Skagit-Samish Basin Intensive Surface Water Sampling for Pesticides in Salmon-Bearing Streams, 2009

A Cooperative Study by the Washington State Departments of Ecology and Agriculture

DEPARTMENT OF
ECOLOGY
State of Washington

August 2010

Publication No. 10-03-043

Publication and Contact Information

This report is available on the Department of Ecology's website at
www.ecy.wa.gov/biblio/1003043.html

Data for this project are available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm. Search User Study ID, DSAR0005.

The Activity Tracker Code for this study is 09-545.

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Cover photo: Skagit valley, Big Ditch waterway, and tidegates (photo by Paul Anderson).

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A Cooperative Study by the Washington State Departments of Ecology and Agriculture

by

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Waterbody Numbers:
WA-03-3100
WA-03-4000

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Abstract

In 2008, the National Oceanic Atmospheric Administration (NOAA), National Marine Fisheries Service (NMFS) released a final biological opinion on the effects of three organophosphates – chlorpyrifos, diazinon, and malathion – on endangered and threatened salmon. In the biological opinion, NMFS recommended a monitoring regime that would evaluate environmental exposure of these pesticides on salmonids. The regime included daily surface water sampling for at least three periods of seven consecutive days during the pesticide-application season.

June 5-11, 2009 results from three sampling regimes were compared: daily sampling for seven consecutive days; weekly sampling; and continuous sampling using a recently developed continuous low-level aquatic monitor (CLAM^{TM}).

Results indicate that daily sampling for a week captured more pesticides and greater variability in concentrations for selected compounds. No organophosphates were detected during the daily or weekly sampling.

This 2009 study indicates that prior knowledge of pesticide-use practices in a drainage is needed to target specific pesticides. The current regime of weekly sampling throughout the application season captures a variety of pesticides. Recommendations include continuing with this weekly regime.

The CLAM^{TM} sampling device did not pump at a consistent rate throughout the placement period. This was likely due to sediment clogging. Therefore, it was not possible to accurately quantify the concentration of pesticides detected with the CLAM^{TM}. The CLAM^{TM} did provide information on the presence or absence of selected pesticides.

Acknowledgements

The authors of this report thank the following people for their contribution to this study:

- Brent Hepner of Aqualytical Inc. for loan of the CLAM^{TM} sampling devices, training, and technical assistance.
- Jim Cowles of the Washington State Department of Agriculture for field assistance, editing, and project support.
- Brad Randall, volunteer citizen, for field assistance.
- Washington State Department of Ecology staff:
  - Michael Friese for field assistance.
  - Manchester Environmental Laboratory staff for sample processing, sample analysis, review of results, and technical assistance: Jeff Westerlund, Nancy Rosenbower, Bob Carrell, Dickey Huntamer, Kamilee Ginder, Dean Momohara, Stuart Magoon, Karin Feddersen, and others.
  - Dan Dugger for review and editing.
  - Dale Norton for review, editing, and guidance.
  - Joan LeTourneau, Gayla Lord, and Cindy Cook for formatting and editing the report.

Background

Since 2003, the Washington State Departments of Agriculture (WSDA) and Ecology (Ecology) have been conducting a monitoring study to evaluate pesticide concentrations in surface waters. The study assesses pesticide presence in salmon-bearing streams during a typical pesticide-use season. The majority of sites are monitored weekly from March through September.

Sampling is conducted in five basins:

- Thornton Creek in the Cedar-Sammamish basin representing urban land use.
- The lower Skagit-Samish basin representing western Washington agricultural practices.
- The lower Yakima basin representing irrigated agriculture.
- The Wenatchee and Entiat basins representing tree fruit agriculture.

Data from this monitoring program are used by the WSDA, the U.S. Environmental Protection Agency (EPA), the National Atmospheric and Oceanic Administration (NOAA) National Marine Fisheries Service (NMFS), and the U.S. Fish and Wildlife Service to refine exposure assessments for pesticides that are registered for use in Washington State. Understanding the fate and transport of pesticides allows regulators to assess potential effects on endangered salmon species while minimizing the economic impacts to agriculture.

Detected pesticide concentrations are evaluated against toxicity criteria used for pesticide registration under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA), EPA National Recommended Water Quality Criteria (NRWQC), and Washington State water quality standards.

NMFS Biological Opinion for Chlorpyrifos, Diazinon, and Malathion

In 2008, the NMFS released a final biological opinion (BiOp) under the authority of the section 7(a)(2) of the Endangered Species Act. The BiOp evaluated the effects of EPA's proposed registration of three pesticides, chlorpyrifos, diazinon, and malathion, on endangered species, threatened species, and critical habitat designated for those species (NMFS, 2008). While both chlorpyrifos and diazinon are no longer registered for homeowner use, all three pesticides are registered for select agricultural use.

In the BiOp, NMFS recommended a monitoring regime for chlorpyrifos, diazinon, and malathion that would evaluate their effects on salmonids. The recommendation included targeting one site in each state where juvenile salmon, listed as endangered, migrate to the Pacific Ocean. The recommended regime included daily surface water sampling for at least three periods of seven consecutive days during the pesticide application season.

The goal of this study is to compare pesticides detected during our weekly sampling regime to NMFS's recommended sample regime, seven days of consecutive sampling (intensive sampling). The more intensive sampling (seven consecutive days) occurred for only one period during the

2009 pesticide application season versus the NMFS recommended three periods. This was due to budget constraints.

CLAM™ Continuous Sample Devices

The surface water pesticide monitoring program uses a depth-integrated sampling technique, which is a snapshot in time, but a single sample event may not capture an overall picture of environmental conditions. Both point and nonpoint pollution events may be missed. Continuous sampling devices can be deployed over a longer time period increasing the likelihood of capturing pollution events. In addition, pollutants are concentrated by the continuous sampler over time, thereby indirectly lowering the detection limits.

This 2009 intensive sampling project provided an opportunity to test a recently developed inexpensive continuous sampling device, the continuous low level aquatic monitor, or CLAM™ (Figure 1). The CLAM™ uses a pre-set pump system operated at a constant rate so the extracted volume can be estimated. Aqualytical, Inc. provided Ecology with six CLAM™ devices to test during the Skagit-Samish intensive survey. Information on CLAM™ devices and collection disks are provided in Appendix B.

Figure 1. Deploying the CLAM™ device at Indian Creek Slough.

Project Description

Seven days of intensive (daily) sampling were conducted at four sites in the Skagit-Samish basin from June 5 – 11, 2009. Regularly scheduled weekly sampling was conducted on June 8, 2009. CLAM^{TM} continuous sample devices were deployed for seven consecutive days during the intensive sampling period.

Surface water grab samples were analyzed for approximately 160 currently registered and historical-use pesticides and degradates. Conventional water quality parameters were also measured to evaluate factors influencing pesticide toxicity, fate and transport, and general water quality. Conventional parameters measured include: total suspended solids (TSS), pH, conductivity, temperature, dissolved oxygen, and streamflow.

To determine if water quality concentrations meet requirements for aquatic life, monitoring data were compared to pesticide registration toxicity criteria and NRWQC, referred to as *assessment criteria*. Data were also compared to the Washington State numeric water quality standards, referred to as *water quality standards*.

Study Area

The lower Skagit-Samish basin is located in Skagit County in northwest Washington (Figure 2). Agricultural land use dominates the western portion of the basin, largely supporting cropland and pasture. The eastern uplands are predominantly forested, with some scattered residential development.

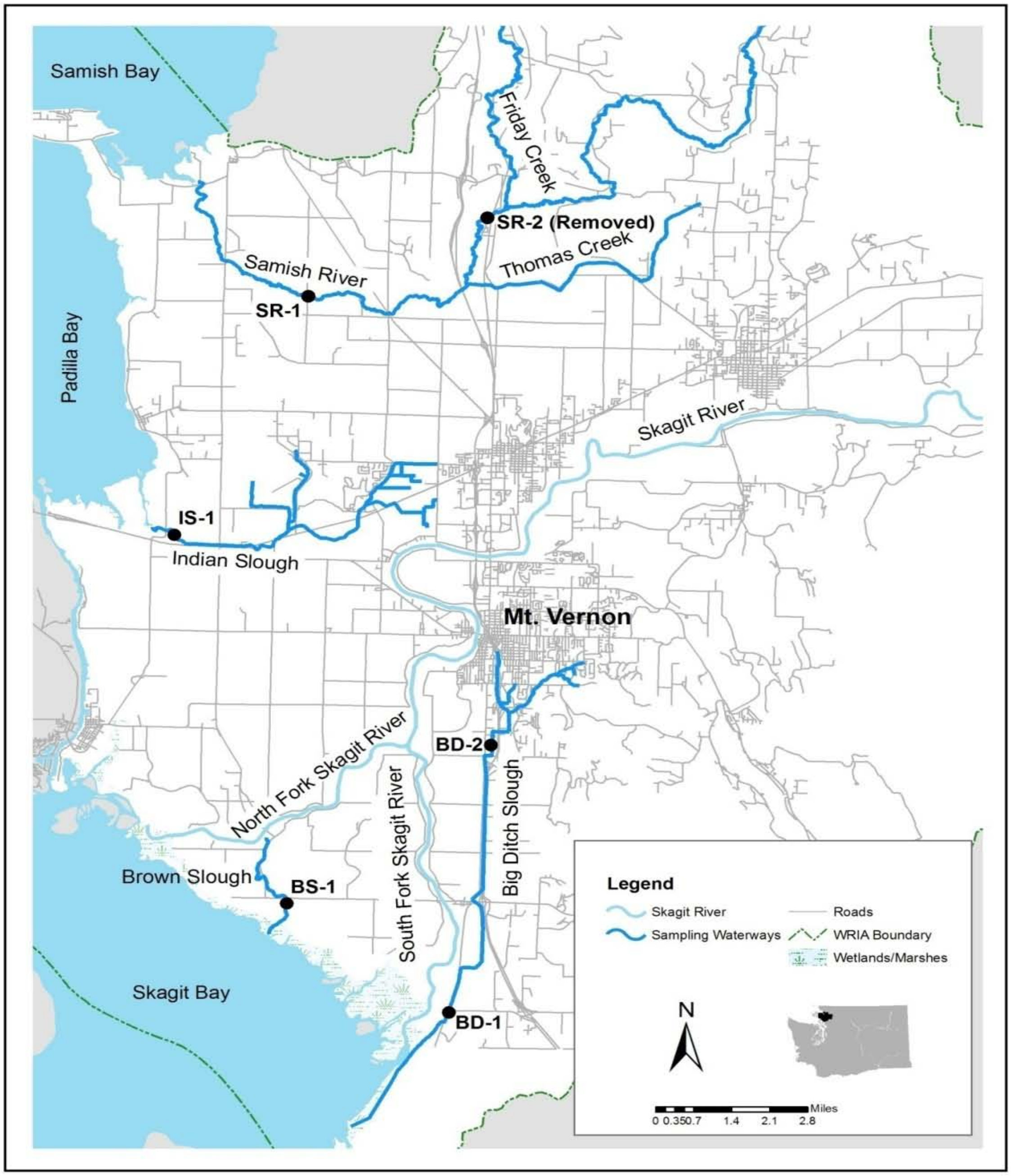

Figure 2. Sampling locations in the lower Skagit-Samish basin.

The estuarine deltas within the basin include the Samish River, sloughs draining to Padilla Bay, Swinomish Channel, North Fork Skagit River, tributaries and sloughs to the lower Skagit River and Bay, South Fork Skagit River, and Douglas Slough. Many of these estuaries are in or near lands used for agriculture. Agriculture is concentrated in the Samish delta, northeast and south Padilla Bay deltas, Skagit delta, and along parts of the Swinomish Channel. Public lands surround the lower South Fork Skagit River.

The intensity of agriculture and importance of salmon habitat make this area a good index watershed for evaluating pesticides associated with western Washington agricultural practices. Weekly monitoring during the pesticide-use season (March – September) of four drainages in the Skagit-Samish basin began in 2006 as described in Burke and Anderson (2006). Three drainages and four sites were sampled for the 2009 intensive monitoring study.

Agricultural Land Use

Each of the Skagit-Samish sites has a portion of its area in agricultural production. The most intensively cultivated subbasins are Browns Slough, Big Ditch, and Indian Slough. A full description of crop area and land-use estimates for the Skagit-Samish subbasins, as well as a description of agricultural commodities produced can be found in Sargeant et al. (2010).

