DEPARTMENT OF ECOLOGY
Environmental Assessment Program

February 28, 2006

TO: Jim Cowles, Washington State Department of Agriculture, Endangered Species Protection Program.

THROUGH: Will Kendra, Watershed Ecology Section Manager, EA Program
Dale Norton, Toxics Studies Unit Supervisor, EA Program

FROM: Chris Burke, Watershed Ecology Section, EA Program
Paul Anderson, Watershed Ecology Section, EA Program

SUBJECT: ADDENDUM TO QA PROJECT PLAN FOR SURFACE WATER MONITORING PROGRAM FOR PESTICIDES IN SALMONID BEARING STREAMS: ADDITION OF SKAGIT-SAMISH WATERSHEDS, AND EXTENSION OF PROGRAM THROUGH JUNE 2009.
PROJECT CODE: 03-501-04
PUBLICATION NUMBER: 03-03-104ADD

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. The first phase of monitoring was conducted during 2003-2005 in two watersheds representing urban and agricultural land use patterns. Thornton Creek in the Cedar-Sammamish watershed (WRIA 8) was chosen as the urban drainage. Marion Drain, Spring Creek, and Sulphur Creek Wasteway in the Lower Yakima watershed (WRIA 37) were selected to represent agricultural land use.

Data from the monitoring program will be used to develop accurate pesticide exposure assessments for ESA-listed salmonid species. This data will be provided to EPA and NOAA-Fisheries for ESA consultations on pesticides and salmon. WSDA will use the data for pesticide registration decisions and may apply data to determine if pesticide mitigation efforts are successful.

This Quality Assurance (QA) Project Plan addendum is designed to add a western Washington agricultural drainage, the Lower Skagit-Samish watershed (WRIA3), to the monitoring program and extend existing project QA through June 2009. This addendum describes changes to the program. Items not specifically addressed in the addendum are governed by the original QA Project Plan (Johnson and Cowles, 2003). Detailed,

ongoing changes are addressed in project deliverables and have been described previously in Anderson et al., 2004 and Burke et al., 2005.

The Skagit-Samish Basin

The Skagit-Samish WRIA 3 supports several Puget Sound salmonid populations (Smith, 2003) and delta drainages produce a variety of agricultural commodities (Appendix A). The intensity of agriculture and proximity to salmonid bearing waters supports selection of the Skagit-Samish WRIA 3 as an index watershed for evaluation of western Washington (agricultural) land use practices.

Four drainages in the Lower Skagit-Samish WRIA 3 will be added to the program: Samish River, Indian Slough, Browns Slough, and Big Ditch (Figure 1). Each watershed may be characterized by a unique combination of agricultural practices, history of pesticide residue detection, and salmonid habitat.

Agriculture

All subject watersheds have a proportion of their area in agricultural production (Table 1). The most intensively utilized watersheds, according to cropped area, include Big Ditch, Browns Slough, and Indian Slough. Virtually 100% of the Browns Slough drainage is occupied by cropped area, except roads, houses, and a small habitat reserve.

Table 1. Watershed statistics (rounded to the nearest 500). All values approximate.

	Watershed Area (acres)	Cropped Area (acres)	Percent Cropped
Big Ditch	8000	4000	50%
Browns Slough	2000	2000	100%
Indian Slough	5000	2500	50%
Samish River	68000	6000	9%

The Samish River is included in this study due to its importance to regional fisheries, as explained in subsequent sections. The Samish River watershed contains 9% cropped area, and the majority of this area is contained in the lower delta. Two sites are located on the Samish to (1) characterize pesticide occurrence below Friday Creek (Figure 1) and (2) integrate the influence of agriculture at the downstream station.

