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PTI

ENVIRONMENTAL SERVICES

1990 Puget Sound Pesticide Reconnaissance Survey

Prepared for

U.S. Environmental Protection Agency
Region 10, Office of Puget Sound
Seattle, Washington

August 1991

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EPA Contract 68D80085
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LIST OF ACRONYMS

CCC	criterion continuous concentration
CMC	criterion maximum concentration
2,4-D	2,4-dichlorophenoxyacetic acid
EPA	U.S. Environmental Protection Agency
IRIS	Integrated Risk Information System
MSMA	monosodium methanearsonate

EXECUTIVE SUMMARY

The 1989-1990 Pesticide Reconnaissance Survey was conducted by the U.S. Environmental Protection Agency Region 10, Office of Coastal Waters, and the Puget Sound Estuary Program to assess the extent and toxicological significance of water-soluble and sediment-bound pesticide residues present in Puget Sound drainages. Fifteen water samples and six sediment samples were collected from five drainage areas that empty into Puget Sound and analyzed for 33 different pesticide residues. Five pesticides were detected in at least one water sample: diazinon, 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, bromacil, and diuron. The most commonly detected pesticide in water samples was 2,4-D, which was detected in 13 samples at concentrations from 0.077 to 0.70 μg/L. Four pesticides, or their degradation products, were detected in at least one sediment sample: dichlobenil, pentachlorophenol, DDT/DDE/DDD, and endosulfan I and II. Pentachlorophenol was detected in all six sediment samples at concentrations up to 33 μg/kg.

Results from water and sediment sampling were compared to toxicological values. Pesticide concentrations detected in water samples were below or did not exceed published acute or chronic toxicological values. Two pesticides, diazinon and endosulfan I, were detected in at least one sediment sample at concentrations that are potentially hazardous to aquatic life that may contact contaminated sediments. Recommendations for future pesticide monitoring efforts include routine monitoring, regional reconnaissance surveys, and detailed research studies.

INTRODUCTION

The 1989-1990 Pesticide Reconnaissance Survey was conducted by the U.S. Environmental Protection Agency (EPA) Region 10, Office of Coastal Waters, and the Puget Sound Estuary Program. The objectives of the survey were to:

- Assess water-soluble pesticide residues during two time intervals immediately following a significant rain event
- Assess sediment-bound pesticide residues at locations consistent with the water-soluble pesticide sampling strategy
- Assess sediment-bound and water-soluble pesticides at areas representing the lower portions of three distinct watersheds: urban, suburban, and semirural land-use patterns
- Compare results of the current survey with results from a previous reconnaissance of pesticide residues in sediments of Puget Sound drainages
- Summarize the results of the present study in the context of the published information on the toxicology of the pesticides detected
- Make recommendations for future pesticide monitoring activities.

In the following section, the design of the reconnaissance survey is described, with emphasis on the rationale for how an appropriate storm event and sampling period were selected for each drainage basin. In subsequent sections, results for the water and sediment analyses conducted in 1989 and 1990 are summarized and a review of toxicity data from the literature is presented. The review provides a biological context for interpreting the concentrations of pesticides detected in the reconnaissance survey and for assessing the adequacy of detection limits attained for undetected compounds. In the final section, a summary is provided in which continued monitoring of selected pesticides is recommended and additional research needs are identified.

SAMPLING PROTOCOLS

SAMPLING LOCATIONS

Twelve water samples and six sediment samples were collected from four Puget Sound drainages (Figure 1) in 1990. Specific sampling locations are provided in Appendix A. The Big Ditch Slough drainage, located near the mouth of the Skagit River, and Padilla Bay sloughs are representative of agricultural runoff. Mercer Creek is representative of urban runoff, and the Swamp Creek/ Sammamish River drainage is representative of suburban runoff. Three additional water samples were collected by EPA staff from Muck Creek in southern Puget Sound. Muck Creek discharges to the Nisqually River and is representative of drainage from the Ft. Lewis military base.

SELECTION OF SIGNIFICANT RAINFALL EVENT FOR WATER SAMPLING

Sampling was conducted during high-rainfall precipitation events to enhance the probability that pesticides would be present in water runoff. A hydrographic model that incorporated area-specific physiographic, hydraulic, and precipitation data was used to predict the amount of precipitation and the length of time after the start of the event needed at each sampling area to produce runoff. A 6-hour duration, 2-year return precipitation event was used as a basis for sampling program design. Model results indicated that 0.5–2.1 inches of rain, depending on the area and the season, must occur in the 5 days preceding the 6-hour, 2-year precipitation event for runoff to occur. Details of model development and criteria used for sampling are found in Appendix B.