Salmonid Fishery

The Skagit-Samish basin supports several Puget Sound salmonid populations (Table 1). Salmonid uses and life cycles are described in Sargeant et al. (2010).

Table 1. Salmonid presence and uses at the Skagit-Samish sample sites (Sargeant et al., 2010).

Species	Big Ditch	Browns Slough	Indian Slough	Samish River
Fall chinook	--	Presence	Presence	Presence
Coho	Rearing	Presence	Presence	Rearing
Fall chum	--	Presence	--	Presence
Pink	--	Presence	--	Presence
Sockeye	--	--	--	Rearing
Bull trout	--	--	--	Presence
Winter steelhead	--	--	--	Rearing

Climate

The climate in the lower Skagit-Samish basin is mild with cool, dry summers and mild, wet winters. The majority of annual precipitation occurs between October and March. Average annual precipitation is 32.3 inches, with the heaviest rainfall during November through January. Average precipitation and air temperature for June is 2.22 inches and 58.6°F. For several days before and during the intensive sampling (June 1-15, 2009), no precipitation occurred (WSU Ag Weather Net, 2010). Average temperatures were slightly above average for June (Table 2).

Table 2. Average, maximum, and minimum daily air temperatures for Mt. Vernon at WSU Cooperative Extension Service, June 5-11, 2009.

Date	Average	Maximum	Minimum
6/5/09	64.9°F	72.2°F	58.8°F
6/6/09	60.4°F	64.6°F	52.2°F
6/7/09	60.5°F	68.1°F	53.0°F
6/8/09	60.0°F	68.9°F	52.1°F
6/9/09	61.3°F	73.8°F	49.2°F
6/10/09	61.1°F	71.7°F	52.9°F
6/11/09	59.1°F	68.6°F	51.9°F

Study Design and Methods

Study Design

Study design and methods are described in Anderson and Sargeant (2009). With the exception of the CLAM^{TM} sampling devices, study methods and sampling procedures are the same as those described in previous reports and Quality Assurance (QA) Project Plans (Johnson and Cowles, 2003; Burke and Anderson, 2006; Burke et al., 2006; Burke and Dugger, al., 2007; Dugger et al., 2008). Table 3 describes sampling locations and type of sampling for each site.

Table 3. Sampling locations, descriptions, and type of sampling for Browns Slough (BS-1), upstream Big Ditch (BD-2), downstream Big Ditch (BD-1), and Indian Slough (IS-1).

Site	Latitude	Longitude	Location Description	CLAM^{TM}	Daily	Weekly
BS-1	48.3405	-122.4140	Downstream of the tidegate on Fir Island Road.	No	Yes	Yes
BD-2	48.3887	-122.3329	Upstream side of the bridge at Eleanor Lane.	No	Yes	Yes
BD-1	48.3086	-122.3473	Upstream side of the bridge at Milltown Road.	Yes[1]	Yes	Yes
IS-1	48.4506	-122.4651	On the upstream side of the tidegate at Bayview-Edison Road.	Yes[1]	Yes	Yes

[1] At this site, three CLAM^{TM} devices were deployed: one for pesticide GCMS analysis, one for carbamate analysis, and one as a replicate (either for pesticide GCMS or carbamate analysis).

Weekly organophosphate pesticide data collected in 2006-2008 were examined to select a time period with the maximum likelihood of detecting chlorpyrifos, malathion, or diazinon. Originally the period selected was the last two weeks in May but due to a laboratory scheduling conflict, the intensive survey was scheduled for June 5-11, 2009.

Intensive Survey Sampling

During a seven-day period, June 5-11, 2009, surface water grab samples were collected every day at four sites in the Skagit-Samish basin: Browns Slough, Indian Slough, and upper and lower Big Ditch (Table 3). Temperature, pH, conductivity, and dissolved oxygen were measured with field meters during each site visit. Grab samples were analyzed at Manchester Environmental Laboratory for TSS and over 160 pesticide and degradate compounds. A full list of analytes is presented in Appendix C, Table C-3. All sites except the upstream Big Ditch site are tidally influenced; therefore, sampling was conducted during the daily low tide.

A regularly scheduled weekly sample event occurred on June 8, 2009.

CLAM^{TM} Devices

CLAM^{TM} continuous sampling devices were deployed on June 5, 2009 at the downstream Big Ditch and Indian Slough sites. Three CLAM^{TM} devices were installed at each site: one for pesticide GCMS analysis, one for carbamate analysis, and a replicate CLAM^{TM} analysis. The replicate pesticide GCMS was deployed at Big Ditch and the replicate carbamate at Indian Slough.

Five of the CLAM^{TM} devices had water pumping rates of 10 mL/minute. One CLAM^{TM} pumped at a rate of 70 mL/ minute. The CLAM^{TM} with the higher pump rate was installed at Indian Slough as a carbamate replicate. Because of the higher pump rate, the solid phase extraction (SPE) disks for this CLAM^{TM} device were changed approximately every two days.

Field Procedures

Field procedures are defined in the QA Project Plan (Anderson and Sargeant, 2009) and in a previous QA Project Plan, QA Project Plan addendum, and the Standard Operating Procedures (SOPs) for the Pesticides in Salmonid Streams Project, referenced in: Johnson and Cowles (2003), Burke and Anderson (2006), and Anderson, (2006), respectively.

Field methods for grab sampling are a direct application or modification of United States Geologic Survey (USGS) or EPA procedures. Surface water samples were collected by hand-compositing grab samples from quarter-point transects across each stream. In situations where streamflow was vertically integrated, a one-liter transfer container was used to dip and pour water from the stream into sample containers. Otherwise samples were collected using depth integrating equipment. Sample/transfer containers were delivered pre-cleaned by the manufacturer to EPA specifications (EPA, 1990). After collection, all samples were labeled and preserved according to the QA Project Plan (Johnson and Cowles, 2003).

Temperature, pH, conductivity, and dissolved oxygen were measured in the field using Environmental Assessment (EA) Program SOPs (Swanson, 2007; Ward, 2007a, 2007b, 2007c; and Nipp, 2006). Grab dissolved oxygen samples were also obtained and analyzed by Winkler titration following EA Program protocol (Ward, 2007c). Discharge for sites was measured using a Marsh-McBirney flow meter and top-setting wading rod, as described in Ecology SOP EAP023 (Sullivan, 2007).

Laboratory Analyses

Ecology's Manchester Laboratory analyzed all pesticide and TSS samples. Laboratory methods are presented in Table 4. A list of target analytes for this study is presented in Appendix C, Table C-3. Laboratory methods are also discussed in the QA Project Plan (Anderson and Sargeant, 2009) and previous publications for the Pesticides in Salmonid Streams Project, referenced in: Johnson and Cowles (2003), Burke and Anderson (2006), and Anderson (2006).

Table 4. Summary of laboratory methods, 2006-2008.

Analyte	Analytical Methods[1]		
	Extraction	Analysis	Reference
Pesticides[2]	3510	GCMS	8270
Herbicides	8151	GCMS	8270
Carbamates	3535M	LCMS-SIM	8321 AM
Total Suspended Solids	n/a	Gravimetric	EPA 160.2

[1] All analytical methods refer to EPA SW 846, unless otherwise noted.
[2] Pesticides refer to all forms tested unless indicated otherwise.
GC: gas chromatograph.
LC: high performance liquid chromatography.
MS: mass spectrometry.
SIM: selected ion monitoring.
n/a: not applicable.

Data Quality

Performance of laboratory analyses is governed by quality assurance and quality control (QA/QC) protocols. The QA/QC protocol employs application of blanks, replicates, surrogates, laboratory control samples, and matrix spike/matrix spike duplicates (MS/MSDs). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components. A summary of laboratory and field data quality are presented below. For a detailed discussion, refer to Appendix C.

Field and laboratory data for the grab sampling analysis met QC objectives with the exception of select carbamate parameters: 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl. During 2009 an anomaly in the analytical method for carbamate pesticides was identified. This analytical anomaly caused the false positive identification of 1-naphthol, aldicarb sulfoxide, aldicarb sulfone, and oxamyl. Data for these parameters are not reported as positive detections. Although QA/QC criteria were met for all reported carbamate values, there is a possibility of some false positives.

Quantitative results from the CLAM^{TM} devices were not reliable due to inconsistent pumping rates. Pesticides detected with the CLAM ^{TM} filters are reported as present or absent, and not as a quantitative value. In addition, due to CLAM^{TM} field blank carbamate detections of carbaryl and oxamyl, detections of these parameters are rejected and not reported.

Results

This study investigated pesticide occurrence for a week (June 5-11, 2009) in Skagit-Samish salmonid-bearing streams during a high pesticide-use period. Samples were collected daily during the week. In addition, CLAM^{TM} devices were installed at two sites during this period. The following sections compare the results of the daily sampling (June 5-11), the weekly sampling (June 8), and the CLAM^{TM} devices.

Pesticides

The assessment of pesticide effects on endangered salmonid species is evaluated by comparing detected pesticide concentrations against three criteria:

- Pesticide registration toxicity and risk assessment criteria.
- EPA National Recommended Water Quality Criteria (NRWQC).
- Washington State water quality standards for the protection of aquatic life (WAC 173-201A).

The EPA and Washington State aquatic life criteria for toxic chemicals are based on evaluating the effects of a single chemical on a specific species (often non-salmonid). These criteria do not take into account the effects of multiple chemicals or pesticide mixtures on an organism.

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are described in Sargeant et al. (2010). Measured concentrations higher than criteria do not necessarily indicate that the water quality criteria have been exceeded. Numeric water quality criteria contain concentrations values and duration of exposure components that must both be compared to the measured concentrations to assess compliance with criteria.

In this report, pesticide registration toxicity, risk assessment criteria, and EPA NRWQC will be referred to as *assessment criteria*. Washington State numeric water quality standards for pesticides will be referred to as *water quality standards*. For a description of Pesticide Registration Toxicity Criteria, EPA NRWQC, Washington State water quality standards, and the numeric criteria used, refer to Appendix D.

Intensive Survey Sampling

During the June 5-11 sampling, all pesticide concentrations met *assessment criteria* and *water quality standards* for all sites sampled. Although sampling was originally set to assess organophosphate exposure, the delay in field work missed this window (when organophosphates were observed in 2006-2008).

Table 5 presents pesticide calendars for all four sites. The calendars provide a chronological overview of pesticide concentrations and detections during the study. TSS results for each day are also included. A full description of pesticide *assessment criteria* and *water quality standards* for the sites is provided in Appendix D.

Table 5. 2009 intensive survey pesticide calendars and total suspended solids (TSS) concentrations, June 5-11, 2009.

Pesticide results are in µg/L.

Date:	6/5/09	6/6/09	6/7/09	6/8/09	6/9/09	6/10/09	6/11/09
Big Ditch (upstream)							
2,4-D	0.040						
Bromacil (µg/L)	0.210	0.190	0.160	0.180	0.160	0.150	0.165
Imidacloprid (µg/L)	0.466	0.306	0.198	0.091	0.117	0.090	0.207
MCPP (µg/L)	0.016						
Metalaxyl (µg/L)	0.094	0.063					0.041
Picloram (µg/L)	0.240	0.290	0.270	0.130	0.230	0.280	0.140
Tebuthiuron (µg/L)	0.035	0.033	0.028				
TSS (mg/L)	12	15	12	11	6	7	14
Big Ditch (downstream)							
TSS (mg/L)	22	12	13	13	11.5	9	9
Indian Slough							
Bentazon (µg/L)			0.033				
Bromacil (µg/L)	0.039		0.034		0.036	0.043	
Dichlobenil (µg/L)	0.009	0.009			0.008	0.007	0.007
Hexazinone (µg/L)	0.080	0.079	0.063	0.064	0.066	0.059	0.054
Tebuthiuron (µg/L)	0.038	0.036	0.036	0.037		0.034	
TSS (mg/L)	7	7	8	6	5	6	5.5
Browns Slough							
2,4-D (µg/L)	0.023	0.043	0.092	0.051			
Atrazine (µg/L)						0.085	0.039
Bentazon (µg/L)		0.073	0.490	0.100	0.034		
Carbaryl (µg/L)						0.034	
DCPA (µg/L)	0.012	0.050	0.050		0.012		
Dicamba I (µg/L)	0.008	0.013	0.034	0.018	0.012	0.008	0.009
Dichlobenil (µg/L)				0.007	0.006		
TSS (mg/L)	5	6	8	7	6	6	5

Blank cell = no detection for that day.

