Washington State Department of Agriculture

Data Report

Pilot Study of Pesticides in Washington State Stream Sediments

December 2018

AGR PUB 102-741 (N/12/18)

This report is available on the Department of Agriculture's website:
http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx

Contact Information:

Lead Author:

Abigail Nickelson
Natural Resource Assessment Section
Phone: (509) 895-9338
21 N 1st Avenue
Yakima, WA 98902
ANickelson@agr.wa.gov

Communications Director:

Hector Castro
Phone: (360) 902-1815
P.O. Box 42560
Olympia, WA 98504-2560
HCastro@agr.wa.gov

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Agriculture.

Do you need this publication in a different format? Contact the WSDA receptionist at (360) 902-1976 or TTY (800) 833-6388

Pilot Study of Pesticides in Washington State Stream Sediments

Abigail Nickelson
Natural Resources Assessment Section
Washington State Department of Agriculture
Olympia, Washington
December 2018

Acknowledgements

Brandi Lubliner, Washington State Department of Ecology for review and cooperative agreement coordinator

Rich Sheibley and United States Geological Survey personnel for sample collection

Stormwater Action Monitoring, a stormwater monitoring program, for study collaboration

Manchester Environmental Laboratory for sample analysis

King County Environmental Laboratory for sample analysis

Yakama Nation: Elizabeth Sanchey, Environmental Management Program Manager for sampling assistance and technical expertise

The Washington State Department of Agriculture, Natural Resources Assessment Section staff including; Matthew Bischof, Joel Demory, George Tuttle, and Margaret Drennan for internal peer-review of this data report. Brian Scott, Jaclyn Hancock and Katie Hurlburt for sampling assistance. Kelly McLain for internal peer review and cooperative agreement coordination.

Table of Contents

List of Figures

List of Tables

Executive Summary

The Washington State Department of Agriculture (WSDA) has been implementing an ambient surface water monitoring program in agricultural and urban areas since 2003. The program has grown to include 14 sites and tests for 122 pesticides during the growing season (March-October). The program's goal is to assess the frequency and magnitude of pesticide detections in surface waters.

In 2015 WSDA decided to assess the presence and magnitude of pesticides specifically in sediment, which has not previously been part of the ambient surface water monitoring program. It is well documented in the literature that chemicals will partition between matrices, and, especially if hydrophobic in nature, will accumulate in bottom sediment (Di Toro et al., 1991). Accumulation of pesticides can have an adverse effect on the invertebrate community and disrupt food webs for higher trophic organisms. This is especially a concern for endangered salmon species and their dependence on invertebrate communities as a source of food (Groot & Margolis, 1991).

Through cooperation with the Manchester Environmental Laboratory, Stormwater Action Monitoring (SAM) program, the Washington State Department of Ecology, the United States Geological Survey and the King County Environmental Laboratory (KCEL) sediment was collected at a total of 86 sites and analyzed for 122 current use and legacy pesticide compounds and Total Organic Carbon (TOC). Sampling took place between April 6 and October 2, 2015.

Of the 93 samples collected, 12 unique compounds were detected in 28 of the samples. The current use insecticide bifenthrin, the legacy pesticide DDT and its degradates DDD and DDE were the most commonly detected, accounting for 36% and 49% of the total detections, respectively. Bifenthrin, a pyrethroid, was found at or above levels considered toxic to benthic invertebrates in 13 of the 16 samples in which it was detected.

The overall detection frequency across all pesticides analyzed was less than 1% and at least 1 analyte was detected in nearly a third of the samples. Reporting limits ranged from 12 µg/kg DW (dry weight) to 110 µg/ Kg DW for different analytes, but also varied between analytical batches. Nearly half of the detections were of legacy pesticides, such as DDT and its breakdown products. Bifenthrin and chlorpyrifos are currently used pesticides that have been found in the surface water. Of the 10 sampling events in which both water and sediment were collected, only one had one detection of the same pesticide in both matrices.

The analytical method was successfully broad in scope with 122 different pesticides analyzed. Overall detections were infrequent, but nearly every time bifenthrin was detected it was at a concentration considered toxic. As new analytical methods and technologies become available the cost effectiveness relative to comprehensive return of useful data will improve. Collaboration and coordination with MEL and the SAM program will continue to be sought for future sediment monitoring efforts.

Introduction

Since 2003 the Washington State Department of Agriculture (WSDA) has received funding from the Model Toxics Control Account (established by Washington's Model Toxics Control Act) and the U.S. Environmental Protection Agency (EPA) to administer a comprehensive program to assess the occurrence of pesticides detected in Washington State surface waters that support aquatic life. To make that assessment WSDA collects 3 kinds of information;

- Pesticide use data: quantities and types of pesticides used on different crops
- Agricultural land use: crop types grown and their locations in the state
- Ambient monitoring data: pesticide concentrations in surface water

It is of critical importance to insure that the potential effects of pesticides on aquatic systems are minimized while also minimizing the economic impacts to agricultural systems that are responsible for providing a sustainable food supply. The program, with its 3 components, is designed to benefit the environment and support the state's agriculture industry in the use of pesticides within the legal constraints of pesticide labels. The data generated by the ambient monitoring is utilized by a wide range of agencies including the EPA, the National Marine Fisheries Service, and the U.S. Fish and Wildlife Service to refine threatened and endangered species exposure assessments for pesticides registered for use. This data also allows WSDA to determine if more protective measures should be required on pesticide labels or restrictions are needed to safeguard water quality. Additionally, WSDA uses this data to conduct education and outreach activities within the agriculture industry to mitigate negative environmental effects of pesticides. Variations in a chemical's physical properties can affect its fate and transport. Some pesticide active ingredients have a tendency to sorb to sediment particles instead of remaining in the water column. The collection of sediment samples in addition to surface water samples yields a more robust assessment of the water body by quantifying pesticide distribution within the waterbody and exposure to invertebrate communities.

This pilot study of pesticides in Washington State stream sediments was conducted to increase WSDA's understanding of the fate and transport of pesticides within the state's fresh water bodies.

The objectives of the 2015 pilot study were as follows;

1) determine if pesticides are present in fine sediment at the selected stream sites,
2) assess if measured pesticide concentrations have the potential for toxicity to benthic invertebrates;
3) and determine if pesticide monitoring in fine sediment should be added to ongoing ambient monitoring.

The additional data acquired through the pilot study adds to the existing ambient monitoring dataset. The additional data allows for further quantification of the fate and transport of pesticide active ingredients by WSDA and other data users.

WSDA partnered with the SAM program, formerly known as the Regional Stormwater Management Program, Puget Lowland Streams study[1], which opened up additional resources and subsequently allowed for more total samples and a more detailed analysis than if both agencies worked separately.

This report summarizes the study area, site selection criteria, study design, sampling procedures, and results. This report concludes with recommendations about future sediment sampling.

[1] https://ecology.wa.gov/Regulations-Permits/Reporting-requirements/Stormwater-monitoring/Stormwater-Action-Monitoring/SAM-status-and-trends/Puget-lowland-streams

Study Area

For the purpose of this report, watershed size was based on the Hydraulic Unit Code (HUC) system. Each 8 digit HUC code designates a subbasin and each 10 digit HUC code designates a watershed (United State Geological Survey, 2016). Figure 1 depicts each subbasin that included one or more sampling locations. All SAM sites were located in the Puget Sound ecoregion. All of the WSDA sites were selected from preexisting ambient monitoring locations, 3 in western Washington and 2 in eastern Washington. See Table A-1 in Appendix A for a complete list of site locations.

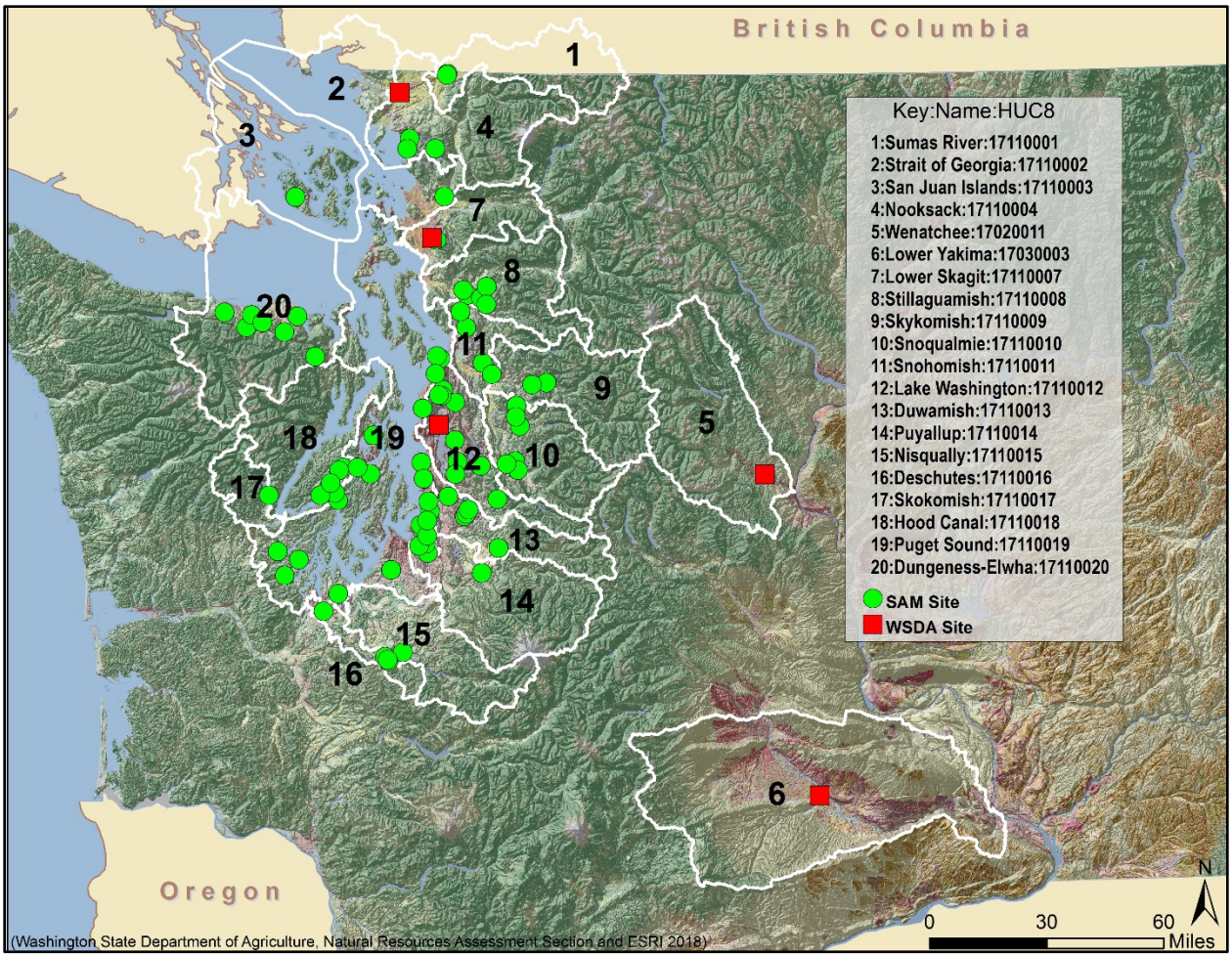

Figure 1 Map of Washington State subbasins containing one or more sediment sampling sites

WSDA Sites

Site selections for the pilot study were based on available funds, past detections and availability of bedded sediment. Of the 14 ambient monitoring sites, 5 were selected for the sediment pilot study.

Lower Bertrand Creek

The Lower Bertrand Creek (BC-1) site is located in the Nooksack River-Frontal Bellingham Bay watershed (HUC 1711000405). The site is approximately 1 mile from where the tributary enters the Nooksack River. Most of the watershed lies south of the United States-Canadian border (83%). Of the portion that is in the United States, about 30% of the land use is agricultural. Roughly 7% of the agricultural acreage on the US side is producing blueberries and caneberries (raspberries, blackberries, and marionberries). The top 3 agricultural crops are grass hay, field corn and caneberry.[2]

Upper Big Ditch

The Upper Big Ditch (BD-2) is located in the Skagit River-Frontal Skagit Bay watershed (HUC 1711000702). Land use in the watershed is 27% agricultural. The top 3 crops in production by acreage are potatoes, field corn, and grass hay. The area is also known for its seed crops. In 2015 there were 1,905 acres of spinach, beet and ryegrass for seed in production[2]. The sampling site is located downstream of the city Mount Vernon, Washington and before the stream enters the main area of agricultural land use in the watershed. This sampling site is therefor considered to be more influenced by urban land use than agricultural land use.

Thornton Creek

The Thornton Creek (TC-3) site is located in the Lake Washington subbasin and lies to the west and just upstream from where the creek enters Lake Washington and downstream of the pedestrian footbridge near Matthews Beach Park. Thornton Creek was selected because the watershed has a mixture of residential and urban land-use that includes recreational turf grass[2].

Marion Drain

The Marion Drain site (MA-2) is located approximately 100 feet upstream of the Indian Church Road bridge in Yakima County, and 0.5 miles upstream of its confluence with the Yakima River. Approximately 69% of the Marion Drain watershed (HUC 1703000304) is devoted to agricultural production. The top 3 crops in production by acreage are field corn, hops, and apples. These top 3 crops make up 54% of all the agricultural land use in the watershed[2]. Marion Drain is documented habitat for summer steelhead and coho salmon as well as spawning grounds for fall Chinook salmon ("WDFW SalmonScape," n.d.).

Brender Creek

The Brender Creek site (BR-1) is located approximately 50 feet upstream of the crossing with Evergreen Drive in Cashmere, Washington. The site is located within the Mission Creek watershed (HUC 1702001106) and only 2.7% of the watershed is used for agricultural production. The watershed is characterized by relatively steep slopes and a close proximity of stream bank to agricultural field edges. The top 3 crops in production (by acreage) are pear, apple and cherry[2].

---

[2] WSDA NRAS agricultural land use mapping program, 2015 data

SAM Sites

WSDA analyzed fine sediments from a total of 81 SAM random sites. The sites were all located in Western Washington. For a description of their location, refer to Table A-1 in Appendix A. The selection of the SAM sites underwent a separate site selection process for small perennial streams. Briefly, SAM candidate sites were selected from EPA's Generalized Random Tesselation Stratified Master Sample List for the Puget Lowland ecoregion based on an evaluation of sampling suitability. Using the GRTS master sample list enables the selection of unbiased and spatially balanced sites within the study frame, which was the Puget lowland ecoregion in this case. Within that area candidate sites were selected inside each of the SAM's assessment areas; Within the Urban Growth Area (WUGA) and Outside the Urban Growth Area (OUGA). Each of the candidate sites were evaluated for suitability for monitoring to create the final site list. For additional information on the site selection process used in the SAM, please refer to the SAM Quality Assurance Project Plan([Ecology], 2014). The availability of WSDA funds meant that 81 of a total 105 SAM sites were analyzed for the purpose of this pilot study.

Study Methodology

This section provides an overview of the study design and methodology for the pilot study. A more detailed description can be found in the *Addendum 7 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds* (2015).

Study Design

This pilot study was designed to collect data of sufficient quality and quantity to assess if pesticide monitoring in sediment should be conducted on a routine basis. Measuring the Total Organic Carbon (TOC) content of the sediment was an essential component of the study design that allows for comparability both between samples and with effects levels from laboratory studies. Comparing pesticide concentrations detected in the sediment to effects thresholds provides a means to assess the potential for risk to aquatic organisms.

All sediment sampling events occurred between July-September 2015. Sediment sampling occurred at each WSDA site 3 separate times; once at the beginning, once in the middle and once at the end of the sampling season. Sediment sampling occurred at each of SAM sites once between June and October.

Field Procedures

Field methods for collecting sediment at the WSDA sites and SAM sites were very similar. In brief the sampling procedure was:

1) Enter the sampling location downstream of where the sediment samples will be collected.
2) Collect a composite sample from 3 to 5 sediment deposition regions at the site using scoops, spoons, or spatulas to remove approximately the top 2.0 cm of sediment.
3) After vigorous mixing of the composite sample, force through a 2.0-mm sieve until an adequate amount of sample is collected.

