DEPARTMENT OF ECOLOGY
Environmental Assessment Program

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Natural Resources Assessment Program

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SUBJECT: **ADDENDUM TO QUALITY ASSURANCE PROJECT PLAN FOR SURFACE WATER MONITORING PROGRAM FOR PESTICIDES IN SALMONID BEARING STREAMS: ADDITION OF WENATCHEE AND ENTIAT WATERSHEDS IN THE UPPER COLUMBIA BASIN**

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Background

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) designed a multi-year monitoring study to characterize pesticide concentrations in salmonid-bearing streams during the typical pesticide use season. Monitoring began in 2003 in two watersheds representing urban and agricultural land-use patterns. Thornton Creek in the Cedar-Sammamish watershed (Water Resource Inventory Area, WRIA 8) was chosen as the urban drainage. Marion Drain, Spring Creek, and Sulphur Creek Wasteway in the Lower Yakima watershed [Water Resources Inventory Area (WRIA 37)] were selected to represent agricultural land use. The second phase of monitoring began in 2006 with the addition of the Lower Skagit-Samish watersheds (WRIA 3) to represent Western Washington agricultural land use.

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

This Quality Assurance (QA) Project Plan addendum is designed to add two Eastern Washington agricultural drainages, the Wenatchee and Entiat (WRIAs 45 & 46 in the Upper Columbia Basin) to the monitoring program. Items not addressed in this addendum are governed by the original QA Project Plan (Johnson & Cowles 2003) and the 2006 Skagit QA Project Plan Addendum (Burke & Anderson 2006). Ongoing changes are addressed in project reports and have been described previously in Anderson et al. (2004), Burke et al. (2005, 2006), and Burke & Anderson (2006).

The Wenatchee and Entiat Watersheds

The Wenatchee and Entiat watersheds (Wenatchee-Entiat) support diverse salmonid populations (Chinook, Coho, Sockeye, Steelhead, and Bull Trout/Dolly Varden [Andonaegui 1999, 2001, PSMFC 2006, WDFW 2006]) and produce a variety of agricultural commodities (Appendix A). The intensity of agriculture, proximity to salmonid bearing waters, dominance of orchard crops, and history of pesticide detection (prior studies) supports selection of the Wenatchee-Entiat as index watersheds for an evaluation of Eastern Washington (tree fruit) agricultural land use practices.

Sampling will be conducted on five drainages in the Wenatchee-Entiat. These include the mainstem Entiat and Wenatchee Rivers and three Wenatchee subbasins: Mission Creek, Brender Creek, and Peshastin Creek (Figure 1). Each watershed is characterized by a unique combination of agricultural practices and salmonid habitat. Sample sites are placed to minimize influence of residential areas (Table 1).

Brender Creek and the Wenatchee River have the highest percentage of cropped area of the selected drainages (Table 1). Brender Creek receives up to 50% of its discharge from the Peshastin Canal and Table 1 illustrates direct runoff to the canal, as a portion of the Brender Creek watershed. Brender Creek discharges into Mission Creek downstream of the confluence with Yaksum Creek. Peshastin and Mission Creeks discharge into the Wenatchee River and the Wenatchee and Entiat rivers discharge to the Columbia River.

Table 1. Watershed statistics. All calculations based on location of sample site.

	Watershed Area (acres)	Cropped Area (acres)	Percent Cropped
Entiat River	265,426	750	0.3
Wenatchee River	845,687	8,282	1.0
Mission Creek	44,322	202	0.5
Brender Creek	6,408	757	11.8
--Peshastin contribution to Brender		210	
Peshastin Creek	86,243	545	0.6