CLAM^{TM} Sampling

The CLAM^{TM} sampling devices did not pump at a consistent rate throughout the placement period. Therefore, it was not possible to accurately quantify concentrations of pesticides detected with the CLAM^{TM}. The CLAM^{TM} did provide information on the presence or absence of select pesticides.

Three CLAM^{TM} devices were installed at the downstream Big Ditch site: one each for carbamate and GCMS analysis, and one for GCMS replicate analysis. The results are presented in Table 6.

Table 6. Summary of CLAM^{TM} pesticide sampling results for the downstream Big Ditch site.

Pesticide	Pesticide Type	CLAM^{TM} Result	CLAM^{TM} Replicate Result
Imidacloprid	Neonicotinoid Insecticide	detected	no replicate
Bromacil	Herbicide	detected	detected
Dichlobenil	Herbicide	detected	detected
Metolachlor	Herbicide	detected	no detection

Three CLAM^{TM} devices were installed at the Indian Slough site: one each for carbamate and GCMS pesticide analysis and one for carbamate replicate analysis. This replicate CLAM^{TM} device had a different pump rate than the other five CLAM^{TM} devices, 70 mL a minute as compared to 10 mL a minute. Because of the higher pump rate, the carbamate replicate CLAM^{TM} filter was changed out every two to three days to prevent exceeding the loading capacity of the collection disk.

Indian Slough CLAM^{TM} results are presented in Table 7.

Table 7. Summary of pesticide sampling results for the Indian Slough site.

Pesticide	Pesticide Type	CLAM^{TM} 7-days	CLAM^{TM} Replicate 2-3 days
Diazinon	Organophosphate Insecticide	detected	not sampled
Methiocarb	Carbamate Insecticide	no detection	detected
Bromacil	Herbicide	detected	not sampled
Dichlobenil	Herbicide	detected	not sampled
Diphenamid	Herbicide	detected	not sampled
Eptam	Herbicide	detected	not sampled
Hexazinone	Herbicide	detected	not sampled
Metolachlor	Herbicide	detected	not sampled
Napropamide	Herbicide	detected	not sampled
Tebuthiuron	Herbicide	detected	not sampled

Conventional Parameters

Washington State water quality standards for conventional water quality parameters are set forth in Chapter 173-201A of the WAC. Waterbodies are required to meet numeric water quality standards based on the beneficial uses of the waterbody. Conventional parameters including temperature, dissolved oxygen, and pH were measured in this study. The numeric water quality standards for temperature, dissolved oxygen, and pH for the Skagit sites sampled are described in Table 8. Browns Slough must meet marine criteria; the other three sites must meet freshwater criteria.

Table 8. Marine and freshwater water quality standards for temperature, dissolved oxygen, and pH for Salmonid Spawning, Rearing, And Migration Habitat-Primary Contact Recreation, June 5-11, 2009.

Parameter	Condition		Value
Temperature	Highest 7- DADMax[1]	Freshwater	17.5º C
		Marine	16° C
Dissolved Oxygen	Lowest 1-day minimum	Freshwater	8.0 mg/L
		Marine	6.0 mg/L
pH	Range, with a human-caused variation within the above range of <0.5 units.	Freshwater	Range within 6.5–8.5 units
		Marine	Range within 7.0-8.5 units

[1] 7-DADMax: 7-day Average of the Daily Maximum Temperatures.

Conventional water quality parameters were measured for TSS, streamflow, pH, conductivity, temperature, and dissolved oxygen. TSS values are presented in Table 5. Table 9 presents summary statistics of sampling for streamflow, pH, conductivity, and dissolved oxygen.

Table 9. Arithmetic mean and range for conventional parameters (grabs), June 5-11, 2009.

Site	Flow (cubic ft/sec)		pH (standard units)		Conductivity (µmhos/cm)		Dissolved Oxygen (mg/L)		Dissolved Oxygen (% Saturation)	
	Range	Mean[1]	Range	Mean[1]	Range	Mean[1]	Range	Mean[1]	Range	Mean[1]
Big Ditch upstream	0.82-1.14	0.97	6.9-7.1	7.0	355-404	371	6.9-9.9	8.6	74-103	93
Big Ditch downstream	17.1-29.6	21.1	7.1-9.4	8.2	46-66	61	10.3-13.8	12.4	103-146	129
Indian Slough	11.1-18.8	15.2	6.8-7.2	7.0	612-1230	800	7.2-8.2	7.6	77-90	82
Browns Slough	2.5-5.9	3.9	7.5-8.2	7.8	7860-9100	8270	8.2-13.0	10.6	99-160	126

All sites, except the downstream Big Ditch site, met the pH standard (6.5 - 8.5) during the 7-day period. The maximum pH value at the downstream Big Ditch site was 9.4. Indian Slough and the upstream Big Ditch site did not meet the dissolved oxygen standard, falling below 8.0 mg/L during the 7-day monitoring period.

The temperature standard for the Skagit-Samish sites, the 7-day average of the daily maximum temperature (7-DADMax), should not exceed 17.5° C. Continuous, 30-minute interval temperature data were collected year-round for all sites. During the 7-day sampling period, none of the sites met the 7-day average of the daily maximum temperature (should not exceed 17.5°C). The downstream Big Ditch site did not meet temperature standards on June 10-11. The rest of the sites did not meet temperature standards for any of the seven days sampled.

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Discussion

Comparison of Sampling Regimes

Three sampling methods were compared:

- Daily sampling for seven days (all sites).
- Weekly sampling for one day (all sites).
- CLAM^{TM} continuous sampling device (two sites: Big Ditch downstream and Indian Slough).

Big Ditch

Both the upstream and downstream Big Ditch sites were sampled daily for seven days. Three CLAM ^{TM} devices were installed at the downstream site. One CLAM^{TM} was designated for carbamate analysis and the other two for pesticide GCMS analysis (one was a replicate sample).

Pesticide results for the upper Big Ditch site are presented in Table 5. The weekly run captured three of the seven pesticides found during the daily sampling. The CLAM^{TM} device was not deployed at this site.

The downstream Big Ditch site had no pesticide detections for the daily and weekly sampling (Table 5). The CLAM^{TM} device detected three herbicides and the insecticide imidacloprid (Table 6).

Indian Slough

Indian Slough was sampled daily during June 5-11. Three CLAM^{TM} devices were installed at this site: one each for carbamate and GCMS pesticide analysis and one for carbamate replicate analysis.

Pesticide results for Indian Slough are presented in Table 5. The weekly run captured two of the five pesticides that were found during the daily sampling. The CLAM^{TM} device detected more pesticides than either of the other two sampling regimes (Table 7). This is not surprising since detection limits are lower for this device (greater volume of water sampled). In addition, the CLAM^{TM} detected the presence of the organophosphate, diazinon, not found during other sampling regimes.

Pesticide results for Browns Slough are presented in Table 5. The weekly run captured four of the seven pesticides found during daily sampling. The CLAM^{TM} device was not deployed at this site.

Insecticide Detections

No organophosphate insecticides were detected during the daily or weekly sample events. The CLAM^{TM} device did detect the presence of diazinon in Indian Slough. The CLAM^{TM} device filters a greater volume of water, and detection limits are lower in general.

There was only one detection of a carbamate insecticide (carbaryl) during daily sampling at Browns Slough. No carbamates were detected during the weekly sample day (June 8). The CLAM^{TM} detected the presence of one carbamate insecticide at downstream Big Ditch and Indian Slough.

Imidacloprid, a neonicotinoid insecticide, was detected in both the daily and weekly sampling at the upstream Big Ditch site. The presence of imidacloprid was also found using the CLAM^{TM} sampler at the downstream Big Ditch site. At the upstream Big Ditch site, imidacloprid has been detected frequently throughout the sampling season since it was added as an analytical parameter in 2008 (Sargeant et al., 2010).

Pesticide Concentrations

In general, daily sampling captured more pesticides and at higher concentrations than the one-day weekly sample event. Some of the differences in pesticide concentrations seen throughout the week are due to data quality fluctuations or normal variability in method accuracy. Field replicate sampling measures these data quality fluctuations, or accuracy of results. A full discussion of quality assurance is described in Appendix C.

To determine if variation in pesticide concentrations is due to normal variability in method accuracy, or due to actual differences in environmental concentrations, variation in accuracy was compared to concentration variation throughout the week (Table 10). Table 10 presents variation in the daily sample results for the week, replicate sampling variation for this 2009 study, replicate sampling variation for the 2006-2008 results, and maximum variation for the 2006-2008 results (Sargeant et al., 2010).

Table 10 shows that for some pesticide concentrations, the daily fluctuation during the week is likely due to variability in method accuracy. The sites and parameters where concentration variation is likely due to method accuracy are *not* shaded in Table 10. For the sites and parameters that are shaded, concentration variation is likely due to environmental variability.

Higher pesticide values were found in the daily sampling for imidacloprid, metalaxyl, and picloram at upper Big Ditch. In Browns Slough, higher values were captured with daily sampling for the herbicides 2,4-D, atrazine, bentazon, DCPA, and dicamba I (Table 10) These values were missed during weekly sampling.

Dugger et al. (2008) found during a similar, but more in-depth, study in Marion Drain in the lower Yakima basin that weekly sampling detected the majority of pesticides found in the daily sampling. In addition, weekly sampling was effective at estimating the median pesticide concentrations detected in the daily results. Weekly sampling failed to detect some isolated peaks in concentration and some rarely detected compounds found in the daily samples.

Table 10. Comparison of daily sample variation in pesticide concentrations to the variations in replicate accuracy.

Pesticide	Weekly Sample Variation (% RSD)	Number of Detections	Intensive 2009 Study Average Replicate Sample Variation (%RSD)	2006-2008 Study Average Replicate Sample Variation (%RSD)	2006-2008 Study Maximum Replicate Sample Variation (%RSD)
Big Ditch (upstream)					
2,4-D	-	1	6%	8% (n=23)	30%
Bromacil	12%	7	13%	6% (n=7)	11%
Imidacloprid	65%	7	4%	0% (n=1)	0%
MCPP	-	1	no data	9% (n=5)	20%
Metalaxyl	40%	3	19%	8% (n=2)	13%
Picloram	29%	7	no data	8% (n=5)	17%
Tebuthiuron	11%	3	4%	7% (n=6)	13%
Indian Slough					
Bentazon	-	1	no data	5% (n=16)	30%
Bromacil	10%	4	13%	6% (n=7)	13%
Dichlobenil	13%	5	no data	11% (n=11)	15%
Hexazinone	15%	7	12%	no data	12%
Tebuthiuron	4%	5	4%	7% (n=6)	30%
Browns Slough					
2,4-D	55%	4	6%	8% (n=23)	30%
Atrazine	52%	2	no data	2% (n=14)	13%
Bentazon	122%	4	no data	5% (n=16)	15%
Carbaryl	-	1	no data	9% (n=2)	12%
DCPA	71%	4	no data	12% (n=5)	30%
Dicamba I	64%	7	16%	6% (n=11)	20%
Dichlobenil	11%	2	no data	11% (n=11)	49%

RSD = relative standard deviation.

Number of Sampling Events

Under the current sampling regime, weekly sampling occurs approximately 27 times, once a week during the pesticide-use season (early March through September). Daily sampling for a one week period three times during the pesticide-use period would be 21 sample events. Using the daily sampling approach would be a savings in resources and laboratory costs.

Sample Timing

If the sampling regime consisted of daily surface water sampling for three periods of seven consecutive days during the pesticide-application season, sample timing would be very important. The sampling weeks would need to occur during the greatest insecticide-use period.

Time periods of insecticide detections and maximum concentrations can vary; this could make choosing three one-week periods for sampling difficult. During 2006-2008, chlorpyrifos levels at the Skagit-Samish sites did not meet (exceeded) the chronic freshwater Washington State water quality standard in February, March, April, May, and June. Diazinon levels exceeded EPA's chronic NRWQC in May and June. As described in Sargeant et al. (2010), the major factor in pesticide detections is season of the year and timing of application for specific crops.