SAMPLE COLLECTION

Water Samples

Twelve water samples were collected during four sampling events in 1990 (Table 1). Samples were collected using 2.5-liter glass bottles held in a ring at the end of a 4.5-meter stainless steel pole. A complete description of the sampling apparatus used for water sampling is included in Appendix C. Samples were taken from below the water surface at a minimum of 3 meters from the bank. Each sample listed in Table 1 was collected as a composite that was divided into a set of twelve 2.5-liter bottles for chemical analysis. Two to eight pairs of 40-mL volatile organic analyte vials were also collected with each sample by transferring water from the sample bottle used to create the composites. Three

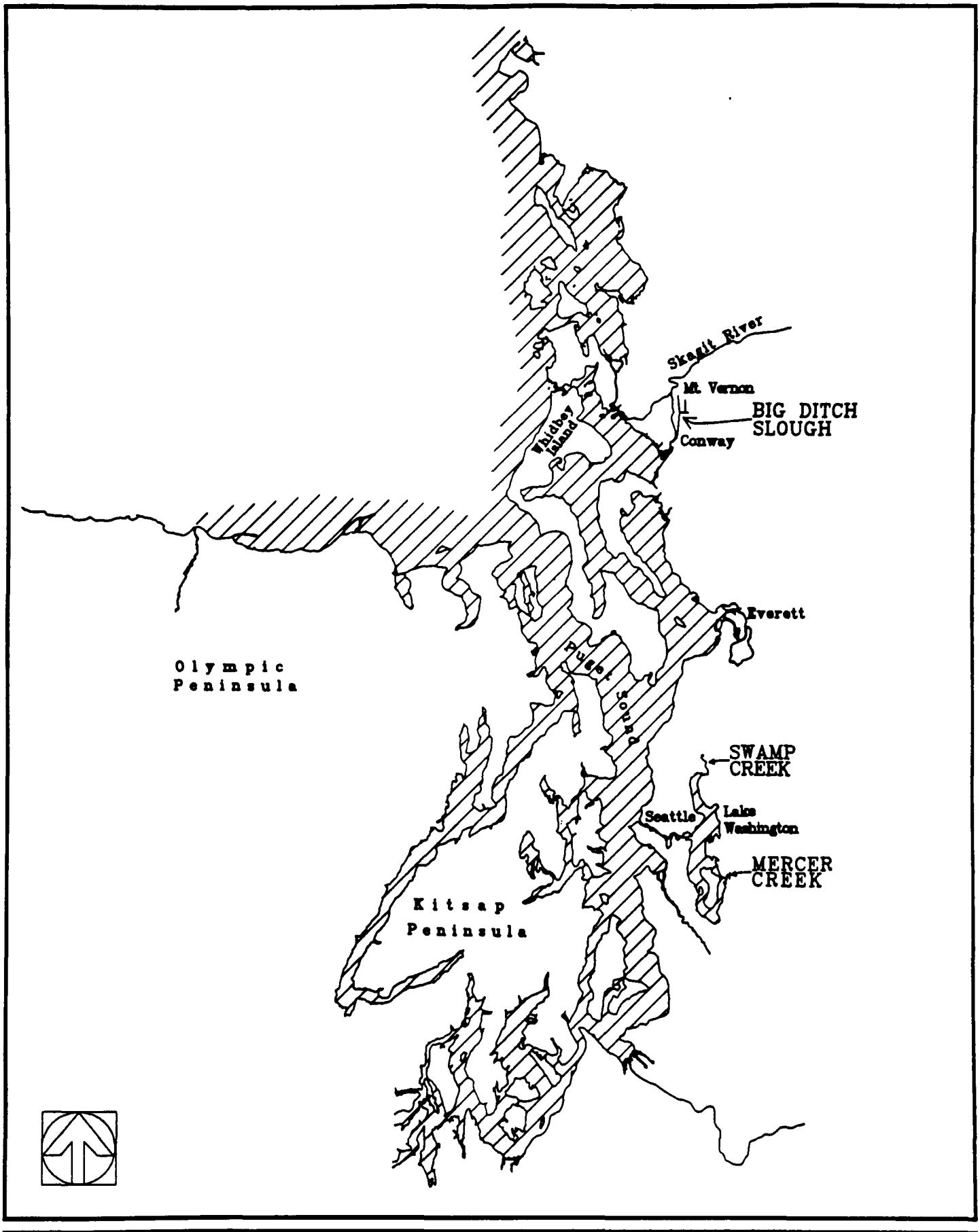

Figure 1. Drainages sampled.

