DEPARTMENT OF
ECOLOGY
State of Washington

WSDA
WASHINGTON STATE
DEPARTMENT OF AGRICULTURE

Pesticides in Salmonid-Bearing Streams: Intensive Sampling in an Agricultural Drain

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

July 2008

Publication No. 08-03-020

Publication Information

This report is available on the Department of Ecology's website at
www.ecy.wa.gov/biblio/0803020.html

Data for this project are available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID, CBUR0005.

Ecology's Study Tracker Code for this study is 07-510.

For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600
Olympia, WA 98504-7600

E-mail: jlet461@ecy.wa.gov
Phone: 360-407-6764

Washington State Department of Ecology - www.ecy.wa.gov/

o Headquarters, Olympia	360-407-6000
o Northwest Regional Office, Bellevue	425-649-7000
o Southwest Regional Office, Olympia	360-407-6300
o Central Regional Office, Yakima	509-575-2490
o Eastern Regional Office, Spokane	509-329-3400

Pesticides in Salmonid-Bearing Streams: Intensive Sampling in an Agricultural Drain

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

by

Dan Dugger, Chris Burke, Jerry Jorden, Paul Anderson, and Dale Norton
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington

and

Jim Cowles
Natural Resources Assessment Program
Washington State Department of Agriculture
Olympia, Washington

July 2008

Waterbody Number: WA-37-1025, Marion Drain

This page is purposely left blank

Table of Contents

Page

List of Figures

Page

Appendix B Figures

List of Tables

Appendix B Tables

This page is purposely left blank

Abstract

The Washington State Department of Ecology and the Washington State Department of Agriculture have monitored pesticides in salmonid-bearing streams during the application season since 2003.

This 2007 project compared pesticide concentrations measured in daily and weekly samples with pesticide residues accumulated by two types of passive samplers, Semi-Permeable Membrane Devices (SPMDs) and Polar Organic Chemical Integrative Samplers (POCISs). The objective was to evaluate short-term variation in pesticide occurrence and concentration, and assess the adequacy of the current weekly sampling regime.

The study site was Marion Drain, a heavily cropped, 19-mile drainage ditch that discharges into the Yakima River. Marion Drain is used by salmonids including chinook, coho, and endangered steelhead. The study was carried out over 22 days in the spring of 2007.

A total of 21 pesticide compounds were detected during the study. Daily grab sampling detected only one more pesticide than the number observed during four pre-scheduled weekly sampling events. Detection frequency and median values were similar between daily and weekly sets. Weekly sampling failed to detect some isolated peaks in concentration and some rarely detected compounds found in the daily samples.

SPMDs detected more hydrophobic and legacy pesticides than grab samples. The additional detections reflect the lower reporting limits in the SPMDs. Results from the POCISs were compromised by pesticide detections in the field blank and by inconsistent detections between sample replicates.

The authors of this study recommend that the monitoring program:

- Continue with weekly sampling for long-term pesticide monitoring.
- Tie additional monitoring to specific pesticide applications.
- Consider using SPMDs for continuous monitoring of hydrophobic pesticides.
- Follow development in polar organic samplers as a complement to the current program.
- Compare pesticide values obtained for this study to endpoint criteria in the 2006-2008 triennial report.

Acknowledgements

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

- Moses Squeochs, James Thomas, and Joanne Cornwall (Yakama Nation) for permission to sample the Marion Drain, technical expertise, outreach coordination, historical and operational knowledge, and ecological insight.
- Staff with the Washington State Department of Agriculture (project sponsor)
    - Deborah Bahs for crop and pesticide use information.
    - Perry Beale for crop diversity and mapping information.
- Staff with the Washington State Department of Ecology
    - Art Johnson and Debby Sargeant for peer review and editing.
    - Rebecca Wood for field collection assistance.
    - Pam Covey, Leon Weiks, and Dean Momohara for shipping assistance.
    - For analysis of samples and reviewing results: Bob Carrell, Dickey Huntamer, Jeff Westerlund, Kamilee Ginder, Dean Momohara, Stuart Magoon, Pam Covey, Karin Feddersen, Dan Baker, Kelly Donegan, Danette Hanttula, Cherlyn Milne, Aileen Richmond, Rebecca Wood, Myrna Mandjikov, John Weakland, and other Manchester Environmental Laboratory staff.
    - Joan LeTourneau and Cindy Cook for editing and formatting the final report.
    - Verna Rae Jeffery, Rebecca Zahler, Jennifer Norby, Carol Norsen, Gayla Lord, Marion England, and Jodi England for operational support.
- Staff with Environmental Sampling Technologies.
    - Terri Spencer for passive sampler and extract preparation.

Introduction

Background and Project Description

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) are conducting a multi-year surface water monitoring study of pesticide concentrations in salmonid[1]-bearing streams during the typical pesticide use season.

Data from the monitoring program are being used to develop pesticide exposure assessments for Endangered Species Act (ESA) listed salmonid species. The data are provided to the U.S. Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA)-Fisheries for ESA consultations on pesticides and salmon. WSDA uses the monitoring data to make decisions about pesticide registration and to determine if pesticide mitigation efforts are needed.

This program monitors sites in the Skagit, Cedar-Sammamish, Lower Yakima, Wenatchee, and Entiat basins (WRIA[2] 3, 8, 37, 45, and 46, respectively). Sampling occurs once a week at each site during the application season. The project and results obtained to date are detailed in the quality assurance (QA) project plan, project amendments, and annual reports (Burke and Dugger, 2007; Dugger et al., 2007; Burke et al., 2006; Burke and Anderson, 2006).

The current weekly sampling regime is designed to provide a long-term assessment of background pesticide levels. Sampling is scheduled independently of pesticide applications, irrigation, and rain events. Short-term pesticide presence and peaks are thus unlikely to be detected.

Streams and agricultural drains are dynamic systems. The extent to which the weekly sampling regime captures short-term changes in pesticide levels has not been evaluated. Understanding short-term variation will assist WSDA, EPA, NOAA-Fisheries, and Ecology to evaluate pesticide exposure to salmonids and other aquatic species.

This project evaluates the variation in pesticide occurrence and concentrations over a 22-day period in a salmonid-bearing agricultural drain. Sampling was conducted using daily and weekly grab samples in conjunction with passive (continuous) sampling.

A list of acronyms used in this report is in Appendix A.

---

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

[2] Water Resource Inventory Area

Marion Drain

Lower Marion Drain (Marion 2) was chosen as the test site for this 2007 study based on the drain's use by salmonids, agricultural diversity, and a pattern of pesticide presence. Marion 2 is located upstream of the intersection of Marion Drain and Indian Church Road (NAD 83, 46.3306W, 120.1989N; Figure 1). This site integrates land-use practices of the entire watershed and has been monitored by the WSDA/Ecology surface water pesticide program since 2003 (Anderson et al., 2004; Burke et al., 2005, 2006).

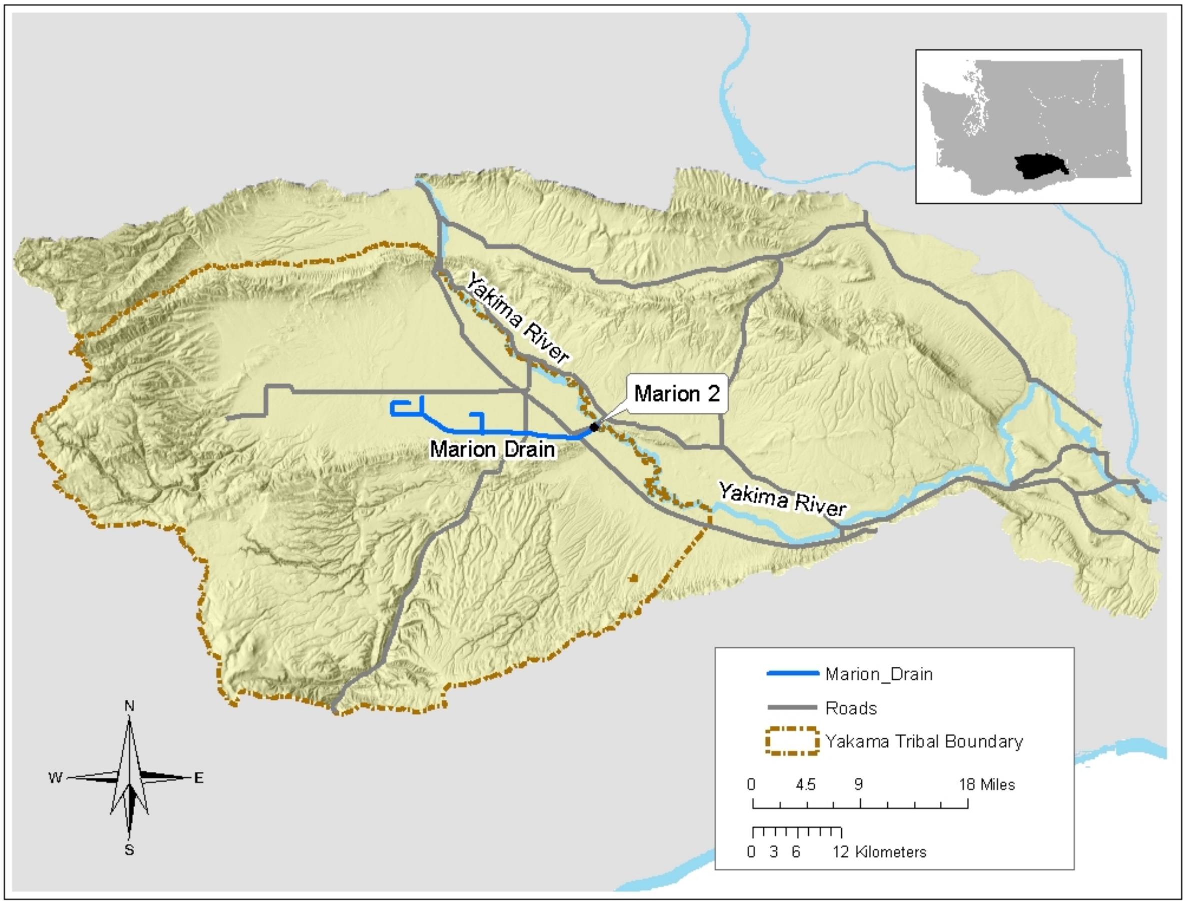

Figure 1. Location of Marion Drain sampling site in the Lower Yakima watershed.

Marion Drain discharges into the Yakima River 2.2 miles upstream of the mouth of Toppenish Creek at Yakima river mile 82.6 and is located within the Yakama Reservation. Marion Drain is a 19-mile-long drainage ditch with a watershed area of approximately 85,786 acres. It primarily collects irrigation return flows from Harrah Drain, Toppenish Creek, Wanity Slough, and groundwater seepage from the northern plain (Haring, 2001; Freudenthal et al., 2005). Approximately 59% of the watershed is in agricultural crops. The majority of this acreage is in apple (9%), hops (9%), and corn (9%) production (Burke et al., 2006).

Although a channelized conveyance, Marion Drain provides spawning habitat for fall chinook, ESA listed summer steelhead, and resident fishes (Freudenthal et al., 2005; Haring, 2001). Coho have also been observed in the drain (Haring, 2001).

From 2003-2006, 31 pesticides and degradates were detected in the Lower Marion Drain (Table 1). The most frequently detected herbicides included 2,4-D, Atrazine, Terbacil, and Trifluralin. Chlorpyrifos and Malathion were the most frequently detected insecticides.

Table 1. Pesticide detections of the Lower Marion Drain for sample years 2003 to 2006. Results in µg/L.