Some minor differences exist between the sampling protocol used at the WSDA sites and the sampling protocol used at the SAM sites. Differences are not believed to have introduced any significant bias or other factor that would have affected the comparability of results from samples collected across all of the sites. The WSDA sites were sampled using all stainless steel scoops, spoons and bowls, while the SAM sites were sampled using Teflon spatulas, glass bowls and stainless steel scoops. A total of 1.5 L of wet sediment was gathered at each SAM site and then split into sub samples for different analyses. Roughly 0.12 L (4 oz) of wet sediment was collected at the WSDA sites because no additional sediment analysis beyond pesticides and TOC were required. Although different sample volumes were collected, both sample collection methods used sediment from multiple areas at each site that was homogenized to create a

composite sample. For more detailed information on the field sampling protocols refer the SOP for WSDA [3] and SAM quality assurance project plan (QAPP), Appendix C-4 ([Ecology], 2014)

Laboratory Analysis

Ecology's Manchester Environmental Laboratory (MEL) conducted the pesticide analysis on all of the sediment samples. Most of the TOC samples were analyzed by MEL using PSEP 1986 for Total Organic Carbon at 70°C. The remainder of the TOC samples were analyzed by the King County Environmental Laboratory using PSEP 1986 with EPA 9060A([Ecology], 2014). The variation in TOC analysis is considered negligible (B. Lubliner, personal communication, August 15, 2018).

Table 1: Analytical methods summary

Parameter	Methods		Instrumentation
	Extraction reference	Analytical reference	
Pesticides in sediment	AOAC2007.01[1]	EPA 8270D[2]	GC/MS
TOC in sediment	n/a	PSEP 1986[3] or PSEP 1986 with EPA 9060A[4]	Gravimetric

n/a: not applicable
GC/MS: gas chromatography/mass spectrometry
[1](AOAC, 2007)
[2](EPA, 1998)
[3](PSEP, 1986)
[4](EPA, 2004)

Data Quality

Data Quality Measures

The quality assurance and quality control (QA/QC) protocol uses blanks, replicates, and surrogate recoveries. Laboratory surrogate recovery, laboratory blanks, laboratory control samples (LCS), and laboratory control sample duplicates (LCSD) are analyzed as the laboratory component of QA/QC. These were implemented at a rate of 1 per batch of samples processed. Field blanks, field replicates, matrix spikes (MS), and matrix spike duplicates (MSD) integrate field and laboratory QA/QC components. In total, 15% of the samples were QA/QC samples. Highlights of the laboratory and field data quality are presented below in Results, and a full analysis of the QA/QC results is contained in Appendix C.

[3] Curtin, A., & McLain, K. (2014) Standard Operating Procedure: Collecting and Processing of Stream Bed Sediment for Pesticide Analysis. Olympia, WA: Washington State Department of Agriculture.

Field replicates are samples that were collected alongside regular composite samples for the purpose of ensuring that the data was of acceptable quality and to gauge the overall variability, and reproducibility of the study results. If one member of a replicate pair was a non-detect while the other was a positive detection, only the positively detected value was used. Results from field replicate pair were averaged for the purpose of making comparisons to pesticide toxicity values from the literature.

Reporting Methods

Data were qualified by the laboratory. The qualifiers described in Table C-1 in Appendix C are consistent with the reporting methods used by WSDA's ambient surface water monitoring program. Unqualified results indicate that the compound was detected at or above the reporting limit. Laboratory results associated with "J" or "E" qualifiers indicate that the compound was detected at or above the method detection limit and the concentration represents an estimate of the concentration of the chemical at the time the sample was collected. Laboratory results associated with "U", "UJ", "N", and ""NJ" qualifiers are considered non-detects and indicate that the compound was not detected in the samples at or above the method detection limit. Results that were qualified with ("U", "UJ", "N", or "NJ") were not included in summary statistics and were not used for comparison to toxicity values from the literature.

Data Analysis

All field site visit information was recorded in a Microsoft Access 2013 database on a Mobile Demand (model number R11AH) tablet. All graphs, plots, and tables were created using Microsoft Excel 2013 software. Maps and spatial analysis were completed using ArcGIS software version 10.5.1.

Toxic Unit and Analysis

To estimate the additive effects of pesticide mixtures and identify major toxicity contributors to organisms a toxic unit (TU) analysis was completed. To calculate TU, the pesticide concentration detected, normalized for the amount of organic carbon (OC) in the sample is divided by the OC-normalized sediment LC_{50} (lethal concentration 50%) values or other assessment criteria from the literature. The sum of these ratios gives the TU for the sediment sample, as described in the equation below;

$$\sum \left(\frac{\mathrm{A}}{\mathrm{LC_{50}A}} + \frac{\mathrm{B}}{\mathrm{LC_{50}B}} + \cdots \right) = \sum \mathrm{TU}$$

where ∑TU is equal to the sum of the individual quotients, A and B are the observed concentrations in the sediment sample, $LC_{50}A$ and $LC_{50}B$ are the whole sediment effect concentrations of the individual compounds A and B. A $\sum TU \geq 1.0$ predicts lethality for 50% of the benthic organisms exposed. Published LC_{50} values originating from 10-day sediment *H. Azteca* bioassays were used. When appropriate other assessment criteria values where chosen in lieu of LC_{50} values, which is described in detail in the Assessment Criteria in Sediments section of this report. For samples with multiple chemicals detected, all chemicals sharing the same mode of action were used to generate the summed toxic unit. For samples where only one

chemical with a specific a mode of action was detected, an individual TU was calculated, but not summed. A single TU is analogous to a risk quotient and is calculated by dividing the sample concentration by the LC_{50} value;

$$\frac{A}{LC_{50}A} = TU$$

where A is the measured concentration of compound A and $LC_{50}A$ is the effect concentration of the compound A.

Assessment Criteria and Washington State Sediment Standards

The results from the 2015 pilot were compared to both assessment criteria derived from the literature and the Washington State Sediment Management Standards (SMS).

Assessment Criteria in Sediments

Sediment dwelling invertebrates may be at risk from pesticides in sediment when pesticides are present at concentrations above assessment criteria. Repeated or prolonged exposure to pesticides concentrations above assessment criteria is likely to result in decreased ability to survive and reproduce. The availability of toxicity data endpoints for sediment dwelling organisms determined which type of assessment criteria was used for each compound in the toxic unit calculation. Four types of assessment criteria were evaluated and described in order of priority below.

After review of the literature, it was decided that a Likely Effect Benchmark (LEB) should be used when possible for the toxic unit assessment. The LEB for a given chemical is defined as a concentration above which there is a high likelihood of adverse effects on benthic invertebrates. A total of 48 LEBs were derived by Nowell et. al (2016) for the purpose of assessing potential toxicity to invertebrates from currently-used pesticides for sites with sediment monitoring data. The study gathered, from the literature, numerous results from spiked sediment bioassays to develop the benchmarks and represents the best available collection of sediment toxicity data.

For compounds that lacked the necessary spiked sediment bioassay results for LEB calculations, the equilibrium partitioning theorem (EqP) was used to derive an alternative estimated LEB using water based bioassay results, denoted as LEB_{eqp}. EqP postulates that the sediment concentration and pore water concentration of a chemical is related by the partitioning coefficient of that chemical, Koc (Di Toro et al., 1991). This is described in the following equation:

$$A_s/Koc = A_{pw}$$

where A_s is the OC-normalized sediment concentration for chemical A, Koc is the organic carbon-water partitioning coefficient of chemical A and A_{pw} is the predicted pore water concentration of chemical A. Furthermore, Di Toro et. al (1991) shows evidence that the observed toxicity of a given chemical correlates better with the estimated pore water concentration than with the sediment concentration. This is likely because the pore water contains the bioavailable fraction of the chemical concentration. By multiplying the Koc of a

given chemical with its corresponding acute toxicity value for invertebrates Nowell et al. (2016) was able to derive estimated benchmarks, LEB_{eqp}s, that can be directly compared to sediment sample concentrations, such as those measured in this study. The advantage of LEB_{eqp} is that Koc and water based bioassay results are available for many compounds that do not have any whole sediment bioassay results in the literature. Unfortunately, there is an increased level of uncertainty introduced when using LEB_{eqp} because these values were extrapolated via calculations that often use estimated Koc and the underlying relationship between sediment toxicity, pore water toxicity, bioavailability and organic carbon content is not yet quantifiable in a precise way. Furthermore, LEB_{eqp} benchmark values assume equilibrium of the chemical-sediment-water system, which is unlikely in fluvial systems like the locations sampled in this pilot study (Nowell et al., 2016).

In the case where LEBs or LEB_{eqp}s were not available, other whole sediment bioassay results were found to be used as a benchmark. Only short term, 10-day LC_{50} results for benthic invertebrates were selected to ensure that the selection would be as comparable as possible to those in Nowell et al. (2016).

In the cases where neither a LEB or a LEB_{eqp} from Nowell et al. (2016) or a whole sediment LC_{50} value is available , the next best option was determined to be using EqP to calculate pore water concentrations of the detected compounds in the sediment samples. The calculated pore water concentrations can then be directly compared to water based bioassay results to assess toxicity. In other words, EqP is used to convert observed sediment concentrations into pore water concentrations, which are then compared to assessment criteria. This is in contrast to the derivation of LEB_{eqp}, where EqP was used to convert water based bioassay results into estimated sediment based bioassay results. The key difference in these methods is that one is converting bioassay results, and the other is converting measured concentrations, both make an assessment of sediment toxicity feasible.

In this study, the assessment criteria were prioritized in this order: LEB, LEB_{eqp}, whole sediment LC_{50} value from the literature, and water based bioassay LC_{50} values. Table 2 lists the selected assessment criteria for each chemical.

Table 2: Assessment criteria

Chemical name	Value	Species	Criteria type	Koc
2, 4'-DDD	1300 µg/g OC[1]	*H. azteca*	Whole sediment 10-day LC_{50}	-
4, 4'-DDD	240 µg/g OC[2]	*H. azteca*	LEB	-
4, 4'-DDE	550 µg/g OC[2]	*H. azteca*	LEB_{eqp}	-
4, 4'-DDT	220 µg/g OC[2]	*H. azteca*	LEB	-
Bifenthrin	0.60 µg/g OC[2]	*H. azteca*	LEB	-
Chlorpyrifos	4.1 µg/g OC[2]	*H. azteca*	LEB	-
cis-Chlordane	520 µg/g OC[2]	*H. azteca*	LEB	-
Dimethoate	3320 µg/L[3]	*D. magna*	Water 48 hr EC_{50}	20[4]
Ethoprop	44 µg/L[5]	*D. magna*	Water 48 hr LC_{50}	70[6]
Fluridone	6300 µg/L[7]	*D. magna*	Water 48 hr LC_{50}	1000[7]

Chemical name	Value	Species	Criteria type	Koc
trans-Chlordane	890 µg/g OC[2]	*H. azteca*	LEB	
trans-Nonachlor[8]	520 µg/g OC[2]	*H. azteca*	LEB	-

[1](Weston, You, & Lydy, 2004)
[2](Nowell et al., 2016)
[3](Garber & Steeger, 2008)
[4](Vogue, Kerle, & Jenkins, 1994)
[5](Patterson, M., 2003)
[6](Lewis, Tzilivakis, Warner, & Green, n.d.)
[7](Lewis et al., n.d.)
[8] The value for cis-chlordane was used for trans-nonachlor in the absence of any available trans-nonachlor specific toxicity data.

Washington State Sediment Management Standards

The Washington State Department of Ecology has established Sediment Management Standards for freshwater sediment. The SMS, Part III, contains the Sediment Quality Standards. This is a 2-tier framework that defines sediment cleanup objectives (SCO) and cleanup screening levels (CSL). The SCO corresponds to the chemical concentration in the sediment that has no adverse effects to the benthic community. The CSL corresponds to the level at which minor effects are expected to the benthic community (Washington State Department of Ecology, 2013). Of the compounds included in the analysis of sediment in this study only DDE, DDD, and DDT have numerical sediment quality standards (see Table 3 below).

Table 3: WA State Sediment Management Standards

Chemical name	SCO (µg/Kg DW)	CSL (µg/Kg DW)
Total DDE	310	860
Total DDD	21	33
Total DDT	100	8100

Results

Quality Assurance & Quality Control (QA/QC)

The following is a brief overview of QA/QC results, for more details please see Appendix C.

In total, 15% of the samples collected in the field were QA samples. Field replicates yielded 15 consistently detected pairs. All but one of those samples met the measurement quality objectives (MQOs) of 40% for pesticides and 20% for TOC. A TOC field replicate pair on April 6, 2015 exceeded the MQO of 20%. The TOC results from that sampling event were requalified as "J" to indicate that the numerical values are an approximation of TOC content. Most (81%) MS/MSD results fell within the control limits, 13% fell above the upper control limit and 6% fell below the lower control limit. More detail on the MS/MSD results for each chemical can be found in Table C-6.The majority of the analytes (79%) had at least 1 MS/MSD result outside of the control limits. The 3 detections from the same batch as the failed MS/MSD recoveries were requalified, 1 for bifenthrin and 2 for 4,4'-DDE.

QC samples were analyzed on a per-batch basis. For TOC, 8 laboratory duplicates were analyzed and all were within the MQO of 20%. MEL uses laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. There were 2 detections of 4,4'-dichlorobenzophenone in laboratory blanks (during the weeks of July 6 and July 20, 2015). There were no detections for 4,4'-dichlorobenzophenone during these weeks, therefore results from these weeks were accepted. All surrogate recoveries for this study fell within the QC limits. Additional detail for the surrogate recovery results can be found in Table C-8. Most (90%) LCS and LCSD sample recoveries fell within the target limits for this method (EPA 8270D). All detections that occurred within the same batch as an inadequate LCS/LCSD results were already qualified as estimates, therefore no further qualification was needed.

Sediment Pesticide Concentration Results

Detection Summary

There were a total of 45 detections of 12 different analytes. Bifenthrin, a pyrethroid insecticide, was the most commonly detected analyte. DDT and its degradates accounted for nearly half of the detections with a combined count of 22. See Table 4 below for a summary of the detections. For more details on each individual detection, please see Table A-2 in Appendix A.

Table 4: Detection summary

Chemical name	Count of detections	Percent Frequency of detection (%, n=96)	Minimum result concentration (µg/kg DW)	Maximum result concentration(µg /kg DW)
2,4'-DDD	1	1	11	11
4,4'-DDD	6	6	6.7	21
4,4'-DDE	12	13	5.1	110
4,4'-DDT	3	3	13	52
Bifenthrin	16	19	11	120
Chlorpyriphos	1	1	24	24
cis-Chlordane	1	1	34	34
Dimethoate	1	1	7.7	7.7
Ethoprop	1	1	18	18
Fluridone	1	1	19	19
trans-Chlordane	1	1	32	32
trans-Nonachlor	1	1	31	31

Comparison to Washington State Sediment Management Standards

Of the chemicals detected in the pilot study, only DDT and its degradates have established criteria in the SMS. Out of all 22 DDT and degradate detections, three exceeded the SCO and one 4, 4'-DDE detection exceeded the CSL. All exceedances occurred at Brender Creek in Cashmere, WA. This site is known for DDT and degradate detections in surface water due to historical use of DDT and bank erosion. WSDA's ambient surface water monitoring program frequently detects DDT and DDT degradates in the surface water at Brender Creek. A Total Maximum Daily Load (TMDL) for DDT in the Brender Creek watershed and the neighboring Mission and Yaksum Creeks currently exists. For more information on the TMDLs refer to the *Mission Creek DDT Total Maximum Daily Load* (Anderson, 2007). Table 5 lists the 3 sediment samples that exceeded SMS criteria.