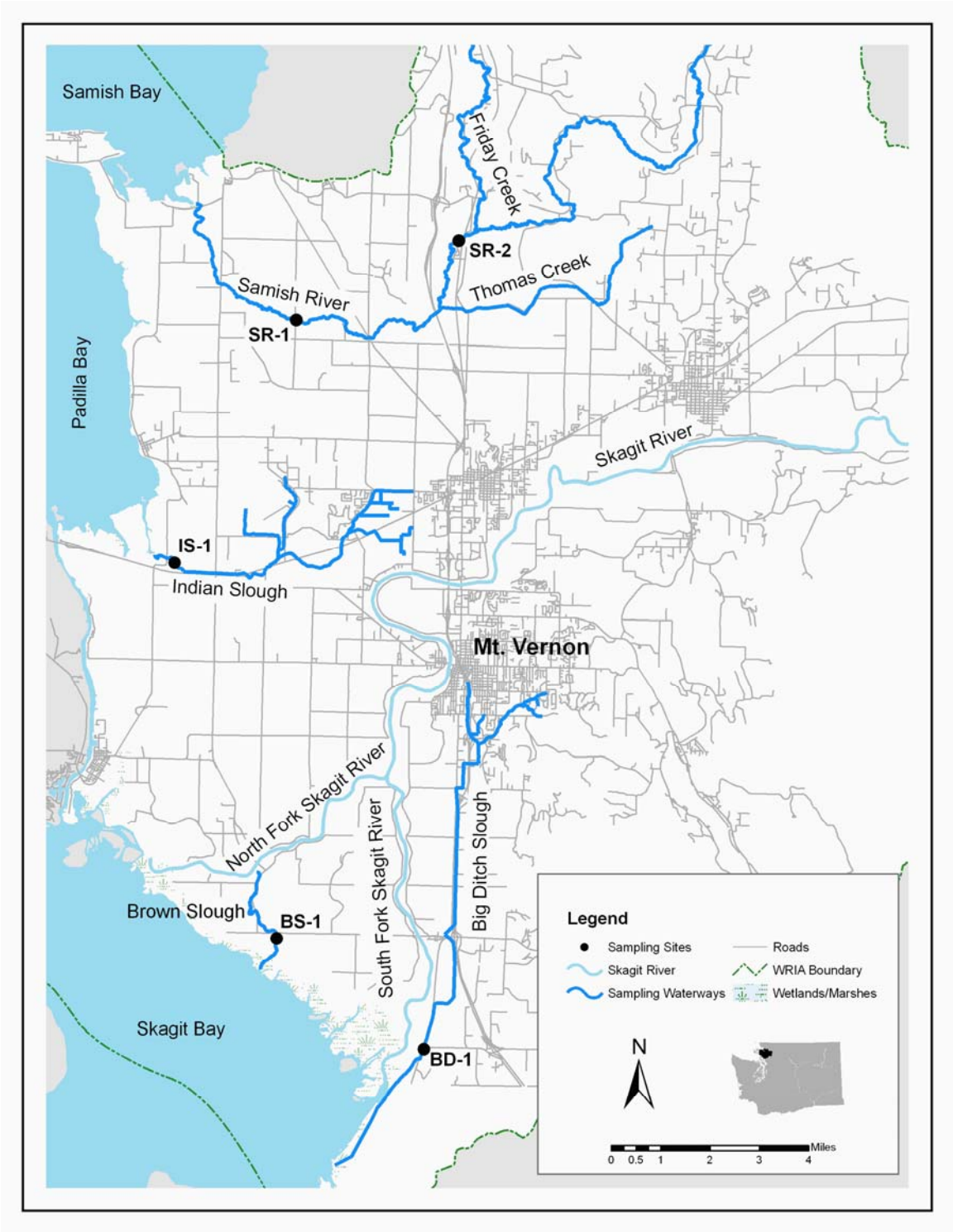

Figure 1. Sample drainages of the Skagit-Samish watershed.

History of Pesticide Residue Detection
While pesticide occurrence has been studied in the lower Skagit River and delta area, few studies address pesticide presence in project drainages (Table 2). 2,4-D was detected in surface water and dicamba in sediments of Indian Slough (Mayer and Elkins, 1990). Bromacil and diuron were detected in surface water, and pentachlorophenol in the sediment of Big Ditch Slough (PTI 1991). This project will address the data gap in selected watersheds.

Table 2. History of pesticide detections in project drainages.

Location	Chemical	Common Name	Category	Media	[1]Dets	Range	Units
Big Ditch	Pentachlorophenol	Penta	Wood Preservative	Sediment	1	0.0039	mg/kg
	Bromacil	Hyvar	Herbicide	Water	1	3.3	µg/L
	Diuron	Karmex	Herbicide	Water	2	1.3-3.3	µg/L
Indian Slough	Dicamba	Banvel	Herbicide	Sediment	2	5.8	mg/kg
	2,4-D	Several	Herbicide	Water	3	0.2-0.7	µg/L

[1]Detections

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	[1]Latitude	[1]Longitude	Description
Big Ditch	BD-1	48.3085	-122.3486	Upstream of bridge at Milltown Rd.
Browns Slough	BS-1	48.3413	-122.4143	Downstream of tidegate at Fir Island Rd.
Indian Slough	IS-1	44.4513	-122.4658	Upstream of tidegate at Bayview-Edison Rd.
Samish River – Lower	SR-1	48.5212	-122.4109	Upstream of bridge at Thomas Rd.
Samish River – Upper	SR-2	48.5460	-122.3374	Downstream of bridge at Old Hwy 99 North Rd.

Datum = NAD 83

[1]Positions shown in decimal fraction.