Figure 3 presents the number of organophosphate and carbamate insecticides detected for each week of the sample season for the Skagit-Samish sites. Monitoring results from 2003-2008 are available through Ecology's Environmental Information Management (EIM) system, www.ecy.wa.gov/eim/. The number of detections generally increase through the sample season, peaking the third week in May then declining thereafter. This is a general pattern for the Skagit-Samish. Individual sites show more variability, with the highest insecticide detections occurring March through May. This pattern also may vary from year to year.

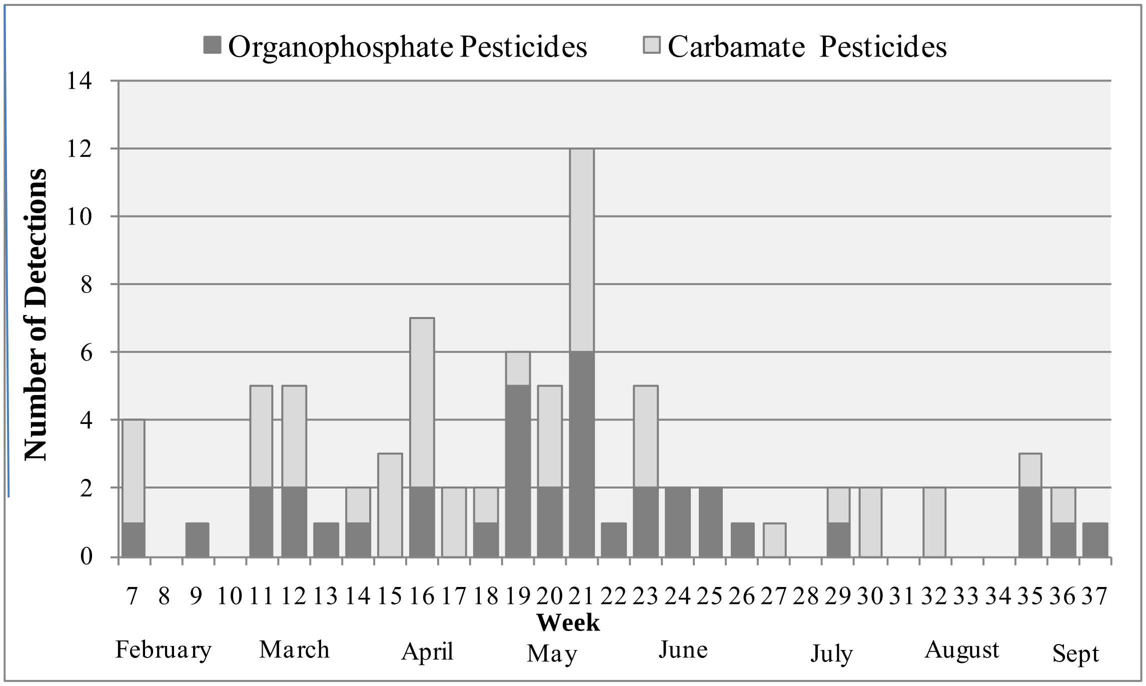

Figure 3. Organophosphate and carbamate insecticide detections per week for the Skagit-Samish sites, 2006-2009.

Conclusions

Sampling Regime

During this 2009 study, daily sampling for a one-week period was tested. Daily surface water sampling for three periods of seven consecutive days during the pesticide-application season is more economical, in terms of resources and laboratory costs, than the current weekly sampling regime.

It is difficult to predict the three weeks during the year when specific pesticides and maximum concentrations will be found. Sampling started one week late (June 5-11, 2009) and missed the window for capturing organophosphate usage. This study illustrates that without prior knowledge of the pesticide-use practices in a drainage, targeting specific compounds of interest can be problematic.

The current weekly sampling regime allows Ecology and WSDA to assess a wide variety of pesticides over a longer period (March-September). Sampling for three periods of seven consecutive days may be suitable for select study purposes. But, the focus of the Pesticides in Salmonid-Bearing Streams project includes different types of pesticides that are applied during different periods. The current weekly sampling regime allows for this broader-scale approach.

CLAM^{TM} Devices

The CLAM^{TM} sampling devices detected more pesticides than either the daily or weekly sampling. All of the pesticides detected with the CLAM^{TM} device were routinely found at the Skagit-Samish sites (Sargeant et al., 2010).

Unfortunately the CLAM^{TM} device did not pump at a consistent rate throughout the placement period. Because of this, it was not possible to accurately quantify the concentration of pesticides detected with the CLAM^{TM} device. The CLAM^{TM} device did provide information on the presence or absence of selected pesticides.

Inaccuracy in pump rates could be due to the length of time the CLAM^{TM} devices were deployed; previously these devices had been deployed for shorter periods. Likely the major factor for this inaccuracy was that water in both Big Ditch and Indian Slough is high in suspended solids.

Recommendations

The results of this study support the following conclusions.

- Continue with the weekly sample regime throughout the pesticide-use season (March through September).
- Perform additional field testing of the CLAM^{TM} devices before use in a monitoring project. Testing should include sites with lower suspended sediment, and pump rates should be checked daily during field testing. Testing also should include additional field blank analysis.

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Appendices

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Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Carbamate insecticide: N-methyl carbamate insecticides are similar to organophosphate insecticides in that they are nerve agents that inhibit cholinesterase enzymes. However they differ in action from the organophosphate compounds in that the inhibitory effect on cholinesterase is brief.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Degradate: Pesticide breakdown product.

Dissolved oxygen: A measure of the amount of oxygen dissolved in water.

Exceeded criteria: Did not meet criteria.

Grab sample: A discrete sample from the water column.

Nonpoint source: Unconfined and diffuse sources of contamination. Pollution that enters water from dispersed land-based or water-based activities. This includes, but is not limited to, atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the National Pollutant Discharge Elimination System program.

Organophosphate pesticide: Organophosphate pesticides are derived from phosphoric acid and are highly neurotoxic, typically inhibiting cholinesterase.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

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

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Source of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Salmonid: Any fish that belong to the family *Salmonidae*. Basically, any species of salmon, trout, or char. www.fws.gov/le/ImpExp/FactSheetSalmonids.htm

Total suspended solids (TSS): The suspended particulate matter in a water sample as retained by a filter.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

7-DADMax or 7-day average of the daily maximum temperatures: The arithmetic average of seven consecutive measures of daily maximum temperatures. The 7-DADMax for any individual day is calculated by averaging that day's daily maximum temperature with the daily maximum temperatures of the three days prior and the three days after that date.

Acronyms and Abbreviations

BiOp	Biological opinion
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
GC	Gas chromatograph
GCMS	Gas chromatograph coupled with mass spectrometer
LCMS	Liquid chromatograph coupled with mass spectrometer
LCMS-SIM	Liquid chromatograph coupled with mass spectrometer, selected ion monitoring
LPQL	Lower practical quantitation limit
MS/MSD	Matrix spike/matrix spike duplicate
n	Number
NRWQC	National Recommended Water Quality Criteria (EPA)
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference

RSD	Relative standard deviation
SOP	Standard operating procedure
SPE	Solid-phase extraction
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area
WSDA	Washington State Department of Agriculture
7-DADMax	(See Glossary above)

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mg	milligrams
mg/L	milligrams per liter (parts per million)
mL	milliliters
mm	millimeters
psu	practical salinity units
s.u.	standard units
µg/g	micrograms per gram (parts per million)
ug/Kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
µm	micrometer
umhos/cm	micromhos per centimeter
µs	microsiemens per centimeter
µS/cm	microsiemens per centimeter, a unit of conductivity

Appendix B. Information on CLAM™ Collection Disks

H2O-Phobic DVB by J.T. Baker

The H2O-Phobic DVB disk was designed by J.T. Baker for use in solid-phase extraction (SPE) in the laboratory. Prior to use, the H2O-Phobic DVB requires laboratory conditioning. Sorbent media in the disk is effective with a wide range of analytes, ranging from slightly polar to non-polar (Mallinckrodt Baker, 2009). H2O-Phobic DVB disk can handle dirty samples while maintaining high speed laminar flow, which makes it a good choice for environmental samples.

H2O-Phobic DVB disks are made from a patented microparticulate sorbent that is packed between two screens and two filters (Mallinckrodt Baker, 2009). The configuration maximizes laminar flow, capacity, adsorption, speed, and resists clogging.

For this 2009 study the H2O-Phobic DVB disk will be used for collection of a wide range of pesticides and herbicides. After being used in the field in conjunction with the CLAM™, the H2O-Phobic DVB disk will be extracted using EPA Method 3535 (EPA, 2004). The H2O-Phobic DVB is currently in use by Manchester Environmental Laboratory to extract water samples, collected in the field, for analysis by GC/MS. After extraction, samples will be analyzed using EPA Method 8270 (EPA, 1998).

Oasis® HLB Disk by Waters

The Oasis® Hydrophobic-Lipophilic-Balanced (HLB) disk was designed by Waters for use in SPE in the laboratory. The Oasis® HLB disk requires little to no laboratory conditioning prior to use, and does not dry out when air is drawn through. The sorbent media in the disk is effective with a large range of analytes, especially polar compounds (Waters, 2009). The Oasis® HLB disk can handle large sample volumes and has increased capacity for dirty samples, making it ideal for environmental samples.

The Oasis® HLB disk is made from a specific ratio of two monomers, hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene (Waters, 2009). This combination of two monomers provides a large reverse-phase capacity for improved retention of polar analytes.

For this 2009 study, the Oasis HLB disk will be used for collection of carbamates. After its use in the field with the CLAM™, the Oasis® HLB disk will be extracted using EPA Method 3535 (EPA, 2004). The Oasis® HLB disk is currently in use by Manchester Laboratory to extract water samples, collected in the field, for analysis using the LCMS. After extraction, samples will be analyzed using EPA Method 8321A (EPA, 1996).

Appendix C. Quality Assurance

Data may be qualified if one or more performance measures are not met (exceeded). Manchester Laboratory qualifies data based on National Functional Guidelines for Organic Data Review (EPA, 1999, 2007). Definitions of data qualifiers are in Table C-1.

Table C-1. Data qualification.

Qualifier	Definition
	Blank; the analyte was detected at the reported concentration. Data are not qualified.
E	Reported result is an estimate because it exceeds 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, 1999, 2007.

Performance measures for QA/QC are in Table C-2. Data that does not meet performance measures may be approved for use by the project manager, but these data will be qualified appropriately. Lowest concentrations of interest for surface water grab samples are below reporting limits. Detections quantified below reporting limits are qualified as estimates.

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

Analysis Method[1]	Analysis[2]	Field/Lab Replicates, MS/MSD[3], and Lab. Control Samples	MS/MSD[3], Surrogates and Lab. Control Samples
		RPD[4]	% Recovery
GCMS	Pesticide-Cl	±40	30-130
	Pesticide-N	±40	30-130
	Pesticide-OP	±40	30-130
	Pesticide-Py	±40	30-130
GCMS-H	Herbicides	±50	40-130
LCMS	Pesticide-C	±40	50-150
TSS	TSS	±20	80-120
TOC	TOC	±20	80-120
DOC	DOC	±20	80-120

[1] GCMS = Gas chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8270M.
GCMS-H = Derivitizable acid herbicides by GCMS, EPA method (modified) SW 846 3535M/8270M.
LCMS = Liquid chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8321AM.
TSS = Total suspended solids, EPA method 2540D.
TOC, DOC = Total and Dissolved Organic Carbon, EPA method 415.1.

[2] Cl=chlorinated, N=nitrogen containing, OP=organophosphorus, Py=pyrethroid, C=carbamate.

[3] MS/MSD = Matrix spike and matrix spike duplicate.

[4] RPD = Relative percent difference.

Lower Practical Quantitation Limits

Lower practical quantitation limits (LPQLs) are the limits at which laboratories may report data without classifying the concentration as an estimate below the lowest calibration standard. The LPQL is determined by averaging the lower reporting values, per analyte, for all batches over each study period. The LPQL has been determined for the 2009 study period, not just for the week of the intensive survey (June 5-11, 2009). LPQL data are presented in Table C-3.

Table C-3. Target analytes and mean performance lower practical quantitation limits (µg/L).