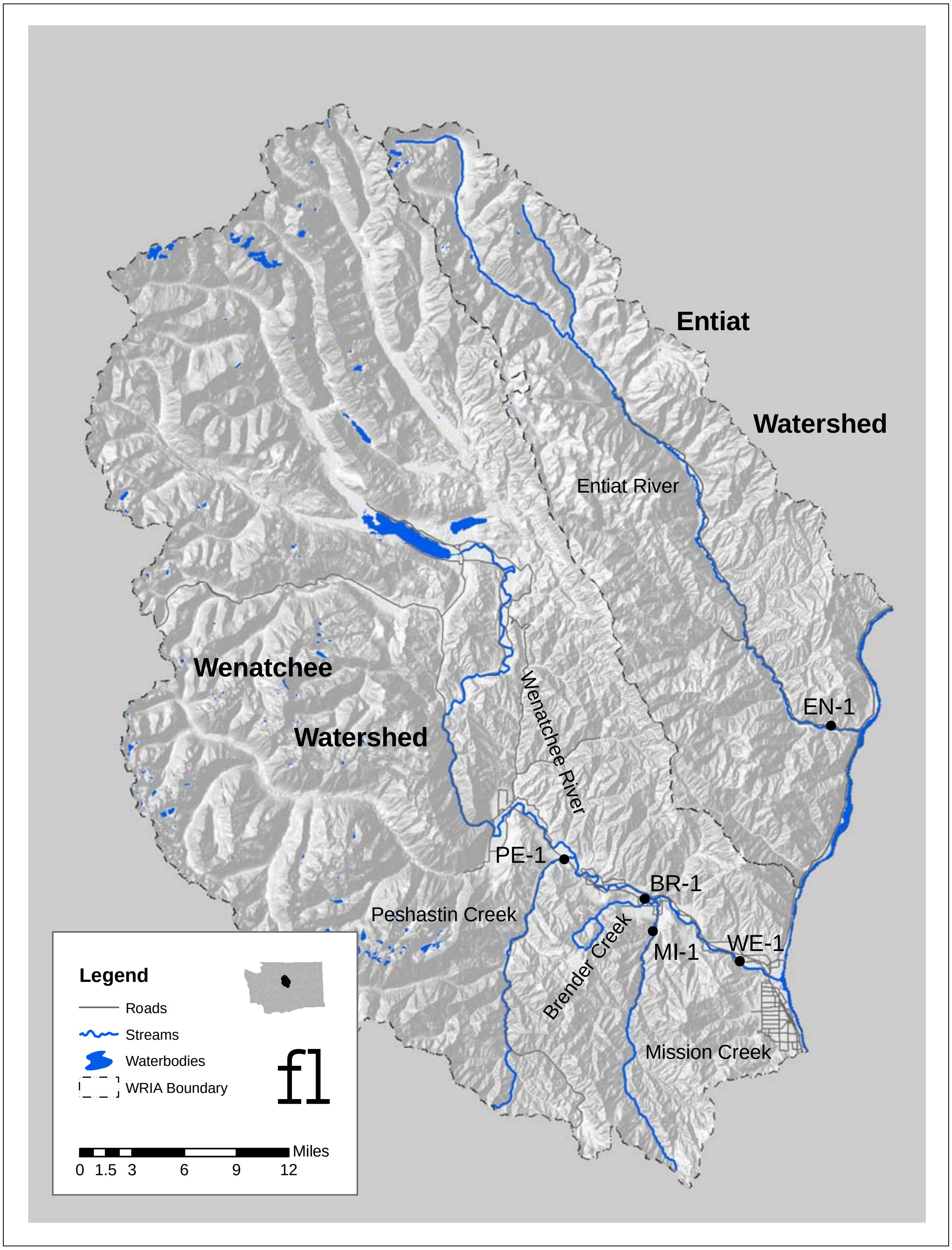

Figure 1. Location of sampling sites in the Wenatchee and Entiat watersheds.

History of Pesticide Residue Detection

Previous studies have indicated pesticide presence in Wenatchee-Entiat surface waters and fish tissues (Table 2). In the Wenatchee watershed 22 pesticides and pesticide breakdown products have been detected. One study analyzing fish tissue from the Entiat River detected high concentrations of the legacy pesticides DDT, DDT breakdown products, and a single detection of hexachlorobenzene.

This project will seek to address data needs for currently registered pesticides in the Wenatchee-Entiat watersheds.

Table 2. History of pesticide detections in the Wenatchee and Entiat watersheds.

Location	Chemical	Category	Media	[1]Dets	Range	Units	Refs[2]
Entiat River	Hexachlorobenzene	insecticide	fish tissue	1	0.63	ng/g	d
	t-DDT	insecticide	fish tissue	2	1363-2024	ng/g	d
Wenatchee River	Oxychlordane	insecticide	fish tissue	1	1	ng/g	c
	Alpha-BHC	insecticide	fish tissue	4	2-23	ng/g	e
	t-DDT	insecticide	fish tissue	6	300-1400	ng/g	c,e
Mission Creek	Endosulfan sulfate	insecticide	fish tissue	1	8	ng/g	c
	t-DDT	insecticide	fish tissue	1	363	ng/g	c
	Pentachlorophenol	fungicide	water	1	2	ng/L	b
	Atrazine	herbicide	water	1	3	ng/L	g
	Bromacil	herbicide	water	2	22-44	ng/L	b
	Glyphosate	herbicide	water	1	1130	ng/L	b
	Simazine	herbicide	water	3	11-41	ng/L	b
	3-hydroxycarbofuran	insecticide	water	1	421	ng/L	b
	Azinphos methyl	insecticide	water	11	1.5-43	ng/L	a,g
	Carbaryl	insecticide	water	1	59	ng/L	g
	Chlorpyrifos	insecticide	water	5	1.6-14	ng/L	a,g
	Diazinon	insecticide	water	3	0.9-31	ng/L	a,g
	Dimethoate	insecticide	water	2	0.5-3	ng/L	g
	Methoxychlor	insecticide	water	1	1.4	ng/L	b
	t-DDT	insecticide	water	16	0.4-25	ng/L	a,b,h
	t-Endosulfan	insecticide	water	6	4.9-48	ng/L	b,g
Yaksum Creek (Tributary to Mission Creek)	Dichlobenil	herbicide	water	1	4.3	ng/L	g
	Azinphos methyl	insecticide	water	8	2.2-80	ng/L	a,b,g
	Chlorpyrifos	insecticide	water	14	0.9-570	ng/L	a,b,g
	Diazinon	insecticide	water	2	1-2	ng/L	b,g
	Dimethoate	insecticide	water	1	9	ng/L	b,g
	t-DDT	insecticide	water	27	11-291	ng/L	a,h
	t-Endosulfan	insecticide	water	5	6.7-102	ng/L	b,g
Brender Creek	Bromacil	herbicide	water	4	12-50	ng/L	b,g
	Azinphos methyl	insecticide	water	8	5-190	ng/L	a,b,g
	Chlorpyrifos	insecticide	water	12	3-140	ng/L	a,b,g
	Diazinon	insecticide	water	4	1-240	ng/L	a,b,g
	Methoxychlor	insecticide	water	1	1.4	ng/L	b
	t-DDT	insecticide	water	23	3.6-136	ng/L	a,h
	t-Endosulfan	insecticide	water	5	3-85	ng/L	b,g
Peshastin Creek	Dialifor	insecticide	water	1	19	ng/L	f
	Chlorpyrifos	insecticide	water	1	16	ng/L	a
	t-DDT	insecticide	water	1	81	ng/L	a

[1]Detections

Shaded compounds are not registered for use in Washington State as of January 2007.