Two sampling sites are located on the Samish River. The upstream site is located downstream of Highway 99, and above the majority of cropped land in the Samish drainage. The downstream site, located at the junction of Thomas Road and the Samish River, serves to integrate diverse land uses, including agriculture. The remaining sites are downstream integrator sites to evaluate agricultural land uses of the Skagit-Samish Delta. The Samish River discharges into Samish Bay, Indian Slough discharges into Padilla Bay, and the remaining sites discharge into Skagit Bay.

Each site represents a reach which drains agricultural lands, and has hydraulic and salmonid connectivity to the outlying estuaries. Connectivity is altered by tidegates, although many are modified to allow fish passage. The Big Dich and Indian Slough sites are located upstream of their respective tidegates, and the Browns Slough site is located

on the seaward side of the Fir Island Road tidegate. A summary of hydraulic impediment, salmonid distribution, and supporting habitat is presented in Table 4.

Table 4. Hydraulic variables and fisheries in the Skagit delta.

Characteristic	Big Ditch	Browns Sl	Indian Sl	Samish R – Lower	Samish R - Upper
Tidegate	Yes	Yes	Yes	No	No
Complete blockage	No	[1]Yes	No		
Fall Chinook		Presence	Presence	Rearing	Spawning
Coho	Rearing	Presence	Presence	Rearing	Spawning
Fall Chum		Presence		Spawning	Spawning
Pink		Presence		Presence	
Sockeye				Rearing-spawning	
Bull Trout				Presence	
Winter Steelhead				Rearing	Spawning

References: Smith 2003, PSMFC 2006, WDFW 2006.
[1]Two tidegates are present in Browns Slough. The seaward tidegate allows unimpeded passage of salmonids (Beamer and LaRock, 1998), while the tidgate located at Fir Island Road represents a complete blockage.

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, and then documented presence (occupation) of a subject species. All sites represent freshwater salmonid habitats; Browns Slough provides freshwater, wetland, and estuarine habitats.

Schedule and Deliverables

Sample Schedule and Frequency

The sample schedule is designed to encompass the typical pesticide use season, estimated as March through October. Using an adaptive management approach, subsequent monitoring may be adjusted to focus on periods with the maximum probability of detecting pesticide residues.

The study design for the Thornton and Lower Yakima watersheds incorporates weekly sampling at stations Thornton 3, Marion 2, Sulphur 1, and Spring 3. Biweekly (every two weeks) sampling will be conducted at sites Thornton 1 and Spring 2. Sampling within the Thornton and Lower Yakima watersheds will be maintained through June 2009. Existing sample locations are described in Burke et al., 2005. Historical site development may be found in Johnson and Cowles, 2003 and Anderson et al., 2004.

Skagit watershed sampling will commence March 2, 2005, continue on a weekly basis through September, and extend over years 2006-2009 in the Skagit watershed.

Laboratory analyses shall be completed by the end of November of each calendar year for all watersheds.

Project Deliverables

August 2006. Tri-Annual Monitoring Report (2003-2005) for Cedar-Sammamish and Lower Yakima watersheds.

March 2007. 2006 Annual Data Summary for Cedar-Sammamish, Lower Yakima, and Skagit watersheds.

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

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

Responsibilities

Changes in project personnel occurred during the previous study period of 2003-2005. Modification of personnel and responsibilities from the original QA Project Plan (Johnson and Cowles, 2003), include:

Jim Cowles, Washington State Department of Agriculture, Sponsor and Project Manager	360.902.2066
Chris Burke, Ecology – Toxics Studies Unit, Project Manager	360.407.6139
Paul Anderson, Ecology – Toxics Studies Unit, EIM and Field Lead	360.407.7548
Dean Momohara, Manchester Laboratory - Chemistry Units Supervisor	360.871.8808
Bill Kammin, Ecology – Manchester QA Officer	360.407.6964
Jeff Westerlund, Manchester Laboratory – GCMS Pesticides	360.871.8813
Bob Carrell, Manchester Laboratory – Herbicides	360.871-8804
Dickey Huntamer, Manchester Laboratory – Carbamates	360.871.8809
Kamilee Ginder, Manchester Laboratory – Carbamates	360.871.8826

Richard Jack, Stew Lombard, and Gregory Perez are no longer involved with the project.

Sampling Procedure

This project is focused on currently registered pesticides, although a number of legacy and degradate compounds are investigated. The primary use classification of investigated compounds include: herbicides, insecticides, and fungicides. Common insecticide functional groups include organophosphorus, organochlorine, carbamate, pyrethroid, and nicotinoid. In order to understand factors affecting pesticide fate, transport, and toxicity to non-target organisms, conventional parameters are analyzed during each sample event, including: discharge, temperature, pH, conductivity, dissolved oxygen, and total suspended solids (TSS).