Pesticides	[1]Use	Parent	[2]Analysis Method	LPQL[3]			
				2006	2007	2008	2009
1-Naphthol	D-C		LCMS	0.065	0.051	0.053	n/a
2,3,4,5-Tetrachlorophenol	D-WP		GCMS-H	0.080	0.062	0.063	0.063
2,3,4,6-Tetrachlorophenol	D-WP		GCMS-H	0.080	0.062	0.063	0.063
2,4,5-T	H		GCMS-H	0.080	0.062	0.063	0.063
2,4,5-TP	H		GCMS-H	0.080	0.062	0.063	0.063
2,4,5-Trichlorophenol	F		GCMS-H	0.080	0.062	0.063	0.063
2,4,6-Trichlorophenol	F		GCMS-H	0.080	0.062	0.063	0.063
2,4-D	H		GCMS-H	0.080	0.062	0.063	0.063
2,4-DB	H		GCMS-H	0.080	0.062	0.063	0.063
2,4'-DDD	D-OC	DDT	GCMS	0.032	0.033	0.033	0.033
2,4'-DDE	D-OC	DDT	GCMS	0.032	0.033	0.033	0.033

Pesticides	[1]Use	Parent	[2]Analysis Method	LPQL[3]			
				2006	2007	2008	2009
2,4'-DDT	D-OC	DDT	GCMS	0.032	0.033	0.033	0.033
3,5-Dichlorobenzoic Acid	H		GCMS-H	0.080	0.062	0.063	0.063
3-Hydroxycarbofuran	D-C	Carbofuran	LCMS	0.063	0.040	0.050	0.050
4,4'-DDD	D-OC	DDT	GCMS	0.032	0.033	0.033	0.033
4,4'-DDE	D-OC	DDT	GCMS	0.032	0.033	0.033	0.033
4,4'-DDT	I-OC		GCMS	0.032	0.033	0.033	0.033
4,4'-Dichlorobenzophenone	D		GCMS				0.101
4-Nitrophenol	D-H		GCMS-H	0.080	0.062	0.063	0.063
Acephate	I-OP		GCMS	0.032			
Acetochlor	H		GCMS				0.101
Acifluorfen	H		GCMS-H	0.080	0.062	0.063	0.063
Alachlor	H		GCMS	0.032	0.033	0.033	0.033
Aldicarb	I-C		LCMS	0.063	0.074	0.100	0.100
Aldicarb Sulfone	D-C	Aldicarb	LCMS	0.094	0.060	0.050	n/a
Aldicarb Sulfoxide	D-C	Aldicarb	LCMS	0.070	0.017	0.020	n/a
Aldrin	I-OC		GCMS	0.032	0.033	0.033	0.033
Alpha-BHC	I-OC		GCMS	0.032	0.033	0.033	0.033
Atrazine	H		GCMS	0.032	0.033	0.033	0.033
Azinphos Ethyl	I-OP		GCMS	0.032	0.033	0.033	0.033
Azinphos Methyl	I-OP		GCMS	0.032	0.033	0.033	0.049
Benefin	H		GCMS	0.032	0.033	0.033	0.033
Bensulide	H		GCMS	0.032	0.033	0.033	
Bentazon	H		GCMS-H	0.080	0.062	0.063	0.063
Benthiocarb	H-C		GCMS		0.099	0.100	0.101
Beta-BHC	I-OC		GCMS	0.032	0.033	0.033	0.033
Beta-Cypermethrin	I-Py		GCMS				0.101
Bifenthrin	I-Py		GCMS				0.101
Bromacil	H		GCMS	0.032	0.034	0.033	0.033
Bromoxynil	H		GCMS-H	0.080	0.062	0.063	0.063
Butachlor	H		GCMS				0.304
Butylate	H		GCMS	0.032	0.033	0.033	0.033
Captan	F		GCMS	0.032	0.033	0.033	0.033
Carbaryl	I-C		LCMS	0.054	0.017	0.020	0.020
Carbofuran	I-C		LCMS	0.063	0.017	0.020	0.020
Carboxin	F		GCMS	0.032	0.033	0.034	0.043
Chlorothalonil	F		GCMS	0.032	0.033	0.033	0.033
Chlorpropham	H		GCMS	0.032	0.033	0.033	0.033
Chlorpyrifos	I-OP		GCMS	0.032	0.033	0.033	0.033
Chlorpyrifos O.A.	D-OP		GCMS				0.101
Cis-Chlordane	I-OC		GCMS	0.032	0.033	0.033	0.033

Pesticides	[1]Use	Parent	[2]Analysis Method	LPQL[3]			
				2006	2007	2008	2009
Cis-Nonachlor	I-OC		GCMS	0.032	0.033	0.033	0.051
cis-Permethrin	I-Py		GCMS		0.050	0.050	0.051
Clopyralid	H		GCMS-H		0.062	0.063	0.063
Coumaphos	I-OP		GCMS	0.032	0.033	0.033	0.051
Cyanazine	H		GCMS	0.032	0.033	0.033	0.033
Cycloate	H		GCMS	0.032	0.033	0.033	0.033
DCPA	H		GCMS				0.051
DCPA	H		GCMS-H	0.080	0.062	0.063	0.063
DDVP	I-OP		GCMS		0.059	0.050	0.051
Delta-BHC	I-OC		GCMS	0.032	0.033	0.033	0.033
Deltamethrin	I-Py		GCMS		0.099	0.100	0.101
Diallate	H		GCMS	0.032	0.033	0.033	0.033
Diazinon	I-OP		GCMS	0.032	0.033	0.033	0.033
Diazoxon	D-OP	Diazinon	GCMS				0.101
Dicamba I	H		GCMS-H	0.080	0.062	0.063	0.063
Dichlobenil	H		GCMS	0.032	0.033	0.033	0.028
Dichlorprop	H		GCMS-H	0.080	0.062	0.063	0.063
Diclofop-Methyl	H		GCMS-H	0.080	0.062	0.063	0.063
Dieldrin	I-OC		GCMS	0.080	0.050	0.050	0.051
Dimethoate	I-OP		GCMS	0.032	0.033	0.033	0.033
Dinoseb	H		GCMS-H	0.080	0.062	0.063	0.063
Dioxocarb	I-C		LCMS		0.050		
Diphenamid	H		GCMS	0.032	0.033	0.033	0.033
Disulfoton	I-OP		GCMS	0.032	0.033	0.052	0.111
Disulfoton Sulfone	I-OP		GCMS		0.099	0.100	0.100
Disulfoton Sulfoxide	D-OP		GCMS				0.132
Diuron	H		GCMS	0.032	0.060	0.050	0.057
Diuron	H		LCMS	0.055			
Endosulfan I	I-OC		GCMS	0.080	0.050	0.050	0.050
Endosulfan II	I-OC		GCMS	0.080	0.050	0.050	0.051
Endosulfan Sulfate	D-OC	Endosulfan	GCMS	0.032	0.033	0.033	0.033
Endrin	I-OC		GCMS	0.080	0.050	0.050	0.051
Endrin Aldehyde	D-OC	Endrin	GCMS	0.080	0.050	0.050	0.051
Endrin Ketone	D-OC	Endrin	GCMS	0.032	0.033	0.033	0.033
EPN	I-OP		GCMS	0.032	0.033	0.033	0.033
Eptam	H		GCMS	0.032	0.033	0.033	0.033
Ethalfluralin	H		GCMS	0.032	0.033	0.033	0.033
Ethion	I-OP		GCMS	0.032	0.033	0.033	0.033
Ethoprop	I-OP		GCMS	0.032	0.033	0.033	0.033
Fenamiphos	I-OP		GCMS	0.032	0.033	0.033	0.039

Pesticides	[1]Use	Parent	[2]Analysis Method	LPQL[3]			
				2006	2007	2008	2009
Fenamiphos Sulfone	D-OP		GCMS				0.101
Fenarimol	F		GCMS	0.032	0.033	0.033	0.033
Fensulfothion	I-OP		GCMS			0.033	0.033
Fenthion	I-OP		GCMS			0.048	0.033
Fenvalerate (2 isomers)	I-Py		GCMS	0.032	0.033	0.033	0.033
Fipronil	I-Pyra		GCMS				0.101
Fipronil Desulfinyl	D-Pyra		GCMS				0.101
Fipronil Sulfide	D-Pyra		GCMS				0.100
Fipronil Sulfone	D-Pyra		GCMS				0.101
Fluridone	H		GCMS	0.065	0.099	0.100	0.101
Fonofos	I-OP		GCMS	0.032	0.033	0.033	0.033
Heptachlor	I-OC		GCMS	0.032	0.033	0.033	0.033
Heptachlor Epoxide	D-OC	Heptachlor	GCMS	0.032	0.033	0.033	0.033
Hexachlorobenzene	F		GCMS	0.032	0.033	0.034	0.033
Hexazinone	H		GCMS	0.080	0.050	0.050	0.051
Imidacloprid	I-N		LCMS			0.020	0.020
Imidan	I-OP		GCMS		0.033	0.033	0.033
Ioxynil	H		GCMS-H	0.080	0.062	0.063	0.063
Kelthane	I-OC		GCMS	0.321	0.295	0.314	0.303
Lambda-Cyhalothrin	I-Py		GCMS				0.101
Lindane	I-OC		GCMS	0.032	0.033	0.033	0.033
Linuron	H		GCMS	0.064	0.059	0.050	0.051
Malathion	I-OP		GCMS	0.032	0.033	0.033	0.033
MCPA	H		GCMS-H	0.080	0.062	0.063	0.063
MCPP	H		GCMS-H	0.080	0.062	0.063	0.063
Metalaxyl	F		GCMS	0.032	0.033	0.033	0.033
Methamidophos	I-OP		GCMS	0.032			
Methidathion	I-OP		GCMS	0.321	0.295	0.293	0.303
Methiocarb	I-C		LCMS	0.100	0.017	0.020	0.020
Methomyl	I-C		LCMS	0.055	0.037	0.050	0.050
Methomyl oxime	D-C	Thiodicarb	LCMS	0.067	0.017	0.020	0.020
Methoxychlor	I-OC		GCMS	0.032	0.033	0.033	0.051
Methyl Chlorpyrifos	I-OP		GCMS	0.032	0.033	0.033	0.033
Methyl Paraoxon	D-OP	Methyl parathion	GCMS		0.099	0.100	0.101
Methyl Parathion	I-OP		GCMS	0.032	0.033	0.033	0.033
Metolachlor	H		GCMS	0.032	0.033	0.033	0.033
Metribuzin	H		GCMS	0.032	0.033	0.033	0.033
Mevinphos	I-OP		GCMS		0.050	0.050	0.051
MGK264	Sy-I		GCMS	0.032	0.033	0.033	0.051
Mirex	I-OC		GCMS	0.032	0.033	0.033	0.036

Pesticides	[1]Use	Parent	[2]Analysis Method	LPQL[3]			
				2006	2007	2008	2009
Monocrotophos	I-OP		GCMS		0.050	0.050	0.051
Naled	I-OP		GCMS	0.032	0.042	0.059	0.035
Napropamide	H		GCMS	0.080	0.050	0.050	0.051
Norflurazon	H		GCMS	0.032	0.033	0.033	0.033
Oryzalin	H		GCMS		0.099	0.100	0.112
Oxamyl	I-C		LCMS	0.072	0.042	0.050	n\a
Oxamyl oxime	D-C	Oxamyl	LCMS	0.091	0.017	0.020	0.020
Oxychlordane	D-OC	Chlordane	GCMS	0.032	0.033	0.033	0.033
Oxyfluorfen	H		GCMS	0.032	0.033	0.033	0.100
Parathion	I-OP		GCMS	0.032	0.033	0.033	0.033
Pebulate	H		GCMS	0.032	0.033	0.033	0.033
Pendimethalin	H		GCMS	0.032	0.033	0.033	0.034
Pentachlorophenol	WP		GCMS-H	0.080	0.062	0.063	0.063
Phenothrin	I-Py		GCMS	0.032	0.033	0.033	0.033
Phorate	I-OP		GCMS	0.321	0.296	0.299	0.289
Phorate O.A.	I-OP		GCMS				0.185
Phosmet	I-OP		GCMS	0.032			
Phosmet O.A.	D-OP		GCMS				0.103
Picloram	H		GCMS-H	0.080	0.062	0.063	0.064
Piperonyl Butoxide	Sy		GCMS				0.100
Promecarb	I-C		LCMS	0.100	0.031	0.020	0.020
Prometon	H		GCMS	0.032	0.033	0.033	0.033
Prometryn	H		GCMS	0.032	0.033	0.033	0.033
Pronamide	H		GCMS	0.032	0.033	0.033	0.033
Propachlor	H		GCMS	0.032	0.033	0.033	0.033
Propargite	I-SE		GCMS	0.032	0.033	0.033	0.051
Propazine	H		GCMS	0.032	0.033	0.033	0.033
Propoxur	I-C		LCMS	0.054	0.040	0.050	0.050
Prothiofos	I-OP		GCMS				0.100
Resmethrin	I-Py		GCMS	0.065	0.050	0.050	0.035
Simazine	H		GCMS	0.032	0.033	0.033	0.033
Simetryn	H		GCMS		0.099	0.100	0.101
Sulfotepp	I-OP		GCMS	0.032	0.033	0.033	0.033
Sulprofos	I-OP		GCMS			0.033	
Tebuthiuron	H		GCMS	0.041	0.033	0.033	0.033
Terbacil	H		GCMS	0.032	0.033	0.033	0.033
Tetrachlorvinphos	I-OP		GCMS		0.050	0.050	0.051
Thiodicarb	I-C		LCMS			0.020	0.100
Tokuthion	I-OP		GCMS		0.050	0.050	
Tralomethrin	I-Py		GCMS		0.099	0.100	0.101