[2]References: [a]Burgoon et al. (2003), [b]Davis (1996), [c]Davis et al. (1995), [d]Davis & Serdar (1996), [e]Hopkins et al. (1985), [f]Seiders & Kinney (2004), [g]Serdar & Era-Miller (2002), [h]Serdar & Era-Miller (2004).

Station Location, Purpose, and Fisheries Characterization
Each sample site serves a specific role in evaluating pesticide fate, transport, and toxicity to aquatic biota. Station locations are described in Table 3 and illustrated in Figure 1.

Table 3. Station location and description.

Site	Station ID	[1]Latitude	[1]Longitude	Description
Entiat River	EN-1	47.6632°N	120.2506°W	Entiat River near Entiat
Wenatchee River	WE-1	47.4719°N	120.3715°W	Wenatchee River at Sleepy Hollow Bridge
Mission Creek	MI-1	47.48747°N	120.48350°W	Mission Creek above Tripp Canyon Rd
Brender Creek	BR-1	47.5211°N	120.4862°W	Brender Creek above Evergreen Drive
Peshastin Creek	PE-1	47.5575°N	120.5756°W	Peshastin Creek above Wenatchee River confluence

Datum = NAD 83.
[1]Positions shown in decimal degrees.

The five sites located in the Wenatchee-Entiat watersheds are selected as downstream integrator sites to evaluate agricultural land uses. The Mission and Brender Creek sample sites were selected upstream of the city of Cashmere to minimize impact from residential pesticide sources. The Mission Creek site is about 2 river miles upstream of the confluence with Brender Creek, while the Brender Creek site is about 0.7 miles above the confluence.

The Peshastin sample site is located 0.1 miles above the confluence with the Wenatchee River. The Wenatchee River sample site is intended to be an integrator for all upstream agricultural sources and is, therefore, located about 7.2 and 14.5 river miles downstream of the Mission and Peshastin Creek confluences, respectively. The Entiat River site is located about 1.2 miles upstream of the Columbia River and integrates upstream agricultural sources for the Entiat Basin.

A summary of salmonid distribution and supporting habitat is presented in Table 4. Salmonid distribution and habitat is classified according to the highest level of habitat supported. The greatest value is placed on spawning habitat followed by rearing, migration, and the documented presence of a species. Habitat is classified for the reach where the sample station is located; higher quality habitat may be available in the upper watershed.

Table 4. Fisheries in the Entiat and Wenatchee watersheds.

Characteristic	Entiat River	Wenatchee River	Mission Creek	Brender Creek	Peshastin Creek
Summer Chinook	Presence	Spawning	—	—	—
Spring Chinook	Rearing	Rearing	—	Presence	Rearing
Coho	Spawning	—	—	—	—
Sockeye	Presence	Rearing	—	—	—
Bull Trout/Dolly Varden	Presence	Rearing	—	—	Presence
Summer Steelhead	Spawning	Rearing	Rearing	Presence	Rearing

References: Andonaegui (1999,2001), PSMFC (2006), WDFW (2006).

Schedule and Deliverables

Sample Schedule and Frequency

Information from growers indicates pesticide applications in the Wenatchee-Entiat begin prior to the spring thaw (Rickel, personal communication). A 10 year average of soil temperature data for the Wenatchee Basin shows soil temperatures remain close to freezing until about mid-February (Figure 2).

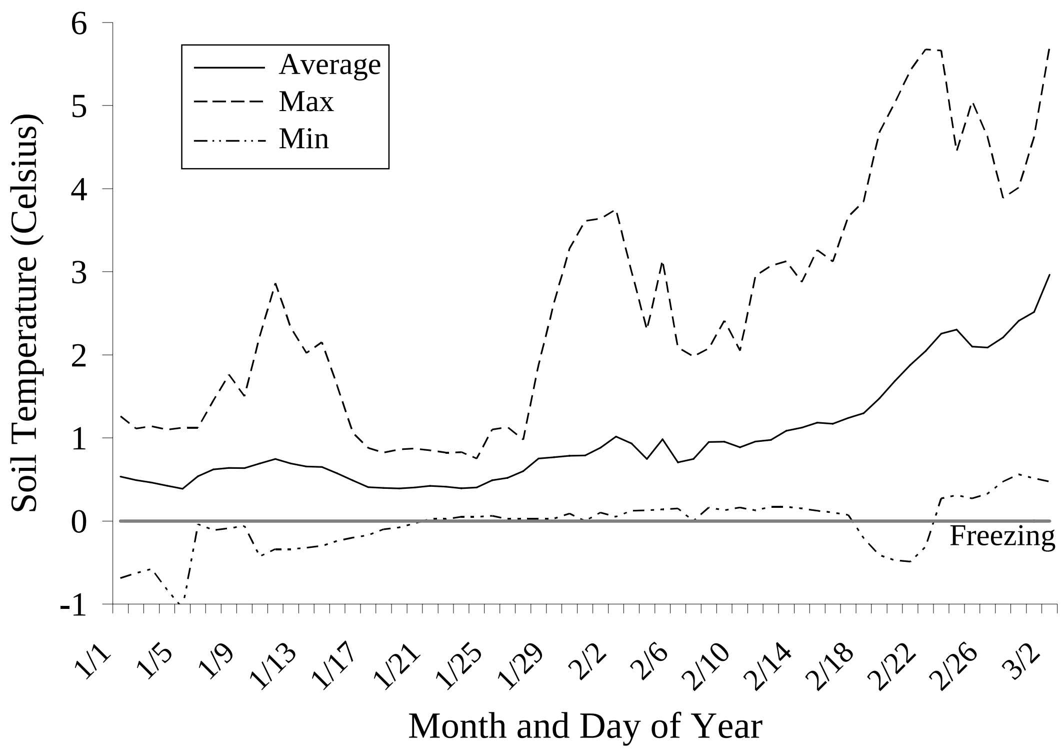

Figure 2. Ten-year statistics for soil temperatures (8-inch depth) in the Wenatchee Basin, January through March, 1996-2006 (WSU PAWS 2007).