Several sites within the Skagit-Samish WRIA 3 have physical characteristics (depth, access) which necessitate the use of sampling procedures that were not included in the original QA Project Plan (Johnson and Cowles, 2003). Integrated sampling protocols are employed to ensure velocity-weighted collection of constituents (vertical axis) and horizontal integration is provided by compositing samples at quarter points across the stream.

When water depths are greater than one foot, samples will be collected with a depth integrating sampler as described in the original QA Project Plan. The model of integrating sampler employed is a result of recommendations based on velocity, and depth characteristics (USGS 2005a). Generally, the USGS DH-81 will be used in wadeable streams at depths greater than 1 ft to a maximum of 4 ft depth. A DH-76 sampler will be used at depths greater than 4 ft. Extra quality assurance samples will be collected while using the DH-76 sampler, as per Horowitz et al., 1994. Sampling and cleaning procedures will be conducted according to USGS 2005a.

Sampling of physicochemical parameters is similarly modified. A vertical profile of measurements will be taken at one foot intervals. If the water column is well mixed, then a cline will not be present and the surface measurement will be recorded. In quiescent waters, a vertical gradient of physicochemical parameters may be encountered, and the profile of physical parameters will be recorded. A check will be made for horizontal gradients and noted in the field book.

Discharge data will be obtained from established stations, wadeable stream methods if less than 3 ft in depth (Rantz et al., 1982; Johnson and Cowles, 2003) or with bridge sampling assemblies (Carter and Daviden, 1968; Riggs, 1972; Rantz et al., 1982; Ward, 2001; Butkus, 2005). Cable/reel discharge procedures are well established and have been used in hydrologic studies since the 1950s.

The upper Samish River site, SR-2, is located just downstream of the bridge crossing at US Highway 99. This site contains an active USGS discharge station entitled 'USGS 12201500 Samish River near Bulington, WA' (USGS 2005b). Discharge data is available at 15-minutes intervals and the measurement occurring during the sample period will be used.

Tidal Influence

The downstream sites of the Skagit watershed are subject to tidal influence. An effort will be made to sample at times when water is discharged at low tide, and the extent of backwater mixing is minimized. Sample events at low tide when discharge can be measured will be evaluated as components of a fate, transport, and exposure characterization, while quiescent water events may be more effectively characterized as fate and exposure components of the study. Assessment will be made according to the best professional judgment of the sample lead, assisted by measurements of discharge, velocity patterns, and conductivity/salinity. Pictures and field notes of site activities will be logged in the Standard Operating Procedures Manual for the project. Examples of tidal influence at each site (low, mean, high) will be recorded over the period of the project.

Laboratory Analysis, Quality Assurance, and Quality Control

Pesticides and TSS are analyzed at the Department of Ecology's Manchester Environmental Laboratory (MEL). TSS are analyzed according to EPA method 160.2, have an expected range of results between 1 and 100 mg/L, and a required reporting limit

of 1 mg/L. The historic analytical schedule, and performance detection limits for pesticides, are presented in Appendix B.

The nature of organic laboratory analysis is 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). Alternative methods may be utilized, providing rigorous quality assurance (QA) guidelines are employed, and performance meets quality control (QC) criteria. Results reported by the Surface Water Monitoring Program for Pesticides in Salmonid Bearing Streams will meet or exceed performance based criteria, or are appropriately qualified and described in annual monitoring reports (Burke et al., 2005). Additionally, analytical modifications will be verified through split sample comparison, obtained from existing sample sites, and represent diverse surface water matrices. Analytical methods and performance of quality assurance/quality control results are presented in Johnson and Cowles, 2003 and data reports (Anderson et al., 2004; Burke et al., 2005). Analytical modifications will be described in subsequent monitoring reports.

The quality assurance and quality control protocol (QA/QC) for all watersheds employs diverse application of blanks, replicates, surrogates, laboratory control samples, and matrix spike/matrix spike duplicates (MS/MSD) (See Burke et al., 2005 and Anderson et al., 2004). Laboratory surrogate, blank, replicate and control samples are analyzed as the laboratory component of QA/QC. Laboratory QA/QC is incorporated into sample charges and is not reflected in the budget discussion below. Field blanks, replicates, and MS/MSDs integrate field and laboratory components.

The budget allocated to QA/QC is substantial and may be modified according to performance. In 2003, 50% of the analytical cost was directed to QA and QC. Field and analytical performance improved over the years, and the proportional QA/QC cost was lowered to 23% (of sample cost) in 2004 and 17% in 2005. No pesticide residues were detected in blanks over the three-year period.