Table 5: SMS criteria exceedances

Chemical name	Site	Date	Result µg/kg DW	SCO µg/kg DW	CSL µg/kg DW
4,4'-DDE	BR-1	4/7/2015	110	21	33
4,4'-DDE	BR-1	6/30/2015	25	21	33
4,4'-DDE	BR-1	9/14/2015	40	21	33

Comparison to Assessment Criteria

To quantify the potential hazard of each sediment sample to benthic invertebrates, each result was compared to assessment criteria. When more than one chemical was detected in a sample with similar modes of actions a summed toxic unit, ∑TU, was calculated. For samples in which only one chemical was detected, or multiple chemicals with dissimilar modes of action, a TU

was calculated. For the purpose of this analysis, when the concentration in a sediment sample meets or exceeds a TU or ∑TU of 1.00 the sample is considered to be toxic.

Table 6: Toxic unit and results

Site code	Stream name	Date	Contributor(s)	∑TU	TU
BD-2	Big Ditch	4/6/2015	Bifenthrin	--	**6.7**
064WUGA	Johnson Creek	9/14/2015	Bifenthrin	--	**5.6**
059OUGA	Mill Creek	9/2/2015	Bifenthrin	--	**3.2**
BD-2	Big Ditch	6/30/2015	Bifenthrin	--	**2.8**
024WUGA	Woodland Creek	8/5/2015	Bifenthrin	--	**2.5**
027OUGA	Thomas Creek	9/23/2015	Bifenthrin	--	**2.5**
070WUGA	Unnamed	8/17/2015	Bifenthrin	--	**2.1**
081WUGA	Unnamed	7/30/2015	Bifenthrin	--	**2.1**
061WUGA	West Hylebos Creek	9/9/2015	Bifenthrin, DDT Degradates	**1.8**	--
077WUGA	Unnamed	9/14/2015	Bifenthrin	--	**1.5**
004WUGA	Wapato Creek	7/24/2015	Bifenthrin, DDT Degradates	**1.5**	--
023WUGA	Wapato Creek	7/17/2015	Bifenthrin, DDT Degradates	**1.3**	--
087WUGA	Bell Creek	7/20/2015	Bifenthrin, DDE	**1.0**	--
082WUGA	North Fork Issaquah Creek	7/22/2015	Bifenthrin	--	0.92
074OUGA	Little Soos Creek	7/23/2015	Bifenthrin	--	0.77
005WUGA	West Hylebos Creek	7/23/2015	Bifenthrin	--	0.65
BR-1	Brender Creek	4/7/2015	Chlorpyrifos	--	0.33
BR-1	Brender Creek	6/30/2015	DDT and DDT degradates	0.0347	--
BR-1	Brender Creek	4/7/2015	DDT and DDT degradates	0.0310	--
BR-1	Brender Creek	9/14/2015	DDT and DDT degradates	0.0300	--
MA-2	Marion Drain	4/6/2015	DDE	--	1.50E-03
TC-3	Thornton Creek	9/16/2015	DDE	--	1.31E-03
MA-2	Marion Drain	6/29/2015	DDE	--	9.04E-04
TC-3	Thornton Creek	6/29/2015	DDE	--	5.80E-04
063WUGA	Clover Creek	8/7/2015	cis-Chlordane, trans-chlordane, trans-Nonachlor	0.00102	--

Table 6 shows that 8 of the 25 samples had multiple compounds that could be summed to give a combined toxic unit. In all samples with a ∑TU >1, bifenthrin was the major contributor with DDT and degradates accounting for less than 1% of the ∑TU in those cases. The majority of the samples only had 1 chemical detected and an individual TU was calculated instead.

The sample at BR-1 on April 7, 2015 had detections of two compounds with differing modes of action, chlorpyrifos and DDT degradates. was the only sample for which individual TUs were calculated despite multiple detections in the sample. Chlorpyrifos and the DDT degradates detected in that sample do not have similar modes of action. Chlorpyrifos is an acetylcholinesterase inhibitor, while DDT is a sodium channel regulator.

Chlordane is an agricultural pesticide that was banned in the U.S. in 1988. Technical grade chlordane is a mixture of chlordane and nonachlor isomers (Przybyla and Wohlers, 2018). A sample from 063WUGA contained 3 compounds found in chlordane. Of those 3, only 2 had available LEB values for the toxic unit approach. No available assessment criteria for trans-nonachlor has been identified in the literature, therefore to complete the comparison, the most conservative of the chlordane LEBs was used in place of an experimental trans-nonachlor value. It is acknowledged and well documented in the literature that isomers of a compound have varying degrees of toxicity (Przybyla and Wohlers, 2018). By using the most conservative (lowest) available LEB value of a similar compound the subsequent toxicity unit sum should be considered an estimate.

The following map shows the spatial relationship of detections for which either ∑TU or TU values were calculated and were greater than > 0.1. Only TUs greater than 0.1 were included on the map for readability purposes only.

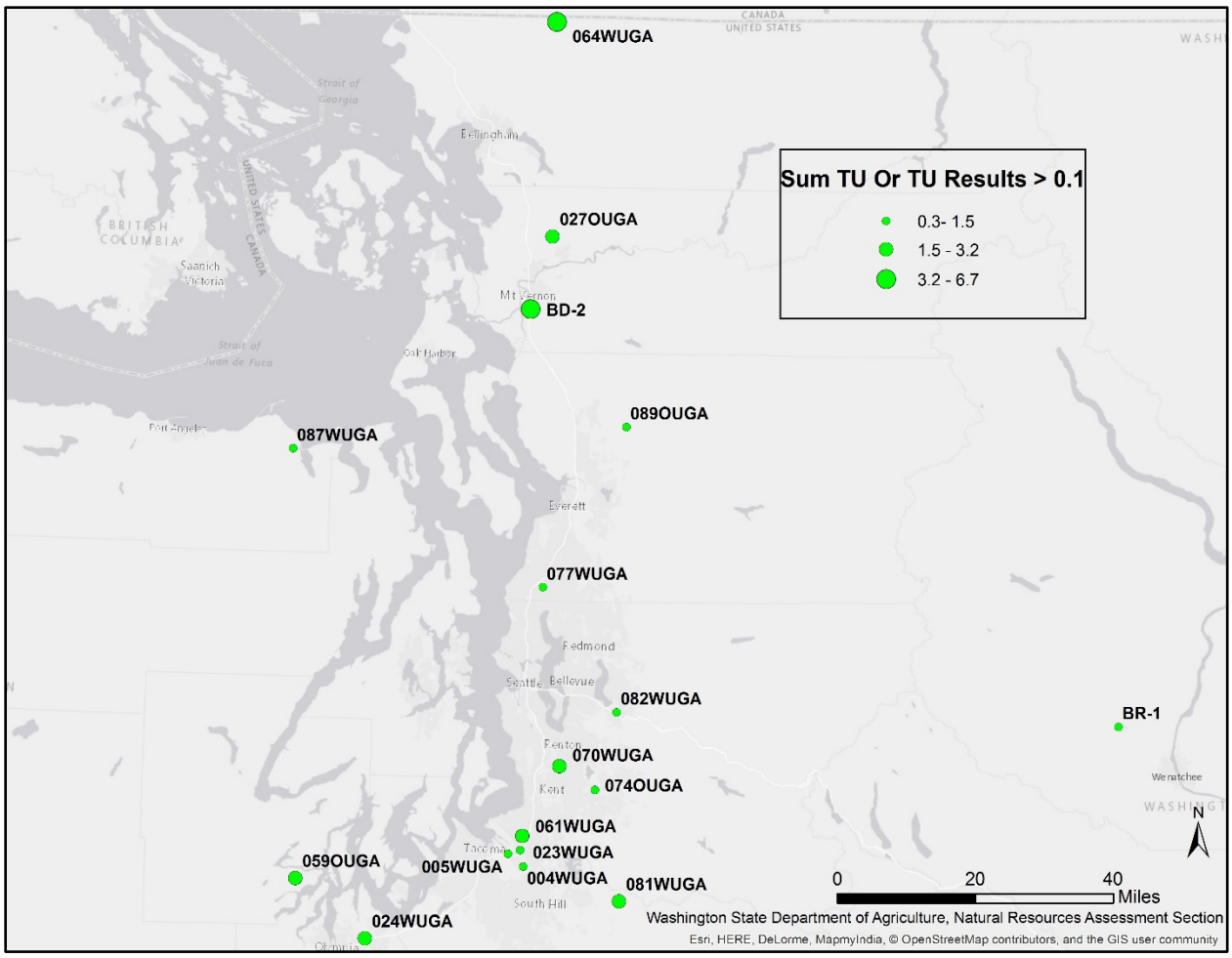

Figure 2 Map of samples with calculated ∑TU or TU values >0.1

For 3 of the compounds detected there were no LEB or whole sediment toxicity results available. Instead of comparing sediment concentrations to sediment bioassay derived criteria, an approach was used to compare calculated pore water concentrations to water bioassay derived criteria. First, pore water concentrations were derived using EqP and Koc values for these chemicals. Then those pore water concentrations were compared against available water based (as opposed to whole sediment) assessment criteria to calculate a TU. Table 7 shows the calculated TU for pore water for those 3 samples.

Table 7: Calculated Pore water TU results; dimethoate, ethoprop and fluridone

Site	Date	Chemical	TU
050WUGA	7/8/2015	Dimethoate	0.057
089OUGA	9/10/2015	Ethoprop	0.62
042OUGA	9/22/2015	Fluridone	2.3E-04

Comparison to water detections

During 2 sampling events, water samples for pesticide analysis were collected in tandem with sediment samples. These tandem events occurred at the 5 WSDA sites during the week of April

6 and June 29. There was only 1 instance where the same chemical was detected in the water and sediment. This occurred at Brender Creek on April 7 with chlorpyrifos. Chlorpyrifos was detected at 0.03 µg/L in the surface water and 24 µg/kg DW in sediment. There was greater variety of chemicals detected in the water samples as opposed to the sediment samples. The ratio of water detections to sediment detections was 4:1. Table 8 below lists the chemicals detected in the water and sediment at the tandem sampling events. The lack of correlation between chemicals detected in the water and the sediment can be attributed to the differences in the environmental fate properties of the chemicals. Hydrophobic compounds like bifenthrin and the DDT degrades have a high affinity for sediment and will accumulate within the sediment particles rather than dissolve into the water column.

Table 8: Chemicals detected at water-sediment tandem sampling events

Site	Date	Water analyte detected	Water concentration detected (µg/L)	Sediment analyte detected	Sediment concentrations detected (µg/kg DW)
BD-2	04/06/2015	Azoxystrobin	0.065	Bifenthrin	110
		Boscalid	0.39		
		Cyprodinil	0.032		
		Dichlobenil	0.022		
		Dinotefuran	0.67		
		Diuron	0.007		
		Etridiazole	0.18		
		Fludioxonil	2.2		
		Imazapyr	0.027		
		Imidacloprid	0.039		
		Metalaxyl	3.3		
		Pyraclostrobin	0.032		
		Thiamethoxam	0.14		
		Trifloxystrobin	0.044		
BD-2	06/30/2015	Azoxystrobin	0.040	Bifenthrin	46
		Boscalid	0.41		
		Dinotefuran	0.14		
		Diuron	0.011		
		Fludioxonil	1.2		
		Imazapyr	0.019		
		Imidacloprid	0.033		
		Thiamethoxam	0.025		
		Triclopyr	0.056		
		Trifloxystrobin	0.018		
BR-1	04/07/2015	Chlorpyrifos	0.03	2,4'-DDD	11
				4,4'-DDD	21
				4,4'-DDE	110

Site	Date	Water analyte detected	Water concentration detected (µg/L)	Sediment analyte detected	Sediment concentrations detected (µg/kg DW)
				4,4'-DDT	52
				Chlorpyriphos	24
BR-1	06/30/2015	4,4'-DDE	0.02	4,4'-DDD	7.3
				4,4'-DDE	25
				4,4'-DDT	14
MA-2	04/06/2015	2,4-D	0.048	4,4'-DDE	15
		Chlorpyrifos	0.026		
		Diuron	0.010		
		Fludioxonil	0.069		
		Pyrimethanil	0.016		
MA-2	06/29/2015	2,4-D	0.042	4,4'-DDE	9.3
		Azoxystrobin	0.005		
		Bentazon	0.30		
		Dicamba	0.019		
		Diuron	0.006		
		Terbacil	0.032		

Conclusion and Recommendations

This pilot study represents the first time WSDA and MEL have attempted to characterize a large number of different analytes in sediment. While a great number of pesticides were successfully characterized, this pilot study highlighted the need to pursue lower method reporting limits. Matrix interferences are inherent when analyzing sediment samples for any compounds, including pesticides. The detection limits for this suite of analytes were generally $1/10^{th}$ the value of the reporting limits. These matrix interferences are in part reflected in the difference between the reporting and detection limits. Reporting limits greater than 12 µg/kg DW have the potential to miss toxic effects to invertebrate organisms. For example, this dataset had a TOC content ranging from <1% to 5%, with a median of 1.3%. Bifenthrin detected at the lowest observed reporting limit of 12 µg/kg DW in sediment with 1.3% TOC has a OC-normalized concentration of 923 µg/kg OC. The assessment criteria chosen for this study was 600 µg/kg OC, well below the reporting limit. Given that the assessment criteria was below the reporting limit, there is the possibility that unmeasurable but considerably harmful concentrations to benthic invertebrates exist in the sediment. The database of LEBs provided by Nowell et al. (2016) shows that 12 other pesticides have LEBs similar in magnitude to bifenthrin at 100-942 µg/kg OC. An improved method with lower reporting limits would be appropriate for those other highly toxic pesticides. Reporting limits found with the method used in this study would be appropriate for relatively less toxic chemicals. The need to quantify highly toxic pesticides at lower concentrations was also described in a similar study by Weston et al. (2004). They focused on pyrethroid insecticides in agricultural areas and found that any detection of those compounds meant that the sediments were likely toxic to benthic organisms. A method with lower reporting limits would allow for a more complete evaluation of sediment toxicity, especially for pyrethroid type pesticides.

Although DDT and its degradates contributed a relatively small amount of toxicity (<1%) when found with other chemicals as seen in the toxic unit analysis, the detections were the most frequent of all pesticides looked for. Almost half of the detections in the study were for DDT and its degradates with a count of 22. The widespread presence of these DDT compounds is not uncommon and is consistent with water samples collected for the ambient monitoring program. The site with the most detections of DDT and its degradates (Brender Creek) has TMDLs in place to mitigate contamination. DDT is a very persistent legacy compound that has been banned in the United States since 1972. The detections in this study and others are attributed to the ability of these compounds to persist in the environment and the widespread historic use of DDT in both urban and agricultural communities. These compounds have been detected in both agricultural and urban dominated watersheds.

Not all of the compounds detected in this study had available LEB or whole sediment toxicity test results available. As a result the detections for dimethoate, ethoprop, fluridone and trans-nonachlor were difficult to quantify of toxicity. No water or sediment based toxicity test results for trans-nonachlor was found in the literature. Trans-nonachlor is one component of technical grade Chlordane, which has been banned in the US since 1988 (Przybyla & Wohlers, 2018). Two

other chlordane components were also found in the same sample from 063WUGA (Clover Creek), cis-chlordane and trans-chlordane. In lieu of an LEB for trans-nonachlor, the lowest LEB of the other 2 components was used to represent trans-nonachlor in the toxicity unit calculation. The resulting ∑TU for that sample should be considered an estimate. Although the physical properties of cis- and trans-chlordane are similar, variable toxicity between isomers is well supported in the literature (Przybyla & Wohlers, 2018). The toxicity of dimethoate, ethoprop and fluridone in 3 samples was quantified using the EqP. Although these calculations made quantification of the toxicity possible in the absence of any LEB or whole sediment LC_{50}, the results should be considered estimates. EqP assumes equilibrium between the pore water and sediment TOC which is unlikely in fluvial systems such as the sites where these samples were collected. Constant renewal of the surface water above the sediment and interconnectivity of sediment pore water at depths of 2 cm below the sediment surface makes equilibrium highly unlikely. Also, there is evidence that the use of EqP may overestimate toxicity due to the presence of black carbon. Black carbon may significantly reduce the bioavailability of compounds in the pore water (Burgess et. al 2013). The results of the TU calculations using for each of the 3 samples containing dimethoate, ethoprop and fluridone suggest a low toxicity (<1.0) to aquatic organisms.