To capture pesticide runoff during the pesticide-use season, sampling for the Wenatchee-Entiat will begin in February and continue through September. Using an adaptive management approach, subsequent monitoring may be adjusted to focus on periods with the maximum probability of detecting pesticide residues.

Wenatchee-Entiat watershed sampling will commence February 12, 2007, and continue on a weekly basis through mid-September, and extend over years 2007-2009. Laboratory analyses shall be completed by the end of November of each calendar year.

Project Deliverables

March 2008. 2007 Annual Data Summary for Cedar-Sammamish, Lower Yakima, Skagit, and Wenatchee-Entiat watersheds.

August 2009. Tri-Annual Monitoring Report (2006-2008) for the Cedar-Sammamish, Lower Yakima, Skagit, and Wenatchee-Entiat watersheds.

Responsibilities

Project responsibilities are similar to the prior QA Project Plan (Johnson & Cowles 2003) and amendment (Burke & Anderson 2006), with some modifications. This project incorporates the efforts of a variety of personnel, key contacts include:

- *Jim Cowles*, Washington State Department of Agriculture, Endangered Species Program Sponsor and Project Manager
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Sampling Procedure

This project is focused on currently registered pesticides, but will include legacy and degradate compounds. Investigated compounds include herbicides, insecticides, and fungicides. To understand factors affecting pesticide fate, transport, and toxicity to non-target organisms, physical data are collected for each sample event including: discharge, temperature, pH, conductivity, dissolved oxygen, and total suspended solids (TSS).

Surface water samples and physical parameters will be collected using the methods described in Johnson & Cowles (2003) and Burke & Anderson (2006) with the following changes.

In 2007, integrated-depth sampling will be conducted in all survey basins as outlined in Burke & Anderson (2006). A DH-95 sampler will be used for depths greater than 4 feet. DH-95 use specifications are outlined in McGregor (2000). Additional quality assurance methods will be employed while using the DH-95, as per Horowitz et al. (1994).

Discharge data will be obtained from established stations, hand-held current meters (Rantz 1982, Johnson & Cowles 2003), or bridge suspended current meters at depths greater than 3 feet (Carter & Daviden 1968, Riggs 1972, Rantz 1982, Ward 2001, Butkus 2005).

Permanent Ecology and United States Geological Survey (USGS) flow stations collect continuous data near the sample sites listed in Table 5. Results from flow stations will be verified for both Wenatchee River and Peshastin Creek sampling with onsite manual measurements. Discharge data for both Ecology and the USGS stations are available at 15-minute intervals. Following verification, the station discharge record closest to the sample time will be used. Manual flow rates will be collected at the time of sampling for both Brender and Mission Creeks.

Table 5. Permanent flow stations near Wenatchee and Entiat sample sites.

Sample site	Operator	Station Name	Location
Entiat River	USGS	USGS 12452990	on site
Wenatchee River	USGS	USGS 12462500	3.60 miles upstream
Peshastin Creek	Ecology	ID 45F070	0.36 miles upstream

Winter water temperatures in the Wenatchee-Entiat often approach freezing (Ehinger 1994; ENTRIX 2003). During freezing conditions, buildup of anchor ice may alter the stream profile and reduce the ability of stage reading tools (such as staff gauges and flow stations) to predict discharge (USGS 1994). To ensure correct flow readings, manual flow measurements will be collected at any site with instream ice. When partial surface ice blocks access to the stream, manual flow will be collected using the accessible surface water. Results from the manual flow readings will be used to verify flow station records.

Sample sites are selected, in part, based on a history of water presence throughout the sampling season. However, Mission and Brender Creeks have recorded low-flow events between July and October (Springer 2005). Flow measurement and water sample collection instruments require a minimum surface water depth of 0.2 feet to function (USGS 2005). Pesticides may transport through the basin in groundwater, even with zero surface flow (Kolpin et al. 1998). To maintain sample collection during low flows, sample locations may be periodically moved to higher flow sites within the basin.

Laboratory Analysis, Quality Assurance, and Quality Control

Pesticides and TSS are analyzed at Ecology's Manchester Environmental Laboratory. Field and laboratory performance is supported by results from the three-year report (Burke et al. 2006). For an explanation of pesticide and TSS analysis and quality assurance (QA) and quality control (QC) protocols refer to Burke & Anderson (2006). The performance detection limits for pesticides are presented in Appendix B**.**

Organic laboratory methods are dynamic and evolving. Recognizing this, the U.S. EPA designed performance based measures in their National Functional Guidelines for Organic Data Review (EPA 1999, 2001, 2005). Alternate methods may be used if rigorous quality assurance guidelines are employed and performance meets quality control measures. Results reported by this study will meet, or exceed, performance based criteria, or are appropriately qualified and described in annual monitoring reports (Burke et al. 2005, 2006). Changes to analyses will be verified through split-sample comparisons collected from existing sample sites with established field methods. Analytical methods and performance of QA/QC results are presented in Johnson and Cowles 2003, and data reports (Anderson et al. 2004; Burke et al. 2005, 2006).