Pesticides	[1]Use	Parent	[2]Analysis Method	LPQL[3]			
				2006	2007	2008	2009
Trans-Chlordane	I-OP		GCMS	0.032	0.033	0.033	0.033
Trans-Nonachlor	I-OC		GCMS	0.032	0.033	0.033	0.051
Trans-Permethrin	I-Py		GCMS				0.101
Triadimefon	F		GCMS	0.032	0.033	0.033	0.033
Triallate	H		GCMS	0.032	0.033	0.033	0.033
Trichloronat	I-OP		GCMS		0.050	0.050	0.050
Triclopyr	H		GCMS-H	0.080	0.062	0.063	0.063
Tricyclazole	F		GCMS				0.101
Trifluralin	H		GCMS	0.032	0.033	0.033	0.033

[1] C = Carbamate, D = Degradate, F=Fungicide, I = Insecticide, H = Herbicide, OC = Organochlorine, OP = Organophosphorus, Py = Pyrethroid, SE = Sulfite Ester, Sy = Synergist, WP = Wood Preservative.
[2] GCMS = Gas chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8270M.
GCMS-H = Derivitizable acid herbicides by GCMS, EPA method (modified) SW 846 3535M/8270M.
LCMS = Liquid chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8321AM.
[3] Blank cells indicate no analysis for the compound in that year.

Quality Assurance Samples

Performance of laboratory analyses is governed by QA/QC protocols. The QA/QC protocol employs application of blanks, replicates, surrogates, laboratory control samples, and matrix spike/matrix spike duplicates (MS/MSD). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components. Results for each QA sample method are outlined in the sections below.

Field and laboratory data for the grab sampling analysis met QC objectives with the exception of select carbamate parameters: 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl. During 2009 an anomaly in the analytical method for carbamate pesticides was identified. This analytical anomaly caused the false positive identification of 1-naphthol, aldicarb sulfoxide, aldicarb sulfone, and oxamyl. Data for these parameters are not reported as positive detections.

Laboratory and Field Data Quality for Daily and Weekly Grab Sampling

Laboratory Blanks

During the intensive daily survey (June 5-11, 2009), there were no target analytes detected in the laboratory blanks for the pesticide GC/MS, the herbicide GC/MS, or the LCMS-SIM carbamate analysis.

Field Blanks

Field blank detections indicate the potential for sample contamination in the field and laboratory and the potential for false detections due to analytical error. During the intensive survey, there were a minimum of three field blanks obtained for each type of laboratory analysis. No field blank contamination was detected for the pesticide GCMS, herbicide, TSS, or carbamate analysis.

Field Replicate Results

Replicate sampling tests the reproducibility or precision of sampling results. Field replicate sampling frequency for the grab sampling was 14% for TSS and carbamates (four replicates) and 11% for herbicides and pesticide GCMS analysis (three replicates).

Precision between replicate pairs was calculated using percent relative standard deviation (% RSD). The % RSD is calculated by dividing the standard deviation of two or more values by their mean, then multiplying by 100 for a percent value.

For TSS, the average % RSD was 10.6, with a maximum of 23.6%.

There are 11 pesticides included in the carbamate analysis (not including 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl); 25 compounds are included in the herbicide analysis, and 128 compounds in the pesticide GCMS analysis.

Table C-4 presents the field replicate results for consistently identified field replicates (at least one pesticide was detected in either the sample or replicate). For most compounds, no detections were observed in the sample or field replicate.

The average RSD for detected compounds was:

- Carbamates 4.0% (3 pairs).
- Herbicides 10.9% (2 pairs).
- Pesticide GCMS 10.1% (9 pairs).

Replicate results met QA objectives for the project.

Table C-4. Pesticide field replicate pairs where one of the pairs was a positive detection.

Chemical	Date	Sample Results (µg/L)	Replicate Results (µg/L)	RSD
Carbamate Analysis				
Imidacloprid	6/8/09	0.092	0.090	1.6 %
	6/9/09	0.120	0.113	4.3 %
	6/10/09	0.094	0.086	6.3 %
Herbicide Analysis				
2,4-D	6/5/09	0.024 J	0.022 J	6.2 %
DCPA	6/5/09	0.062 U	0.012 J	-
Dicamba I	6/5/09	0.010 NJ	0.008 J	15.7 %
Bentazon	6/7/09	0.033 J	0.062 U	-
Pesticide GCMS Analysis				
Bromacil	6/5/09	0.039	0.033 U	-
	6/11/09	0.150	0.180	12.9 %
Diazinon	6/5/09	0.015 NJ	0.015 NJ	0.0 %
Dichlobenil	6/5/09	0.009 J	0.009 U	-
Diphenamid	6/5/09	0.019 NJ	0.017 NJ	7.9 %
Eptam	6/5/09	0.025 NJ	0.031 NJ	15.2 %
Hexazinone	6/5/09	0.086	0.073	11.6 %
Tebuthiuron	6/5/09	0.039 J	0.037 J	3.7 %
Metalaxyl	6/11/09	0.035	0.046	19.2 %

Surrogates, Laboratory Control Samples, and Matrix Spikes

Surrogates are used to evaluate recovery for a group of compounds. For the daily and weekly grab sampling, surrogate recoveries fell within the control limits established by Manchester Laboratory.

Laboratory control samples (LCS) evaluate accuracy of pesticide residue recovery for a specific pesticide and are applied on a rotating basis. The four TSS LCS met QC requirements. Two of the three pesticide MS LCS met QC requirements of a 30-130% recovery rate for compounds measured. One of the LCS met QC requirements, but the following pesticides were recovered at a high rate: alachlor, atrazine, chlorothalonil, cis-permethrin, delta and gamma-BHC, dimethoate, endosulfan II, methoxychlor, parathion, and simazine. These compounds were not detected during the study.

The three herbicide LCS recoveries were acceptable, with recoveries between 40-130% for all but clopyralid. Clopyralid recovery was low in one LCS. This compound was not detected, and results were qualified as an estimate.

The three carbamate LCS met QC requirements (recoveries between 50-150%) with the exception of methomyl oxime and oxamyl oxime. Recoveries for these compounds were low in all LCS. Neither of these parameters was detected; results were qualified as an estimate. In addition, carbamate LCS was analyzed for the carbamate CLAM^{TM}. QC requirements were met for most parameters with the exception of methomyl, imidacloprid, aldicarb, propoxur, and carbaryl. These compounds had low recoveries, and results were qualified as an estimate.

Matrix spike/matrix spike duplicates (MS/MSD) provide an indication of bias due to interferences from components of the sample matrix. The duplicate spike can be used to estimate analytical precision at the concentration of the spiked samples. The average recovery of MS compounds and the average RSD between MS/MSD pairs is presented in Table C-5. For most compounds, the recovery and RSDs of MS/MSD pairs showed acceptable performance and were within defined limits for the project.

Table C-5. Matrix spike and matrix spike duplicate QA/QC results.

Laboratory Analysis	Number of MS/MSD Samples	Average Percent Recovery of Matrix Spiked Compounds	Average RSD of MS/MSD Pairs
Pesticide GCMS	1	103.2%	7.5 %
Herbicides	2	66.4% 78.2%	21.2% 4.5%
Carbamates	2	71.3% 68.6%	16.0% 15.4%

Field Measurements

Field meters were calibrated at the beginning of the field day according to manufacturers' specifications, using SOP EAP033 (Swanson, 2007). Meters were post checked at the end of the field day using known standards. Post checks met QC control objectives.

Dissolved oxygen meter results were compared to Winkler laboratory titration results from grab samples. Dissolved oxygen meter readings met data quality objectives with an average 1.6% RSD between meter and Winkler results, and all results were < 5.2 % RSD.

CLAM^{TM} Data Quality

CLAM^{TM} Pump Rates

The pump rate of the CLAM^{TM} devices was checked pre- and post-deployment. Pump rates were checked by timing the pumping rate of a set volume of deionized water. Pre-deployment pump rates were fairly accurate, between 0.8 - 17.7 % RSD (Table C-6). But pump rates at retrieval were not accurate, between 125 - 140 % RSD (Table C-6).

Due to the variation in pumping rate for pre and post deployment it is impossible to determine the volume of water pumped through the sampler during deployment of the CLAMs^{TM}. Therefore pesticides detected with the CLAM^{TM} SPE disks are reported as present or absent, and not a quantitative value.

Table C-6. Pre- and post-deployment pump rates for the CLAM™ devices.

CLAM™ site and specified pump rate	Analysis	Dates deployed	Hours de-ployed	Pre-deployment pump rate	% RSD for specified and pre-deployment pump rate.	Post-deployment pump rate	% RSD for specified and post-deployment pump rate.
BD-1 (10 mL/min)	PestMS	6/5-6/11/09	145	8.1 mL/min	14.7	0.05 mL/min	140
BD-1 (10 mL/min)	Carbamates	6/5-6/11/09	145	9.5 mL/min	3.6	0.6 mL/min	125
BD-1 (replicate) (10 mL/min)	PestMS	6/5-6/11/09	145	8.7 mL/min	9.5	0.3 mL/min	133
IS-1 (10 mL/min)	PestMS	6/5-6/11/09	147	8.9 mL/min	8.6	0.385 mL/min	131
IS-1 (10 mL/min)	Carbamates	6/5-6/11/09	147	7.8 mL/min	17.7	0.5 mL/min	128
IS-1 (replicate) (70 mL\min)	Carbamates	6/5-6/7/09	49	70.8 mL/min	0.8	Not tested	-
IS-1 (replicate) (70 mL\min)	Carbamates	6/7-6/9/09	< 48	Not tested	-	Pump not running	-
IS-1 (replicate) (70 mL\min)	Carbamates	6/9-6/11/09	50	Not tested	-	Not tested	-

Six CLAM™ devices were available for testing. Five CLAM™ devices were deployed for seven days; the pre-set pump rate was 10 mL per minute. One CLAM™ device was deployed for three 2-day periods; the pump rate was 70 mL per minute.

Laboratory Data Quality

Laboratory Blanks

The discussion above under Laboratory and Field Data Quality for Daily and Weekly Grab Sampling, Laboratory Blanks, applies to the CLAM™ results.

Field Blank Results

Field blanks were used to assess contamination of the CLAM™ device before sample water passes through the collection disk. The field blanks were collected by exposing clean, un-used collection disks to air. Each disk was exposed to air two times. One exposure occurred after the CLAM™ device was placed in the water, and the second occurred after the CLAM™ device was retrieved. The length of each blank exposure was equivalent to the time the sample collection disk was exposed to air. Before, after, and between exposures, the disk was stored in a pre-labeled, organics-free glass container.

At Indian Slough there were detections of carbaryl and oxamyl above detection limits. CLAM™ device detections of these parameters were rejected due to field blank contamination. There were no field blank detections for pesticide GCMS at Big Ditch.