Bifenthrin is a pyrethroid insecticide that is registered for both home and agricultural use in Washington (Puyallup Research and Extension Center, n.d.). 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). The detections occurred at both urban and agriculturally dominated areas. When bifenthrin was detected, it was almost always at levels considered to be toxic with a TU > 1.0. Weston et al. (2004) also found pyrethroids in sediment to be highly toxic when they were detected in agricultural communities in California. A study on sediment toxicity in the midwestern US found that bifenthrin in particular was commonly a major contributor of pesticide related toxicity whenever it was detected (Moran et al., 2017).

Differences between detections in the surface water and sediment support the fact that water sampling alone does not completely characterize the risk to aquatic organisms by pesticides. Although there was an overall low frequency of detections, this study suggests bifenthrin toxicity in sediment is a concern. As new analytical methods and technologies become available the cost effectiveness relative to comprehensive return of useful data will improve. Collaboration and coordination with MEL, SAM and other interested parties for future sediment monitoring is recommended.

References

Amweg, E. L., Weston, D. P., & Ureda, N. M. (2005). Use and toxicity of pyrethroid insecticides in the central valley, California, USA. *Environmental Toxicology and Chemistry*, *24*(4), 966–972.

Anderson, R. (2007). *Mission Creek Watershed DDT Total Maximum Daily Load* (Water Quality Improvement Report No. 07-10–046). Retrieved from https://fortress.wa.gov/ecy/publications/documents/0710046.pdf

AOAC. (2007). Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate. Retrieved from http://www.thenfl.com/pdf/AOAC%202007.1.pdf

Burgess, R. M., Berry, W. J., Mount, D. R., & Di Toro, D. M. (2013). Mechanistic sediment quality guidelines based on contaminant bioavailability: Equilibrium partitioning sediment benchmarks. *Environmental Toxicology and Chemistry*, *32*(1), 102–114. https://doi.org/10.1002/etc.2025

Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., … Paquin, P. R. (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*, *10*, 1541–1583.

Ding, Y., Harwood, A. D., Foslund, H. M., & Lydy, M. J. (2010). Distribution and toxicity of sediment-associated pesticides in urban and agricultural waterways from Illinois, USA. *Environmental Toxicology and Chemistry*, *29*(1), 149–157.

Drennan, M., & Curtin, A. (2015). *Addendum 7 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds* (No. 103- 512(N/3/16)) (p. 25). Olympia, WA.

[Ecology]. (2014). *Quality Assurance Project Plan for Status and Trends Monitoring of Small Streams in the Puget Lowlands Ecoregion for Monitoring Conducted using Pooled RSMP Funds contributed by Western Washington Municipal Stormwater Permittees* (No. 14-10–054). Olympia, WA: Washington State Department of Ecology. Retrieved from https://fortress.wa.gov/ecy/publications/SummaryPages/1410054.html

EPA. (1998, January). Semivolitile Organic Compounds by GC/MS. Retrieved from https://www.epa.gov/sites/production/files/2015-07/documents/epa-8270d.pdf

EPA. (2004, November). Method 9060aTotal Organic Carbon. Retrieved from https://www.epa.gov/sites/production/files/2015-12/documents/9060a.pdf

Garber, K., & Steeger, T. (2008). *Risks of Dimethoate Use to the Federally-Listed California Red Legged Frog* (Pesticide Effects Dertermination) (p. 137). Office of Pesticide Programs, Environmental Protection Agency.

Groot, C., & Margolis, L. (1991). *Pacific Salmon Life Histories*. Vancouver, BC: UBC Press.

Lewis, K. A., Tzilivakis, J., Warner, D., & Green, A. (n.d.). An international database for pesticide risk assessments and management. *Human and Ecological Risk Assessment: An International Journal*, *22*(4), 1050–1064. https://doi.org/10.1080/10807039.2015.1133242

Moran, P. W., Nowell, L. H., Kemble, N. E., Mahler, B. J., Waite, I. R., & Van Metre, P. C. (2017). Influence of sediment chemistry and sediment toxicity on macroinvertebrate communities across 99 wadable streams of the Midwestern USA. *Science of The Total Environment*, *599–600*, 1469–1478. https://doi.org/10.1016/j.scitotenv.2017.05.035

Nowell, L. H., Norman, J. E., Ingersoll, C. G., & Moran, P. W. (2016). Development and application of freshwater sediment-toxicity benchmarks for currently used pesticides. *Science of The Total Environment*, *550*, 835–850. https://doi.org/10.1016/j.scitotenv.2016.01.081

Przybyla, J., & Wohlers, D. W. (2018). *Toxicological Profile for Chlordane* (No. CS274127- A) (p. 252). Atlanta, GA: Agency for Toxic Substances and Disease Registry. Retrieved from https://www.atsdr.cdc.gov/ToxProfiles/tp31.pdf

PSEP, P. S. E. P. (1986). *Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound.* (No. TC-3991-04). Seattle, WA: USEPA Region 10. Retrieved from https://nepis.epa.gov/Exe/ZyPDF.cgi/9101X5BM.PDF?Dockey=9101X5BM.PDF

Puyallup Research and Extension Center. (n.d.). Pesticide Information Center Online(PICOL) Databases. Retrieved December 15, 2015, from http://picol.cahe.wsu.edu/LabelTolerance.html

Spurlock, F. (2008). Distribution and variance/covariance structure of pesticide environmental fate data. *Environmental Toxicology and Chemistry*, *27*(8), 1683–1690.

United State Geological Survey. (2016, August 16). Watershed Boundary Dataset. Retrieved September 20, 2016, from http://nhd.usgs.gov/

US EPA. (2008). *National Functional Guidelines for Superfund Organic Methods Data Review* (No. USEPA-540-R-08-01). Washington, DC: United State Environmental Protection Agency Office of Superfun Remediation and Technology Innovation.

Vogue, P. A., Kerle, E. A., & Jenkins, J. J. (1994, July 24). OSU Extension Pesticide Properties Database. Retrieved June 13, 2017, from http://npic.orst.edu/ingred/ppdmove.htm

WDFW SalmonScape. (n.d.). Retrieved November 3, 2016, from http://apps.wdfw.wa.gov/salmonscape/map.html

Weston, D. P., You, J., & Lydy, M. J. (2004). Distribution and Toxicity of Sediment-Associated Pesticides in Agriculture-Dominated Water Bodies of California's Central Valley. *Environmental Science & Technology*, *38*(10), 2752–2759. https://doi.org/10.1021/es0352193

Appendices

Appendix A: Supplemental Information

Site List

The following table compiles a complete list of sites sampled during the Pesticides in Washington State Pilot Study. The site name and location information was gathered from the SAM and WSDA QAPPS ([Ecology], 2014) (Drennan & Curtin, 2015). The HUC boundaries were queried from the Watershed Boundary Dataset(United State Geological Survey, 2016). The percent of total HUC10 acreage in agricultural production was calculated using WSDA agricultural land use data for 2015 and the corresponding HUC10 boundary for the site.

Table A-1: Site location table

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	000WUGA	Goldsborough Creek	47.2122	-123.1388	1711001906	Goldsborough Creek-Frontal Puget Sound	17110019012957	1.05
SAM	001OUGA	-	47.4072	-122.8176	1711001906	Goldsborough Creek-Frontal Puget Sound	17110019000643	1.05
SAM	001WUGA	Coal Creek	47.5599	-122.1701	1711001204	Lower Sammamish River	17110012000226	1.02
SAM	002WUGA	-	47.3753	-122.3151	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000680	0.724
SAM	003WUGA	North Creek	47.7798	-122.188	1711001203	Middle Sammamish River	17110012000115	2.26
SAM	004WUGA	Wapato Creek	47.2192	-122.3226	1711001902	Lunds Gulch-Frontal Puget Sound	17110019020834	0.724
SAM	005WUGA	West Hylebos Creek	47.2535	-122.3335	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000729	0.724
SAM	006OUGA	-	48.5262	-123.099	1711000305	San Juan Island	17110003000119	9.71
SAM	006WUGA	Blackjack Creek	47.5082	-122.6446	1711001907	Ollala Valley-Frontal Puget Sound	17110019012828	1.47
SAM	008OUGA	-	47.2429	-121.9377	1711001303	Lower Green River	17110013002264	8.28
SAM	009OUGA	Canyon Creek	48.0242	-123.1382	1711002003	Dungeness River	17110020003107	1.58
SAM	009WUGA	Swamp Creek	47.8256	-122.2553	1711001203	Middle Sammamish River	17110012005112	2.26

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	016WUGA	Whatcom Creek	48.7533	-122.468	1711000406	Whatcom Creek-Frontal Bellingham Bay	17110004013762	0.726
SAM	018WUGA	May Creek	47.8572	-121.6877	1711000906	Wallace River-Skykomish River	17110009000942	0.933
SAM	019OUGA	-	48.3794	-122.3066	1711000702	Skagit River-Frontal Skagit Bay	17110007000036	26.9
SAM	019WUGA	-	47.5289	-122.794	1711001801	Tahuya River-Frontal Hood Canal	17110018000603	0.284
SAM	021WUGA	Johnson Creek	48.9969	-122.2642	1711000104	Sumas River	17110001000005	36.4
SAM	023WUGA	Wapato Creek	47.2453	-122.3705	1711001902	Lunds Gulch-Frontal Puget Sound	17110019020834	0.724
SAM	024OUGA	Mud Creek	47.5647	-121.8534	1711001004	Upper Snoqualmie River	17110010000645	3.44
SAM	024WUGA	Woodland Creek	47.061	-122.8043	1711001905	McLane Creek-Frontal Puget Sound	17110019013153	2.62
SAM	025OUGA	Skookum Creek	47.1231	-123.0969	1711001906	Goldsborough Creek-Frontal Puget Sound	17110019000213	1.05
SAM	025WUGA	-	47.4347	-122.8348	1711001801	Tahuya River-Frontal Hood Canal	17110018014669	0.284
SAM	026OUGA	Tumwater Creek	48.0907	-123.4726	1711002004	Morse Creek-Frontal Port Angeles Harbor	17110020000295	1.71
SAM	027OUGA	Thomas Creek	48.5412	-122.2679	1711000202	Samish River	17110002001771	14.6

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	028OUGA	Powell Creek	46.8494	-122.4464	1711001502	Middle Nisqually River	17110015000293	2.71
SAM	030OUGA	Deschutes River	46.8316	-122.543	1711001601	Upper Deschutes River	17110016000016	1.99
SAM	030WUGA	-	47.6508	-122.6324	1711001907	Ollala Valley-Frontal Puget Sound	17110019012695	1.47
SAM	033WUGA	Gorst Creek	47.5303	-122.715	1711001907	Ollala Valley-Frontal Puget Sound	17110019000121	1.47
SAM	034WUGA	Little Soos Creek	47.3579	-122.1258	1711001303	Lower Green River	17110013002281	8.28
SAM	036WUGA	-	47.5541	-122.3668	1711001902	Lunds Gulch-Frontal Puget Sound	17110019019025	0.724
SAM	037OUGA	Surveyor Creek	48.0377	-123.3486	1711002004	Morse Creek-Frontal Port Angeles Harbor	17110020000348	1.71
SAM	038OUGA	Cherry Creek	47.7706	-121.8503	1711001006	Lower Snoqualmie River	17110010000467	12.6
SAM	038WUGA	Munson Creek	48.0579	-122.1336	1711001102	Quilceda Creek-Frontal Possession Sound	17110011003033	15.8
SAM	039OUGA	-	47.8493	-121.7663	1711000906	Wallace River-Skykomish River	17110009000617	0.933
SAM	040WUGA	Kimball Creek	47.5322	-121.8378	1711001004	Upper Snoqualmie River	17110010000477	3.44
SAM	042OUGA	Snow Creek	47.9374	-122.9639	1711002001	Snow Creek-Frontal Discovery Bay	17110020000244	1.27

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	042WUGA	-	47.3224	-122.3655	1711001902	Lunds Gulch-Frontal Puget Sound	17110019007775	0.724
SAM	044WUGA	-	48.1778	-122.1305	1711000803	Stillaguamish River-Frontal Port Susan	17110008000546	11.8
SAM	045OUGA	Carey Creek	47.4232	-121.9484	1711001202	Lake Sammamish	17110012000105	1.20
SAM	046OUGA	Bear Creek	47.5185	-122.8166	1711001801	Tahuya River-Frontal Hood Canal	17110018000620	0.284
SAM	047WUGA	-	48.1163	-122.1673	1711001102	Quilceda Creek-Frontal Possession Sound	17110011000527	15.8
SAM	048WUGA	-	47.8035	-122.2631	1711001203	Middle Sammamish River	17110012000545	2.26
SAM	050OUGA	Jim Creek	48.168	-122.055	1711000802	South Fork Stillaguamish River	17110008000129	0.955
SAM	050WUGA	Powder Mill Gulch Retention Basin	47.9409	-122.2748	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000524	0.724
SAM	055WUGA	-	47.6401	-122.1858	1711001204	Lower Sammamish River	17110012001060	1.02
SAM	056OUGA	Dow Creek	47.4184	-123.1959	1711001702	Skokomish River-Frontal Hood Canal	17110017000272	1.05
SAM	059OUGA	Mill Creek	47.1833	-123.0235	1711001906	Goldsborough Creek-Frontal Puget Sound	17110019013041	1.05
SAM	060OUGA	Deschutes River	46.8162	-122.5242	1711001601	Upper Deschutes River	17110016005168	1.99

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	061WUGA	West Hylebos Creek	47.2833	-122.3272	1711001902	Lunds Gulch-Frontal Puget Sound	17110019008055	0.724
SAM	062WUGA	Deschutes River	46.9954	-122.8819	1711001602	Lower Deschutes River	17110016000007	6.04
SAM	063WUGA	Clover Creek	47.1538	-122.5203	1711001903	Chambers Creek-Frontal Puget Sound	17110019013511	1.37
SAM	064WUGA	Johnson Creek	48.9913	-122.267	1711000104	Sumas River	17110001000007	36.4
SAM	065WUGA	-	47.9499	-122.2933	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000527	0.724
SAM	067WUGA	Little Soos Creek	47.3673	-122.1163	1711001303	Lower Green River	17110013002281	8.28
SAM	068WUGA	-	47.8841	-122.299	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000533	0.724
SAM	069OUGA	Stossel Creek	47.695	-121.8313	1711001005	Tolt River	17110010000452	0.0472
SAM	070WUGA	-	47.4305	-122.2165	1711001303	Lower Green River	17110013000134	8.28
SAM	072OUGA	Raging River	47.5545	-121.9008	1711001004	Upper Snoqualmie River	17110010000209	3.44
SAM	074OUGA	Little Soos Creek	47.3822	-122.105	1711001303	Lower Green River	17110013002281	8.28
SAM	074WUGA	Boeing Creek	47.7542	-122.3649	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000550	0.724
SAM	076OUGA	Jim Creek	48.2097	-122.0258	1711000802	South Fork Stillaguamish River	17110008000134	0.955