Field and method performance has been substantiated by results provided in Anderson et al., 2004; Burke et al., 2005; and will be detailed in the three-year monitoring report (publication in late summer, 2006). In established watersheds of Thornton Creek and the Lower Yakima, application of QA/QC procedures will remain at greater than 10% of sample cost for the duration of monitoring. Sufficient funding of QA/QC ensures field and laboratory performance will be preserved and closely monitored at current levels in existing watersheds.

Sampling in the Skagit-Samish watershed will occur weekly, during March through September, at five sites. Field and laboratory performance in existing watersheds has been established, yet the matrices specific to the Skagit-Samish watershed will be different from surface waters obtained in the Thornton and Lower Yakima watersheds. Notably, the conductivity of samples obtained from Browns Slough will be in the range of 5000-20000 µS/cm, while conductivity of existing watersheds ranged from 30 to 750 µS/cm. As such, ~20% of the Skagit watershed analytical budget is reserved for QA/QC.

An example of the calendar year 2006, the Skagit QA/QC schedule is provided in Table 4. 'Blind' replicates and blanks ensure unbiased assessment of contamination and performance; therefore, the actual schedule is not provided. The greatest QA/QC effort (cost) is placed on MS/MSD samples, followed by replicates and blanks. Effort is applied according to historical performance and variation (expected) associated with alternative sampling methods or environmental matrices. Additional considerations include timing of use in watershed (chemistry specific), and critical life stages of salmonids.

Table 5. Calendar year 2006, QA/QC schedule for the Skagit watershed. (Example, not actual schedule.)

	Sample sites of the Skagit-Samish WRIA 3				
Week	Big Ditch	Browns Slough	Indian Slough	Lower Samish River	Upper Samish River
1-Mar-06		MS/MSD			
8-Mar-06			Replicate		
15-Mar-06				Blank	
22-Mar-05	MS/MSD	Replicate			
29-Mar-06					
5-Apr-06			MS/MSD		
12-Apr-06					Replicate
19-Apr-06					
26-Apr-06		MS/MSD			
3-May-06	Replicate				
10-May-06				MS/MSD	
17-May-06					
24-May-06		MS/MSD			
31-May-06					
7-Jun-06	Blank				
14-Jun-06					
21-Jun-06			MS/MSD		
28-Jun-06					
5-Jul-06				Replicate	
12-Jul-06		Replicate			
19-Jul-06					Blank
26-Jul-06					
2-Aug-06	Replicate				
9-Aug-06			Blank		
16-Aug-06					MS/MSD
23-Aug-06					
30-Aug-06		Blank		Replicate	
6-Sep-06	MS/MSD				
13-Sep-06			Replicate		

A total of 174 pesticide samples are scheduled for the calendar year 2006 submission in the Skagit watershed. Of the total, 29 will be QA/QC samples including: 18 MS/MSD (9 pairs), 9 replicates, and 5 blanks. The QA/QC effort will be continuously monitored in the Skagit watershed, and distribution among MS/MSD, replicate, and blank samples may be modified to target unanticipated performance issues.

cc: Bridget Moran, WSDA Endangered Species Coordinator
Stuart Magoon, Manchester Environmental Laboratory
Cliff Kirchmer, EA Program QA Coordinator
Bill Kammin, Ecology QA Officer

References

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 Number 04-03-048. www.ecy.wa.gov/biblio/0403048.html

Beamer, E. M. and R. G. LaRock. 1998. Fish Use and Water Quality Associated with a Levee Crossing the Tidally Influenced Portion of Browns Slough, Skagit River Estuary, Washington. System Cooperative. La Conner, WA. Report prepared on behalf of Skagit County Diking District No. 22.

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 Number 05-03-025. http://www.ecy.wa.gov/biblio/0503025.html

Butkus, S. 2005. Quality Assurance Monitoring Plan, Streamflow Gauging Network. Washington State Department of Ecology, Publication Number 05-03-304. http://www.ecy.wa.gov/biblio/0503204.html

Carter, W. and J. Daviden. 1968. Chapter A6, General Procedure for Gauging Streams; Book 3, Applications of Hydraulics. United States Geological Survey. U.S. Government Printing Office, Washington D.C., USA.

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 2001. Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review. EPA 540-R-00-006. http://www.epa.gov/superfund/programs/clp/download/olcnfg.pdf

EPA 2005. Draft – National Functional Guidelines for Superfund Organic Methods Data Review. EPA 540-R-04-009. http://www.epa.gov/superfund/programs/clp/download/somnfg.pdf

Horowitz, A. J., C. R. Demas, K. K. Fitzgerald, T. L. Miller, and D. A. Rickert. 1994. U.S. Geological Survey Protocol for the Collection and Processing of Surface Water Samples for the Subsequent Determination of Inorganic Constituents in Filtered Water: U.S. Geological Survey Open-File Report 94-539, 57p.