TABLE 1. SAMPLING DATES
FOR WATER SAMPLES

Sample	Date Sampled
Muck Creek[a]	
MKCR-1	21 June 1989
MKCR-2	21 June 1989
MKCR-3	21 June 1989
Big Ditch Slough	
BGDHJ1	7 June 1990
BGDHJ2	7 June 1990
BGCHJ3	7 June 1990
BGDH01	16 October 1990
BGDH02	16 October 1990
BGDH03	16 October 1990
Mercer Creek	
MRCR-1	30 August 1990
MRCR-2	30 August 1990
MRCR-2	30 August 1990
Swamp Creek	
SWMP-1	4 October 1990
SWMP-2	4-5 October 1990
SWMP-3	5 October 1990

[a] Muck Creek, near Ft. Lewis, was not resampled in 1990, and no hydrograph was prepared for this location.

sets of twelve bottles each were collected at each location during a storm event, representing three time periods on the flow curve. All samples were stored on ice until delivery to the laboratory. Chain-of-custody records were completed each day for each sample and are included in Appendix D.

Water samples collected in 1989 near Ft. Lewis were obtained using a battery-powered submersible pump. Water drawn through Tygon® tubing was collected in 2.5-liter bottles for chemical analysis. This system was replaced with the apparatus shown in Appendix C to eliminate any concern about the possibility of pesticides being absorbed into the walls of the tubing.

Sediment Samples

Six composite sediment samples were collected on 25 and 26 October 1990 using a hand-held Ekman grab sampler (0.023 m^2). Each composite sample consisted of three to four grab samples at each location. Grab samples were taken in water depths of 6 inches to 3 feet and, unless insufficient fine-grained material was found, were generally collected within 10 feet of each other. Exceptions were grab samples collected within 300 feet of each other along the slough near Conway (Figure 1) and grab samples collected within 1,300 feet of each other along Swamp Creek. Samples were stored on ice until delivery to the laboratory. Chain-of-custody records were completed each day for each sample, and are included in Appendix D.

CHEMICAL ANALYSES

Water and sediment samples were analyzed for the pesticides listed in Table 2 by EPA-approved methods (Table 3). Target pesticides were selected from the list found in *Pesticides of Concern in the Puget Sound Basin: A Review of Contemporary Pesticide Usage* (Tetra Tech 1988). Some pesticides suggested in the 1988 report were not determined because of 1) analytical difficulties (e.g., benomyl in sediment); 2) nonspecific analysis [e.g., vernolate or butylate by carbon disulfide generation, monosodium methanearsonate (MSMA) by arsenic detection]; or 3) environmental interferences (e.g., substitution of bromine in methyl bromide by chlorine in natural waters).

TABLE 2. PESTICIDES ANALYZED FOR IN PUGET SOUND WATERS AND SEDIMENTS

Organophosphate Pesticides	Chlorinated Pesticides[a]	Chlorinated Herbicides	Triazine Herbicides
Diazinon	Trifluralin	2,4-D	Alachlor
Malathion	Chlordane	Dicamba	Atrazine
Dichlorvos	Endosulfan	Dinoseb	Amitrole
Fenamiphos	Lindane	Triclopyr	Hexazinone
Chlorpyrifos	Dichlobenil		Prometon
Parathion (ethyl)	DDT		Simazine
Disulfoton	DDE		
Methyl parathion	DDD		
Azinphos-methyl			
Phorate			

Polar Phosphorous Pesticides[b]	Carbamates and Urea Pesticides	Miscellaneous
Acephate	Bromacil	1,3-Dichloropropene[b] and Chloropicrin[b]
Methamidophos	Carbaryl	Glyphosate
	Propham	Benfluralin
	Methomyl	Pentachlorophenol[a]
	Diphenamid	Fenvalerate[b]
	Tebuthiuron	
	Diuron	
	Pronamide	
	Bendiocarb	
	Terbacil	

[a] Sediment samples only.

[b] Water samples only.