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	077WUGA	-	47.8055	-122.2786	1711001203	Middle Sammamish River	17110012000545	2.26
SAM	078OUGA	March Creek	48.1959	-122.1536	1711000803	Stillaguamish River-Frontal Port Susan	17110008000410	11.8
SAM	079OUGA	-	47.9273	-122.0398	1711001101	Pilchuck River	17110011000247	1.14
SAM	079WUGA	-	47.8858	-121.9879	1711001102	Quilceda Creek-Frontal Possession Sound	17110011000259	15.8
SAM	080WUGA	Salmon Creek	47.4948	-122.3535	1711001902	Lunds Gulch-Frontal Puget Sound	17110019006552	0.724
SAM	081WUGA	-	47.1495	-122.026	1711001401	Carbon River	17110014004706	0.801
SAM	082WUGA	North Fork Issaquah Creek	47.5461	-122.042	1711001202	Lake Sammamish	17110012000223	1.20
SAM	083OUGA	Stimson Creek	47.4237	-122.914	1711001801	Tahuya River-Frontal Hood Canal	17110018000675	0.284
SAM	084OUGA	Bagley Creek	48.0841	-123.3222	1711002004	Morse Creek-Frontal Port Angeles Harbor	17110020000306	1.71
SAM	087WUGA	Bell Creek	48.0845	-123.0691	1711002002	Jimmycomelately Creek-Frontal Sequim Bay	17110020000315	4.62
SAM	089OUGA	Jordan Creek	48.1445	-122.0254	1711000802	South Fork Stillaguamish River	17110008000439	0.955
SAM	093OUGA	Pederson Creek	48.0583	-123.2616	1711002004	Morse Creek-Frontal Port Angeles Harbor	17110020012986	1.71

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
SAM	093WUGA	Honey Dew Creek	47.5134	-122.1792	1711001204	Lower Sammamish River	17110012000231	1.02
SAM	095WUGA	Des Moines Creek	47.4104	-122.3244	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000665	0.724
SAM	097WUGA	-	47.34	-122.3294	1711001902	Lunds Gulch-Frontal Puget Sound	17110019000699	0.724
SAM	098OUGA	Stossel Creek	47.7292	-121.8517	1711001005	Tolt River	17110010000456	0.0472
SAM	100OUGA	-	47.4704	-122.8599	1711001801	Tahuya River-Frontal Hood Canal	17110018000713	0.284
SAM	102WUGA	Padden Creek	48.7153	-122.4817	1711000406	Whatcom Creek-Frontal Bellingham Bay	17110004015058	0.726
SAM	105OUGA	Austin Creek	48.7185	-122.3247	1711000406	Whatcom Creek-Frontal Bellingham Bay	17110004013567	0.726
SAM	113OUGA	Deschutes River	46.8213	-122.5291	1711001601	Upper Deschutes River	17110016000016	1.99
WSDA	BC-1	Lower Bertrand Creek 1	48.9241	-122.53	1711000405	Nooksack River-Frontal Bellingham Bay	17110004000396	30.5
WSDA	BD-2	Upper Big Ditch 2	48.3882	-122.333	1711000702	Skagit River-Frontal Skagit Bay	17110007002428	26.9
WSDA	BR-1	Brender Creek 1	47.5211	-120.4864	1702001106	Mission Creek	17020011001199	2.71

Agency	Site code[1]	Site name	Latitude	Longitude	HUC10[2]	HUC10[2] name	NHD reach code[3]	Percent of total HUC 10 acreage in agricultural production
WSDA	MA-2	Marion Drain 2	46.3307	-120.2	1703000304	Marion Drain	17030003003251	68.7
WSDA	TC-3	Thornton Creek 3	47.6959	-122.2757	1711001204	Lower Sammamish River	17110012000182	1.02

[1]"WUGA" designates that the site was within the Urban Growth Area; "OUGA" designates that the site was outside of the Urban Growth Area

[2]HUC10: Hydraulic Unit Code

[3]NHD: National Hydrography Dataset

Results Data

Table A-2: Supplemental detection data

Chemical name	Site	Date	Result µg/kg DW	Minimum reporting limit µg/kg DW	Minimum detection limit µg/kg DW	TOC	Result µg/kg DW -OC
2,4'-DDD	BR-1	4/7/2015	11	29	4.5	0.0179	614.5
4,4'-DDD	BR-1	4/7/2015	21	29	3.5	0.0179	1173.2
4,4'-DDD	BR-1	6/30/2015	7.3	16	1.9	0.0042	1738.1
4,4'-DDD	023WUGA	7/17/2015	21	47	5.7	0.0483	434.8
4,4'-DDD	004WUGA	7/24/2015	17	45	5.5	0.0521	326.3
4,4'-DDD	061WUGA	9/9/2015	6.7	15	1.8	0.0248	270.2
4,4'-DDD	BR-1	9/14/2015	10.3	15	1.8	0.0060	1708.3
4,4'-DDE	MA-2	4/6/2015	15	29	2.9	0.0181	828.7
4,4'-DDE	BR-1	4/7/2015	110	29	2.9	0.0179	6145.3
4,4'-DDE	MA-2	6/29/2015	9.3	29	2.9	0.0187	497.3
4,4'-DDE	TC-3	6/29/2015	9.7	19	1.9	0.0304	319.1
4,4'-DDE	BR-1	6/30/2015	25	16	1.6	0.0038	5952.4
4,4'-DDE	023WUGA	7/17/2015	19	47	4.8	0.0483	393.4
4,4'-DDE	087WUGA	7/20/2015	12	38	3.9	0.135	88.9
4,4'-DDE	004WUGA	7/24/2015	17	45	4.6	0.0521	326.3
4,4'-DDE	061WUGA	9/9/2015	8.85	15	1.5	0.0248	356.9
4,4'-DDE	021WUGA	9/14/2015	14	36	3.7	0.0532	263.2
4,4'-DDE	BR-1	9/14/2015	40	15	1.5	0.0060	6666.7
4,4'-DDE	TC-3	9/16/2015	5.1	13	1.3	0.0071	718.3
4,4'-DDT	BR-1	4/7/2015	52	29	5.7	0.0179	2905.0
4,4'-DDT	BR-1	6/30/2015	14	16	3.1	0.0042	3333.3
4,4'-DDT	BR-1	9/14/2015	13	15	3	0.0060	2166.7
Bifenthrin	BD-2	4/6/2015	110	43	4.6	0.0275	4000.0
Bifenthrin	BD-2	6/30/2015	46	31	3.3	0.0272	1691.2
Bifenthrin	023WUGA	7/17/2015	37	47	5	0.0483	766.0
Bifenthrin	087WUGA	7/20/2015	83	38	4.1	0.135	614.8
Bifenthrin	082WUGA	7/22/2015	26	26	2.7	0.0470	554.4
Bifenthrin	005WUGA	7/23/2015	28	27	2.9	0.0715	391.6
Bifenthrin	074OUGA	7/23/2015	35	28	3	0.0750	465.7
Bifenthrin	004WUGA	7/24/2015	46	45	4.8	0.0521	882.9
Bifenthrin	081WUGA	7/30/2015	91	45	4.8	0.0731	1244.9
Bifenthrin	024WUGA	8/5/2015	79	65	6.9	0.0530	1490.6
Bifenthrin	070WUGA	8/17/2015	13	14	1.5	0.0100	1261.5
Bifenthrin	059OUGA	9/2/2015	27	17	1.8	0.0141	1914.9
Bifenthrin	061WUGA	9/9/2015	27	18	1.9	0.0248	1088.7
Bifenthrin	064WUGA	9/14/2015	120	42	4.5	0.0357	3361.3

Chemical name	Site	Date	Result µg/kg DW	Minimum reporting limit µg/kg DW	Minimum detection limit µg/kg DW	TOC	Result µg/kg DW -OC
Bifenthrin	077WUGA	9/14/2015	11	15	1.6	0.0120	887.1
Bifenthrin	027OUGA	9/23/2015	13	17	1.9	0.0088	1477.3
Chlorpyriphos	BR-1	4/7/2015	24	29	18	0.0179	1340.8
cis-Chlordane	063WUGA	8/07/2015	34	100	19	0.157	216.6
Dimethoate	050WUGA	7/8/2015	7.7	13	5.9	0.0020	3793.1
Ethoprop	089OUGA	9/10/2015	18	19	12	0.0095	1894.7
Fluridone	042OUGA	9/22/15	19	17	2.5	0.0134	1417.9
trans-Chlordane	063WUGA	8/07/2015	32	100	31	0.157	203.8
trans-Nonachlor	063WUGA	8/07/2015	31	100	12	0.157	197.5

Appendix B: Glossary, Acronyms, Abbreviations

Glossary

Analyte: Chemical being measured by a laboratory method.

Current use pesticide: A pesticide that is currently registered for use in Washington state.

Degradate: Pesticide breakdown product.

EC_{50}: The "effect concentration" causing an effect in 50% of test species. This value is calculated by plotting the dose response curve and fitting a mathematical equation to the data and using that equation to calculate the concentration for any level of effect, in this case the 50% value.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Laboratory control sample/ Laboratory control sample duplicate (LCS/LCSD): Laboratory control samples are a type of quality control samples in which a known amount of pure analytical grade compound is intentionally introduced, or "spiked", into pure water. LCSs are included with every batch of samples and are treated in exactly the same manner as the field samples throughout the sample extraction and sample analysis processes. LCSs are used in conjunction with LCSDs to evaluate the performance of the analytical method. Analyte recoveries are used to assess the accuracy of the analytical method and, the relative standard difference between LCS and LCSD recoveries is used to assess the precision of the analytical method. LCSs and LCSDs are used to assess the reproducibility between batches and can also be compared to MS and MSD recoveries to assess if results that fall outside of the acceptance criteria may be due to matrix effects and not due to the analytical method itself.

LC_{50}: The "lethal concentration" causing mortality in 50% of test species. This value is calculated by plotting the dose response curve and fitting a mathematical equation to the data and using that equation to calculate the concentration for any level of effect, in this case the 50% value.

Legacy pesticide: A pesticide that is no longer registered for use, but persists in the environment.

Likely effect benchmark: A concentration above which there is a high probability of adverse effects on benthic invertebrates.

Matrix spike/Matrix spike duplicate (MS/MSD): Spiked samples are used to determine whether there are interferences in the analysis of a particular sample matrix and their effect on analyte recovery. An aliquot of a sample is "spiked" with a known amount of the analyte of interest and analyzed along with the associated samples. The recovery of the spiked analyte is calculated as the amount of analyte found minus the amount of analyte found in the unspiked sample. Spiked samples are sometimes viewed as a way of measuring the efficiency with which an analyte is recovered from the sample.

Pesticide: Any substance or mixture of substances intended for killing, repelling or mitigating any pest. Pests include nuisance microbes, plants, fungus, and animals.

Pyrethroid: A synthetic analog or derivative of pyrethrins, similar to the natural compound pyrethrum that is produced by *Chrysanthemum cineum* and *cenerariaefolium*

Quality assurance and quality control (QA/QC): Quality Assurance and Quality Control refer to the combined process of evaluating the performance of laboratory and field methods. Quality Assurance refers to aspects of the monitoring program that are designed to evaluate the monitoring as a whole including field methods and other process outside of the laboratory analysis. Quality control relates specifically to aspects of the monitoring program that are designed to evaluate laboratory performance and ensure that the laboratory data is of reliable quality.

Risk quotient: A risk quotient is calculated by dividing a point estimate of environmental exposure by a point estimate of effect. Risk quotients are an expression of concentration over toxicity and are used by EPA and others to assess risk given just two pieces of information for screening level risk assessments.

*Toxic Unit (TU):*Amount or concentration of a toxicant expressed in units of lethality

Acronyms and Abbreviations

DDD	Dichloro-diphenyl-dichloroethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
DW	Dry weight
EEC	Estimated environmental concentration
EPA	United States Environmental Protection Agency
EQP	Equilibrium partitioning
GCMS	Gas chromatograph coupled with mass spectrometer
GRTS	Generalized random tesselation stratified
HUC10	Hydraulic unit code 10- digit
KCEL	King County Environmental Laboratory
Koc	Organic carbon-water partitioning coefficient
LC50	Lethal concentration to cause mortality in 50% of test species
LCS/LCSD	Laboratory control sample/laboratory control sample duplicate
LEB	Likely effect benchmark
LOC	Level(s) of concern
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
MS/MSD	Matrix spike/matrix spike duplicate
OC	Organic carbon
OUGA	Outside urban growth boundary
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
RPD	Relative percent difference
SAM	Stormwater Action Monitoring
SMS	Sediment Management Standards
SOP	Standard operation procedures
TMDL	Total maximum daily load
TOC	Total organic carbon
TU	Toxic unit
WSDA	Washington State Department of Agriculture
WUGA	Within urban growth boundary

Units of Measure

°C	Degrees centigrade
m	Meter
µg/L	Micrograms per liter (parts per billion)
µg/kg DW	Micrograms per kilogram dry weight

Appendix C: Laboratory Data Quality

Data may be qualified if one or more analytical factors affect confidence in the prescribed data value. MEL qualifies data according to the National Functional Guidelines for Superfund Organic Data Review (US EPA, 2008). Definitions of data qualifiers are presented below. The following QA/QC analysis does not include results for TOC from King County Environmental Laboratory.

Table C-1: Laboratory data quality qualifiers

Qualifier	Definition
D	The analyte was positively identified and was detected at the reported concentration.
E	Reported result is an estimate because it falls outside of the calibration range.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified," and the associated numerical value represents its approximate concentration.
NAF	Not analyzed for.
NC	Not calculated.
REJ	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
U	The analyte was not detected at or above the reported sample quantitation limit.
UJ	The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

MEL, 2000, 2008; EPA, 2008

Performance measures are used by the laboratory and field staff to determine when data should be qualified. Relative percent difference (RPD) is used as a performance measure to represent the precision of the analysis by comparing the difference between replicate pairs for matrix spikes, laboratory control samples and field replicates. Percent recovery is also used as a performance measure to represent the bias of the analysis by comparing the difference between replicate pairs for matrix spikes, laboratory control samples, and surrogate recovery. RPD and % Recovery are also used by the analyst to qualify the results of the grab samples when quality assurance (QA) and quality control (QC) samples fall below the lower control limits or fall above the upper control limits. Control limits can be either be analyte specific control limits as determined by the analysts or default limits specified by the EPA method. Upper and lower analyte specific control limits are calculated from the mean of the most recent one hundred pairs, ± three standard deviations. The sediment sample analysis process was a new process for MEL at the time of the Pilot Study, therefore all of the performance measures match that of the default

limits for the pesticides, 50-150 %. Performance measures for QA and QC samples are presented in **Error! Reference source not found.**.