Field Replicate Results

Two of the CLAM^{TM} devices represented field replicates. One was a replicate for carbamate analysis (including a neonicotinoid insecticide), and the other was a replicate for GC/MS pesticide analysis.

Over 120 compounds are included in the pesticide GCMS analysis, and 11 compounds are included in the carbamate analysis (not including 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl). The sample and replicate results are included in Table C-7. The carbamate CLAM^{TM} replicate included three filters placed for a 2-day period each in Indian Slough. Table 6 includes results of the CLAM^{TM} pesticide GCMS and carbamate analysis, including the replicates.

The CLAM^{TM} carbamate replicates are not true replicates because the time period deployed is different than the CLAM^{TM} carbamate sample. The CLAM^{TM} replicates deployed for two to three days detected six carbamate compounds that were not detected in the CLAM^{TM} deployed for seven days. This may be due to different deployment periods or due to laboratory issues with carbamate analysis.

Table C-7. Replicate results for the pesticide GCMS and carbamate CLAM^{TM} devices.

Compounds detected	BD-1 Sample	BD-1 Replicate
Diuron	tentatively identified	present
Dichlobenil	present	present
Bromacil	present	present
Metolachlor	present	Not present
Compounds detected	IS-1 Sample (7-day)	IS-1 Replicate (2-3 day)
Methiocarb	not present	present
Imidacloprid	not present	present
Methomyl oxime	not present	present

Surrogates

Surrogates are used to evaluate recovery for a group of compounds. The majority of surrogate recoveries fell within the control limits established by Manchester Laboratory. Pesticide GCMS analysis surrogate recovery for the Big Ditch CLAM^{TM} filter retrieved on June 11, 2009 had low surrogate recoveries. The decachlorobiphenyl (DCB) recovery was 20%, and the 4, 4'-DDE-D8 recovery was 18%. In addition, the Big Ditch CLAM^{TM} blank filter for June 11, had a high recovery of 1, 3-dimethyl-2-nitrobenzene (136%). No pesticides were detected in this blank.

Appendix D. Assessment Criteria and Water Quality Criteria

EPA pesticide assessment documents were reviewed to determine the most comparable and up-to-date toxicity guidelines for freshwater (Table D-1) and marine species (Table D-2). The 2006-2008 maximum concentration for each chemical is listed on the table, and values in bold indicate the result was above aquatic species toxicity or water quality criteria.

EPA Pesticide Assessment Toxicity Criteria

Rainbow trout are a surrogate for freshwater endangered and threatened species. Daphnia magna (invertebrate) and Selenastrum capricornutum (green algae also called pseudokirchneria subcapitata) represent components of the aquatic food web that may be affected by pesticide use. Alternative species are used only if no data are available for rainbow trout, Daphnia magna, or Selenastrum capricornutum.

Marine toxicity criteria were evaluated for detections at sites with estuarine influence. These sites were all in the Skagit-Samish watersheds and included lower Big Ditch, Browns Slough, and Indian Slough. Criteria were generated for marine species including sheepshead minnow and tidewater silverside for fish; pink shrimp, eastern oyster, grass shrimp, acartia tonsa (copepod), and mysid shrimp for invertebrates; and isochrysis galbana, and skeletonema costatum for aquatic plants.

EPA classifies a laboratory study as ‘core’ if it meets guidelines appropriate for inclusion in pesticide registration. Usually, a core designation may be made if the study is appropriately designed, monitored, conditions controlled, and duration of exposure is consistent with other studies. Core study criteria are used in the assessment table. Keeping with pesticide review precedent, the most toxic, acceptable criteria from core studies are used.

Water Quality Criteria

The most recent versions of Washington State water quality standards and EPA National Recommended Water Quality Criteria (NRWQC) were applied. The NRWQC remained largely unchanged from the 2003 update through 2008.

The toxic standards for Washington State waters also remain essentially unchanged following the 1997 rule and 2003 updates (Washington Administrative Code (WAC), Chapter 173-201A).

Table D-1. Freshwater toxicity and regulatory guideline values. All values reported in µg/L.

Chemical	Maximum Detection 2006-8	[1]Freshwater Toxicological and Reregistration Criteria													Freshwater Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
1-Naphthol	0.641*	1400		70	RT	10	700		DM	10	1100		SC	10				
2,4-D (Acids, Salts, Amines)[m]	6.57	101000	14200	5050	RT; FM	1	25000	16050	DM	1	3880	1440	ND	1				
2,4-D (BEE Ester)[m]		428		21.4	BS	1	4970	200	DM	1	1020	538	ND	1				
2,4'-DDD	0.018*																	
2,4'-DDT	0.053																	
3-Hydroxycarbofuran	0.34	362	5.7	18.1	RT	54; 60	2.23	0.75	CD	54								
		88		4.4	BG	54	29	9.8/27	DM	60								
4,4'-DDD	0.025																	
4,4'-DDE	0.071														1.1[a,b]	0.001[a,c]	1.1[a]	0.001[a]
4,4'-DDT	0.3														1.1[a,b]	0.001[a,c]	1.1[a]	0.001[a]
4-Nitrophenol	0.78																	
Alachlor	0.15	2100	187	105	RT	2	1550	110	DM	2	1.64	0.35	SC	2				
Aldicarb	0.22	560	78	28	RT;FM	3	410	20	DM	3								
Aldicarb Sulfone	0.51*	42000	78	2100	RT;FM	3	280	20	DM	3								
Aldicarb Sulfoxide	0.15*	7140	78	357	RT-A; FM-C	3	696	20	DM	3								
Atrazine	0.15	5300	65	265	RT; BT	4	6900	140	DM	4	49		SC	4				
Azinphos Methyl	0.53*	2.9	0.23	0.145	RT	5	1.1	0.25	DM	5								0.01
		3.2		0.16	Coho	5												
Bentazon	0.28	>100000		>5000	RT	6	>100000		DM	6	4500		SC	6				
Bromacil	0.75	36000		1800	RT	7	121000		DM	7	6.8		SC	7				
Bromoxynil	0.64	50	18/ 39	2.5	RT-A; FM-C	8	11	2.5/5.9	DM	8	80		SC	8				
Carbaryl	1.26	1200		60	RT	9	5.6	1.5	DM	10	1100	370	SC	10				
		2400		120	Chinook	10												
		2400		120	Coho	10												
Carbofuran	0.16	362	5.7	18.1	RT	54; 60	2.23	0.75	CD	54								
		88		4.4	BG	54	29	9.8/27	DM	60								
Chlorothalonil	0.024*	42.3	3	2.12	RT; FM	46	68	39	DM	46	190		SC	46				
Chlorpropham	5.6	5700		285	RT	47	3700		DM	47								
Chlorpyrifos	0.27	3	0.57	0.15	RT; FM	11; 12	0.1	0.04	DM	11					0.083d	0.041e	0.083	0.041

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Table D-1 (continued). Freshwater toxicity and regulatory guideline values.

Chemical	Max Detection 2006-8	[1]Freshwater Toxicological and Reregistration Criteria													Freshwater Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
cis-Permethrin[n]	0.11*	2.9;17	0.30/ 0.41	0.145	RT;CS-A FM-C	58	0.039	0.039/ 0.084	DM	58								
		0.79		0.0395	BG	58												
Clopyralid	0.065*	1968000	N/A	98400	RT	59, 64	113000	N/A	DM	59, 64	6900		SC	59				
Cycloate	1.2	4500		225	RT	48	24000		DM	48								
DCPA	0.55	6600	N/A	330	RT	56	27000	N/A	DM	56	>12380		SC	56				
Diazinon	0.7	90	0.8	4.5	RT; BT	13; 14	0.8	0.17	DM	13	3700		SC	13			0.17	0.17
Dicamba I	0.11*	28000		1400	RT	15	34600	16400	DM	15	3700	5	SC; AFA	15				
Dichlobenil	0.36	4930	330	246.5	RT	16; 17	6200	560	DM	17	1500	160	SC	17				
Dimethoate	0.45*	6200	430	310	RT	18	3320	40	DM	18								
Diphenamid	0.033*	97000		4850	RT	59	58000		DM	59								
Disulfoton sulfone	0.039*	9200		460	RT	20, 66	35.2	0.14/ 0.27	DM	20, 66								
Diuron	4.1	1950	26.4	97.5	RT; FM	21; 22	1400	200	DM	22	2.4		SC	22				
Endosulfan I	0.13	0.8	0.1	0.04	RT	23	166	2	DM	23					0.22[b,f]	0.056[c,f]	0.22[i]	0.056[i]
Endosulfan II	0.12	0.8	0.1	0.04	RT	23	166	2	DM	23					0.22[b,f]	0.056[c,f]	0.22[i]	0.056[i]
Endosulfan Sulfate	0.16	2.2		0.11	ND	23	580		DM	23								
Endrin Aldehyde	0.027*																	
Eptam	0.99*	14000		700	ND	24	6500		ND	24	1360		SC	24				
Ethoprop	0.14	1020	180	51	RT; FM	25	44	0.8	DM	25								
Fenarimol	0.038*	2100	430	105	RT	67	6800	113	DM	67		100	SC	67				
Hexachlorobenzene	0.016*	1000	3.68	50	CH-A; RT-C	59, 26	30	16	DM	26	30		SC	26				
Hexazinone	0.12	180000	17000	9000	RT; FM	27; 28	151600	20000	DM	27	7	4	SC	27				
		317000		15850	Chinook	27												
		246000		12300	Coho	27												
		317000		15850	Sockeye	27												
Imidacloprid	0.11	>83000	1200/ 2500	4150	RT	61	69	1800/ 3600	CT-A; DM-C	61								
							85200		DM	59								
Linuron	0.054*	3000	<42	150	RT	49	120		DM	50	67		SC	49				

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Table D-1 (continued). Freshwater toxicity and regulatory guideline values.

Chemical	Max Detection 2006-8	[1]Freshwater Toxicological and Reregistration Criteria													Freshwater Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
Malathion	0.082	4.1	21	0.205	RT	30	1	0.06	DM	30								0.1
		170		8.5	Coho	31												
MCPA	0.67	1150	916	57.5	RT	32	280	77	DM	32	250	32	SC	32				
MCPP	0.14	93000	N/A	4650	RT	65	91000	50800/102700	DM	65	14	9	SC	65				
Metalaxyl	0.51	132000	9100	6600	RT; FM	51	29000	1270	DM	51	140000		SC	51				
Methiocarb	0.034*	436		21.8	RT	C	19		DM	C								
Methomyl	0.17*	860	57/117	43	RT-A; FM-C	57	5	>0.4	DM	57								
Methomyl oxime	0.039*																	
Metolachlor	31	3900	780	195	ND	33	25100		DM	33								
Metribuzin	0.23	77000		3850	RT	52	4200	1290	DM	52	11.9	8.9	NP	51				
Napropamide	0.24	6400	1100	320	RT	53	14300	1100	DM	53	3400		SC					
Norflurazon	0.25	8100	770/1500	405	RT	34	15000	1000/2600	DM	34	9.7	3.2	SC	34-A 59-C				
Oryzalin	0.44*	3260		163	RT	D	1400		DM	D								
Oxamyl	0.21	4200	770/1500	210	RT	62	180	1000/4200	CP-A; DM-C	62	120	4.6	SC	62				
Oxamyl oxime	0.14																	
Oxyfluorfen	0.034*	250	38/74	12.5	RT-A; FM-C	35, 36	80	13/28	DM	35, 36	0.29	0.1	SC	35, 36				
Pendimethalin	0.098*	138	6.3	6.9	RT; FM	37	280	14.5	DM	37	5.4	3	SC	37				
Pentachlorophenol	0.053*	15	11	0.75	RT	38	450	240	DM	38	50		SC	38	8.2-41.0[d,g]	5.2-25.9[e,h]	7.9-107.6[j]	6.1-82.6[k]
Picloram	0.58	5500	N/A	275	RT	53	34400	N/A	DM	53								
Promecarb	0.2*																	
Prometon	0.12	12000	9500	600	RT-A; FM-C	68	25700	3500/6800	DM	68	98	32	SC	68				
Propargite	0.043*	118	16	5.9	RT; FM	40	74	9	DM	40	66.2	5	SC	40				
Propoxur	0.03*	3700		185	RT	63	11		DM	63								
Simazine	1.6	70500	1200	3525	RT; FM	41	1100		DM	41	100		SC	41				

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Table D-1 (continued). Freshwater toxicity and regulatory guideline values.