Chemical	[1]Common Name	[2]Type	2006, n=31			2005, n=29			2004, n=31			2003, n=18		
			Freq	Median	Max	Freq	Median	Max	Freq	Median	Max	Freq	Median	Max
Terbacil	Sinbar	H	84%	0.096	0.68	86%	0.12	0.46	67%	0.088	0.37	76%	0.0785	0.26
Chlorpyrifos	Lorsban	I-OP	68%	0.013	0.12	24%	0.02	0.4	37%	0.02	0.1	43%	0.023	0.085
Atrazine	(several)	H	61%	0.011	0.078	72%	0.019	0.035	60%	0.014	0.142	62%	0.0059	0.017
2,4-D	(several)	H	42%	0.047	0.53	38%	0.056	0.17	77%	0.045	0.22	76%	0.061	0.29
Trifluralin	Treflan	H	32%	0.015	0.034	24%	0.02	0.025	7%	0.0153	0.023	19%	0.0096	0.016
Metolachlor	Dual Magnum	H	26%	0.011	0.033	28%	0.011	0.012	7%	0.0024	0.0038			
Bentazon	Basagran	H	23%	0.1	0.27	14%	0.0755	0.15	53%	0.125	2.5	14%	0.053	0.063
Pendimethalin	Prowl	H	16%	0.035	0.061	28%	0.028	0.065	13%	0.046	0.126	43%	0.044	0.1
Malathion	(several)	I-OP	13%	0.018	0.024	30%	0.0215	0.23	20%	0.0275	3.05	10%	0.0136	0.024
Alachlor	Intrro, Lariat	H	13%	0.014	0.11	14%	0.021	0.058	10%	0.005	0.04	10%	0.0041	0.0061
MCPA	(several)	H	10%	0.028	0.033	10%	0.052	0.075	23%	0.032	0.297	33%	0.044	0.068
Simazine	(several)	H	6%	0.0175	0.018	45%	0.021	0.033	17%	0.022	0.031	5%	0.002	0.002
Diuron	Direx, Karmex	H	6%	0.06	0.11	21%	0.0165	0.092	53%	0.0255	0.16	24%	0.015	0.041
Ethoprop	Mocap	I-OP	6%	0.02	0.022	15%	0.03	0.27	20%	0.0485	0.18	5%	0.046	0.046
EPTC	Eptam	H	6%	0.0185	0.022	7%	0.025	0.032	27%	0.008	0.027	5%	0.038	0.038
Bromoxynil	Buctril	H	6%	0.055	0.066	3%	0.04	0.04	23%	0.034	0.081	38%	0.0285	0.052
Carbaryl	Sevin	I-C	6%	0.0795	0.09							5%	0.14	0.14
Metribuzin	Sencor	H	3%	0.049	0.049									
Propargite	Comite, Omite	I-SE				3%	0.092	0.092	3%	2.144	2.144	5%	0.015	0.015
Bromacil	Hyvar	H							23%	0.0072	0.052	14%	0.01	0.013
Dimethoate	(several)	I-OP							13%	0.0305	0.14	19%	0.00625	0.13
Hexazinone	Velpar	H							10%	0.009	0.036			
Prometon	Pramitol	H							7%	0.0218	0.036			
Disulfoton	(several)	I-OP							3%	0.023	0.023			
Azinphos methyl	Guthion	I-OP										10%	0.0048	0.0064
Diazinon	(several)	I-OP										5%	0.007	0.007
Dicamba I	(several)	H										19%	0.0105	0.012
Diphenamid		H										5%	0.093	0.093
Endosulfan II	Thionex	I-OC										5%	0.004	0.004
Endosulfan sulfate		D										5%	0.36	0.36
Pentachlorophenol	Penta	WP										5%	0.01	0.01

Results as reported by Manchester Environmental Laboratory.

[1]Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Competing labels listed as 'several'.

[2]Use type descriptors: D = degradate compound, H = herbicide, I-C = carbamate insecticide, I-OC = chlorinated insecticide,
I-OP = organophosphorus insecticide, I-SE = sulfite ester insecticide, WP = wood preservative.

Study Design

Daily grab samples were collected and passive samplers were deployed from April 24 to May 15, 2007. A subset of four weekly samples that were part of scheduled sampling in the Lower Yakima (April 24 and May 1, 8, and 15) were compared to the full set of daily samples to assess if weekly sampling adequately captures pesticide variation. Passive sampler results were compared to daily grab samples to assess continuous exposure methods against discrete sampling. Conventional water quality parameters were analyzed to examine correlations with the pesticides.

Sampling frequency, field procedures, and laboratory methods are described in previous reports and QA project plans (Ward, 2001; Johnson and Cowles, 2003; Anderson et al., 2004, 2007; Burke et al., 2005, 2006; Burke and Anderson, 2006; Dugger et al., 2007; Burke and Dugger, 2007). All laboratory analyses were conducted by Ecology's Manchester Environmental Laboratory (MEL) according to standard protocols (MEL, 2005, 2006).

Passive Samplers

Passive devices provided continuous sampling over the deployment period. A Semipermeable Membrane Device (SPMD; Figure 2) and a Polar Organic Chemical Integrative Sampler (POCIS; Figure 3) were used. SPMDs and POCISs measure the dissolved fraction of a compound as compared to whole water grab samples which represent the total amount (dissolved + particulate fractions). Under conditions of the present 2003-2008 study, the pesticides detected would be expected to be primarily in the dissolved form.

An SPMD is composed of a thin-walled, layflat polyethylene tube filled with triolein, a neutral lipid. When placed in water, dissolved lipophilic organic compounds diffuse through the SPMD membrane and are concentrated over time. The SPMD targets hydrophobic, nonpolar, compounds with a log octanol-water partition coefficient (log K_{ow}[3]) > 3. These include pyrethroids and organochlorine pesticides such as Chlorpyrifos and DDT.

The POCIS consists of a resin/adsorbent mix between polyethersulfone membranes. The POCIS adsorbs hydrophilic, polar organic compounds with a log $K_{ow} < 3$. Most current-use pesticides fall into this category.

The water concentrations of SPMD-detected compounds are estimated using performance reference compounds (PRC). PRCs are spiked into the SPMDs prior to deployment. PRC loss rates are used to derive an exposure adjustment factor (EAF) to calibrate for the effects of water velocity, temperature, and biofouling on chemical uptake. PRCs can be used to predict the EAFs of chemicals over a wide range of log K_{ow}s. Studies have shown that chemical concentrations derived from SPMDs are comparable to other low-level sampling methods such as solid-phase

---

[3] The log octanol-water partition coefficient (log K_{ow}) is an indicator of a compound's hydrophilic or lipophilic (hydrophobic) properties. It is the ratio of a chemical's concentration in octanol to its concentration in water of an octanol-water mixture at equilibrium. Higher values of log K_{ow} indicate more lipophilic compounds.

and liquid-liquid extraction, generally agreeing within a factor of 2 (Ellis et al., 1995; Rantalainen et al., 1998, Hyne et al. 2004).

POCIS uptake rates for most of the pesticides are not yet available. Therefore, POCIS-derived water concentrations could not be calculated.

Figure 2. Standard SPMD membrane mounted on a spider carrier.

Figure 3. Three standard POCISs on a deployment carrier.

Figure 4. Passive sampler protective deployment canister. (Photos courtesy of EST Labs)

SPMD and POCIS samplers are sold under United States Geological Survey (USGS) patent by Environmental Sampling Technologies (EST), www.est-lab.com/. Additional passive sampler properties and function are described in detail in the QA project plan (Burke and Dugger, 2007). USGS research on SPMDs and POCISs is online at www.cerc.usgs.gov/Research/passive_samplers.htm.

For the purpose of this project, passive sampling data are considered experimental and used to complement the existing monitoring program. Results should be viewed with this caveat in mind.

Methods

Active (Grab) Sampling

Pesticides and conventional water quality parameters were collected by hand-compositing grab samples from quarter-point transects across the stream. A one-liter transfer container was used to dip into the stream and pour water into the sample containers. Sampling and preservation methods followed the existing monitoring project, allowing for direct comparison of daily- and weekly-measured concentrations (Johnson et al., 2003; Anderson et al., 2004, 2007; Burke et al., 2005; Burke et al., 2006; Dugger et al., 2007; Burke and Dugger, 2007). Samples were collected about 10 meters downstream from the passive sampler deployments.

Passive (Continuous) Sampling

EST shipped the passive samplers to Ecology in sealed containers packed in ice. Passive samplers were kept frozen prior to deployment.

SPMDs were deployed according to Ecology Standard Operating Procedures (SOPs) for SPMDs (Ecology, 2007). POCISs lack an SOP, but deployment methods were similar to SPMDs.

Sampler protective canisters (Figure 4) were submerged and attached to a cable in a slow moving eddy as shown in Figure 5. Samplers were moved from the sealed shipment containers to the submerged canister. Air exposure time was minimized and recorded at deployment and retrieval to indicate potential for airborne pesticide contamination. Empty shipment containers were sealed to prevent contamination during deployment.

Each passive sampler unit was a composite of either five SPMDs or six POCISs in the same canister. The samplers were deployed in duplicate. Following deployment, passive samplers were resealed in their shipment containers and placed on ice. The samplers were shipped frozen to EST.

Estimated water concentrations of compounds detected in SPMDs were calculated using an Excel® spreadsheet developed by USGS[4] (Alvarez, 2006).

---

[4] The SPMD Water Concentration Calculator v5-1 is available at www.cerc.usgs.gov/Research/spmd.htm.

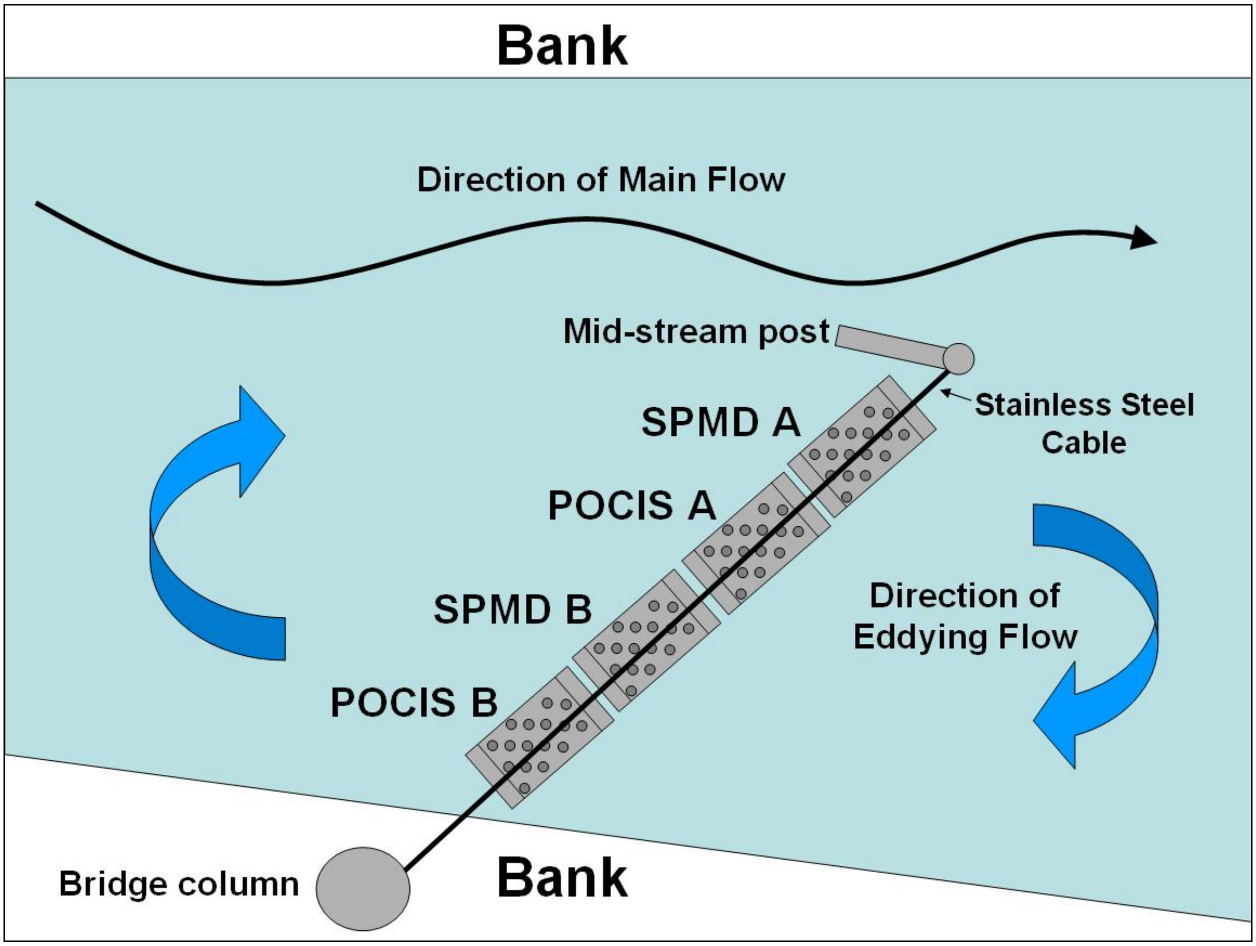

Figure 5. Passive sampler deployment in Marion Drain (not to scale).

Analysis

The analyses conducted for the study are shown in Table 2. The full list of target pesticides is in Appendix B Table B-3. Registered and legacy pesticides were analyzed (Table 2). SPMDs were not analyzed for acid herbicides or carbamates.

Table 2. Analyses conducted.

Analysis[1]	Target	Grab Sample	POCIS	SPMD
GCMS	Chlorinated pesticides	X	X	X
	Nitrogen pesticides	X	X	X
	Organophosphorus pesticides	X	X	X
	Pyrethroid pesticides	X	X	X
GCMS-H	Acid herbicides	X	X	
LCMS	Carbamate pesticides	X	X	
EPA method 415.1	Total organic carbon	X		
Filter (0.45 µm) and EPA method 415.1	Dissolved organic carbon	X		
Standard methods 2540 D	Total suspended solids	X		

[1] GCMS = Gas chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8270M.
GCMS-H = EPA method (modified) SW 846 3535M/8270M.
LCMS = Liquid chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8321AM.

Total suspended solids (TSS), dissolved organic carbon (DOC), and total organic carbon (TOC) were analyzed from grab samples. Other conventional parameters (listed below) were recorded daily using field meters. Discharge was calculated from flow rates measured on site.

- Discharge (cfs)
- Dissolved oxygen (mg/L)
- pH
- Conductivity (µS)
- Water temperature (°C)

All field meters were calibrated according to the manufacturers' specifications, using Ecology SOPs where available (Ecology, 2007) and established methods. All field methods may be referenced to the USGS, American Public Health Association (Standard Methods), or American Society for Testing Materials (USGS, 2007; APHA, 2005; ASTM, 2005-2007).

EST extracted the passive samplers and performed a gel permeation chromatography cleanup on the extracts. MEL analyzed the samples.