TABLE 3. SUMMARY OF ANALYTICAL METHODS

Analytical Group	Instrument Technique	Method
Organophosphate pesticides	GC/FPD[a]	EPA Method 1618
Chlorinated pesticides (sediment only)	GC/ECD[b]	EPA Method 608
Chlorinated herbicides and trichlopyr	GC/ECD	EPA Method 615
Triazine herbicides and alachlor	GC/NPD[c]	EPA Method 619
Carbamate pesticides and terbacil	HPLC[d]	EPA Method 632
Polar phosphorous pesticides (water only)	GC/FPD	Method AB 1803
Miscellaneous (water only)		
Chloropicrin and 1,3-dichloropropene	GC/ECD	EPA Method 504
Glyphosate	HPLC	Modified EPA Method 547[e]
Miscellaneous (sediment only)		
Benfluralin	GC/ECD or HPLC	Modified EPA Method 608 or modified Method 619
Pentachlorophenol	GC/ECD	EPA Method 8040
Pydrin and Fenvalerate	GC/ECD	Modified EPA Method 608

[a] Gas chromatography/flame photometric detection.

[b] Gas chromatography/electron capture detection.

[c] Gas chromatography/nitrogen-phosphorous detection.

[d] High performance liquid chromatography.

[e] Fluorescence detection.

RESULTS

Five pesticides were detected in water samples: diazinon, 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, bromacil, and diuron (Table 4a). Diuron and 2,4-D were the only pesticides detected in water samples from Muck Creek in the June 1989 sampling event (Table 4b). Diazinon and 2,4-D were detected in water samples from Big Ditch Slough from the June 1990 (BGDHJ) sampling event, but were not detected during the October 1990 sampling event (BGDHO). Diazinon was also detected in samples from Mercer Creek (MRCR) and Swamp Creek (SWMP). Dicamba was detected in samples from Swamp Creek. Dicamba and 2,4-D were the only pesticides detected in water samples from a study of Padilla Bay and surrounding sloughs conducted in 1987 and 1988 (Table 5) (Mayer 1989). The concentrations of 2,4-D found in the present survey are similar to those found in the previous Padilla Bay study, but the concentrations of dicamba found in the previous Padilla Bay study were 1-2 orders of magnitude higher than those found in the present Swamp Creek samples. Water samples from the June 1990 sampling of Big Ditch Slough also had detectable concentrations of bromacil and diuron, while no detectable concentrations of these pesticides were observed in Big Ditch Slough samples collected in October 1990.

Four pesticides were detected in sediment samples: dichlobenil, DDT and its breakdown products (DDE and DDD), endosulfan, and pentachlorophenol (Table 6). Pentachlorophenol was detected in all six sediment samples at concentrations from 0.0021 to 0.033 mg/kg. Pentachlorophenol was also detected in all 17 sediment samples collected for the 1988 pesticide survey, at similar concentrations to those found in the present study (Table 7) (Crecelius et al. 1989). Dichlobenil was detected in three sediment samples in the present study [MRCR-S, SWMP-S, and LACO-S (Padilla Bay sloughs/north Skagit delta)]. During the 1988 survey, dichlobenil was detected in four samples collected from around Lake Washington, at similar concentrations. The sediment sample from Mercer Creek (MRCR-S) had a detectable concentration of endosulfan. DDT and/or its breakdown products were detected in samples MRCR-S, SWMP-S, LACO-S, and CNWY-S at levels from 0.0078 to 0.0209 mg/kg (total DDT+DDE+DDD). Endosulfan, DDT, DDE, and DDD were not analyzed for during the 1988 survey.

During the 1988 survey, several pesticides were reported as detected: clorpyrifos was detected at three stations, lindane (γ-hexachlorocyclohexane) at nine stations, dicamba at two stations, and 2,4-D at four stations. Dicamba was also detected in sediment samples from Padilla Bay drainages during 1987 (Mayer 1989).

TABLE 4a. CONCENTRATIONS OF PESTICIDES IN WATER SAMPLES (μg/L)[a]