Coarse pre-filtering of Liquid Chromatography/Mass Spectrometry (LCMS) carbamate analytes will be employed in 2007. The sample is passed through a 1-2 µm polytetrafluoroethylene (PTFE) filter and the filtrate is discharged to an amber glass bottle with preservative. During filtration, the entire system is sealed with PTFE thread sealer tape. All components of the field filtration system are PTFE, to ensure clean transfer of target analytes to the filtrate. Field Matrix Spike and Matrix Spike Duplicates (MS/MSD) have been tested with samples above 340 nephlometric turbidity units (NTU) and no carbamate products were retained on the filter or solid fraction (Ginder and Huntamer, personal communication). Carbamate product recoveries were within range as described in the National Functional Guidelines for Organic Data Review (EPA 2006). This method of pre-filtration is a modification of the USGS National Field Manual sections 5.2.2 and solid phase extraction (at the laboratory) through method 5.2.3 (Wilde et al. 2004).

Sampling in the Wenatchee-Entiat watersheds will occur weekly (during February through September) at five sites. At least 15% of the Wenatchee-Entiat laboratory budget will be spent on QA/QC to ensure field and laboratory performance. The surface water sample matrix in the Wenatchee-Entiat watersheds will be similar to Lower Yakima sites.

The budget assigned to QA/QC may change based on performance. Changes to methods will be described in annual reports.

The quality assurance and quality control protocol for all watersheds employs blanks, replicates, and MS/MSD (see Anderson et al. 2004; Burke et al. 2005, 2006). Starting in 2007, QA/QC samples are evenly divided among sample sites and pesticide assays (Table 6).

Table 6. Pesticide assay and reference method.

Assay	Target	Methods (EPA SW 846)
High Performance Liquid Chromatography/ Mass Spectrometry	Carbamate insecticides and specialty products	3535M and 8321AM
Gas Chromatography/ Mass Spectrometry	Pesticides	3535M and 8270M
Gas Chromatography/ Mass Spectrometry	Derivitizable pesticides	8151M and 8270M

The greatest QA/QC effort (cost) will be placed on MS/MSD samples, followed by replicates and blanks. An example of the QA/QC schedule is presented in Appendix C. The actual QA/QC schedule is not submitted as the blanks and replicates would no longer constitute *blind* evaluations.

cc: Kirk Cook, WSDA Natural Resources Assessment Coordinator
Stuart Magoon, Manchester Environmental Laboratory
Bill Kammin, Ecology Quality Assurance Officer

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Appendix A. Agricultural Commodities.

Entiat Watershed

Crop	Area (acres)
Pear	529
Apple	175
Cherry	27
Fallow	12
Alfalfa/Grass hay	7
Total Crop Area	750
Watershed Area	265,426
Percent Agriculture	0.3%

Peshastin Creek

Crop	Area (acres)
Pear	502
Apple	33
Cherry	10
Total Crop Area	545
Watershed Area	86,243
Percent Agriculture	0.6%

Wenatchee Watershed

Crop	Area (acres)
Pear	6,559
Apple	1,020
Cherry	302
Fallow	152
Alfalfa/Grass hay	110
Golf course	113
Nectarine/Peach	10
Grape, Wine	8
Christmas Tree	5
Apricot	1
Nursery, Lavender	1
Total Crop Area	8,281
Watershed Area	845,687
Percent Agriculture	1.0%

Brender Creek

Crop	Area (acres)
Pear	530
Apple	111
Cherry	57
Golf Course	36
Fallow	23
Total Crop Area	757
Watershed Area	6,408
Percent Agriculture	11.8%

Mission Creek

Crop	Area (acres)
Pear	177
Alfalfa/Grass Hay	12
Cherry	7
Christmas Tree	5
Total Crop Area	201
Watershed Area	44,322
Percent Agriculture	0.5%

Brender Creek - contribution from Peshastin C.

Crop	Area (acres)
Pear	195
Apple	8
Cherry	6
Total Crop Area	209

Appendix B. Mean Performance Lower Practical Quantitation Limits.