Grab samples for LCMS on April 25 and GCMS-H on May 10 were lost in shipment and could not be analyzed.

All summary statistics were calculated by substituting the lower practical quantitation limit (LPQL) for non-detections.

This page is purposely left blank

Data Quality

MEL prepared written case narratives assessing the quality of the data collected for this project. These reviews include a description of analytical methods and assessments of holding times, initial and continuing calibration and degradation checks, method blanks, surrogate recoveries, matrix spike recoveries, laboratory control samples, and laboratory duplicates (MEL, 2005, 2006). The reviews and the complete Manchester data reports are available from the author on request.

Appendix B includes a detailed review of data quality. At least two quality assurance samples (field blanks, field replicates, or matrix spike/matrix spike duplicate [MS/MSD] pairs) were evaluated per 11 samples.

In some cases, pesticides were positively identified below the LPQL. These detections were qualified as approximate concentrations.

Most grab sample and SPMD quality control samples met project quality objectives (Appendix B Table B-2). Specific compounds which did not meet quality objectives were qualified as estimates as described in Appendix B. All POCIS results were qualified as estimates based on poor laboratory control sample (LCS) and surrogate recovery, and inconsistency between replicates.

Field blanks were analyzed for both grab and passive samples. At least one field blank was used for each grab sample analysis method. SPMD and POCIS samplers each had one field blank.

Field blanks for grab samples were composed of deionized water that was transferred into a sample bottle at the field site. Passive sampler field blanks were identical to the deployed samples but were exposed only to ambient air at the test site during retrieval and deployment. Transfer blanks underwent the same handling, shipment, and analyses as standard samples; therefore transfer blanks indicate contamination from sources encountered in the survey.

Analysis of the SPMD field blank showed a detection of Trans-Chlordane. This compound was not detected among passive or grab samples.

The LCMS extract of the POCIS field blank was contaminated with five carbamate compounds: 3-Hydroxycarbofuran, Carbaryl, Methiocarb, Oxamyl oxime, and Propoxur. Among these, Oxamyl oxime and Methiocarb were also detected in the deployed POCISs.

No contamination was detected in the grab sample blanks.

The relative percent differences (RPDs) between most grab sample replicates were within 30%. A few detections occurred only in one replicate, but in each case the detection was below the LPQL (Appendix B Tables B-4 and B-5).

SPMD replicates agreed within performance measures with one exception: Trans-Nonachlor was found in only one SPMD at a concentration below the LPQL (Appendix B Table B-6).

Of 10 pesticides detected in the POCISs, only four occurred in both replicates. Concentrations of the mutually detected pesticides were inconsistent between replicates (Appendix B Table B-7).

Results

Conventional Field Parameters

A summary of conventional parameter results is presented in Table 3.

Table 3. Summary of results for conventional parameters.

Parameter	n	Minimum	Median	Mean	Maximum
Discharge (cfs)	21	99	111	117	169
TSS (mg/L)	22	6	10.5	10	14
TOC (mg/L)	22	1.5	1.9	1.9	2.1
DOC (mg/L)	21	1.3	1.5	1.5	2
pH	22	7.5	8	8.1	8.9
Dissolved oxygen (mg/L)	20	9.6	12.1	12.1	14.8
Conductivity (µS)	21	175	189	190	222
Water temperature (°C)	22	10.8	13.5	13.5	16.1

Stream discharge in Marion Drain generally decreased throughout the April-May 2007 study period, from an initial high of 180 cfs to an average of 109 cfs after the first five days (Figure 6). TSS, however, generally increased with time, perhaps reflecting increasing irrigation of farmland. Other conventional parameters remained relatively unchanged.

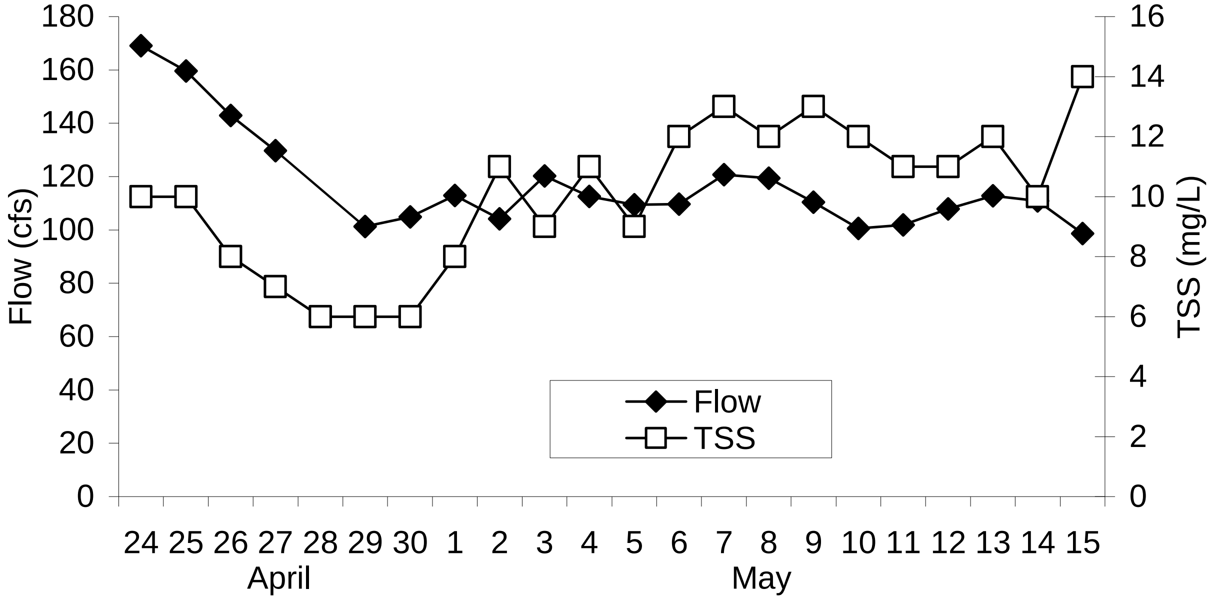

Figure 6. Flow and total suspended solids during the monitoring period.

Sample Method Comparison

Daily versus Weekly Grab Sampling

Daily grab sampling from April 24 through May 15, 2007 detected 16 pesticides, including 13 herbicides and 3 insecticides (Table 4). Most pesticide concentrations were near detection limits (Appendix B Table B-3).

The number of detected pesticides per grab sample tended to increase over time (Figure 7).

Pesticides that were detected initially tended to be found on consecutive days. Weekly samples were therefore a good indicator for detection frequency when compared to daily samples.

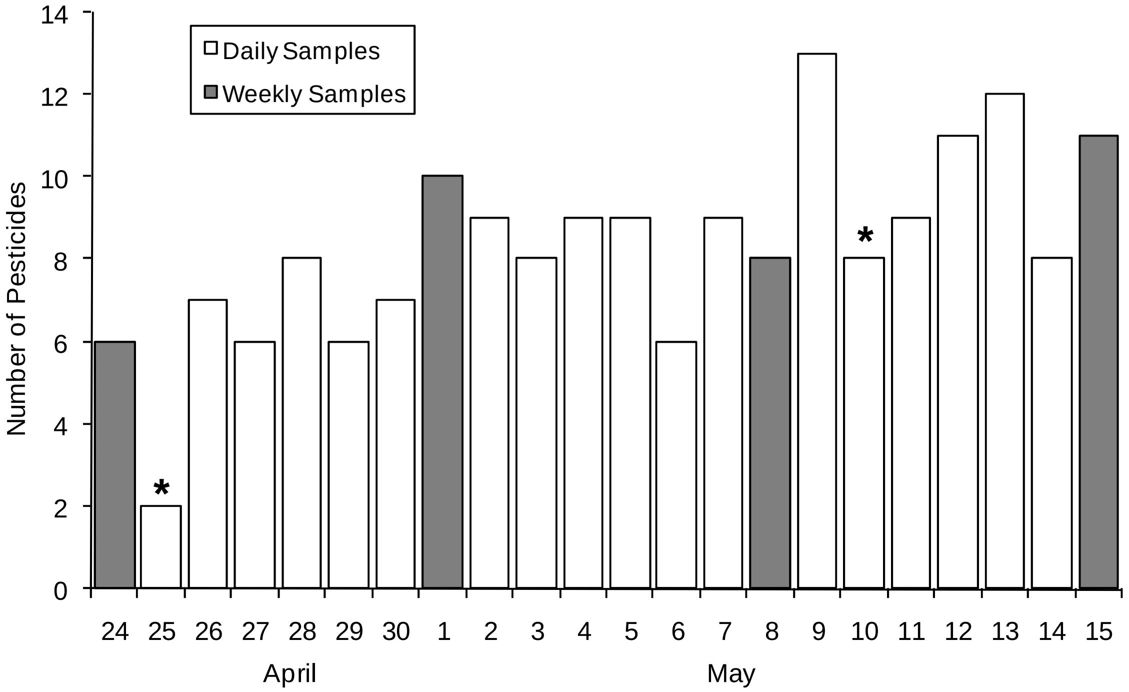

Figure 7. Number of pesticides detected per day.

*Samples for LCMS on April 25 and GCMS-H on May 10 were lost and could not be analyzed.

The weekly samples were representative of daily concentrations. Most weekly medians were within 10% of the daily medians. Weekly samples also detected the maximum or near maximum concentrations for Bentazon, Bromoxynil, Chlorpyrifos, Clopyralid, and Malathion (Table 4 and Figures 8-12).

Table 4. Summary of grab sample results (ng/L).[1]

Chemical	[2]Type	Detection frequency		Minimum		Median		Maximum	
		Weekly[3]	Daily[4]	Weekly	Daily	Weekly	Daily	Weekly	Daily
2,4-D[4]	H	100%	67%	35	32	50	<64	68	500
Atrazine	H	50%	68%	9	9	27	25	21	36
Bentazon[4]	H	50%	38%	22	19	58	<62	53	53
Bromoxynil[4]	H	100%	67%	21	19	31	56	61	63
Carbaryl[4]	H	0%	19%	<19	10	<19	<19	<19	35
Chlorpyrifos	H	50%	77%	6	6	26	20	20	22
Clopyralid[4]	I-OP	25%	5%	27	27	<62	<62	27	27
Dicamba I[4]	H	25%	57%	16	3	<62	33	16	61
Diuron	H	25%	14%	28	15	<49	<49	28	47
Eptam	H	25%	41%	24	13	<32	<32	24	71
Malathion	H	25%	5%	<32	<32	<32	<32	82	82
MCPA[4]	H	75%	57%	43	20	66	<61	86	130
Pendimethalin	H	100%	95%	27	27	43	53	74	98
Simazine	H	50%	50%	7	7	59	67	19	36
Terbacil	I-OP	100%	100%	34	31	115	200	280	490
Trifluralin	I-C	75%	82%	21	18	27	27	28	40

[1] Non-detections are reported as <LPQL.

[2] H = Herbicide, I-C = Insecticide/Carbamate, I-OP = Insecticide/Organophosphate.

[3] Weekly results are a subset of four daily results that occurred during pre-scheduled weekly sampling days (April 24, May 1, May 8, and May 15).

[4] Due to sample losses on April 25 and May 10, only 21 daily grab samples were analyzed for the indicated pesticides. The remaining pesticides had 22 daily grab samples.

Weekly sampling did poorly for pesticides that showed isolated spikes (e.g., 2,4-D, Dicamba I, Eptam, and MCPA; Figures 13-16). Maximum daily concentrations for these pesticides were often much higher than for weekly samples. Weekly samples also did poorly at detecting some rarely occurring pesticides such as Carbaryl and Diuron (Figures 17 and 18).

Figures 19-23 show detections for Atrazine, Pendimethalin, Simazine, Terbacil, and Trifluralin.