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 Number 03-03-104. www.ecy.wa.gov/biblio/0303104.html

Mayer, J. R. and N. R. Elkins. 1990. Potential for Agricultural Pesticide Runoff to a Puget Sound Estuary – Padilla Bay, Washington. Bulletin of Environmental Contamination and Toxicology (45):215-222.

Pacific States Marine Fisheries Commission. 2006. Streamnet Interactive Mapper. Pacific Northwest Mapper. http://www.streamnet.org

PTI Environmental Services. 1991. 1990 Puget Sound Pesticide Reconnaissance Survey: Bellevue, Washington. Prepared for the U.S. Environmental Protection Agency Region 10, contract 68D80085. 39p.

Rantz, S.E. et al., 1982. Measurement and Computation of Streamflow: Volume I. Measurement of Stage and Discharge. U.S. Geological Survey Water-Supply Paper 2175. U.S. Government Printing Office, Washington D.C.

Riggs, H. C. 1972. Low-Flow Investigations. United States Geological Survey, TWRI Book 4, Chapter B1.

Smith, C. 2003. Salmon and Steelhead Habitat Limiting Factors, Water Resources Inventory Areas 3 and 4, the Skagit and Samish Basins. Washington State Conservation Commission. Lacey, Washington.

U.S. Geological Survey. 2005a. 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
(Note: All versions that were published previously in a printed format have been superseded by the online manual.)

United States Geological Survey. 2005b. Surface Water Discharge Station, USGS 12201500 Samish River near Bulington, WA
http://waterdata.usgs.gov/usa/nwis/uv?site_no=12201500

Ward, B. 2001. Stream Sampling Protocols for the Environmental Monitoring and Trends Section. Washington State Department of Ecology, Olympia, WA. Publication Number 01-03-036. www.ecy.wa.gov/biblio/0103036.html

Washington State Department of Fish and Wildlife (WDFW). 2006. Salmonscape Application, version 4.0. http://wdfw.wa.gov/mapping/salmonscape/

Appendix A. Crops in Production within the Skagit-Samish Study Drainages.

Alfalfa	Lettuce
Apple	Market Crops
Barley	Nursery Crops
Bean, Green	Oat
Beet, Seed	Pasture
Blueberry	Pea, Green
Broccoli	Poplar, Hybrid
Bulb, Daffodil	Potato
Bulb, Iris	Pumpkin
Cabbage, Seed	Raspberry
Clover/Grass, Hay	Ryegrass, Hay
Corn, Seed	Ryegrass, Seed
Corn, Silage	Sod Farm
Corn, Sweet	Spinach, Seed
Cucumber	Strawberry
Grass, Hay	Tea
	Wheat

Appendix B. Method Detection, and Practical Quantitation Limits (µg/L).

Chemical	[1]EPA	[2]Manchester	[3]WSDA	
			2003	2004
	MDL	MDL	LPQL	LPQL
1-Napthtol			0.19	0.13
2,3,4,5-Tetrachlorophenol	0.022	0.022	0.087	0.079
2,3,4,6-Tetrachlorophenol	0.023	0.018	0.087	0.079
2,4,5-T	0.033	0.018	0.125	0.079
2,4,5-TP (Silvex)	0.033	0.0099	0.125	0.079
2,4,5-Trichlorophenol	0.025	0.02	0.500	0.079
2,4,6-Trichlorophenol	0.025	0.019	0.495	0.079
2,4-D	0.042	0.019	0.160	0.079
2,4-DB	0.05	0.022	0.190	0.079
2,4'-DDD	0.02	0.02	0.018	0.079
2,4'-DDE	0.01	0.01	0.018	0.079
2,4'-DDT	0.02	0.02	0.018	0.079
3,5-Dichlorobenzoic Acid	0.042	0.017	0.160	0.079
3-Hydroxycarbofuran			0.19	0.13
4,4'-DDD	0.02	0.02	0.018	0.079
4,4'-DDE	0.02	0.02	0.018	0.079
4,4'-DDT	0.03	0.03	0.018	0.079
4-Nitrophenol	0.073	0.023	0.290	0.079
Acephate				1.594
Acifluorfen (Blazer)	0.15	0.15	0.640	0.079
Alachlor	0.1	0.1	0.335	0.112
Aldicarb			0.19	0.13
Aldicarb sulfoxide+s			0.19	0.13
Aldrin	0.006	0.006	0.018	0.079
Alpha-BHC	0.03	0.03	0.018	0.079
Ametryn	0.04	0.04	0.033	0.031
Atraton	0.13	0.13	0.052	0.047
Atrazine	0.05	0.05	0.039	0.032
Azinphos (Guthion)	0.025	0.02	0.053	0.050
Azinphos Ethyl	0.02	0.025	0.053	0.050
Bendiocarb			0.19	0.13
Benefin	0.15	0.15	0.050	0.047
Bensulide				14.187
Bentazon	0.006	0.0064	0.235	0.079
Benzamide, 2,6-dichloro-			0.22	
Beta-BHC	0.03	0.03	0.018	0.079
Bolstar (Sulprofos)	0.011	0.02	0.023	0.022
Bromacil	0.27	0.27	0.135	0.126
Bromoxynil	0.042	0.022	0.160	0.079
Butachlor	0.16	0.16	0.199	0.189
Butylate	0.14	0.14	0.066	0.063
Captafol	0.25	0.25	0.063	0.394
Captan	0.18	0.18	0.089	0.213
Carbaryl			0.19	0.13