Chemical	[1]Use	Parent	[2]Analysis Method	[3]WSDA 2003 LPQL	2004 LPQL	2005 LPQL	2006 LPQL
1-Napthtol	Degradate/C	carbaryl	LCMS	0.19	0.13		0.065
3-Hydroxycarbofuran	Insecticide/C	carbofuran	LCMS	0.19	0.13	0.11	0.063
Aldicarb	Insecticide/C		LCMS	0.19	0.13	0.1	0.063
Aldicarb sulfone	Degradate/C	aldicarb	LCMS			0.10	0.095
Aldicarb sulfoxide	Degradate/C	aldicarb	LCMS			0.11	0.069
Aldicarb sulfoxide+s	Degradate/C	aldicarb	LCMS	0.19	0.13	0.16	
Bendiocarb	Insecticide/C		LCMS	0.19	0.13	0.131	
Carbaryl	Insecticide/C		LCMS	0.19	0.13	0.11	0.054
Carbofuran	Insecticide/C		LCMS	0.19	0.13	0.104	0.063
Dioxacarb	Insecticide/C		LCMS	0.19	0.13		
Diuron	Herbicide		LCMS				0.055
Linuron	Herbicide		LCMS				0.064
Methiocarb	Insecticide/C		LCMS	0.19	0.13	0.11	0.100
Methomyl	Insecticide/C		LCMS	0.19	0.13	0.12	0.055
Methomyl oxime	Degradate/C	methomyl	LCMS				0.070
Oxamyl	Insecticide/C		LCMS	0.19	0.13	0.11	0.071
Oxamyl oxime	Degradate/C	oxamyl	LCMS				0.092
Promecarb	Insecticide/C		LCMS	0.19	0.13	0.093	0.101
Propoxur	Insecticide/C		LCMS	0.19	0.13	0.11	0.054
2,3,4,5-Tetrachlorophenol	Degradate/WP	PCP	GCMS-H	0.087	0.079	0.081	0.079
2,3,4,6-Tetrachlorophenol	Degradate/WP	PCP	GCMS-H	0.087	0.079	0.081	0.079
2,4,5-T	Herbicide		GCMS-H	0.125	0.079	0.081	0.079
2,4,5-TP (Silvex)	Herbicide		GCMS-H	0.125	0.079	0.081	0.079
2,4,5-Trichlorophenol	Fungicide		GCMS-H	0.5	0.079	0.081	0.079
2,4,6-Trichlorophenol	Fungicide		GCMS-H	0.495	0.079	0.081	0.079
2,4-D	Herbicide		GCMS-H	0.16	0.079	0.081	0.078
2,4-DB	Herbicide		GCMS-H	0.19	0.079	0.081	0.079
3,5-Dichlorobenzoic Acid	Herbicide		GCMS-H	0.16	0.079	0.084	0.079
4-Nitrophenol	Degradate/H-OP	parathion	GCMS-H	0.29	0.079	0.238	0.079
Acifluorfen (Blazer)	Herbicide		GCMS-H	0.64	0.079	0.085	0.079
Bentazon	Herbicide		GCMS-H	0.235	0.079	0.082	0.078
Bromoxynil	Herbicide		GCMS-H	0.16	0.079	0.093	0.079
Dacthal (DCPA)	Herbicide		GCMS-H	0.125	0.079	0.081	0.079
Dicamba I	Herbicide		GCMS-H	0.16	0.079	0.081	0.078
Dichlorprop	Herbicide		GCMS-H	0.17	0.079	0.081	0.079
Diclofop-Methyl	Herbicide		GCMS-H	0.24	0.079	0.081	0.079
Dinoseb	Herbicide		GCMS-H	0.24	0.079	0.083	0.079
Ioxynil	Herbicide		GCMS-H	0.16	0.079	0.103	0.079
MCPA	Herbicide		GCMS-H	0.315	0.079	0.081	0.079
MCPP (Mecoprop)	Herbicide		GCMS-H	0.315	0.079	0.077	0.079
Pentachlorophenol	Wood Preservative		GCMS-H	0.08	0.079	0.080	0.079
Picloram	Herbicide		GCMS-H	0.16	0.079	0.081	0.079
Triclopyr	Herbicide		GCMS	0.13	0.079	0.079	0.079
2,4'-DDD	Degradate/OC		GCMS	0.018	0.079	0.083	0.032

Continued…

Appendix B continued. Mean Performance Lower Practical Quantitation Limits.

Chemical	[1]Use	Parent	[2]Analysis Method	[3]WSDA			
				2003	2004	2005	2006
				LPQL	LPQL	LPQL	LPQL
2,4'-DDE	Degradate/OC		GCMS	0.018	0.079	0.083	0.032
2,4'-DDT	Degradate/OC		GCMS	0.018	0.079	0.082	0.032
4,4'-DDD	Degradate/OC		GCMS	0.018	0.079	0.083	0.032
4,4'-DDE	Degradate/OC		GCMS	0.018	0.079	0.082	0.032
4,4'-DDT	Degradate/OC		GCMS	0.018	0.079	0.082	0.032
Acephate	Insecticide/OP		GCMS		1.594	1.500	0.032
Alachlor	Herbicide		GCMS	0.335	0.112	0.12	0.032
Aldrin	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Alpha-BHC	Insecticide/OC		GCMS	0.018	0.079	0.077	0.032
Ametryn	Herbicide		GCMS	0.033	0.031	0.035	
Atraton	Herbicide		GCMS	0.052	0.047	0.048	
Atrazine	Herbicide		GCMS	0.039	0.032	0.037	0.032
Azinphos Ethyl	Insecticide/OP		GCMS	0.053	0.05	0.06	0.032
Azinphos methyl	Insecticide/OP		GCMS	0.053	0.05	0.052	0.032
Benefin	Herbicide		GCMS	0.05	0.047	0.208	0.032
Bensulide	Herbicide/OP		GCMS		14.187	1.500	0.032
Benzamide, 2,6-dichloro-	Degradate/H-OP	dichlobenil	GCMS	0.22			
Beta-BHC	Insecticide/OC		GCMS	0.018	0.079	0.076	0.032
Bolstar (Sulprofos)	Insecticide/OP		GCMS	0.023	0.022	0.034	
Bromacil	Herbicide		GCMS	0.135	0.126	0.126	0.032
Butachlor	Herbicide		GCMS	0.199	0.189	0.185	
Butylate	Herbicide		GCMS	0.066	0.063	0.080	0.032
Captafol	Fungicide		GCMS	0.063	0.394	0.41	
Captan	Fungicide		GCMS	0.089	0.213	0.21	0.032
Carbophenothion	Insecticide/OP		GCMS	0.033	0.031	0.049	
Carboxin	Fungicide		GCMS	0.199	0.189	0.186	0.032
Chlorothalonil (Daconil)	Herbicide		GCMS	0.079	0.075	0.084	0.032
Chlorpropham	Herbicide		GCMS	0.132	0.127	0.121	0.032
Chlorpyrifos	Insecticide/OP		GCMS	0.026	0.025	0.029	0.032
Cis-Chlordane (Alpha-Chlordane)	Insecticide/OC		GCMS	0.017	0.079	0.083	0.032
Cis-Nonachlor	Insecticide/OC		GCMS	0.018	0.079	0.258	0.032
Coumaphos	Insecticide/OP		GCMS		1.504	1.497	0.032
Cyanazine	Herbicide		GCMS	0.05	0.047	0.051	0.032
Cycloate	Herbicide		GCMS	0.066	0.063	0.067	0.032
Delta-BHC	Insecticide/OC		GCMS	0.018	0.079	0.078	0.032
Demeton (O+S)	Insecticide/OP		GCMS			0.023	
Demeton-O	Insecticide/OP		GCMS	0.033	0.022	0.022	
Demeton-S	Insecticide/OP		GCMS	0.033	0.022	0.093	
Di-allate (Avadex)	Herbicide		GCMS	0.345	0.221	0.211	0.032
Diazinon	Insecticide		GCMS	0.027	0.026	0.032	0.032
Dichlobenil	Herbicide		GCMS	0.065	0.063	0.068	0.032
Dicofol (Kelthane)	Insecticide/OC		GCMS	0.051	0.315	0.274	0.319
Dieldrin	Insecticide/OC		GCMS	0.018	0.079	0.076	0.080
Dimethoate	Insecticide/OP		GCMS	0.027	0.025	0.032	0.032

Continued…

Appendix B continued. Mean Performance Lower Practical Quantitation Limits.