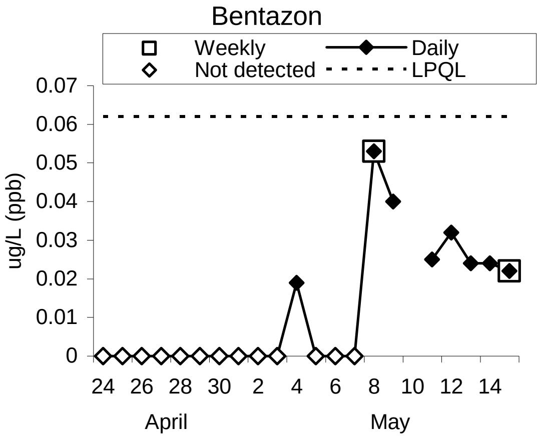

Figure 8. Bentazon

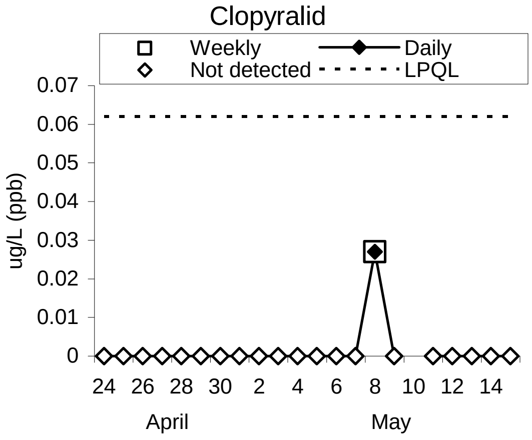

Figure 11. Clopyralid

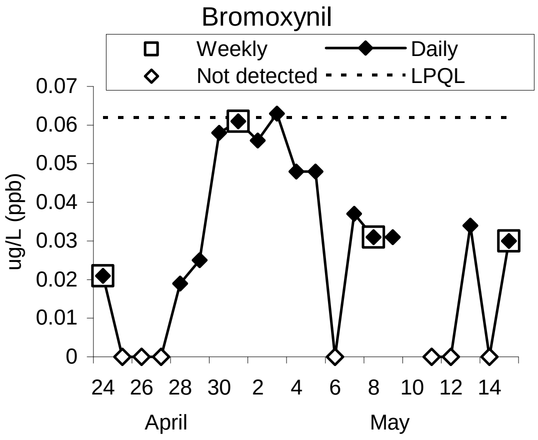

Figure 9. Bromoxynil

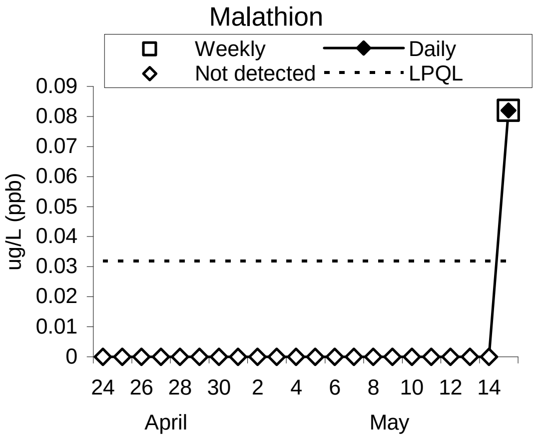

Figure 12. Malathion

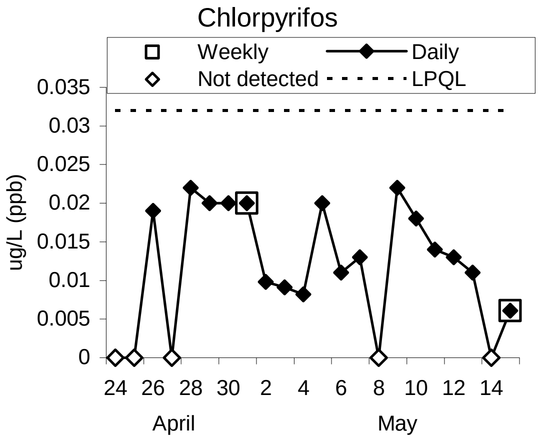

Figure 10. Chlorpyrifos

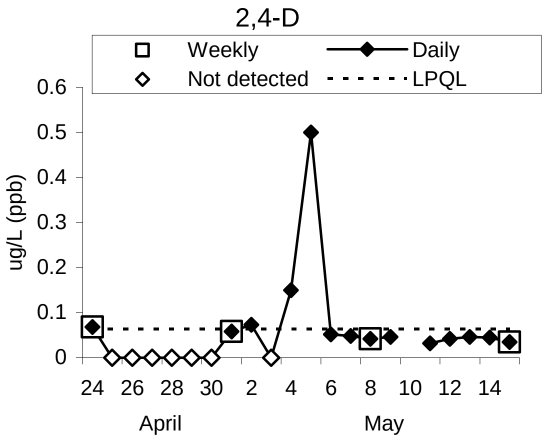

Figure 13. 2,4-D

Figures 8-23. Daily versus weekly pesticide concentrations. Non-detections are plotted as zero.

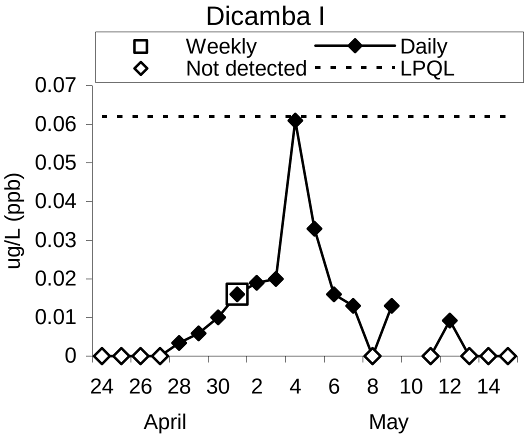

Figure 14. Dicamba I

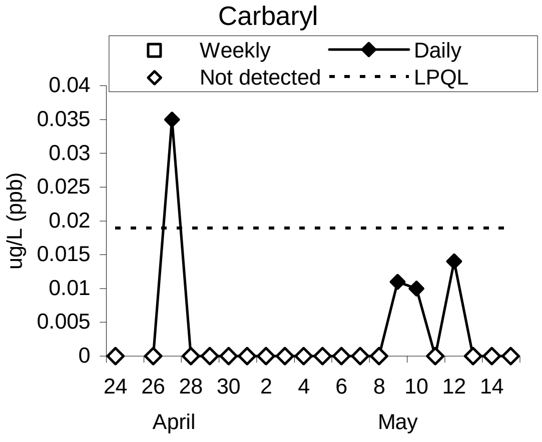

Figure 17. Carbaryl

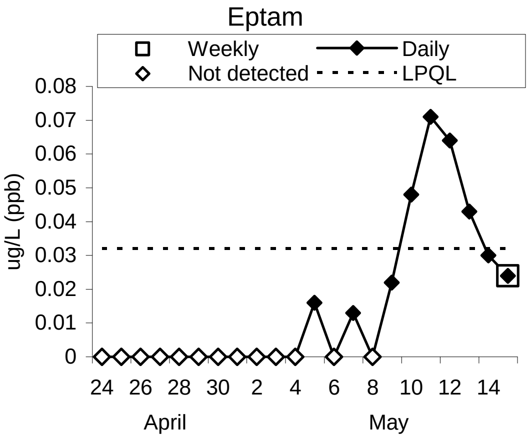

Figure 15. Eptam

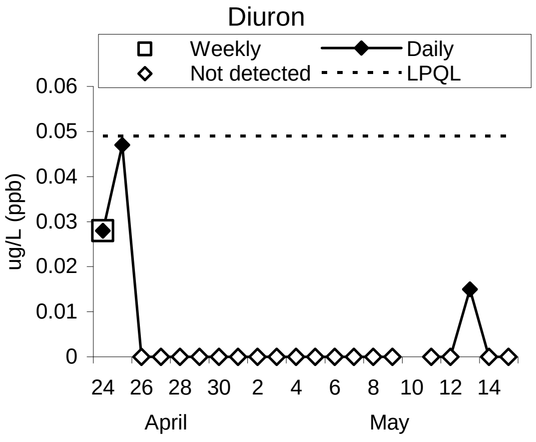

Figure 18. Diuron

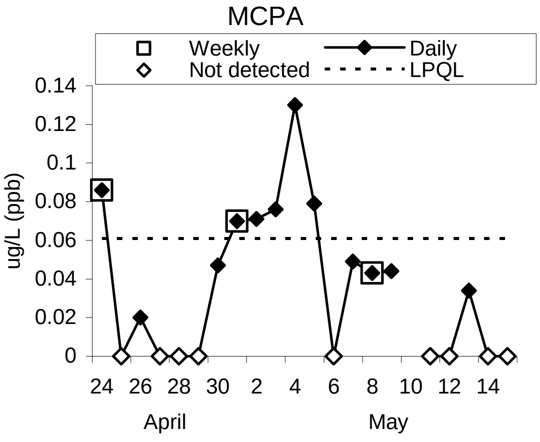

Figure 16. MCPA

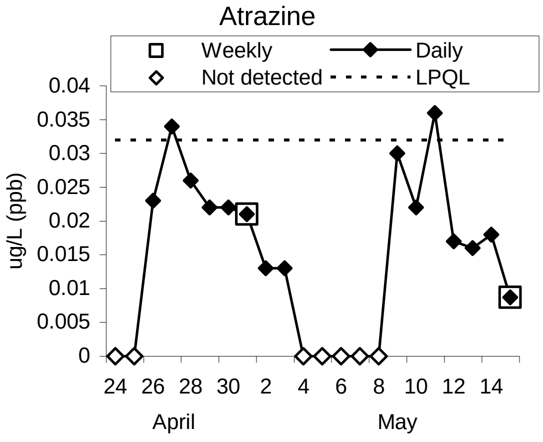

Figure 19. Atrazine

Figures 8-23 (continued).

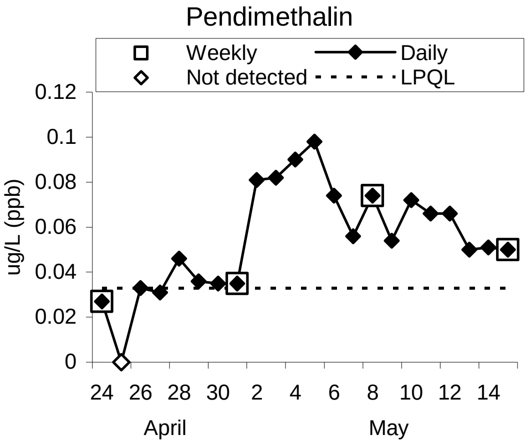

Figure 20. Pendimethalin

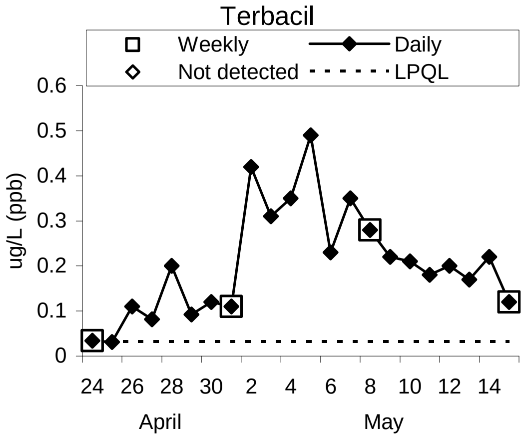

Figure 22. Terbacil

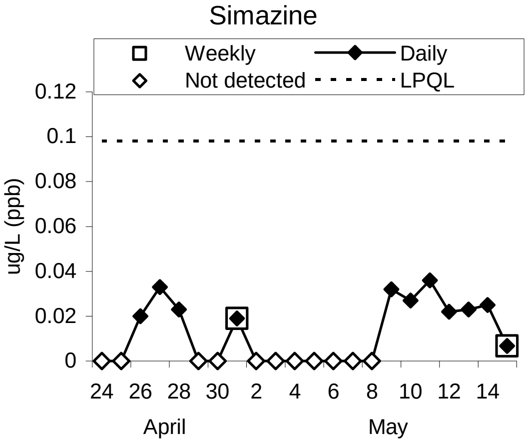

Figure 21. Simazine

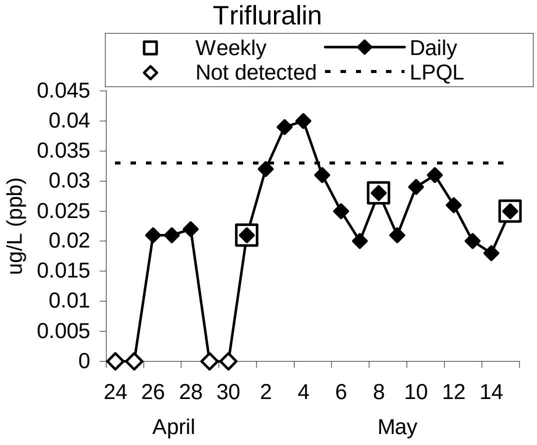

Figure 23. Trifluralin

Figures 8-23 (continued).

Conventional Parameters and Pesticides

Weekly sample means for detected pesticides and conventional parameters were compared to the daily sample means using t-tests. Weekly and daily variances were assumed to be equal. Only the pesticides listed in Table 5 had enough detections in both the weekly and daily samples for conducting t-tests. None of the weekly means were significantly different than the daily means at a p-value of 0.05 (Tables 5 and 6).

Table 5. T-Tests of daily versus weekly sample means for selected pesticides.

Chemical	t	df[1]	p-value
Atrazine	1.271	11	0.23
Bentazon	-0.431	6	0.68
Chlorpyrifos	0.587	10	0.57
Pendimethalin	0.480	21	0.64
Simazine	0.620	3	0.58
Terbacil	1.078	24	0.29
Trifluralin	0.503	17	0.62

[1] df = degrees of freedom

Table 6. T-Tests of daily versus weekly sample means for conventional parameters.

Parameter	t	df[1]	p-value
Discharge	-0.694	23	0.49
TSS	-0.725	24	0.48
TOC	-0.146	24	0.89
DOC	0.671	23	0.51
Staff gauge	-1.393	21	0.18
Dissolved oxygen	-0.186	22	0.85
pH	-0.842	24	0.41
Conductivity	0.723	23	0.48
Water temperature	-0.894	24	0.38

[1] df = degrees of freedom

Conventional parameters were linearly regressed first on the number and then on the concentrations of detected pesticides. No linear relationships were found.

Daily Grab Sampling versus SPMD

The SPMD samples were analyzed for a subset of the GCMS analytes in the grab samples (see Appendix B Table B-3). The effective reporting limit for SPMDs was much lower due to their high affinity for many of these compounds.