(Continued)

Appendix B, Continued.

Chemical	[1]EPA	[2]Manchester	[3]WSDA	
			2003	2004
	MDL	MDL	LPQL	LPQL
Carbofuran			0.19	0.13
Carbophenothion	0.009	0.009	0.033	0.031
Carboxin	0.41	0.41	0.199	0.189
Chlorothalonil (Daconil)	0.18	0.18	0.079	0.075
Chlorpropham	0.26	0.26	0.132	0.127
Chlorpyrifos	0.004	0.004	0.026	0.025
Cis-Chlordane (Alpha-Chlordane)	0.04		0.017	0.079
Cis-Nonachlor	0.035		0.018	0.079
Coumaphos	0.01	0.010		1.504
Cyanazine	0.06	0.06	0.050	0.047
Cycloate	0.19	0.19	0.066	0.063
Dacthal (DCPA)	0.033	0.008	0.125	0.079
Delta-BHC	0.035	0.03	0.018	0.079
Demeton-O	0.021	0.021	0.033	0.022
Demeton-S	0.07	0.08	0.033	0.022
Di-allate (Avadex)	0.17	0.17	0.345	0.221
Diazinon	0.014	0.014	0.027	0.026
Dicamba I	0.042	0.022	0.160	0.079
Dichlobenil	0.06	0.06	0.065	0.063
Dichlorprop	0.046	0.014	0.170	0.079
Diclofop-Methyl	0.063	0.013	0.240	0.079
Dieldrin	0.02	0.02	0.018	0.079
Dimethoate	0.05	0.05	0.027	0.025
Dinoseb	0.063	0.016	0.240	0.079
Dioxacarb			0.19	0.13
Diphenamid	0.13	0.13	0.099	0.094
Disulfoton (Di-Syston)	0.016	0.016	0.020	0.019
Diuron	0.21	0.21	0.195	0.189
Endosulfan I	0	0	0.018	0.079
Endosulfan II	0	0	0.018	0.079
Endosulfan Sulfate	0.03	0.03	0.018	0.079
Endrin	0.03	0.03	0.018	0.079
Endrin Aldehyde	0.02	0.02	0.018	0.079
Endrin Ketone	0.01	0.01	0.018	0.079
EPN	0.008	0.008	0.033	0.031
Eptam	0.22	0.22	0.066	0.063
Ethalfluralin (Sonalan)	0.08	0.08	0.050	0.047
Ethion	0.006	0.006	0.023	0.022
Ethoprop	0.012	0.012	0.027	0.025
Fenamiphos	0.03		0.050	0.047
Fenarimol	0.23	0.23	0.099	0.094
Fenitrothion	0.004	0.004	0.023	0.022
Fensulfothion	0.08	0.12	0.033	0.031

(Continued)

Appendix B, Continued.