Chemical	[1]Use	Parent	[2]Analysis Method	[3]WSDA			
				2003	2004	2005	2006
				LPQL	LPQL	LPQL	LPQL
Diphenamid	Herbicide		GCMS	0.099	0.094	0.091	0.032
Disulfoton (Di-Syston)	Insecticide/OP		GCMS	0.02	0.019	0.035	0.032
Diuron	Herbicide		GCMS	0.195	0.189	0.19	0.033
Endosulfan I	Insecticide/OC		GCMS	0.018	0.079	0.083	0.080
Endosulfan II	Insecticide/OC		GCMS	0.018	0.079	0.083	0.080
Endosulfan Sulfate	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Endrin	Insecticide/OC		GCMS	0.018	0.079	0.083	0.080
Endrin Aldehyde	Degradate/OC		GCMS	0.018	0.079	0.083	0.080
Endrin Ketone	Degradate/OC		GCMS	0.018	0.079	0.077	0.032
EPN	Insecticide/OP		GCMS	0.033	0.031	0.036	0.032
Eptam	Herbicide		GCMS	0.066	0.063	0.064	0.032
Ethalfluralin (Sonalan)	Herbicide		GCMS	0.05	0.047	0.047	0.032
Ethion	Insecticide/OP		GCMS	0.023	0.022	0.023	0.032
Ethoprop	Insecticide/OP		GCMS	0.027	0.025	0.029	0.032
Fenamiphos	Insecticide/OP		GCMS	0.05	0.047	0.054	0.032
Fenarimol	Fungicide		GCMS	0.099	0.094	0.091	0.032
Fenitrothion	Insecticide/OP		GCMS	0.023	0.022	0.024	
Fensulfothion	Insecticide/OP		GCMS	0.033	0.031	0.032	
Fenthion	Insecticide/OP		GCMS	0.023	0.022	0.026	
Fenvalerate (2 isomers)	Insecticide/Py		GCMS			0.083	0.032
Fluridone	Herbicide		GCMS	0.199	0.189	0.180	0.064
Fonofos	Insecticide/OP		GCMS	0.02	0.019	0.023	0.032
Gamma-BHC (Lindane)	Insecticide/OC		GCMS	0.018	0.079	0.082	0.032
Heptachlor	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Heptachlor Epoxide	Degradate/OC		GCMS	0.018	0.079	0.083	0.032
Hexachlorobenzene	Fungicide		GCMS	0.018	0.079	0.079	0.032
Hexazinone	Herbicide		GCMS	0.05	0.047	0.048	0.080
Imidan	Insecticide/OP		GCMS	0.036	0.035	0.041	0.032
Malathion	Insecticide/OP		GCMS	0.027	0.025	0.032	0.032
Merphos (1 & 2)	Herbicide/OP		GCMS	0.04	0.038	0.055	
Metalaxyl	Fungicide		GCMS	0.199	0.189	0.34	0.032
Methamidophos	Insecticide/OP		GCMS		1.594	1.7	0.032
Methidathion	Insecticide/OP		GCMS		1.594	1.47	0.319
Methoxychlor	Insecticide/OC		GCMS	0.088	0.079	0.076	0.032
Methyl Chlorpyrifos	Insecticide/OP		GCMS	0.027	0.025	0.026	0.032
Methyl Parathion	Insecticide/OP		GCMS	0.023	0.022	0.034	0.032
Metolachlor	Herbicide		GCMS	0.133	0.127	0.121	0.032
Metribuzin	Herbicide		GCMS	0.033	0.031	0.056	0.032
MGK264	Synergist/I		GCMS	0.263	0.252	0.26	0.032
Mirex	Insecticide/OC		GCMS	0.018	0.079	0.081	0.032
Molinate	Herbicide		GCMS	0.066	0.063	0.223	
Naled	Insecticide/OP		GCMS		1.594	1.502	0.032
Napropamide	Herbicide		GCMS	0.099	0.094	0.096	0.080
Norflurazon	Herbicide		GCMS	0.066	0.063	0.071	0.032
Oxychlordane	Degradate/OC		GCMS	0.018	0.079	0.088	0.032

Continued…

Appendix B continued. Mean Performance Lower Practical Quantitation Limits.