SPMD samplers detected 8 pesticides, including 2 herbicides, 3 insecticides, and 3 degradates (Table 7). Five of these compounds were not found by daily grab sampling (4,4'-DDT, 4,4'-DDD, 4,4'-DDE, Endosulfan 1, and Trans-Nonachlor) due to higher detection limits.

SPMD results and LPQLs are reported in Table 7 as estimated water concentrations calculated using an Excel® spreadsheet developed by USGS (Alvarez, 2006).

Table 7. SPMD results compared to grab sample results (ng/L).[1] SPMD calculated water concentrations include only the dissolved residue.

Chemical	Log K_{ow}	[2]Type	Daily Grab Samples (n = 22)			SPMD (n = 2)		
			Freq	Min	Max	Freq	Min	Max
4,4'-DDT	6.91	I-OC	0%	<32	<32	100%	0.016	0.019
4,4'-DDE	6.51	D	0%	<32	<32	100%	0.056	0.058
4,4'-DDD	6.02	D	0%	<32	<32	100%	0.015	0.016
Endosulfan I	3.83	D	0%	<49	<49	100%	1.806	2.207
Trans-Nonachlor[3]	6.35	I-OC	0%	<32	<32	50%	0.003	0.003
Trifluralin	5.34	H	82%	18	40	100%	0.033	0.036
Pendimethalin	5.18	H	95%	27	98	100%	0.759	1.040
Chlorpyrifos	4.96	I-OP	77%	6.1	22	100%	1.092	1.224
Eptam	3.21	H	41%	13	71	0%	<3.5	<3.5
Diuron	2.68	H	14%	15	47	0%	<28	<28
Atrazine	2.61	H	68%	8.7	36	0%	<23	<23
Malathion	2.36	I-OP	5%	<32	82	0%	<56	<56
Simazine	2.18	H	50%	6.7	36	0%	<108	<108
Terbacil	1.89	H	100%	31	490	0%	<328	<328

[1] Non-detections are reported as <LPQL.

[2] D = Degradate, H = Herbicide, I-OC = Insecticide/Organochlorine, I-OP = Insecticide/Organophosphate.

[3] Trans-Nonachlor was detected in only one SPMD.

Pendimethalin, Trifluralin, and Chlorpyrifos were the only compounds detected in both SPMDs and grab samples. Calculated water concentrations were much lower in the SPMDs than the average of the daily grab samples. The reason for the difference could not be determined.

The daily grab sampling detected six compounds that were not found by the SPMDs (Table 7). All of these have log K_{ow}s ≤ 3.21 and, thus, have a low affinity for SPMDs.

Daily Grab Sampling versus POCIS

POCIS water concentrations for detected pesticides could not be calculated due to a lack of calibration data. Grab sample concentrations in Table 8 are listed for relative comparison only.

POCIS field blank contamination compromised the comparison with grab sample results. Excluding the blank contamination, the POCISs detected 8 pesticides: 6 herbicides, 1 insecticide, and 1 degradate (Table 8). Most pesticide concentrations in the POCIS extracts were near detection limits (see Appendix B Table B-3).

Two compounds, Methomyl and Oxamyl, were found by POCIS samplers and not in daily samples. Daily grab sampling detected ten compounds that were not found in the POCISs. Six compounds were mutually identified by both the grab and POCIS samples: Bromoxynil, MCPA, 2,4-D, Atrazine, Bentazon, and Terbacil.

Table 8. POCIS results (ng) compared to grab sample results (ng/L).[1]

Chemical	Log K_{ow}	[2]Type	Daily Grab Samples (n = 21 or 22)[3]			POCIS (n = 2)		
			Freq	Min	Max	Freq	Min	Max
2,4-D[3]	2.81	H	67%	32	500	50%	<190	270
Atrazine	2.61	H	68%	8.7	36	50%	<99	150
Terbacil	1.89	H	100%	31	490	50%	<190	1100
Bentazon[3]	2.34	H	38%	19	53	100%	71	130
Bromoxynil[3]	3.39	H	67%	19	63	100%	140	270
MCPA[3]	3.25	H	57%	20	130	100%	39	190
Chlorpyrifos	4.96	I-OP	77%	6.1	22	0%	<99	<99
Clopyralid[3]	1.06	H	5%	27	27	0%	<190	<190
Dicamba I[3]	2.21	H	57%	3.4	61	0%	<190	<190
Diuron	2.68	H	14%	15	47	0%	<150	<150
Eptam	3.21	H	41%	13	71	0%	<99	<99
Malathion	2.36	I-OP	5%	<32	82	0%	<99	<99
Pendimethalin	5.18	H	95%	27	98	0%	<99	<99
Simazine	2.18	H	50%	6.7	36	0%	<99	<99
Trifluralin	5.34	H	82%	18	40	0%	<99	<99
Carbaryl[3]	2.36	I-C	19%	10	35	0%	<41	<41
Methiocarb[3,4]	2.92	I-C	0%	<19	<19	50%	<6	15
Methomyl[3]	0.6	D	0%	<47	<47	50%	<15	44
Oxamyl[3]	-0.47	I-C	0%	<48	<48	50%	9.5	9.5
Oxamyl oxime[3,4]	-0.71	D	0%	<19	<19	100%	5.4	23

[1] Non-detections are reported as <LPQL.

[2] D = Degradate, H = Herbicide, I-C = Insecticide/Carbamate, I-OP = Insecticide/Organophosphate.

[3] Due to sample losses on April 25 and May 10, only 21 daily grab samples were analyzed for the indicated pesticides. The remaining pesticides had 22 daily grab samples.

[4] Methiocarb and Oxamyl oxime were each detected in the POCIS field blank at 10 ng and 47 ng, respectively.

This page is purposely left blank

Discussion

Grab Samples

The increase in the number of compounds detected through the April-May 2007 monitoring period probably coincides with the onset of spring pesticide application. This detection pattern appears to match previous seasons, 2003-2006. Detected pesticides continued to be identified on consecutive days. Successive detections may have been related to chemical persistence or continued field applications.

Weekly sampling detected the majority of pesticides found in the daily regime. Pesticides tended to persist for multiple days allowing weekly grab sampling to detect most occurrences. Weekly sampling was also effective at estimating the median pesticide concentrations detected in the daily results.

Weekly sampling missed periodic pesticide peaks detected by daily samples. Thus, weekly sampling may not detect the maximum concentrations of certain pesticides present in the sample season. However, weekly samples did succeed in detecting the highest or near highest concentrations for many compounds.

The current weekly sample regime was designed for long-term monitoring and was not intended to detect short-term pesticide events. In most cases, the weekly samples were effective at detecting pesticide presence at median background levels.

Because increasing the standard sampling rate is cost prohibitive, targeted samples may be used to increase detection of pesticide peaks. Timing additional samples to coincide with pesticide applications would target the most likely harmful pesticide concentrations.

SPMDs

SPMDs detected more hydrophobic compounds than grab samples. These included both legacy and current use hydrophobic pesticides, not found in the grab samples. The additional detections reflect the lower reporting limits in the SPMDs. Alternative methods such as large volume injection (LVI) or Gas Chromatography with Electron Capture Detection (GC/ECD) could lower the grab sample reporting limit and improve the detection frequency.

SPMD-calculated water concentrations were much lower than the average grab sample results for mutually detected compounds. The cause of this discrepancy is unknown. Other studies have found closer relationships between water and passive sampler concentrations. Rantalainen et al. (1998) found comparable concentrations of PCBs from SPMDs and in water samples processed through an Infiltrex resin column. Hyne et al. (2004) found pesticide concentrations to be similar between trimethylpentane (TRIMPS) passive samplers and water samples. And Ellis et al. (1995) found links between organochlorine SPMD concentrations and the measured values of ultrafilter permeates from water samples.

In this study, SPMDs and grab samples were both effective at detecting hydrophobic pesticides. But SPMDs were better at detecting legacy pesticides at low concentrations. Alternative analysis methods can lower grab sample detection limits. However, the need for continuous exposure data may point to SPMDs as a useful complement to the current sampling regime.

POCISs

The POCISs detected some compounds that were not identified in grab samples. And six pesticides were mutually identified by both POCISs and grab samples. However, the majority of pesticides identified by grab sampling were not detected by the POCISs.

POCIS quality control samples indicated shortcomings in the data. POCIS surrogates and laboratory control sample recoveries failed to meet project performance criteria (see Appendix B). The inconsistent detections between replicates, contamination of the field blank, and poor sample recoveries indicate problems that may be unique to this study.

Although there were data quality problems with the POCISs in this study, other studies have successfully used POCISs to monitor current-use pesticides and other polar compounds. Charlestra (2005) used POCISs to compare relative pesticide concentrations between stream sites. Vermeirssen et al. (2005) found detections of environmental estrogens were correlated between POCISs, surface water grab samples, and caged fish tissue. Other studies have also used POCISs successfully in surface water sampling (e.g., Mazella et al., 2007; Sharpe and Nichols, 2007). The USGS (2004) also has recommended the POCIS as a sampling tool for polar compounds including pesticides.

Although POCIS results were inconclusive in the present study, these samplers have the potential to complement grab samples by continuously sequestering polar current-use pesticides during deployment. Further research into polar compound passive sampling by USGS and others is ongoing.

Recommendations

As a result of this 2007 study, the following recommendations are made:

- Continue with the current program of weekly sampling for long-term pesticide monitoring.
- Identify chemicals where intensive monitoring is needed, and organize additional sampling events to coincide with pesticide applications.
- Consider using SPMDs for continuous monitoring of hydrophobic pesticides.
- Follow development in POCIS and other polar organic samplers as a potentially useful complementary approach to the current program.
- Compare pesticide values obtained for this study to endpoint criteria in the 2006-2008 triennial report, including:
    - Pesticide registration toxicity and risk assessment endpoints criteria.
    - Washington Administrative Code (WAC) water quality standards for the protection of aquatic life.
    - EPA National Recommended Water Quality Criteria.

This page is purposely left blank

References

Alvarez, D.A., 2006. SPMD Calculator version 5-1 (downloaded 11/18/2007). USGS/Columbia Environmental Research Center. 4200 New Haven Road, Columbia, MO 65202 http://137.227.231.90/Research/spmd.htm.

APHA (American Public Health Association), 2005. Standard Methods for the Analysis of Water and Wastewater, 21st Edition. Joint publication of the APHA, American Water Works Association, and Water Environment Federation. www.standardmethods.org/

ASTM (American Society for Testing Materials), 2005-2007. Book of Standards, Section 11, Various years. www.normas.com/ASTM/STDS/index.html

Anderson, P., D. Dugger, and C. Burke, 2007. Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2006 Monitoring Data Summary. Washington State Department of Ecology. Ecology Publication No. 07-03-016. www.ecy.wa.gov/biblio/0703016.html

Anderson, P., R. Jack, C. Burke, J. Cowles, and B. Moran, 2004. Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, April to December, 2003. Washington State Departments of Agriculture and Ecology. Ecology Publication No. 04-03-048. www.ecy.wa.gov/biblio/0403048.html

Burke, C. and D. Dugger, 2007. Quality Assurance Project Plan: Marion Drain Intensive Surface Water Sampling for Pesticides In Salmonid-Bearing Streams. Washington State Departments of Agriculture and Ecology. Ecology Publication No. 07-03-105. www.ecy.wa.gov/biblio/0703105.html

Burke, C. and P. Anderson, 2006. Addendum to the Quality Assurance Project Plan for the Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, Addition of the Skagit-Samish Watersheds and Extension of Program Through June 2009. www.ecy.wa.gov/biblio/0303104add.html

Burke, C., P. Anderson, D. Dugger, and J. Cowles, 2006. Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2003-2005. Washington State Departments of Agriculture and Ecology. Ecology Publication No. 06-03-036. www.ecy.wa.gov/biblio/0603036.html

Burke, C., P. Anderson, J. Cowles and B. Moran, 2005. Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, April through October, 2004. Washington State Departments of Agriculture and Ecology. Ecology Publication No. 05-03-025. www.ecy.wa.gov/biblio/0503025.html

Charlestra, L., 2005. Detection of pesticides in Washington County (Maine) surface waters using Polar Organic Chemical Integrative Samplers (POCIS). Senator George J. Mitchell Center For Environmental and Watershed Management, University of Maine, Orono, ME 04469-5764.

Dugger, D., P. Anderson, and C. Burke, 2007. Addendum to the Quality Assurance Project Plan for the Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams: Addition of Wenatchee and Entiat Watersheds in the Upper Columbia Basin. www.ecy.wa.gov/biblio/0303104add2.html

Ecology, 2007. Standard Operating Procedures for the Environmental Assessment Program (EAP). SOP for Determining Conductivity/Salinity in Water, Provisional, EAP 010; SOP for Determining Instantaneous Temperature in Water, Provisional, EAP 011; and SOP for Using Semipermeable Membrane Devices to Monitoring Hydrophobic Organic Compounds in Surface Water, EAP 001. www.ecy.wa.gov/programs/eap/quality.html

Ellis, G.S., J.N. Huckins, C.E. Rostad, C.J. Schmitt, J.D. Petty, and P. MacCarthy, 1995. Evaluation of Lipid-Containing Semipermeable Membrane Devices (SPMDs) for Monitoring Organochlorine Contaminants in the Upper Mississippi River. Environ. Toxicol. Chem. 14:1875-1884.