Table C-2: Performance measures for quality assurance and quality control

Analysis method[1]	Parameter type	Parameter	Lower control limit (%)	Upper control limit (%)	Upper RPD control limit (%)
GCMS	Surrogate	1,3-Dimethyl-2nitrobenzene	30	130	-
	Pesticide	2,4'-DDD	50	150	40
GCMS	Pesticide	2,4'-DDE	50	150	40
	Pesticide	2,4'-DDT	50	150	40
	Pesticide	4,4'-DDD	50	150	40
	Pesticide	4,4'-DDE	50	150	40
	Surrogate	4,4'-DDE-13C12	20	117	-
	Pesticide	4,4'-DDT	50	150	40
	Pesticide	4,4'-Dichlorobenzophenone	50	150	40
	Pesticide	Acetochlor	50	150	40
	Pesticide	Alachlor	50	150	40
	Pesticide	Aldrin	50	150	40
	Pesticide	Alpha-BHC	50	150	40
	Pesticide	Atrazine	50	150	40
	Surrogate	Atrazine-D5	45	167	-
	Pesticide	Azinphos-ethyl	50	150	40
	Pesticide	Azinphos-methyl	50	150	40
	Pesticide	Benefin	50	150	40
	Pesticide	Benthiocarb	50	150	40
	Pesticide	Beta-BHC	50	150	40
	Pesticide	Bifenthrin	50	150	40
	Pesticide	Boscalid	50	150	40
	Pesticide	Bromacil	50	150	40
	Pesticide	Butachlor	50	150	40
	Pesticide	Butylate	50	150	40
	Pesticide	Captan	50	150	40
	Pesticide	Chlorothalonil (Daconil)	50	150	40
	Pesticide	Chlorpropham	50	150	40
	Surrogate	Chlorpyrifos-D10	30	178	-
	Pesticide	Chlorpyriphos	50	150	40
	Pesticide	cis-Chlordane	50	150	40
	Pesticide	Cis-Nonachlor	50	150	40
	Pesticide	cis-Permethrin	50	150	40
	Pesticide	Coumaphos	50	150	40

Analysis method[1]	Parameter type	Parameter	Lower control limit (%)	Upper control limit (%)	Upper RPD control limit (%)
	Pesticide	Cyanazine	50	150	40
	Pesticide	Cycloate	50	150	40
	Pesticide	Cypermethrin	30	130	40
	Surrogate	Decachlorobiphenyl (DCB)	30	135	-
	Pesticide	Delta-BHC	50	150	40
GCMS	Pesticide	Di-allate (Avadex)	50	150	40
	Pesticide	Diazinon	50	150	40
	Pesticide	Dichlobenil	50	150	40
	Pesticide	Dieldrin	50	150	40
	Pesticide	Dimethoate	50	150	40
	Pesticide	Diphenamid	50	150	40
	Pesticide	Endosulfan I	50	150	40
	Pesticide	Endosulfan II	50	150	40
	Pesticide	Endosulfan Sulfate	50	150	40
	Pesticide	Endrin	50	150	40
	Pesticide	Endrin Ketone	50	150	40
	Pesticide	EPN	50	150	40
	Pesticide	Eptam	50	150	40
	Pesticide	Ethalfluralin (Sonalan)	50	150	40
	Pesticide	Ethion	50	150	40
	Pesticide	Ethoprop	50	150	40
	Pesticide	Fenamiphos	50	150	40
	Pesticide	Fenamiphos Sulfone	50	150	40
	Pesticide	Fenarimol	50	150	40
	Pesticide	Fenvalerate	50	150	40
	Pesticide	Fipronil	50	150	40
	Pesticide	Fipronil Disulfinyl	50	150	40
	Pesticide	Fipronil Sulfide	50	150	40
	Pesticide	Fipronil Sulfone	50	150	40
	Pesticide	Fluridone	50	150	40
	Pesticide	Fonofos	50	150	40
	Pesticide	Gamma-BHC	50	150	40
	Pesticide	Heptachlor	50	150	40
	Pesticide	Heptachlor Epoxide	50	150	40
	Pesticide	Hexachlorobenzene	50	150	40
	Pesticide	Hexazinone	50	150	40
	Pesticide	Imidan	50	150	40
	Pesticide	Kelthane	50	150	40
	Pesticide	Malathion	50	150	40

Analysis method[1]	Parameter type	Parameter	Lower control limit (%)	Upper control limit (%)	Upper RPD control limit (%)
	Pesticide	Metalaxyl	50	150	40
	Pesticide	Methidathion	50	150	40
	Pesticide	Methoxychlor	50	150	40
	Pesticide	Methyl Chlorpyrifos	50	150	40
	Pesticide	Methyl Paraoxon	50	150	40
	Pesticide	Methyl Parathion	50	150	40
GCMS	Pesticide	Metolachlor	50	150	40
	Pesticide	Metribuzin	50	150	40
	Pesticide	Mevinphos	50	150	40
	Pesticide	MGK264	50	150	40
	Pesticide	Mirex	50	150	40
	Pesticide	Molinate	50	150	40
	Pesticide	Monocrotophos	50	150	40
	Pesticide	Napropamide	50	150	40
	Pesticide	Norflurazon	50	150	40
	Pesticide	Oryzalin	50	150	40
	Pesticide	Oxychlordane	50	150	40
	Pesticide	Oxyfluorfen	50	150	40
	Pesticide	Parathion	50	150	40
	Pesticide	Pebulate	50	150	40
	Pesticide	Pendimethalin	50	150	40
	Pesticide	Phenothrin	50	150	40
	Pesticide	Phorate	50	150	40
	Pesticide	Piperonyl Butoxide (PBO)	50	150	40
	Pesticide	Prometon	50	150	40
	Pesticide	Prometryn	50	150	40
	Pesticide	Pronamide (Kerb)	50	150	40
	Pesticide	Propachlor (Ramrod)	50	150	40
	Pesticide	Propargite	50	150	40
	Pesticide	Propazine	50	150	40
	Pesticide	Resmethrin	50	150	40
	Pesticide	Simazine	50	150	40
	Pesticide	Simetryn	50	150	40
	Pesticide	Sulfotepp	50	150	40
	Pesticide	Terbacil	50	150	40
	Pesticide	Tetrachlorvinphos (Gardona)	50	150	40
	Pesticide	Tetrahydrophthalimide	50	150	40
	Pesticide	Tokuthion	50	150	40

Analysis method[1]	Parameter type	Parameter	Lower control limit (%)	Upper control limit (%)	Upper RPD control limit (%)
	Pesticide	trans-Chlordane	50	150	40
	Pesticide	Trans-Nonachlor	50	150	40
	Pesticide	Treflan (Trifluralin)	50	150	40
	Pesticide	Triadimefon	50	150	40
	Pesticide	Triallate	50	150	40
	Pesticide	Trichloronate	50	150	40
	Pesticide	Tricyclazole	50	150	40
	Surrogate	Trifluralin-D14	26	180	-
	Surrogate	Triphenyl Phosphate	30	130	-
TOC	TOC	Total Organic Carbon	75	125	20

[1]GCMS – Gas chromatography/mass spectroscopy, AOAC2007.1(modified)/SW8270D(modified)
TOC- Total Organic Carbon, PSEP-TOC

Lower Practical Quantitation Limits

Lower practical quantitation limits (LPQLs) are the lowest concentrations at which laboratories may report data without classifying the concentration as an estimate below the lowest calibration standard. The LPQL is determined by calculating the average of the method detection limit (MDL) per analyte for all batches over the study period. The MDL is defined by the Federal code of Regulation 40 Appendix B to Part 136 as, "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." In addition to the MDL, the lab also reports the method reporting limit (MRL) which is the lowest concentration standard in the calibration range of each parameter. The concentration of the result reported by the laboratory that fall above the MDL but below the MRL are estimates because they fall outside of the calibration range. LPQL data for the Pilot Study are presented in **Error! Reference source not found.**.

Table C-3: Mean performance lower practical quantitation limits (LPQL) in µg/L

CAS number	Parameter	Parent chemical	Use / Type	Analysis method[1]	LPQL	Standard deviation
53-19-0	2,4'-DDD	DDT	Degradate	GCMS	2.75	2.02
3424-82-6	2,4'-DDE	DDT	Degradate		2.55	1.87
789-02-6	2,4'-DDT	DDT	Insecticide		2.31	1.74
72-54-8	4,4'-DDD	DDT	Degradate		2.10	1.55
72-55-9	4,4'-DDE	DDT	Degradate		1.76	1.30
50-29-3	4,4'-DDT		Insecticide		3.43	2.52
90-98-2	4,4'-Dichlorobenzophenone		Degradate		2.58	1.90
34256-82-1	Acetochlor		Herbicide		11.03	8.19

CAS number	Parameter	Parent chemical	Use / Type	Analysis method[1]	LPQL	Standard deviation
15972-60-8	Alachlor		Herbicide		8.36	6.18
309-00-2	Aldrin		Insecticide		12.36	9.13
319-84-6	Alpha-BHC		Insecticide		7.43	5.50
1912-24-9	Atrazine		Herbicide		3.16	2.36
2642-71-9	Azinphos-ethyl		Insecticide		2.06	1.51
86-50-0	Azinphos-methyl		Insecticide		3.69	2.76
1861-40-1	Benefin		Herbicide		12.71	9.43
28249-77-6	Benthiocarb		Herbicide		8.19	6.06
319-85-7	Beta-BHC		Insecticide		8.66	6.40
82657-04-3	Bifenthrin		Insecticide		1.87	1.38
188425-85-6	Boscalid		Fungicide		3.13	2.38
314-40-9	Bromacil		Herbicide		8.13	5.98
23184-66-9	Butachlor		Herbicide		5.34	3.94
2008-41-5	Butylate		Herbicide		8.10	5.98
133-06-2	Captan		Fungicide		5.08	3.77
1897-45-6	Chlorothalonil (Daconil)		Fungicide		6.85	5.23
101-21-3	Chlorpropham		Herbicide		7.47	5.51
5598-15-2	Chlorpyrifos O.A.		Degradate		11.09	6.32
2921-88-2	Chlorpyriphos		Insecticide		11.09	8.16
5103-71-9	cis-Chlordane		Insecticide		3.16	2.36
5103-73-1	Cis-Nonachlor		Insecticide		3.43	2.52
54774-45-7	cis-Permethrin		Insecticide		3.62	2.66
56-72-4	Coumaphos		Insecticide		13.66	10.12
21725-46-2	Cyanazine		Herbicide		2.24	1.64
1134-23-2	Cycloate		Herbicide		6.61	5.09
52315-07-8	Cypermethrin		Insecticide		6.51	4.88
319-86-8	Delta-BHC		Insecticide		5.93	4.38
52918-63-5	Deltamethrin		Insecticide		4.17	3.01
2303-16-4	Di-allate (Avadex)		Herbicide			
333-41-5	Diazinon		Insecticide		6.46	4.79
962-58-3	Diazinon O Analog	Diazinon	Degradate		15.43	11.15
1194-65-6	Dichlobenil		Herbicide		8.35	6.18
60-57-1	Dieldrin		Insecticide		2.92	2.16
60-51-5	Dimethoate		Insecticide		7.76	5.73
957-51-7	Diphenamid		Herbicide		1.61	1.19
2497-06-5	Disulfoton Sulfone		Insecticide		10.34	7.50
959-98-8	Endosulfan I		Insecticide		9.92	7.35
33213-65-9	Endosulfan II		Insecticide		9.20	6.80
1031-07-8	Endosulfan Sulfate	Endosulfan	Degradate		2.74	2.01

CAS number	Parameter	Parent chemical	Use / Type	Analysis method[1]	LPQL	Standard deviation
72-20-8	Endrin		Insecticide		2.41	1.76
53494-70-5	Endrin Ketone	Endrin	Degradate		3.44	2.52
2104-64-5	EPN		Insecticide		15.40	11.41
759-94-4	Eptam		Herbicide		11.05	8.15
55283-68-6	Ethalfluralin (Sonalan)		Herbicide		16.50	12.22
563-12-2	Ethion		Insecticide		1.51	1.12
13194-48-4	Ethoprop		Insecticide		10.91	8.04
153233-91-1	Etoxazole		Insecticide		5.07	3.68
22224-92-6	Fenamiphos		Insecticide		3.25	2.36
31972-44-8	Fenamiphos Sulfone		Degradate		5.58	4.15
60168-88-9	Fenarimol		Fungicide		4.65	3.42
51630-58-1	Fenvalerate		Insecticide		30.13	22.40
120068-37-3	Fipronil		Insecticide		2.36	1.74
205650-65-3	Fipronil Disulfinyl		Degradate		7.32	5.44
120067-83-6	Fipronil Sulfide		Degradate		2.13	1.62
120068-36-2	Fipronil Sulfone		Degradate		2.10	1.57
59756-60-4	Fluridone		Herbicide		2.47	1.87
944-22-9	Fonofos		Insecticide		9.00	6.66
58-89-9	Gamma-BHC		Insecticide		8.17	6.02
76-44-8	Heptachlor		Insecticide		14.11	10.46
1024-57-3	Heptachlor Epoxide	Heptachlor	Degradate		5.02	3.72
118-74-1	Hexachlorobenzene		Fungicide		7.25	5.34
51235-04-2	Hexazinone		Herbicide		2.93	2.16
732-11-6	Imidan		Insecticide		3.28	2.47
115-32-2	Kelthane		Insecticide		4.65	3.42
121-75-5	Malathion		Insecticide		6.26	4.62
57837-19-1	Metalaxyl		Fungicide		11.28	8.33
950-37-8	Methidathion		Insecticide		4.57	3.40
72-43-5	Methoxychlor		Insecticide		2.50	1.88
5598-13-0	Methyl Chlorpyrifos		Insecticide		8.31	6.19
950-35-6	Methyl Paraoxon	Methyl parathion	Degradate		8.69	6.42
298-00-0	Methyl Parathion		Insecticide		14.48	10.69
51218-45-2	Metolachlor		Herbicide		7.19	5.32
21087-64-9	Metribuzin		Herbicide		9.70	7.14
7786-34-7	Mevinphos		Insecticide		12.98	9.63
113-48-4	MGK264		Synergist		21.48	16.23

CAS number	Parameter	Parent chemical	Use / Type	Analysis method[1]	LPQL	Standard deviation
2385-85-5	Mirex		Insecticide		2.28	1.69
2212-67-1	Molinate		Herbicide		9.60	7.20
6923-22-4	Monocrotophos		Insecticide		6.14	4.57
15299-99-7	Napropamide		Herbicide		13.19	9.74
27314-13-2	Norflurazon		Herbicide		3.17	2.36
19044-88-3	Oryzalin		Herbicide		4.84	3.49
27304-13-8	Oxychlordane	Chlordane	Degradate		1.91	1.41
42874-03-3	Oxyfluorfen		Herbicide		10.82	8.03
56-38-2	Parathion		Insecticide		13.99	10.33
1114-71-2	Pebulate		Herbicide		13.00	9.64
40487-42-1	Pendimethalin		Herbicide		5.37	3.97
26002-80-2	Phenothrin		Insecticide		1.90	1.40
298-02-2	Phorate		Insecticide		10.78	7.98
2600-69-3	Phorate O.A.		Insecticide		15.62	11.29
51-03-6	Piperonyl Butoxide (PBO)		Synergist		2.11	1.57
1610-18-0	Prometon		Herbicide		6.66	4.93
7287-19-6	Prometryn		Herbicide		10.01	7.39
23950-58-5	Pronamide (Kerb)		Herbicide		8.05	5.99
1918-16-7	Propachlor (Ramrod)		Herbicide		7.92	5.82
2312-35-8	Propargite		Insecticide		16.47	12.21
139-40-2	Propazine		Herbicide		8.67	6.41
10453-86-8	Resmethrin		Insecticide		2.02	1.47
122-34-9	Simazine		Herbicide		11.65	8.64
1014-70-6	Simetryn		Herbicide		8.56	6.36
3689-24-5	Sulfotepp		Insecticide		9.61	7.16
5902-51-2	Terbacil		Herbicide		5.78	4.29
961-11-5	Tetrachlorvinphos (Gardona)		Insecticide		5.89	4.37
27813-21-4	Tetrahydrophthalimide	Captan	Degradate		10.94	8.18
153719-23-4	Thiamethoxam		Insecticide		7.51	5.48
34643-46-4	Tokuthion		Insecticide		3.49	2.60
66841-25-6	Tralomethrin		Insecticide		4.17	3.01
5103-74-2	trans-Chlordane		Insecticide		5.21	3.86
39765-80-5	Trans-Nonachlor		Insecticide		2.09	1.55
61949-77-7	trans-Permethrin		Insecticide		1.47	1.07
1582-09-8	Treflan (Trifluralin)		Herbicide		8.49	6.27
43121-43-3	Triadimefon		Fungicide		9.57	7.07
2303-17-5	Triallate		Herbicide		8.73	6.50
327-98-0	Trichloronate		Insecticide		5.83	4.32

CAS number	Parameter	Parent chemical	Use / Type	Analysis method[1]	LPQL	Standard deviation
41814-78-2	Tricyclazole		Fungicide		2.30	1.75
-	Total Organic Carbon		-	TOC	3.00	5.04

[1]GCMS – Gas chromatography/mass spectroscopy, AOAC2007.1(modified)/SW8270D(modified)
TOC- Total Organic Carbon, PSEP 1986

Quality Assurance and Quality Control Samples

Quality assurance (QA) samples are collected alongside grab samples in the field and analyzed. Quality control (QC) samples are generated by the laboratory for every batch of field samples submitted. QA and QC samples assure consistency and accuracy throughout sample collection, sample analysis, and the data reporting process.

For this project, QA samples include: field replicates, and matrix spike and matrix spike duplicates (MS/MSD). Laboratory control samples (LCS), LCS duplicates (LCSD), surrogate spikes, and method blanks are included as QC samples in each batch of samples analyzed for pesticides as are method blanks and split sample duplicates for each batch of TOC samples.