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3]			
				2003	2004	2005	2006
				LPQL	LPQL	LPQL	LPQL
Oxyfluorfen	Herbicide		GCMS	0.134	0.127	0.121	0.032
Parathion	Insecticide/OP		GCMS	0.027	0.025	0.030	0.032
Pebulate	Herbicide		GCMS	0.066	0.063	0.064	0.032
Pendimethalin	Herbicide		GCMS	0.05	0.046	0.051	0.032
Pentachloroanisole	Degradate/WP	PCP	GCMS	0.018	0.079	0.080	
Pentachlorophenol	Wood Preservative		GCMS	0.08	0.079	0.080	0.080
Phenothrin	Insecticide/Py		GCMS			0.061	0.032
Phorate	Insecticide/OP		GCMS	0.023	0.022	0.029	0.319
Profluralin	Herbicide		GCMS	0.079	0.075	0.081	
Prometon (Pramitol 5p)	Herbicide		GCMS	0.032	0.031	0.033	0.032
Prometryn	Herbicide		GCMS	0.033	0.031	0.043	0.032
Pronamide (Kerb)	Herbicide		GCMS	0.169	0.127	0.127	0.032
Propachlor (Ramrod)	Herbicide		GCMS	0.079	0.075	0.078	0.032
Propargite	Insecticide/SE		GCMS	0.066	0.063	0.063	0.032
Propazine	Herbicide		GCMS	0.033	0.031	0.035	0.032
Resmethrin	Insecticide/Py		GCMS			0.061	0.064
Ronnel	Insecticide/OP		GCMS	0.023	0.022	0.024	
Simazine	Herbicide		GCMS	0.033	0.031	0.031	0.032
Sulfotepp	Insecticide/OP		GCMS	0.02	0.019	0.023	0.032
Tebuthiuron	Herbicide		GCMS	0.05	0.047	0.054	0.037
Terbacil	Herbicide		GCMS	0.099	0.093	0.090	0.032
Terbutryn (Igran)	Herbicide		GCMS	0.033	0.031	0.035	
Trans-Chlordane (Gamma)	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Trans-Nonachlor	Insecticide/OC		GCMS	0.018	0.079	0.080	0.032
Triadimefon	Fungicide		GCMS	0.086	0.082	0.087	0.032
Triallate	Herbicide		GCMS	0.099	0.094	0.098	0.032
Trifluralin (Treflan)	Herbicide		GCMS	0.05	0.047	0.054	0.032
Vernolate	Herbicide		GCMS	0.066	0.063	0.066	

[1]I = insecticide, OC = organochlorine, OP = organophosphorus, Py = pyrethroid, SE = sulfite ester, WP = wood preservative.
[2]LCMS = High performance liquid chromatography/mass spectroscopy. Carbamate analyses run by HPLC in 2003. 2003 results run by PSC/Maxxum analytical laboratory in Vancouver, BC
GCMS = Gas chromatography/mass spectroscopy. 2003 results run by GCMS and Atomic Emission Detection (AED).
GCMS-H = Herbicide GCMS method SW 846 8270M has been used throughout entirety of project.
[3]Average of lower performance (reporting) values, per analyte for all batches over each study year (14-31 batches per year).
LPQL: Lower performance practical quantitation limit.

Appendix C. Calendar Year 2007, QA/QC Schedule for the Wenatchee-Entiat Watersheds. (Example, Not Actual Schedule).

	Sample sites of the Wenatchee-Entiat WRIAs 45 & 46				
Week	Entiat River	Wenatchee River	Peshastin Creek	Mission Creek	Brender Creek
15-Feb-07		MS/MSD (LCMS)	Replicate (LCMS)	Replicate (LCMS)	
22-Feb-07	Replicate (LCMS)		MS/MSD (GCMS)		
1-Mar-07		Blank (GCMS)		MS/MSD (LCMS)	Replicate (GCMS)
8-Mar-07			Blank (GCMS)		MS/MSD (GCMS-H)
15-Mar-07			MS/MSD (LCMS)	Replicate (GCMS)	
22-Mar-07	Blank (GCMS)	Replicate (GCMS-H)			
29-Mar-07	Blank (LCMS)		Replicate (GCMS)		
5-Apr-07		Replicate (LCMS, GCMS)	MS/MSD (GCMS, GCMS-H), Replicate (LCMS)	MS/MSD (LCMS)	
12-Apr-07					Blank (LCMS), MS/MSD (GCMS)
19-Apr-07	MS/MSD (LCMS)			Replicate (GCMS-H), MS/MSD (GCMS)	MS/MSD (LCMS)
26-Apr-07	MS/MSD (GCMS-H)				
3-May-07					
10-May-07		MS/MSD (GCMS-H)			
17-May-07			Blank (GCMS)		
24-May-07			Blank (GCMS-H)		MS/MSD (LCMS)
31-May-07		MS/MSD (LCMS)			Replicate (GCMS)
7-Jun-07	Replicate (GCMS)				
14-Jun-07	Replicate (GCMS)				Blank (LCMS)
21-Jun-07					Replicate (LCMS)
28-Jun-07	MS/MSD (GCMS)	MS/MSD (GCMS)			
5-Jul-07	Replicate (GCMS-H)		MS/MSD (GCMS-H)		
12-Jul-07				Replicate (LCMS)	
19-Jul-07				MS/MSD (GCMS)	
26-Jul-07			Replicate (GCMS)	MS/MSD (GCMS-H)	Replicate (GCMS-H)
2-Aug-07	Blank (LCMS)	Replicate (LCMS)			
9-Aug-07					
16-Aug-07			Replicate (GCMS-H)	Blank (GCMS-H)	
23-Aug-07		MS/MSD (GCMS)			
30-Aug-07	MS/MSD (LCMS)				MS/MSD (GCMS)
6-Sep-07		Blank (GCMS-H)		Blank (GCMS)	
13-Sep-07					
20-Sep-07					
27-Sep-07	MS/MSD (GCMS)				Replicate (LCMS)

GCMS – Gas Chromatography/Mass Spectrometry for pesticides.
GCMS-H – Gas Chromatography/Mass Spectrometry for derivitizable pesticides, especially acidic herbicides.
LCMS – Liquid Chromatography/Mass Spectrometry for carbamate insecticides and specialty products.
MS/MSD – Matrix Spike paired with a Matrix Spike Duplicate.