EPA, 1999. Contract Laboratory Program National Functional Guidelines for Organic Data Review. EPA 540/R-99/008. www.epa.gov/superfund/programs/clp/download/fgorg.pdf

EPA, 2007. USEPA Contract Laboratory Program. National Functional Guidelines for Superfund Organic Methods Data Review. EPA-540-R-04-009. www.epa.gov/superfund/programs/clp/download/somnfg.pdf

Freudenthal, J., D. Lind, R. Visser, and P. Mess, 2005. Yakima Subbasin Salmon Recovery Plan, Draft October 19, 2005. Prepared for the Yakima Subbasin Fish and Wildlife Planning Board. www.co.yakima.wa.us/YakSubbasin/Draft%20plan/RecPlanFinal.pdf

Haring, D., 2001. Yakima River Watershed: Water Resource Inventory Areas 37-39, Final Report. Washington Conservation Commission, Olympia, WA.

Hyne, R., F. Pablo, M. Aistrope, A.W. Leonard, and N. Ahmad, 2004. Comparison of Time-Integrated Pesticide Concentrations Determined from Field-Deployed Passive Samplers with Daily River-Water Extractions. Environ. Toxicol. Chem. 23(9):2090-2098.

Johnson, A. and J. Cowles, 2003. Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat: A Study for the Washington State Department of Agriculture Conducted by the Washington State Department of Ecology. Publication No. 03-03-104. www.ecy.wa.gov/biblio/0303104.html

Mazella, N., J.F. Duberneta, and F. Delmasa, 2007. Determination of kinetic and equilibrium regimes in the operation of polar organic chemical integrative samplers. Application to the passive sampling of the polar herbicides in aquatic environments. Journal of Chromatography A 1154(1-2): 42-51.

MEL, 2005. Manchester Environmental Laboratory Lab Users Manual, Eighth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL, 2006. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Rantalainen, A.L., M.G. Ikonomou, and I.H. Rogers, 1998. Lipid-Containing Semipermeable Membrane Devices (SPMDs) as Concentrators of Toxic Chemicals in the Lower Fraser River, British Columbia. Chemosphere 37:1119-1138.

Sharpe, A.J. and E.G. Nichols, 2007. Use of stable nitrogen isotopes and permeable membrane devices to study what factors influence freshwater mollusk survival in the Conasauga River. Environmental Monitoring and Assessment 132 (1-3): 275-295.

USGS (U.S. Geological Survey), 2004. Polar Organic Chemical Integrative Sampler (POCIS). U.S. Geological Survey. Columbia Environmental Research Center. www.cerc.usgs.gov/pubs/center/pdfDocs/POCIS.pdf

USGS (U.S. Geological Survey), 2007. National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, http://pubs.water.usgs.gov/twri9A

Vermeirssen, E.L.M., O. Korner, R. Schonenberger, M.J.F. Suter, and P. Burkhardt-Holm, 2005. Characterization of environmental estrogens in river water using a three pronged approach: active and passive water sampling and the analysis of accumulated estrogens in the bile of caged fish. Environmental Science and Technology 39: 8191-8198.

This page is purposely left blank

Appendix A: List of Acronyms

Following are acronyms and abbreviations used frequently in this report.

DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
EPA	United States Environmental Protection Agency
ESA	United States Endangered Species Act
EST	Environmental Sampling Technologies (Laboratory)
GCMS	Gas chromatography/mass spectrometry
GCMS-H	Gas chromatography/mass spectrometry for acid herbicides
LCMS	Liquid chromatography/mass spectrometry
LCS	Laboratory control sample
LPQL	Lower practical quantitation limit
MEL	Manchester Environmental Laboratory (Department of Ecology)
MS/MSD	Matrix spike/matrix spike duplicate
NOAA	National Oceanic and Atmospheric Administration
POCIS	Polar Organic Chemical Integrative Sampler
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedure
SPMD	Semipermeable membrane device
TOC	Total organic carbon
TSS	Total suspended sediment
USGS	United States Geological Survey
WSDA	Washington State Department of Agriculture

This page is purposely left blank

Appendix B: Quality Assurance

Data may be qualified if one or more analytical factors affect confidence in the prescribed data value. Manchester Environmental Laboratory qualifies data according to the National Functional Guidelines for Organic Data Review (EPA, 1999, 2007). Data qualification is presented in Table B-1.

Table B-1. Data qualification.

Qualifier	Definition
U	The analyte was not detected at or above the reported sample quantitation limit.
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample (either certain quality control criteria were not met or the concentration of the analyte was below the 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 be imprecise.
REJ	The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.
NAF	Not analyzed for.
NJ	The analysis indicates the presence of an analyte that has been tentatively identified, and the associated numerical value is the approximate concentration.
NC	Not calculated.

MEL, 2000, 2007; EPA, 2007

Performance measures for quality assurance and control are presented in Table B-2. The lowest concentration of interest for SPMD/POCIS reflects the lower reporting limits achievable from MEL, EST, and contract laboratories. Lowest concentrations of interest for grab samples are below reporting limits. Detections quantified below reporting limits are qualified as estimates.

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

Analysis[1]	Field/Lab Replicates	MS/MSD	Surrogates and Lab. Control Samples	Lowest Concentration of Interest	
	RPD[2]	RPD[2]	% Recovery	Grab Samples	SPMD/POCIS
Herbicides	±40	±40	40-130	30 ng/L	10ng/POCIS or POCIS
Pesticide-Cl	±40	±40	50-120	1 ng/L	10ng/SPMD or POCIS
Pesticide-N	±40	±40	30-105	20 ng/L	10ng/SPMD or POCIS
Pesticide-OP	±40	±40	30-150	5 ng/L	10ng/SPMD or POCIS
Pesticide-Py	±40	±40	30-130	5 ng/L	10ng/SPMD or POCIS
Pesticide-C	±40	±40	30-130	5 ng/L	10ng/POCIS
TSS	±20	±20	80-120	1 mg/L	
TOC	±20	±20	80-120	1 mg/L	
DOC	±20	±20	80-120	1 mg/L	

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

[2] 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. LPQLs were calculated for all active and passive sample methods. LPQL data are presented in Table B-3. LPQL for passive samplers represent the concentration in the sample extract, unadjusted for total water volume sampled.

Table B-3. Mean performance Lower Practical Quantitation Limits (ng/L).

Chemical	[1]Use	Parent	[2]Analysis Method	LPQL		
				Grab Sample	SPMD[3] extract	POCIS[3] extract
1-Naphthol	D	Carbaryl	LCMS	50		15
2,3,4,5-Tetrachlorophenol	D	PCP	GCMS-H	62		190
2,3,4,6-Tetrachlorophenol	D	PCP	GCMS-H	62		190
2,4,5-T	H		GCMS-H	62		190
2,4,5-TP (Silvex)	H		GCMS-H	62		190
2,4,5-Trichlorophenol	F		GCMS-H	62		190
2,4,6-Trichlorophenol	F		GCMS-H	62		190
2,4-D	H		GCMS-H	64		190
2,4-DB	H		GCMS-H	62		190
2,4'-DDD	D	DDT	GCMS	32	33	99
2,4'-DDE	D	DDT	GCMS	32	33	99
2,4'-DDT	D	DDT	GCMS	32	33	99
3,5-Dichlorobenzoic Acid	H		GCMS-H	62		190
3-Hydroxycarbofuran	I-C	Carbofuran	LCMS	48		15
4,4'-DDD	D	DDT	GCMS	32	33	99
4,4'-DDE	D	DDT	GCMS	32	33	99
4,4'-DDT	D	DDT	GCMS	32	33	99
4-Nitrophenol	D	Parathion, Others	GCMS-H	61		190
Acifluorfen (Blazer)	H		GCMS-H	62		190
Alachlor	H		GCMS	32	33	99
Aldicarb	I-C		LCMS	94		30
Aldicarb sulfone	D	Aldicarb	LCMS	52		15
Aldicarb sulfoxide	D	Aldicarb	LCMS	19		6
Aldrin	I-OC		GCMS	32	33	99
Alpha-BHC	I-OC		GCMS	32	33	99
Atrazine	H		GCMS	32	33	99
Azinphos Ethyl	I-OP		GCMS	32	33	99
Azinphos methyl	I-OP		GCMS	32	33	99
Benefin	H		GCMS	32	33	99
Bensulide	H-OP		GCMS	32	33	99
Bentazon	H		GCMS-H	62		190
Benthiocarb			GCMS	98	100	300
Beta-BHC	I-OC		GCMS	32	33	99
Bromacil	H		GCMS	32	33	99

Continued…

Table B-3 continued. Mean performance Lower Practical Quantitation Limits (ng/L).

Chemical	[1]Use	Parent	[2]Analysis Method	LPQL		
				Grab Sample	SPMD[3] extract	POCIS[3] extract
Bromoxynil	H		GCMS-H	62		190
Butylate	H		GCMS	32	33	99
Captan	F		GCMS	32	33	99
Carbaryl	I-C		LCMS	19		41
Carbofuran	I-C		LCMS	19		6
Carboxin	F		GCMS	32	33	99
Chlorothalonil (Daconil)	H		GCMS	32	33	99
Chlorpropham	H		GCMS	32	33	99
Chlorpyrifos	I-OP		GCMS	32	33	99
Cis-Chlordane (Alpha-Chlordane)	I-OC		GCMS	32	33	99
Cis-Nonachlor	I-OC		GCMS	32	33	99
cis-Permethrin	I-Py		GCMS	49	50	150
Clopyralid	H		GCMS-H	62		190
Coumaphos	I-OP		GCMS	32	33	99
Cyanazine	H		GCMS	32	33	99
Cycloate	H		GCMS	32	33	99
Dacthal (DCPA)	H		GCMS-H	62		190
Delta-BHC	I-OC		GCMS	32	33	99
Deltamethrin	I-Py		GCMS	98	100	300
Di-allate (Avadex)	H		GCMS	32	33	99
Diazinon	I		GCMS	32	33	99
Dicamba I	H		GCMS-H	62		190
Dichlobenil	H		GCMS	32	33	99
Dichlorprop	H		GCMS-H	62		190
Dichlorvos (DDVP)	D		GCMS	49	50	150
Diclofop-Methyl	H		GCMS-H	62		190
Dieldrin	I-OC		GCMS	49	50	150
Dimethoate	I-OP		GCMS	32	33	99
Dinoseb	H		GCMS-H	62		190
Diphenamid	H		GCMS	32	33	99
Disulfoton (Di-Syston)	I-OP		GCMS	32	33	99
Disulfoton sulfone	I-OP		GCMS	98	100	300
Diuron	H		GCMS	49	50	150
Endosulfan I	I-OC		GCMS	49	50	150
Endosulfan II	I-OC		GCMS	49	50	150
Endosulfan Sulfate	I-OC		GCMS	32	33	99
Endrin	I-OC		GCMS	49	50	150
Endrin Aldehyde	D		GCMS	49	50	150
Endrin Ketone	D		GCMS	32	33	99
EPN	I-OP		GCMS	32	33	99
Eptam	H		GCMS	32	33	99
Ethalfluralin (Sonalan)	H		GCMS	32	33	99
Ethion	I-OP		GCMS	32	33	99
Ethoprop	I-OP		GCMS	32	33	99

Continued…

Table B-3 continued. Mean performance Lower Practical Quantitation Limits (ng/L).

Chemical	[1]Use	Parent	[2]Analysis Method	LPQL Grab Sample	LPQL SPMD[3] extract	LPQL POCIS[3] extract
Fenamiphos	I-OP		GCMS	32	33	99
Fenarimol	F		GCMS	32	33	99
Fenvalerate (2 isomers)	I-Py		GCMS	32	33	99
Fluridone	H		GCMS	98	100	300
Fonofos	I-OP		GCMS	32	33	99
Gamma-BHC (Lindane)	I-OC		GCMS	32	33	99
Heptachlor	I-OC		GCMS	32	33	99
Heptachlor Epoxide	D	Heptachlor	GCMS	32	33	99
Hexachlorobenzene	I-OC		GCMS	32	33	99
Hexazinone	H		GCMS	49	50	150
Imidacloprid	I-OC		LCMS	50		
Imidan	I-OP		GCMS	32	33	99
Ioxynil	H		GCMS-H	62		190
Kelthane	I-OC		GCMS	293	300	900
Linuron	H		GCMS	49	50	150
Malathion	I-OP		GCMS	32	33	99
MCPA	H		GCMS-H	61		190
MCPP (Mecoprop)	H		GCMS-H	62		190
Metalaxyl	F		GCMS	32	33	99
Methidathion	I-OP		GCMS	293	300	900
Methiocarb	I-C		LCMS	19		6
Methomyl	I-C		LCMS	47		15
Methomyl oxime	D	Methomyl	LCMS	19		6
Methoxychlor	I-OC		GCMS	32	33	99
Methyl Chlorpyrifos	I-OP		GCMS	32	33	99
Methyl Paraoxon	I-OP		GCMS	98	100	300
Methyl Parathion	I-OP		GCMS	32	33	99
Metolachlor	H		GCMS	32	33	99
Metribuzin	H		GCMS	32	33	99
Mevinphos	I-OP		GCMS	49	50	150
MGK264	Sy-I		GCMS	32	33	99
Mirex	I-OC		GCMS	32	33	99
Monocrotophos			GCMS	49	50	150
Naled	I-OP		GCMS	32	33	99
Napropamide	H		GCMS	49	50	150
Norflurazon	H		GCMS	32	33	99
O-Ethyl-S-PO-Dieste			LCMS	50		
Oryzalin			GCMS	98	100	300
Oxamyl	I-C		LCMS	48		15
Oxamyl oxime	D	Oxamyl	LCMS	19		15
Oxychlordane	D	Chlordane	GCMS	32	33	99
Oxyfluorfen	H		GCMS	32	33	99
Parathion	I-OP		GCMS	32	33	99
Pebulate	H		GCMS	32	33	99
Pendimethalin	H		GCMS	33	33	99

Continued…

Table B-3 continued. Mean performance Lower Practical Quantitation Limits (ng/L).