Quality Assurance Samples

For the Pilot Study, 15% of the samples collected in the field were QA samples. There were 10 field replicates collected in total; 3 for TOC, and 7 for the EPA 8270D analyses. Also, 8 of the collected samples were subsampled for MS/MSD analysis.

Field Replicate Results

Precision between replicate pairs was calculated using the relative percent difference (RPD) statistic. The RPD is calculated by dividing the absolute value of the difference between the replicates by their mean, then multiplying by 100 for a percent value.

In the Pilot Study there were 8 consistently identified pairs of replicates: 5 for the pesticide analysis and 3 for TOC, see **Error! Reference source not found.**. *Consistent identification* refers to compounds identified in both the original sample and field replicate.

Table C-4 presents the data, data qualification, and relative percent difference (RPD) for analytes consistently identified in both the sample and replicate sample.

Table C-4: Consistently detected pairs within field replicate results

Parameter	Sample date	Site code	Reporting limit	Averaged result	Unit of measurement	Sample and replicate sample details (results and corresponding qualifiers)	RPD (%)
4,4'-DDD	9/14/2015	BR-1	15	10.250	µg/kg dw	9.5 µg/kg dw 'J' 11 µg/kg dw 'J'	14.63
4,4'-DDE	9/9/2015	061WUGA	18	8.850	µg/kg dw	9.8 µg/kg dw 'J' 7.9 µg/kg dw 'J'	21.47
4,4'-DDE	9/14/2015	BR-1	15	40.000	µg/kg dw	35 µg/kg dw 'D' 45 µg/kg dw 'D'	25.00
4,4'-DDE	6/29/2015	TC-3	19	9.700	µg/kg dw	10 µg/kg dw 'J' 9.4 µg/kg dw 'J'	6.19
4,4'-DDT	9/14/2015	BR-1	15	13.000	µg/kg dw	12 µg/kg dw 'J' 14 µg/kg dw 'J'	15.38
Total Organic Carbon	6/30/2015	BR-1	0.1	0.415	%	0.45 % 'D' 0.38 % 'D'	16.87
Total Organic Carbon	9/14/2015	MA-2	0.1	0.635	%	0.61 % 'D' 0.66 % 'D'	7.87
Total Organic Carbon	4/06/2015	BD-2	0.1	2.745	%	2.47 % 'D' 3.02 % 'D'	20.04

For pesticides, the average RPD of the consistently detected pairs was 16.53% and all of the replicate pairs met the RPD MQO of 40%. For TOC, the average RPD of the consistently detected pairs was 14.93% and all of the replicate pairs met the RPD MQO of 20% with the exception of a sample on April 6, 2015 at BD-2. An exceedance of the MQO for TOC indicates a failure of the sampling procedure to produce a homogenized sample. The results from that sampling event were requalified as "J" to indicate that the numerical values are an approximation of TOC in the samples.

In contrast with a consistently detected replicates pair, an inconsistently identified replicate pair denotes when an analyte was positively identified in either the replicate sample or the grab sample but not in both.

There were four inconsistently identified replicate pairs. All of the inconsistencies were due to the detections being very close to the detection limit. Three of the four inconsistently detected pairs were bifenthrin, a highly hydrophobic compound with a $\log K_{oc}$ of 5.4 (Spurlock, 2008) and therefore is known to predominately partition into the TOC (Di Toro et al, 1991). These inconsistencies reflect the nature of sediment sampling in that TOC content can vary throughout a sampling site and creating truly homogenous sub sample can be difficult.

Table C-5 : Inconsistently detected pairs within field replicate results

Parameter	Sample date	Site code	Reporting limit	Averaged result	Unit of measurement	Sample and replicate sample details	RPD (%)
4,4'-DDD	9/9/2015	061WUGA	15	7.0	µg/kg dw	7.3 µg/kg dw 'NJ' 6.7 µg/kg dw 'J'	8.57
Bifenthrin	9/9/2015	061WUGA	18	19.0	µg/kg dw	27 µg/kg dw 'D' 11 µg/kg dw 'NJ'	84.21
Bifenthrin	8/17/2015	070WUGA	14	10.4	µg/kg dw	13 µg/kg dw 'J' 7.8 µg/kg dw 'NJ'	50.00
Bifenthrin	7/23/2015	074OUGA	28	31.5	µg/kg dw	35 µg/kg dw 'D' 28 µg/kg dw 'U'	22.22

Field Blank Results

Sediments vary from area to area by grain size, TOC content and other factors. Due the complexities involved in obtaining pesticide free sediment with identical composition to that of the sampling site, sediment sampling blanks are generally not included in sediment sampling studies.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Results

MS/MSD results reflects the process of sample duplication (field), analyte degradation, matrix interaction, extraction efficiency, and analyte recovery. This measure is the best overall indicator of accuracy and reproducibility in the sampling process.

Table C-6 presents the mean, minimum, and maximum percent recovery for the MS/MSD and the RPD for each MS and MSD pair.

Table C-6: MS/MSD summary statistics

Parameter Name	Analysis	Number of results	Average recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
2,4'-DDD	SW8270D	18	83	158	58	7	9	2
2,4'-DDE	SW8270D	18	73	143	49	8	12	3
2,4'-DDT	SW8270D	18	70	82	53	7	13	2
4,4'-DDD	SW8270D	18	92	170	64	8	12	1
4,4'-DDE	SW8270D	18	66	134	45	5	12	1
4,4'-DDT	SW8270D	18	68	82	27	11	34	1

Parameter Name	Analysis	Number of results	Average recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
4,4'-Dichlorobenzophenone	SW8270D	16	74	144	57	12	12	11
Acetochlor	SW8270D	16	85	163	60	12	20	2
Alachlor	SW8270D	18	80	142	60	12	18	1
Aldrin	SW8270D	18	59	125	41	15	26	4
Alpha-BHC	SW8270D	18	91	183	48	7	16	5
Atrazine	SW8270D	18	78	155	54	7	11	1
Azinphos-ethyl	SW8270D	16	175	283	129	7	9	3
Azinphos-methyl	SW8270D	18	165	220	131	14	18	3
Benefin	SW8270D	18	97	241	15	41	166	1
Benthiocarb	SW8270D	18	81	160	61	4	15	0
Beta-BHC	SW8270D	18	85	140	54	6	20	1
Bifenthrin	SW8270D	16	115	235	76	10	11	9
Boscalid	SW8270D	16	176	298	116	8	9	6
Bromacil	SW8270D	18	88	149	68	6	17	2
Butachlor	SW8270D	16	91	172	72	11	13	5
Butylate	SW8270D	18	83	148	50	29	52	7
Captan	SW8270D	18	92	172	54	7	19	0
Chlorothalonil (Daconil)	SW8270D	14	13	23	0	0	0	0
Chlorpropham	SW8270D	18	100	172	74	16	25	9
Chlorpyriphos	SW8270D	18	84	173	61	11	20	1
cis-Chlordane	SW8270D	18	73	135	51	10	17	1
Cis-Nonachlor	SW8270D	18	77	153	56	8	11	1
cis-Permethrin	SW8270D	18	135	217	92	9	15	2
Coumaphos	SW8270D	18	187	302	147	6	10	1
Cyanazine	SW8270D	18	104	286	74	8	12	1
Cycloate	SW8270D	14	78	128	53	58	86	9
Cypermethrin	SW8270D	16	213	288	109	18	29	2
Delta-BHC	SW8270D	18	111	288	55	7	16	4
Di-allate (Avadex)	SW8270D	2	132	133	130	1	1	1
Diazinon	SW8270D	18	82	167	56	5	9	1
Dichlobenil	SW8270D	18	82	149	62	17	23	9
Dieldrin	SW8270D	18	82	160	55	3	4	1
Dimethoate	SW8270D	18	92	131	65	7	13	3
Diphenamid	SW8270D	18	88	170	56	9	12	2
Endosulfan I	SW8270D	18	79	150	58	17	23	7
Endosulfan II	SW8270D	18	72	140	34	29	53	5
Endosulfan Sulfate	SW8270D	18	80	146	58	10	17	2
Endrin	SW8270D	18	88	161	68	7	16	2

Parameter Name	Analysis	Number of results	Average recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Endrin Ketone	SW8270D	18	93	142	61	14	32	4
EPN	SW8270D	18	166	296	135	6	16	2
Eptam	SW8270D	18	77	140	51	24	52	4
Ethalfluralin (Sonalan)	SW8270D	18	144	287	107	8	13	3
Ethion	SW8270D	18	122	223	91	7	9	5
Ethoprop	SW8270D	18	100	243	66	6	14	2
Fenamiphos	SW8270D	18	221	380	138	11	22	3
Fenamiphos Sulfone	SW8270D	16	176	267	142	2	6	1
Fenarimol	SW8270D	18	132	223	93	15	20	4
Fenvalerate	SW8270D	18	205	359	140	11	16	1
Fipronil	SW8270D	16	128	269	92	13	19	10
Fipronil Disulfinyl	SW8270D	16	91	173	69	7	10	3
Fipronil Sulfide	SW8270D	16	97	184	72	10	14	7
Fipronil Sulfone	SW8270D	16	115	185	84	15	19	6
Fluridone	SW8270D	18	239	344	139	3	5	1
Fonofos	SW8270D	18	86	161	57	8	32	0
Gamma-BHC	SW8270D	18	69	136	49	15	22	3
Heptachlor	SW8270D	18	92	147	78	9	23	5
Heptachlor Epoxide	SW8270D	18	65	141	44	13	25	5
Hexachlorobenzene	SW8270D	18	60	132	40	10	16	0
Hexazinone	SW8270D	18	83	146	56	8	16	1
Imidan	SW8270D	14	61	117	22	36	58	2
Kelthane	SW8270D	18	132	223	93	15	20	4
Malathion	SW8270D	18	100	157	84	12	15	2
Metalaxyl	SW8270D	18	81	146	53	11	23	1
Methidathion	SW8270D	18	92	153	59	16	26	1
Methoxychlor	SW8270D	18	76	99	28	14	45	2
Methyl Chlorpyrifos	SW8270D	16	68	132	50	12	15	5
Methyl Paraoxon	SW8270D	18	102	146	57	13	26	0
Methyl Parathion	SW8270D	18	94	176	58	22	33	1
Metolachlor	SW8270D	18	89	162	68	4	10	1
Metribuzin	SW8270D	18	88	156	61	16	20	5
Mevinphos	SW8270D	18	89	177	63	10	15	1
MGK264	SW8270D	18	99	203	60	19	31	10
Mirex	SW8270D	18	69	124	49	6	9	0
Molinate	SW8270D	16	72	143	52	9	17	2
Monocrotophos	SW8270D	16	90	129	0	8	10	5
Napropamide	SW8270D	18	99	183	66	7	11	3
Norflurazon	SW8270D	18	125	209	94	3	6	1
Oryzalin	SW8270D	2	0	0	0	33	33	33

Parameter Name	Analysis	Number of results	Average recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Oxychlordane	SW8270D	18	103	184	72	10	14	7
Oxyfluorfen	SW8270D	18	138	220	113	7	11	1
Parathion	SW8270D	18	127	221	103	11	18	0
Pebulate	SW8270D	18	81	139	64	11	17	1
Pendimethalin	SW8270D	18	111	211	83	6	10	1
Phenothrin	SW8270D	18	115	234	84	10	21	3
Phorate	SW8270D	18	95	208	62	17	25	5
Piperonyl Butoxide (PBO)	SW8270D	16	107	187	75	8	11	1
Prometon	SW8270D	18	93	182	61	14	18	1
Prometryn	SW8270D	18	79	147	56	8	16	3
Pronamide (Kerb)	SW8270D	18	89	173	61	8	13	2
Propachlor (Ramrod)	SW8270D	18	95	275	63	10	20	1
Propargite	SW8270D	17	97	217	0	19	29	4
Propazine	SW8270D	18	78	149	54	11	16	3
Resmethrin	SW8270D	18	73	273	21	7	11	0
Simazine	SW8270D	18	75	151	50	5	9	2
Simetryn	SW8270D	18	80	141	61	5	10	2
Sulfotepp	SW8270D	18	90	186	65	15	19	5
Terbacil	SW8270D	18	105	183	77	9	13	6
Tetrachlorvinphos (Gardona)	SW8270D	18	82	111	70	8	12	3
Tetrahydrophthalimide	SW8270D	16	119	212	96	13	18	10
Tokuthion	SW8270D	18	94	194	67	5	16	0
trans-Chlordane	SW8270D	18	70	141	52	8	19	2
Trans-Nonachlor	SW8270D	18	70	149	48	10	15	5
Treflan (Trifluralin)	SW8270D	18	105	215	83	14	32	2
Triadimefon	SW8270D	18	95	195	61	19	28	4
Triallate	SW8270D	18	77	164	53	7	12	3
Trichloronate	SW8270D	16	80	185	51	13	22	3
Tricyclazole	SW8270D	16	118	189	96	7	11	1

In total, 81% of all MS/MSD results fell within the control limits, 13% fell above the upper control limit and 6% fell below the lower control limit. The majority of the analytes, 79%, had at least one MS/MSD result outside of the control limits.

Analytes not meeting the target recovery range and the percentage of occurrences are described in Table C-7. Table C-7 also describes the number of detections for each analyte not meeting the target recovery range. Any detections that occurred within the same batch as an MS/MSD recovery criteria were requalified.

Table C-7: Sediment MS/MSD parameters outside of control limits

Parameter name	Percentage of recoveries outside control limits (%)	Fell below or exceeded control limits	Lower control limit (%)	Upper control limit (%)	Number of detections in 2015
2,4'-DDD	6	Exceeded	50	150	1
2,4'-DDE	19	Fell Below	50	150	0
4,4'-DDD	13	Exceeded	50	150	7
4,4'-DDE	63	Fell Below	50	150	15
4,4'-DDT	19	Fell Below	50	150	4
Acetochlor	14	Exceeded	50	150	0
Aldrin	63	Fell Below	50	150	0
Alpha-BHC	31	Both	50	150	0
Atrazine	6	Exceeded	50	150	0
Azinphos-ethyl	71	Exceeded	50	150	0
Azinphos-methyl	69	Exceeded	50	150	0
Benefin	25	Both	50	150	0
Benthiocarb	13	Exceeded	50	150	0
Bifenthrin	14	Exceeded	50	150	16
Boscalid	71	Exceeded	50	150	0
Butachlor	14	Exceeded	50	150	0
Captan	13	Exceeded	50	150	0
Chlorothalonil	100	Fell Below	50	150	0
Chlorpropham	6	Exceeded	50	150	0
Chlorpyriphos	6	Exceeded	50	150	1
Cis-Nonachlor	6	Exceeded	50	150	0
cis-Permethrin	13	Exceeded	50	150	0
Coumaphos	75	Exceeded	50	150	0
Cyanazine	13	Exceeded	50	150	0
Cypermethrin	71	Exceeded	30	130	0
Delta-BHC	25	Exceeded	50	150	0
Diazinon	13	Exceeded	50	150	0
Dieldrin	13	Exceeded	50	150	0

Parameter name	Percentage of recoveries outside control limits (%)	Fell below or exceeded control limits	Lower control limit (%)	Upper control limit (%)	Number of detections in 2015
Diphenamid	13	Exceeded	50	150	0
Endosulfan II	19	Fell Below	50	150	0
Endrin	6	Exceeded	50	150	0
EPN	50	Exceeded	50	150	0
Ethalfluralin (Sonalan)	25	Exceeded	50	150	0
Ethion	13	Exceeded	50	150	0
Ethoprop	19	Exceeded	50	150	1
Fenamiphos	88	Exceeded	50	150	0
Fenamiphos Sulfone	71	Exceeded	50	150	0
Fenarimol	13	Exceeded	50	150	0
Fenvalerate	75	Exceeded	50	150	0
Fipronil	21	Exceeded	50	150	0
Fipronil Disulfinyl	14	Exceeded	50	150	0
Fipronil Sulfide	14	Exceeded	50	150	0
Fipronil Sulfone	14	Exceeded	50	150	0
Fluridone	88	Exceeded	50	150	1
Fonofos	13	Exceeded	50	150	0
Gamma-BHC	19	Fell Below	50	150	0
Heptachlor Epoxide	63	Fell Below	50	150	0
Hexachlorobenzene	63	Fell Below	50	150	0
Imidan	50	Fell Below	50	150	0
Kelthane	13	Exceeded	50	150	0
Malathion	6	Exceeded	50	150	0
Methidathion	13	Exceeded	50	150	0
Methoxychlor	31	Fell Below	50	150	0
Methyl Parathion	6	Exceeded	50	150	0
Metolachlor	6	Exceeded	50	150	0
Metribuzin	6	Exceeded	50	150	0
Mevinphos	13	Exceeded	50	150	0