Chemical	Max Detection 2006-8	[1]Freshwater Toxicological and Reregistration Criteria													Freshwater Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
Tebuthiuron	0.31*	143000	9300	7150	RT; FM	42	297000	21800	DM	42	50	13	SC	42				
Terbacil	0.68	46200		2310	RT	43	65000		DM	43	18	4	SC	43				
Triadimefon	0.019*	4100	41/ 116	205	RT	55	1600	52/119	DM	55	100/1710		SC	55				
Triclopyr	1.3	650		32.5	RT	44	12000		DM	44	2300	2	SC; NP	44				
Trifluralin	0.047	41	1.14	2.05	RT	45	560	2.4	DM	45	7.52	5.37	SC	45				

*Values are not analytically qualified. Non-asterisk values have been J-qualified as estimates, normally below the practical quantitation limit.

[1]Criteria identified in EPA reregistration and review documents or peer reviewed literature. References listed separately.

Time component of standards explained in body of report.

ESLOC refers to Endangered Species Level of Concern.

Species abbreviated in table include: RT-Rainbow Trout, CS-Coho Salmon, CH-Chinook Salmon, FM- Fathead Minnow, BT-Brook Trout, BS-Bluegill Sunfish, ND-not described, DM-Daphnia magna, CD–Ceriodaphnia dubia, SC-Selenastrum capricornutum (aka Pseudokirchneria subcapitata), Anabaena flos-aquae, and Navicula pellicosa, SM-sheepshead Minnow, CT-Chironomus tentans (midge).

[2]WAC: Promulgated standards according to Chapter 173-201A WAC.

[3]EPA National Recommended Water Quality Criteria (EPA-822-R-02-047).

CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

[a]Criteria applies to DDT and its metabolites (ΣDDT).

[b]An instantaneous concentration not to be exceeded at any time.

[c]A 24-hour average not to be exceeded.

[d]A 1-hour average concentration not to be exceeded more than once every three years on average.

[e]A 4-day average concentration not to be exceeded more than once every three years on average.

fChemical form of Endosulfan is not defined in WAC 173-201A. Endosulfan sulfate may be applied in this instance.

[g]≤ e[1.005(pH)-4.830], pH range of 6.9 to 9.5 shown.

[h]≤ e[1.005(pH)-5.29], pH range of 6.9 to 9.5 shown.

[i]Value refers to ∑α and β-endosulfan.

[j]≤ e[1.005(pH)-4.869], pH range of 6.9 to 9.5 shown.

[k]≤ e[1.005(pH)-5.134], pH range of 6.9 to 9.5 shown.

[l]There are many forms of 2,4-D that include acids, salts, amines, and esters, all of which have unique toxicity values. The criteria presented are in acid equivalents and are intended to provide a range of possible effects. Toxicity values for each form of 2,4-D are available in the referenced document.

[m]Assessment criteria for permethrin are based on a formulation of cis-and trans-permethrin isomers. Manchester Laboratory analysis includes only the cis-permethrin isomer, the more toxic of the two; and cis-permethrin concentrations are compared to the assessment criteria for permethrin.

Table D-2. Marine toxicity and regulatory guideline values for three estuarine sites. All values reported in µg/L.

Chemical	Maximum Detection 2006-8	Marine Toxicological and Registration Criteria													Marine Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
1-Naphthol	0.641*	1200		60	SM	10	2100		EO	10								
2,4-D (Acids, Salts, Amines) [m]	6.57	>80,000 (175,000 definitive)	no data	4000	TS	1	57000	no data	EO	1								
2,4-D (BEE Ester)[m]		no data	555		SM	1	1800	no data	EO	1								
2,4'-DDD	0.018*																	
2,4'-DDT	0.053																	
3-Hydroxycarbofuran	0.34	33	2.6	1.65	AS; SM	60	4.6	0.4	PS; MS	60								
4,4'-DDD	0.025																	
4,4'-DDE	0.071														0.13[a]	0.001[b]		
4,4'-DDT	0.3														0.13[a]	0.001[b]		
4-Nitrophenol	0.78																	
Alachlor	0.15																	
Aldicarb	0.22																	
Aldicarb Sulfone	0.51*																	
Aldicarb Sulfoxide	0.15*																	
Atrazine	0.15	2000	2542	100	SM	4	94	80	AT; M	4	22		IG	4				
Azinphos Methyl	0.53*																	
Bentazon	0.28	136		6.8	SM	6	>132.5; >109		PS; EO	6								
Bromacil	0.75	162		8.1	SM		12.9; 130		M; EO	7								
Bromoxynil	0.64																	
Carbaryl	1.26	2600		130	SM	10	32; >2		PS; EO	10								
Carbofuran	0.16	33	2.6	1.65	AS; SM	60	4.6	0.4	PS; MS	60								
Chlorothalonil	0.024*	32		1.6	SM	46	154; 3.6	1.2	PS; EO; M	46								
Chlorpropham	5.6																	
Chlorpyrifos	0.27	270	0.38	13.5	SM; TS	11	2.4	<0.0046	PS; M	11					0.011[c]	0.0056[d]	0.011[G]	0.0056[G]
cis-Permethrin[n]	0.11*	2.2	0.83	0.11	AS; SM	58	0.019	0.011	M	58								
Clopyralid	0.065*																	
Cycloate	1.2																	

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Table D-2 (continued). Marine toxicity and regulatory guideline values for three estuarine sites.

Chemical	Max Detection 2006-8	Marine Toxicological and Registration Criteria													Marine Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
DCPA	0.55	>1000		50	SM	56	620		EO	56	>11000		SkC	56				
Diazinon	0.7						4.2	0.23	M	13							0.82	0.82
Dicamba I	0.11*	>180000		>9000	SM	15												
Dichlobenil	0.36	14000		700	SM	16	>1000; 2500		PS; EO	16								
Dimethoate	0.45*																	
Diphenamid	0.033*																	
Disulfoton sulfone	0.039*																	
Diuron	4.1	6700		335	SM	22		270	M	22								
Endosulfan I	0.13														0.034[a]	0.0087[b]	0.034[a]	0.0087[b]
Endosulfan II	0.12														0.034[a]	0.0087[b]	0.034[a]	0.0087[b]
Endosulfan Sulfate	0.16																	
Endrin Aldehyde	0.027*																	
Eptam	0.99*																	
Ethoprop	0.14																	
Fenarimol	0.038*																	
Hexachlorobenzene	0.016*																	
Hexazinone	0.12																	
Imidacloprid	0.11	163000		8150	SM	61	37	>0.6/1.3	MS	61								
Linuron	0.054*	890		44.5	SM	49	4500; 890		M; EO									
Malathion	0.082																	
MCPA	0.67	>4100	4100	>205	SM	32	150000	115000	EO	32	300	15	SkC	32				
MCPP	0.14																	
Metalaxyl	0.51						25700; 4600		M; EO	51								
Methiocarb	0.034*																	
Methomyl	0.17*	1160		58	SM	57	>140000; 230		EO; M	57								
Methomyl oxime	0.039*																	
Metolachlor	31	7900	1000	395	ND	33												

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Table D-2 (continued). Marine toxicity and regulatory guideline values for three estuarine sites.

Chemical	Max Detection 2006-8	Marine Toxicological and Registration Criteria													Marine Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
Metribuzin	0.23	85000		4250	SM	52	48300; 49800		M; EO	52	8.7	5.8	SkC	52				
Napropamide	0.24	14000		700	SM	53	4200; 1400		M; EO									
Norflurazon	0.25																	
Oryzalin	0.44*																	
Oxamyl	0.21	2600		130	SM	62	0.4		EO	62								
Oxamyl oxime	0.14																	
Oxyfluorfen	0.034*																	
Pendimethalin	0.098*																	
Pentachlorophenol	0.053*	240		12	SM	38	48		PO	38	27		SkC	38	13.0[c]	7.9[d]		
Picloram	0.58																	
Promecarb	0.2*																	
Prometon	0.12	47300		2365	SM	68	18000		MS	68								
Propargite	0.043*																	
Propoxur	0.03*																	
Simazine	1.6	>4300		215	SM	41	113000; >3700		PS; EO	41	600		SkC	41				
Tebuthiuron	0.31*						62000		PS	42	31		SkC	42				
Terbacil	0.68																	
Triadimefon	0.019*																	
Triclopyr	1.3	450		22.5	TS	44	2470		GS	44	1170	209	SkC	44				
Trifluralin	0.047	190		9.5	SM	45	638.5		GS	45	28		SkC	45				

*Values are not analytically qualified. Non-asterisk values have been J-qualified as estimates, normally below the practical quantitation limit.

[1] Criteria identified in EPA reregistration and review documents or peer reviewed literature. References listed separately.

Time component of standards explained in body of report.

ESLOC refers to Endangered Species Level of Concern.

Species abbreviated in table include: ND-not determined, AS-Atlantic silverside, IS-Inland silverside, TS-Tidewater silverside, PS-Pink shrimp, EO-Eastern oyster, AT-Acartia tonsa (copepod), M-Mysid, IG-Isochrysis galbana, LG-Lemna gibba, CT-Chironomus tentans (midge), GS - Grass shrimp, SkC - Skeletonema costatum, PO-Pacific Oyster.

[2] WAC: Promulgated standards according to Chapter 173-201AWAC.

[3] EPA National Recommended Water Quality Criteria (EPA-822-R-02-047).

CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

[a] Criteria applies to DDT and its metabolites (ΣDDT).

[b] An instantaneous concentration not to be exceeded at any time.

[c] A 24-hour average not to be exceeded.

[d] A 1-hour average concentration not to be exceeded more than once every three years on average.

[e] A 4-day average concentration not to be exceeded more than once every three years on average.

[f] Chemical form of Endosulfan is not defined in WAC 173-201A. Endosulfan sulfate may be applied in this instance.

[g] $\leq$ e[1.005(pH)-4.830], pH range of 6.9 to 9.5 shown

[h] $\leq$ e[1.005(pH)-5.29], pH range of 6.9 to 9.5 shown

[i] Value refers to $\sum\alpha$ and β-endosulfan

[j] $\leq$ e[1.005(pH)-4.869], pH range of 6.9 to 9.5 shown

[k] $\leq$ e[1.005(pH)-5.134], pH range of 6.9 to 9.5 shown

[l] There are many forms of 2,4-D that include acids, salts, amines. and esters, all of which have unique toxicity values. The criteria presented are in acid equivalents and are intended to provide a range of possible effects. Toxicity values for each form of 2,4-D are available in the referenced document.

[m] Assessment criteria for permethrin are based on a formulation of cis-and trans-permethrin isomers. Manchester Laboratory analysis includes only the cis-permethrin isomer, the more toxic of the two; and cis-permethrin concentrations are compared to the assessment criteria for permethrin.

Appendix D: References

[1] Draft EFED Chapter for 2,4-D Reregistration Eligibility Decision (RED). As modified 12-2004. www.epa.gov/oppfead1/endanger/litstatus/effects/24d-efedchap.pdf.

[2] Alachlor Reregistration Eligibility Decision (RED). 12-1998. www.epa.gov/oppsrrd1/REDs/0063.pdf.

[3] Revised EFED Risk Assessment for the Aldicarb reregistration Eligibility Decision (RED). Docket number EPA-HQ-OPP-2005-0163-0005. www.regulations.gov/.

[4] Atrazine Reregistration Eligibility Decision (RED). 4-2006. www.epa.gov/oppsrrd1/REDs/atrazine_combined_docs.pdf.

[5] Azinphos-methyl Insecticide: Ecological Risk Assessment for the Use of Azinphos-methyl on Caneberries, Cranberries, Peaches, Potatoes, and Southern Pine Seeds (Group 2 Uses). Docket number EPA-HQ-OPP-2005-0061-0027.

[6] Bentazon Reregistration Eligibility Decision (RED). 12-1994. www.epa.gov/oppsrrd1/REDs/0182.pdf.

[7] Bromacil Reregistration Eligibility Decision (RED). 8-1996. www.epa.gov/oppsrrd1/REDs/0041red.pdf.

[8] Bromoxynil Reregistration Eligibility Decision (RED). 12-1998. www.epa.gov/oppsrrd1/REDs/2070red.pdf.

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