Chemical	[1]Use	Parent	[2]Analysis Method	LPQL		
				Grab Sample	SPMD[3] extract	POCIS[3] extract
Pentachlorophenol	WP		GCMS-H	62		190
Phenothrin	I-Py		GCMS	32	33	99
Phorate	I-OP		GCMS	293	300	900
Picloram	H		GCMS-H	62		190
Promecarb	I-C		LCMS	22		6
Prometon (Pramitol 5p)	H		GCMS	32	33	99
Prometryn	H		GCMS	32	33	99
Pronamide (Kerb)	H		GCMS	32	33	99
Propachlor (Ramrod)	H		GCMS	32	33	99
Propargite	I-SE		GCMS	32	33	99
Propazine	H		GCMS	32	33	99
Propoxur	I-C		LCMS	48		15
Resmethrin	I-Py		GCMS	49	50	150
Simazine	H		GCMS	32	33	99
Simetryn			GCMS	98	100	300
Sulfotepp	I-OP		GCMS	32	33	99
Tebuthiuron	H		GCMS	32	33	99
Terbacil	H		GCMS	33	33	99
Tetrachlorvinphos (Gardona)			GCMS	49	50	150
Thiodicarb	I-C		LCMS	50		
Tokuthion	I-OP		GCMS	49	50	150
Tralomethrin	I-Py		GCMS	98	100	300
Trans-Chlordane (Gamma)	I-OC		GCMS	32	33	99
Trans-Nonachlor	I-OC		GCMS	32	33	99
Treflan (Trifluralin)			GCMS	33	33	99
Triadimefon	F		GCMS	32	33	99
Triallate	H		GCMS	32	33	99
Trichloronat			GCMS	49	50	150
Triclopyr	H		GCMS-H	62		190

[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] LCMS = Liquid chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8321AM.
GCMS = Gas chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8270M.
GCMS-H = Acid Herbicide GCMS, EPA method (modified) SW 846 3535M/8270M.

[3] SPMD and POCIS LPQLs are quantitation limits for the sampler extract. SPMD results are reported in ng/L. POCIS results are reported in ng.

Replicates

Results for pesticide replicate grab samples are presented in Tables B-4 and B-5. Table B-4 presents the data value, data qualification (if assigned), and relative percent difference (RPD) between the results for compounds which were consistently identified in both the grab sample and replicate. Consistent identification refers to compounds which had a positive identification in both the original sample and field replicate. Inconsistently identified replicate pairs are those in which the compound was identified in one sample but not the other. Inconsistently identified grab sample replicates are presented in Table B-5. Replicate results for SPMDs and POCISs are presented in Tables B-6 and B-7.

Each type of grab sample analysis had at least one replicate. LCMS (carbamate) grab samples were replicated three times. All other pesticide and TSS grab samples were replicated twice. DOC and TOC grab samples were replicated once. SPMD and POCIS samples each had one replicate.

All replicate results for consistently identified compounds in grab and SPMD samples met the RPD criterion of ±40% (Table B-2). Oxamyl Oxime, Bentazon, Bromoxynil, and MCPA were consistently identified in the POCIS replicates, but failed to meet the RPD criterion (Table B-7).

Among grab samples, MCPA was inconsistently identified in one replicate pair, but consistently identified in another replicate. Carbaryl was inconsistently identified in one grab sample replicate, and not found in the other. Simazine was inconsistently identified for both grab sample replicates (Table B-5). In the SPMDs, Trans-Nonachlor was found in only one replicate at an estimated concentration below the SPMD LPQL (Table B-6). For each of the inconsistently identified grab and SPMD compounds, the concentration was below the LPQL.

In the POCIS replicates, 2,4-D, Oxamyl, Atrazine, Terbacil, Methiocarb, and Methomyl were inconsistently identified (Table B-7). Oxamyl and Methiocarb were identified at concentrations below the POCIS LPQL. 2,4-D, Atrazine, Terbacil, and Methomyl were identified above the POCIS LPQL (Table B-3).

Blanks

All grab sample field blanks had no detections, indicating both field and laboratory methods were free from contamination.

Trans-chlordane was positively identified in the SPMD blank at 16 ng/L. The concentration was qualified as approximate because it falls below the Trans-chlordane LPQL of 33 ng/L (Table B-8).

The LCMS extract of the POCIS field blank was contaminated with five carbamate compounds: 3-Hydroxycarbofuran, Carbaryl, Methiocarb, Oxamyl oxime, and Propoxur. Among these, Oxamyl oxime and Methiocarb were also detected in the deployed POCISs (Table B-8).

Table B-4. Detected pairs within grab sample replicate results (µg/L).

Chemical	Sample	Replicate	RPD
2,4-D	0.073	0.076	4.03
Atrazine	0.021 J	0.021 J	0.00
	0.0087 J	0.0087 J	0.00
		Mean =	0.00
Bromoxynil	0.019 NJ	0.016 NJ	17.14
	0.056 NJ	0.053 NJ	5.50
		Mean =	11.32
Chlorpyrifos	0.02 J	0.02 NJ	0.00
	0.061 J	0.064 J	4.80
		Mean =	2.40
Dicamba I	0.019 J	0.02 J	5.13
	0.034 J	0.044 J	25.64
		Mean =	15.38
Eptam	0.024 J	0.023 J	4.26
MCPA	0.71	0.77	8.11
Malathion	0.82	0.81	1.23
Pendimethalin	0.35	0.34	2.90
	0.05	0.049	2.02
		Mean =	2.46
Terbacil	0.11	0.084	26.80
	0.12	0.12	0.00
		Mean =	13.40
Treflan (Trifluralin)	0.021 J	0.022 J	4.65
	0.025 J	0.025 J	0.00
		Mean =	2.33
Dissolved Organic Carbon (mg/L)	1.4	1.4	0.00
Total Organic Carbon (mg/L)	1.9	1.5	23.53
Total Suspended Solids (mg/L)	6	6	0.00
	9	9	0.00
		Mean =	0.00

Table B-5. Unpaired detections between grab sample replicates (µg/L).[1]

Chemical	Sample	Replicate	RPD
Carbaryl	0.014 J	<0.020 UJ	35%
MCPA	<0.061 U	0.015 NJ	121%
Simazine	0.019 J	<0.033 U	54%
	0.0067 J	<0.031 U	129%
		Mean =	91%

[1] Non-detections are listed as less than the LPQL (<LPQL). RPD is calculated between the detected value and the LPQL for non-detections.

Table B-6. SPMD replicate results (ng/L).[1,2]

Chemical	SPMD A		SPMD B		RPD
4,4'-DDD	58		58		0%
4,4'-DDE	190		200		5%
4,4'-DDT	51		49		4%
Chlorpyrifos	580		650		11%
Endosulfan I	440		360		20%
Pendimethalin	1900		2700		35%
Trans-Nonachlor	<33	U	12	J	93%
Treflan	94		110		16%

[1] SPMD results in this table are in extract concentrations, unadjusted for the water volume sampled.
[2] Non-detections are listed as less than the LPQL (<LPQL). RPD is calculated between the detected value and the LPQL for non-detections.

Table B-7. POCIS replicate results (ng/POCIS).[1,2]

Chemical	POCIS A		POCIS B		RPD
2,4-D	270	NJ	<190	U	35%
Atrazine	150		<99	UJ	41%
Bentazon	130	J	71	NJ	59%
Bromoxynil	270	NJ	140	NJ	63%
MCPA	190		39	NJ	132%
Methiocarb	<6	U	15	J	86%
Methomyl	<15	UJ	44	J	98%
Oxamyl	10	J	<15	UJ	45%
Oxamyl oxime	23	J	5	J	124%
Terbacil	1100		<99	UJ	167%

[1] POCIS results are in extract concentrations.
[2] Non-detections are listed as less than the LPQL (<LPQL). RPD is calculated between the detected value and the LPQL for non-detections.

Table B-8. Passive sampler field blank detections.[1,2]

Chemical	SPMD (ng/L)		POCIS (ng/POCIS)	
3-Hydroxycarbofuran	---		7.7	J
Carbaryl	---		3.1	J
Methiocarb	---		10.0	J
Oxamyl oxime	---		47.0	
Propoxur	---		4.6	J
Trans-Chlordane	16.0	J	---	

[1] SPMD and POCIS results in this table are in extract concentrations, unadjusted for the water volume sampled.
[2] "---" = not detected.

Surrogates

Surrogate analyses evaluate accuracy of recovery for a group of compounds, and are analyzed in each sample set. For instance, Triphenyl Phosphate is a surrogate for organophosphorus insecticides. Three pesticide surrogates were added to the protocol for passive sampler analysis: 4,4-Dibromo-octafluorobiphenyl (DBOB) for POCIS herbicides, Chlorpyrifos-d10 for SPMD organophosphorus pesticides, and Trans-Permethrin -13C6 for SPMD pyrethroid pesticides (Table B-9). High pesticide surrogate recovery requires related detections to be qualified as estimates. Low pesticide surrogate recovery requires all related data to be qualified as estimates.

Table B-9. Pesticide surrogates.

Surrogate Compound	Surrogate	% Recovery
C-13 Carbaryl	Carbamate pesticides	30-130
2,4,6-Tribromophenol	Herbicide	40-130
2,4-Dichlorophenylacetic acid	Herbicide	40-130
1,3 Dimethyl-2-nitrobenzene	Nitrogen pesticides	30-105
4,4'-DDE-d8	Chlorinated pesticides	50-120
Decachlorobiphenyl	Chlorinated pesticides	50-120
gamma-BHC-d6	Chlorinated pesticides	50-120
Triphenyl phosphate	Organophosphorus pesticides	30-150
4,4-Dibromo-octafluorobiphenyl (DBOB)	Herbicide	30-130
Chlorpyrifos-d10	Organophosphorus pesticides	not available
Trans-Permethrin -13C6	Pyrethroid pesticides	not available

Grab sample surrogate recoveries are presented in Figure B-1. Box plots show the medians and the mean ± 1 and 2 standard deviations (SD).

The box plots in Figure B-1 illustrate the ability of Manchester Environmental Laboratory (MEL) to accurately analyze standards, and the tendency of organic analysis to underestimate environmental concentration. The median and majority of all values fall within the control limits established by MEL. Outlier values are outside of control limits for nitrogen, chlorinated, phosphorous, and herbicide surrogates.

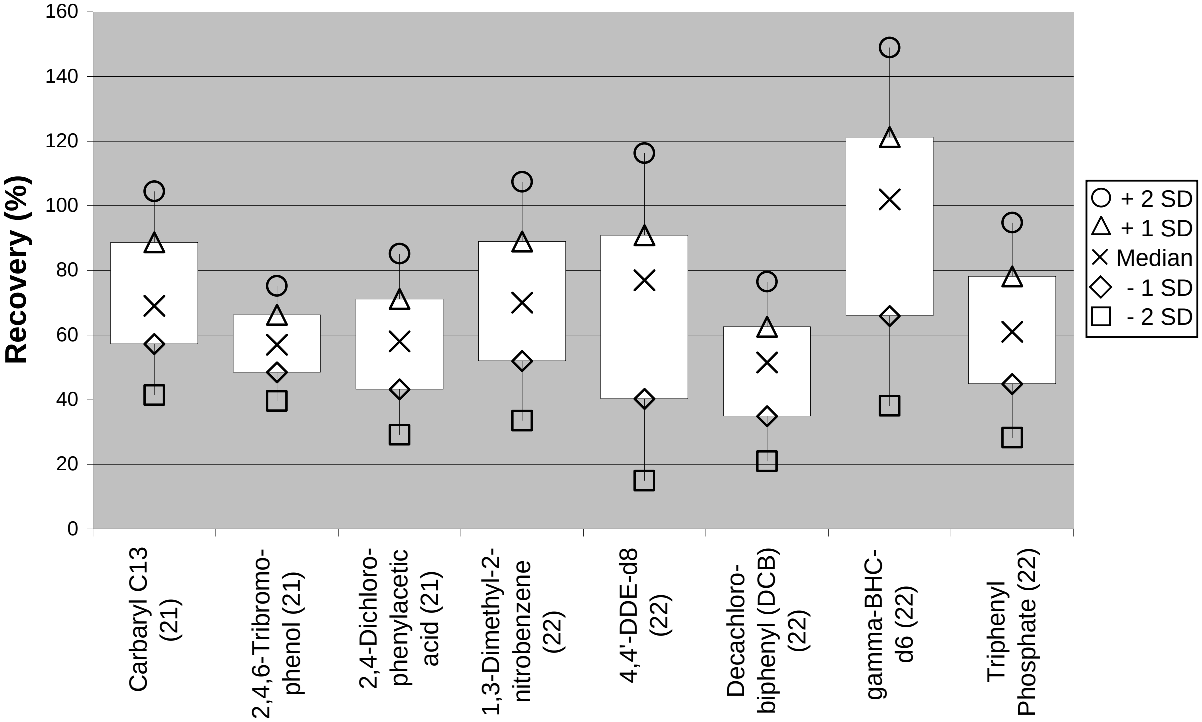

Figure B-1. Grab sample surrogate recoveries (%).