Chemical	[1]EPA	[2]Manchester	[3]WSDA	
			2003	2004
	MDL	MDL	LPQL	LPQL
Fenthion	0.011	0.011	0.023	0.022
Fluridone	0.66	0.66	0.199	0.189
Fonofos	0.004	0.004	0.020	0.019
Gamma-BHC (Lindane)	0.03	0.03	0.018	0.079
Heptachlor	0.01	0.01	0.018	0.079
Heptachlor Epoxide	0.008	0.008	0.018	0.079
Hexachlorobenzene	0.04	0.04	0.018	0.079
Hexazinone	0.05	0.05	0.050	0.047
Imidan	0.007	0.007	0.036	0.035
Ioxynil	0.042	0.0063	0.160	0.079
Kelthane	0.17		0.051	0.315
Malathion	0.01	0.01	0.027	0.025
MCPA	0.083	0.022	0.315	0.079
MCPP (Mecoprop)	0.083	0.029	0.315	0.079
Merphos (1 & 2)	0.024	0.06	0.040	0.038
Metalaxyl	0.35	0.35	0.199	0.189
Methamidophos				1.594
Methidathion				1.594
Methiocarb			0.19	0.13
Methomyl			0.19	0.13
Methoxychlor	0.03	0.03	0.088	0.079
Methyl Chlorpyrifos	0.008	0.008	0.027	0.025
Methyl Parathion	0.005	0.005	0.023	0.022
Metolachlor	0.15	0.15	0.133	0.127
Metribuzin	0.02	0.02	0.033	0.031
MGK264	0.26	0.26	0.263	0.252
Mirex	0.04	0.04	0.018	0.079
Molinate	0.17	0.17	0.066	0.063
Naled				1.594
Napropamide	0.11	0.11	0.099	0.094
Norflurazon	0.07	0.07	0.066	0.063
Oxamyl			0.19	0.13
Oxychlordane	0.035		0.018	0.079
Oxyfluorfen	0.1	0.1	0.134	0.127
Parathion	0.009	0.009	0.027	0.025
Pebulate	0.11	0.11	0.066	0.063
Pendimethalin	0.06	0.06	0.050	0.046
Pentachloroanisole	0.035		0.018	0.079
Pentachlorophenol	0.021	0.007	0.080	0.079
Phorate	0.006	0.006	0.023	0.022
Picloram	0.042	0.004	0.160	0.079
Profluralin	0.07	0.07	0.079	0.075
Promecarb			0.19	0.13
Prometon (Pramitol 5p)	0.04	0.04	0.032	0.031

(Continued)

Appendix B, Continued.

Chemical	[1]EPA	[2]Manchester	[3]WSDA	
			2003	2004
	MDL	MDL	LPQL	LPQL
Prometryn	0.04	0.04	0.033	0.031
Pronamide (Kerb)	0.13	0.13	0.169	0.127
Propachlor (Ramrod)	0.12	0.12	0.079	0.075
Propargite	0.14	0.14	0.066	0.063
Propazine	0.05	0.05	0.033	0.031
Propoxur			0.19	0.13
Ronnel	0.005	0.005	0.023	0.022
Simazine	0.05	0.05	0.033	0.031
Sulfotepp	0.006	0.006	0.020	0.019
Tebuthiuron	0.03	0.03	0.050	0.047
Terbacil	0.13	0.13	0.099	0.093
Terbutryn (Igran)	0.05	0.05	0.033	0.031
Trans-Chlordane (Gamma)	0.03		0.018	0.079
Trans-Nonachlor	0.035		0.018	0.079
Treflan (Trifluralin)	0.09	0.09	0.050	0.047
Triadimefon	0.13	0.13	0.086	0.082
Triallate	0.26	0.26	0.099	0.094
Triclopyr	0.035	0.0091	0.130	0.079
Vernolate	0.22	0.22	0.066	0.063

[1]Environmental Protection Agency. Target method detection limits (MDLs). Provided for comparative purposes only. Actual MDL for a specific matrix will vary. Each laboratory should determine its own MDL.
Lowest detection level abstracted from Tables 1-8 (EPA 2000).
MDL – Method detection limit is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom. (Appendix B to 40 CFR Part 136).
EPA 1996, 2000, 2005.

[2]Manchester Environmental Laboratory.
MDL – Method detection limit is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom. (Appendix B to 40 CFR Part 136).

[3]WSDA Pesticides Study, 2003-2004
LPQL: Lower performance practical quantitation limit. Average of lower performance (reporting) values, per analyte for all batches over each study year (14-31 batches per year).

Appendix B References

EPA. 1996. Guidelines and Format for Methods to be Proposed at 40 CFR Part 136 or Part 141. www.epa.gov/waterscience/methods/guide/guidfor5.pdf

EPA. 2000. Method 8085: Compound-Independent Elemental Quantitation of Pesticides by Gas Chromatography with Atomic Emission Detection. Revision 0, November 2000. www.epa.gov/epaoswer/hazwaste/test/pdfs/8085.pdf

EPA 2005. Draft – National Functional Guidelines for Superfund Organic Methods Data Review. EPA 540-R-04-009.
http://www.epa.gov/superfund/programs/clp/download/somnfg.pdf

MEL. 2000. Standard Operating Procedure for Pesticides Screening and Compound Independent Elemental Quantitation by Gas Chromatography with Atomic Emission Detection (AED), Method 8085, version 2.0. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.