Parameter name	Percentage of recoveries outside control limits (%)	Fell below or exceeded control limits	Lower control limit (%)	Upper control limit (%)	Number of detections in 2015
MGK264	13	Exceeded	50	150	0
Mirex	13	Fell Below	50	150	0
Monocrotophos	14	Fell Below	50	150	0
Napropamide	13	Exceeded	50	150	0
Norflurazon	13	Exceeded	50	150	0
Oryzalin	100	Fell Below	50	150	0
Oxychlordane	19	Exceeded	50	150	0
Oxyfluorfen	13	Exceeded	50	150	0
Parathion	13	Exceeded	50	150	0
Pendimethalin	13	Exceeded	50	150	0
Phenothrin	19	Exceeded	50	150	0
Phorate	13	Exceeded	50	150	0
Piperonyl Butoxide (PBO)	14	Exceeded	50	150	0
Prometon	13	Exceeded	50	150	0
Pronamide (Kerb)	13	Exceeded	50	150	0
Propachlor (Ramrod)	13	Exceeded	50	150	0
Propargite	13	Both	50	150	0
Resmethrin	50	Both	50	150	0
Simazine	6	Exceeded	50	150	0
Sulfotepp	13	Exceeded	50	150	0
Terbacil	13	Exceeded	50	150	0
Tetrahydrophthalimide	14	Exceeded	50	150	0
Tokuthion	13	Exceeded	50	150	0
Trans-Nonachlor	19	Fell Below	50	150	1
Treflan (Trifluralin)	13	Exceeded	50	150	0
Triadimefon	13	Exceeded	50	150	0
Triallate	6	Exceeded	50	150	0
Trichloronate	14	Exceeded	50	150	0
Tricyclazole	14	Exceeded	50	150	0

Quality Control Samples

Laboratory Duplicates

MEL uses laboratory split sample duplicates to ensure consistency of TOC and Solids analysis. In the the Pilot Study, there were 71 replicate pairs for Solids and 8 for TOC. None of the replicate pairs exceeded the 20% RPD criterion. For Solids, the pooled average RPD was 0.69%; the maximum RPD was 5.0%. For TOC the pooled average was 7.0%; the maximum RPD was 12%.

Laboratory Blanks

MEL uses laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. There were two instances of positive detections of 4,4'-dichlorobenzophenone in the laboratory blanks for the weeks of July 6 and July 20, 2015. There were no detections for 4,4'-Dichlorobenzophenone during the aforementioned weeks, therefore values from these weeks are accepted.

Surrogates

Surrogates are compounds spiked into field samples at the laboratory. Surrogates are used to assess recovery for a group of structurally related compounds. For instance, triphenyl phosphate is a surrogate for organophosphorus insecticides. Structurally related compounds, summary statistics, and control limits for surrogate recoveries are presented in Table 8.

All of the surrogate recoveries for this study fell within the QC limits. Consequently, no results needed to be qualified.

Table C-8: Pesticide surrogates for method SW8270D, modified for sediment

Parameter name	Structurally related compounds	Average recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Lower control limit (%)	Upper control limit (%)
1,3-Dimethyl-2-nitrobenzene	Nitrogen containing pesticides	67	33	125	30	130
4,4'-DDE-13C12	Chlorinated pesticides	55	32	107	20	117
Atrazine-D5	Chlorinated and nitrogen containing pesticides	86	41	125	45	167
Chlorpyrifos-D10	Organophosphorus pesticides	73	46	130	30	178
Decachlorobiphenyl (DCB)	Chlorinated pesticides	41	29	91	30	130
Decachlorobiphenyl (DCB)	Chlorinated pesticides	93	-	93	30	140
Trifluralin-D14	Nitrogen containing pesticides	119	49	162	26	180
Triphenyl Phosphate	Organophosphorus pesticides	59	36	119	30	130

Laboratory Control Samples

Laboratory control samples (LCS) are analyte compounds spiked into deionized water at known concentrations and subjected to extraction and analysis conditions. They are used to evaluate accuracy of pesticide residue recovery for a specific analyte. Detections may be qualified based on low recovery and/or high RPD between the paired LCS and LCSD.

Table C-9 presents the mean, minimum, and maximum percent recovery for the LCS and LCSD for three types of analysis, as well as RPD between the LCS and the paired LCSD for this study.

Table C-9: Summary statistics for LCS and LCSD Recovery and RPD, PESTMS (GC/MS) for sediment

Parameter name	Number of results	Average recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Average RPD	Min. RPD	Max. RPD
2,4'-DDD	50	71	53	120	10	0.5	28
2,4'-DDE	50	68	48	99	12	1	22
2,4'-DDT	50	86	66	134	12	1	25
4,4'-DDD	50	78	60	111	8	2	20
4,4'-DDE	50	67	50	106	10	0.6	20
4,4'-DDT	50	87	64	121	8	2	16
4,4'-Dichlorobenzophenone	48	72	51	94	8	0.8	18
Acetochlor	48	79	59	107	14	0.5	32
Alachlor	50	71	58	104	11	0.5	28
Aldrin	50	59	36	102	12	0.2	19
Alpha-BHC	50	55	9	135	13	0.6	34
Atrazine	50	68	57	116	6	1	29
Azinphos-ethyl	48	121	88	175	7	0.2	20
Azinphos-methyl	50	100	52	204	14	0.8	38
Benefin	50	118	82	161	11	0.8	27
Benthiocarb	50	81	48	102	7	1	27
Beta-BHC	50	88	54	187	12	3	47
Bifenthrin	48	90	63	116	8	0.8	16
Boscalid	48	120	78	168	9	1	20
Bromacil	50	78	53	115	11	2	26
Butachlor	48	80	63	93	10	0.9	26
Butylate	50	85	37	131	11	0.9	33
Captan	50	75	50	118	13	3	39
Chlorothalonil (Daconil)	40	17	0	48	17	3	42

Parameter name	Number of results	Average recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Average RPD	Min. RPD	Max. RPD
Chlorpropham	50	124	68	427	31	1	115
Chlorpyriphos	50	65	50	101	7	0.7	18
cis-Chlordane	50	69	49	109	9	3	22
Cis-Nonachlor	50	69	51	107	11	0.6	36
cis-Permethrin	50	93	0	144	6	0.4	12
Coumaphos	50	122	88	166	8	0.08	16
Cyanazine	50	54	16	117	8	1	22
Cycloate	48	92	0	240	20	0.6	59
Cypermethrin	48	116	82	180	18	0.1	42
Delta-BHC	50	74	21	136	12	0.02	37
Di-allate (Avadex)	2	114	102	126	20	20	20
Diazinon	50	78	59	108	10	0.1	22
Dichlobenil	50	82	40	120	13	1	24
Dieldrin	50	69	51	115	10	0.1	20
Dimethoate	50	68	0	136	16	3	30
Diphenamid	50	82	58	116	10	0.7	24
Endosulfan I	50	69	45	107	10	2	31
Endosulfan II	50	73	47	111	10	0.2	30
Endosulfan Sulfate	50	66	48	122	12	2	25
Endrin	50	79	58	120	11	2	26
Endrin Ketone	50	66	36	135	12	2	36
EPN	50	137	96	201	10	0.2	31
Eptam	50	77	36	103	13	2	26
Ethalfluralin (Sonalan)	50	126	93	176	11	3	22
Ethion	50	106	84	143	6	1	14
Ethoprop	50	91	30	136	22	0.8	93
Fenamiphos	50	189	117	258	9	0.8	20
Fenamiphos Sulfone	48	125	28	229	16	0.3	125
Fenarimol	50	96	62	133	10	2	18
Fenvalerate	50	130	99	210	6	0.1	18
Fipronil	48	97	69	153	9	0.7	18
Fipronil Disulfinyl	48	88	69	116	8	1	15
Fipronil Sulfide	48	93	66	119	8	1	19
Fipronil Sulfone	48	93	59	116	9	0.2	25
Fluridone	50	157	97	203	10	1	30
Fonofos	50	77	52	103	13	0.2	37
Gamma-BHC	50	57	40	102	12	4	25
Heptachlor	50	84	63	128	10	0.3	27
Heptachlor Epoxide	50	62	45	98	11	1	24

Parameter name	Number of results	Average recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Average RPD	Min. RPD	Max. RPD
Hexachlorobenzene	50	57	41	75	15	2	28
Hexazinone	50	71	48	101	14	2	30
Imidan	40	26	0	135	5	0.2	12
Kelthane	50	96	62	133	10	2	18
Malathion	50	56	16	137	20	3	62
Metalaxyl	50	81	56	118	17	0.8	36
Methidathion	50	69	36	132	16	0.7	42
Methoxychlor	50	96	62	129	9	0.6	20
Methyl Chlorpyrifos	48	34	5	76	14	3	40
Methyl Paraoxon	50	62	0	150	16	2	53
Methyl Parathion	50	70	35	117	16	1	50
Metolachlor	50	81	64	119	10	0.4	28
Metribuzin	50	79	52	120	11	2	25
Mevinphos	50	65	34	147	12	2	22
MGK264	50	86	66	131	8	0.3	20
Mirex	50	62	42	96	11	4	16
Molinate	48	71	47	93	13	3	23
Monocrotophos	50	70	0	144	19	0.6	89
Napropamide	50	91	63	126	8	0.5	22
Norflurazon	50	104	80	139	11	0.8	22
Oxychlordane	50	94	66	124	8	0.2	19
Oxyfluorfen	50	118	93	158	8	0.1	23
Parathion	50	116	87	142	6	0.1	15
Pebulate	50	74	34	97	15	1	59
Pendimethalin	50	97	76	126	7	0.5	15
Phenothrin	50	97	69	160	10	2	18
Phorate	50	99	66	141	15	5	28
Piperonyl Butoxide (PBO)	48	90	69	124	8	1	17
Prometon	50	85	62	129	13	5	24
Prometryn	50	77	53	104	11	2	26
Pronamide (Kerb)	50	82	63	116	9	0.1	23
Propachlor (Ramrod)	50	72	51	95	12	4	21
Propargite	50	78	53	111	18	0.5	46
Propazine	50	73	54	114	12	2	26
Resmethrin	50	84	54	177	12	4	20
Simazine	50	68	49	99	12	3	26
Simetryn	50	77	50	109	13	2	25
Sulfotepp	50	58	15	117	23	2	98

Parameter name	Number of results	Average recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Average RPD	Min. RPD	Max. RPD
Terbacil	50	90	46	136	13	0.2	49
Tetrachlorvinphos (Gardona)	50	54	22	119	11	1	25
Tetrahydrophthalimide	48	93	55	138	17	2	39
Tokuthion	50	81	63	109	8	0.09	13
trans-Chlordane	50	66	51	95	11	1	22
Trans-Nonachlor	50	65	43	88	11	0.2	23
Treflan (Trifluralin)	50	102	84	135	7	0.3	22
Triadimefon	50	80	55	109	11	4	30
Triallate	50	73	54	109	9	0.1	17
Trichloronate	48	68	50	93	10	1	23
Tricyclazole	48	91	34	125	25	2	65

The percentage of LCS and LCSD samples having recoveries that fell within the target limits for this method (PESTMS GC/MS) was 89.4%. Overall, 3.1% fell above the control limits and 7.5% fell below the control limits. The majority of the analytes, 51%, had at least one LCS result outside of the control limits.

Analytes not meeting the target recovery range and the percentage of occurrences are described in Table C-10. Table C-10 also describes the number of detections for each analyte not meeting the target recovery range. All detections that occurred within the same batch as an inadequate LCS/LCSD result were already qualified as estimates, therefore no requalification occurred.

Table C-10: Sediment LCS/LCSD parameters are not meeting criteria

Parameter name	Percentage of recoveries outside control limits (%)	Fell below or exceeded control limits	Lower control limit (%)	Upper control limit (%)	Number of detections in 2015
2,4'-DDE	4	Fell Below	50	150	0
Aldrin	28	Fell Below	50	150	0
Alpha-BHC	44	Fell Below	50	150	0
Azinphos-ethyl	12.5	Exceeded	50	150	0
Azinphos-methyl	20	Exceeded	50	150	0
Benefin	4	Exceeded	50	150	0
Benthiocarb	2	Fell Below	50	150	0
Beta-BHC	4	Exceeded	50	150	0
Boscalid	10.4	Exceeded	50	150	0
Butylate	4	Fell Below	50	150	0
Chlorothalonil (Daconil)	100	Fell Below	50	150	0

Parameter name	Percentage of recoveries outside control limits (%)	Fell below or exceeded control limits	Lower control limit (%)	Upper control limit (%)	Number of detections in 2015
Chlorpropham	12	Exceeded	50	150	0
cis-Chlordane	4	Fell Below	50	150	1
cis-Permethrin	8	Fell Below	50	150	0
Coumaphos	6	Exceeded	50	150	0
Cyanazine	36	Fell Below	50	150	0
Cycloate	41.7	Both	50	150	0
Cypermethrin	25	Exceeded	30	130	0
Delta-BHC	12	Fell Below	50	150	0
Dichlobenil	8	Fell Below	50	150	0
Dimethoate	16	Fell Below	50	150	1
Endosulfan I	4	Fell Below	50	150	0
Endosulfan II	8	Fell Below	50	150	0
Endosulfan Sulfate	8	Fell Below	50	150	0
Endrin Ketone	32	Fell Below	50	150	0
EPN	16	Exceeded	50	150	0
Eptam	12	Fell Below	50	150	0
Ethalfluralin (Sonalan)	16	Exceeded	50	150	0
Ethoprop	8	Fell Below	50	150	1
Fenamiphos	84	Exceeded	50	150	0
Fenamiphos Sulfone	31.3	Both	50	150	0
Fenvalerate	16	Exceeded	50	150	0
Fipronil	2.1	Exceeded	50	150	0
Fluridone	54	Exceeded	50	150	1
Gamma-BHC	16	Fell Below	50	150	0
Heptachlor Epoxide	8	Fell Below	50	150	0
Hexachlorobenzene	32	Fell Below	50	150	0
Hexazinone	4	Fell Below	50	150	0
Imidan	75	Fell Below	50	150	0
Malathion	36	Fell Below	50	150	0
Methidathion	16	Fell Below	50	150	0
Methyl Chlorpyrifos	66.7	Fell Below	50	150	0
Methyl Paraoxon	46	Fell Below	50	150	0
Methyl Parathion	26	Fell Below	50	150	0
Mevinphos	32	Fell Below	50	150	0
Mirex	16	Fell Below	50	150	0
Molinate	4.2	Fell Below	50	150	0
Monocrotophos	16	Fell Below	50	150	0
Oxyfluorfen	4	Exceeded	50	150	0
Pebulate	4	Fell Below	50	150	0

Parameter name	Percentage of recoveries outside control limits (%)	Fell below or exceeded control limits	Lower control limit (%)	Upper control limit (%)	Number of detections in 2015
Phenothrin	4	Exceeded	50	150	0
Resmethrin	4	Exceeded	50	150	0
Simazine	4	Fell Below	50	150	0
Sulfotepp	38	Fell Below	50	150	0
Terbacil	4	Fell Below	50	150	0
Tetrachlorvinphos (Gardona)	40	Fell Below	50	150	0
Trans-Nonachlor	8	Fell Below	50	150	1
Tricyclazole	4.2	Fell Below	50	150	0