SPMD surrogate recovery is outlined in Table B-10. Surrogate recovery was generally poor for SPMD samples. There were some losses of surrogates due to either extraction cleanup procedures, or to poor extraction efficiencies in the triolein matrix. It does not appear that the surrogates used in the SPMDs recover as well as in other matrices.

Table B-10. SPMD surrogate recoveries (%).

SPMD Surrogate	Field Blank	Original	Replicate
Triphenyl Phosphate	7.9	8.8	10
1,3-Dimethyl-2-nitrobenzene	27	19	18
Decachlorobiphenyl (DCB)	70	71	75
4,4'-DDE-d8	86	89	100
gamma-BHC-d6	78	91	98
Chlorpyrifos-d10	54	33	42
Trans-Permethrin -13C6	8.4	7.5	9.2

POCIS surrogate recovery is outlined in Table B-11. DBOB was used as the POCIS GCMS surrogate. The POCIS original sample and the field blank had acceptable recoveries of DBOB and were unqualified for this analysis. The POCIS replicate and extraction blanks had zero and low surrogate recovery. GCMS results for these samples were qualified as estimates.

Table B-11. POCIS surrogate recoveries (%).

Surrogate	Field Blank	Original	Replicate
Carbaryl C13	85	249	0
2,4-Dichlorophenylacetic acid	65	76	50
2,4,6-Tribromophenol	77	75	104
4,4-Dibromo-octafluorobiphenyl (DBOB)	94	82	0

All POCIS GCMS-H surrogate recoveries were acceptable.

All LCMS detects in the POCIS original were qualified as estimates due to high surrogate recovery. All LCMS detects in the POCIS replicate were qualified as estimates due to zero surrogate recovery. Surrogate recovery for the LCMS field blank was acceptable.

Matrix Spike/Matrix Spike Duplicates (MS/MSD)

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

The average RPD between MS/MSD pairs was 24.4%, and the average recovery of reviewed compounds was 63.4%. For most compounds, the RPD and recovery of MS/MSD pairs showed acceptable performance, and were within defined limits for the project (Table 2 in Burke and Dugger, 2007). Due to low recoveries, 4-Nitrophenol, Acifluorfen, and Dinoseb had an average RPD outside the ± 40% criteria and were qualified as estimates.

Laboratory Control Samples (LCSs)

LCSs evaluate accuracy of pesticide residue recovery for a specific pesticide and are applied on a rotating basis. Detections may be qualified based on low LCS recovery and/or high RPD between paired LCS.

Figures B-2 to B-4 show LCS recovery results for selected pesticides. Grab sample LCS tests were applied for acid herbicides (GCMS-H, n=16), carbamates (LCMS, n=7), and general pesticides (GCMS, n=1 to 7). All LCS tests for the intensive sampling project must be evaluated as estimates because sample sizes were insufficient to meet the requirements of the central limit theorem (i.e.; n>29).

Most grab sample LCS recoveries fell within the acceptance criteria established by MEL (Table B-2). Extract results associated with high or low LCS recoveries were qualified as estimates. Extracts qualified for low recoveries included 4-Nitrophenol, Acifluorfen, Aldicarb, and Dinoseb. High recoveries were found for Tebuthiuron, Ethoprop, Kelthane, Trans-Nonachlor, Butylate, Cyanazine, Hexachlorobenzene, 2,4'-DDD, 2,4'-DDT, and Captan.

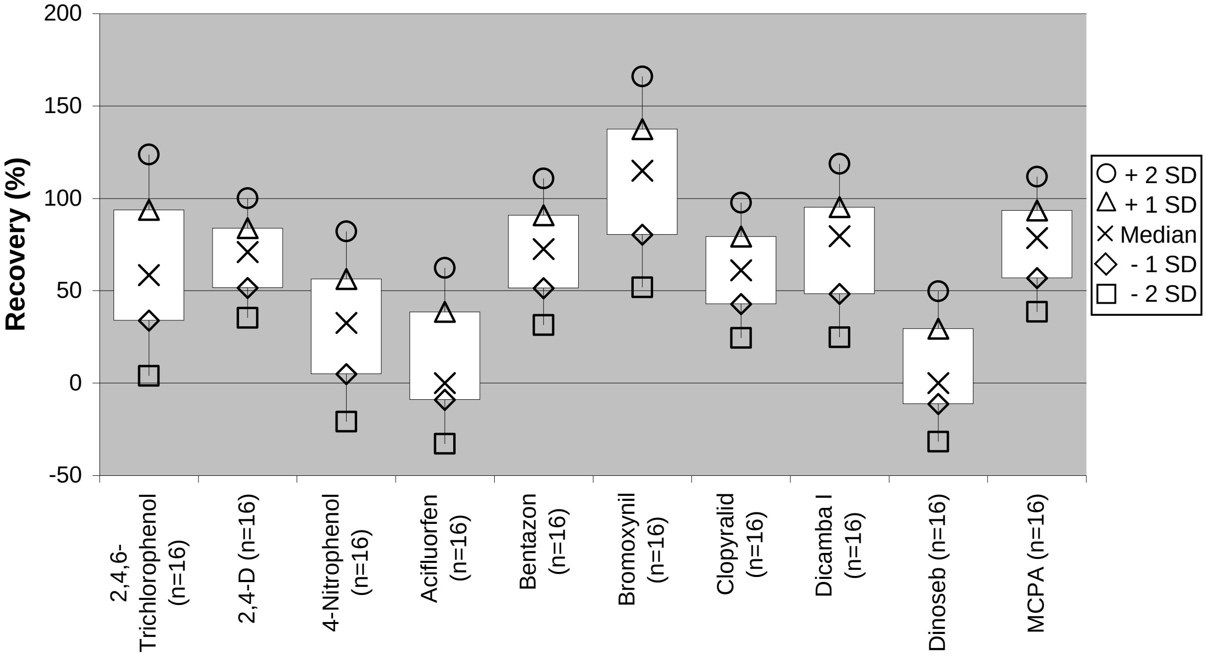

Figure B-2. Laboratory control sample recoveries for selected acid herbicides.

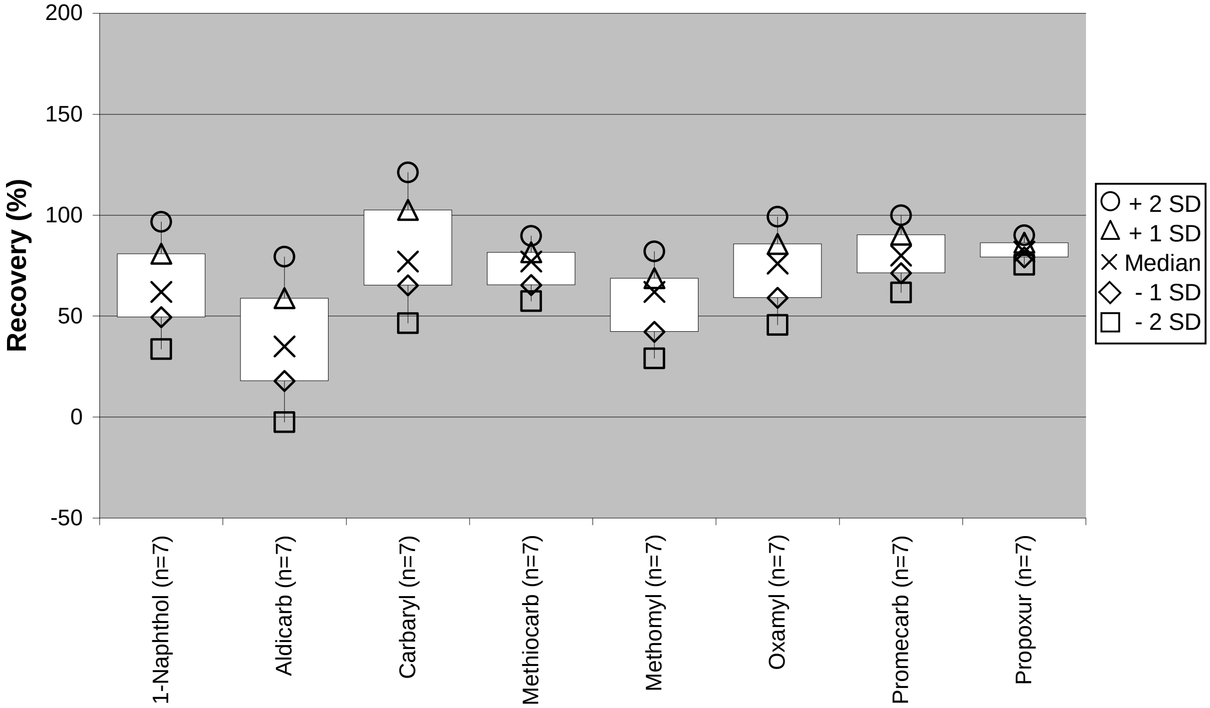

Figure B-3. Laboratory control sample recoveries for selected carbamate pesticides.

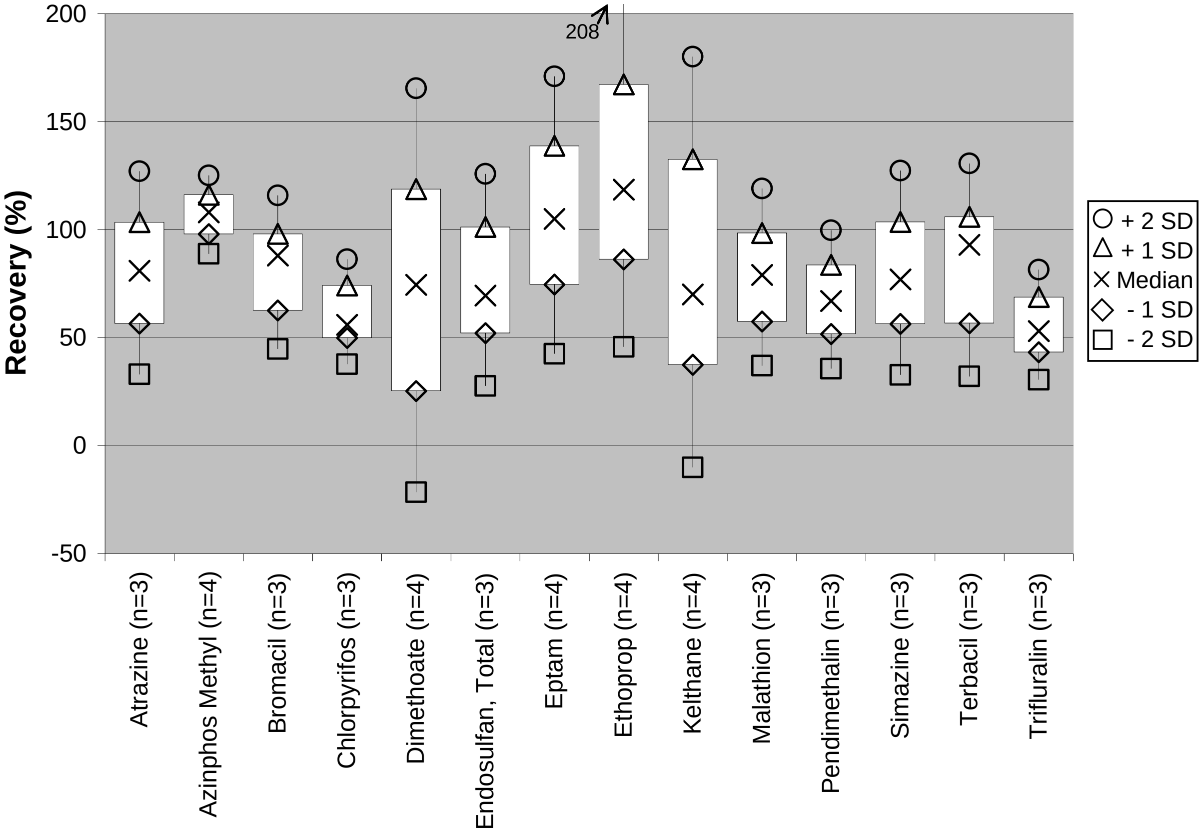

Figure B-4. Laboratory control sample recoveries for selected pesticides by GCMS.

For SPMDs, many compounds were recovered below the quality control acceptance limits outlined in the QA project plan (Table 2 in Burke and Dugger, 2007). Of the low recovery compounds, only Pendimethalin had a detected result and was qualified as estimated.

POCIS LCS recoveries varied widely, from 0% to 386%. All LCMS extract results were qualified based on low spike recoveries and poor RPD, except for Methomyl oxime and Oxamyl oxime. LCS recoveries for POCIS GCMS-H extracts were poor, but no qualifications were made because of a suspected problem in the extract preparation. No POCIS GCMS extracts were spiked for LCS recovery except the surrogate to minimize interferences with analytes in other requested analyses.