Compound	Sample												
	BGDHJ1	BGDHJ2	BGDHJ3	BGDHJC[b]	MRCR-1	MRCR-2	MRCR-3	SWMP-1	SWMP-2	SWMP-3	BGDHO1	BGDHO2	BGDHO3
Azinophos methyl	--	--	--	0.2 *U*[b]	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*
Chlorpyrifos	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Diazinon	--	--	--	**0.072**[b]	0.05 *U*	**0.054**	0.05 *U*	**0.14**	**0.14**	**0.12**	0.05 *U*	0.05 *U*	0.05 *U*
Dichlorvos	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Disulfoton	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Fenamiphos	--	--	--	0.06 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*	0.1 *U*
Malathion	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Methyl parathion	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Parathion	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Phorate	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Chloropicrin	--	--	--	0.22 *UE*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*
1,3-Dichloropropene	--	--	--	0.22 *UE*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*	0.22 *U*
2,4-D	--	--	--	**0.077**	**0.14**	**0.16**	**0.18**	**0.29**	**0.54**	**0.48**	0.05 *U*	0.05 *U*	0.05 *U*
Dicamba	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	**0.11**	**0.19**	**0.27**	0.05 *U*	0.05 *U*	0.05 *U*
Dinoseb	--	--	--	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*	0.05 *U*
Trichlopyr	--	--	--	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*	0.17 *U*
Alachlor	--	--	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Atrazine	--	--	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Hexazinone	--	--	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Prometon	--	--	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Simazine	--	--	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*

TABLE 4a. (Continued)

Compound	Sample												
	BGDHJ1	BGDHJ2	BGDHJ3	BGDHJC[b]	MRCR-1	MRCR-2	MRCR-3	SWMP-1	SWMP-2	SWMP-3	BGDHO1	BGDHO2	BGDHO3
Amimole	NR[b]	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Methomyl	5.0 *U*	5.0 *U*	5.0 *U*	--	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*
Tebuthiuron	2.0 *U*	2.0 *U*	2.0 *U*	--	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Bromacil	2.0 *U*	2.0 *U*	**3.3**	--	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Terbacil	2.0 *U*	2.0 *U*	2.0 *U*	--	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Bendiocarb	5.0 *U*	5.0 *U*	5.0 *U*	--	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*
Carbaryl	2.0 *U*	2.0 *U*	2.0 *U*	--	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Diuron	1.0 *U*	**1.3**	**3.3**	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Propham	2.0 *U*	2.0 *U*	2.0 *U*	--	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Diphenamid	2.0 *U*	2.0 *U*	2.0 *U*	--	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Pronamide	1.0 *U*	1.0 *U*	1.0 *U*	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Acephate	1.0 *U*	1.0 *U*	1.0 *U*	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Methamidophos	1.0 *U*	1.0 *U*	1.0 *U*	--	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Gyphosate	5.0 *U*	5.0 *U*	5.0 *U*	--	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*

[a] BGDHJC - composite of BGDHJ1, BGDHJ2, and BGDHJ3. Results are reported for the composited sample (BGDHJC), except for polar phorphorous pesticides, carbamate and urea pesticides, and glyphosate, which were analyzed in individual samples rather than as a composited sample.

[b] *U* – Undetected at the detection limit shown.
Bold – Detected values.
NR – Analysis not required.

TABLE 4b. CONCENTRATIONS OF PESTICIDES IN WATER SAMPLES (μg/L)[a]

Compound	Sample			
	MKCR-1[d]	MKCR-2[c]	MKCR-3[d]	MKCR-4[a]
Azinophos methyl	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Chlorpyrifos	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Diazinon	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Dichlorvos	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Disulfoton	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Fenamiphos	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Malathion	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Methyl parathion	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Parathion	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Phorate	NR	NR	NR	NR
Chloropicrin	0.22 *U*	0.22 *U*	0.22 *U*	.22 *U*
1,3-Dichloropropene	0.22 *U*	0.22 *U*	0.22 *U*	.22 *U*
2,4-D	**0.7**	**0.69**	**0.58**	0.4 *U*
Dicamba	0.40 *U*	0.4 *U*	0.4 *U*	0.4 *U*
Dinoseb	0.40 *U*	0.4 *U*	0.4 *U*	0.4 *U*
Trichlopyr	0.40 *U*	0.4 *U*	0.4 *U*	0.4 *U*
Alachlor	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Atrazine	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Hexazinone	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Prometon	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Simazine	1.0 *U*	1.0 *U*	1.0 *U*	1.0 *U*
Amimole	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*
Methomyl	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*
Tebuthiuron	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Bromacil	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Terbacil	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Bendiocarb	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*
Carbaryl	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Diuron	**2.9**	**2.1**	**2.2**	1.0 *U*
Propham	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Diphenamid	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Pronamide	2.0 *U*	2.0 *U*	2.0 *U*	2.0 *U*
Acephate	10.0 *U*	10.0 *U*	10.0 *U*	10.0 *U*
Methamidophos	10.0 *U*	10.0 *U*	10.0 *U*	10.0 *U*
Gyphosate	5.0 *U*	5.0 *U*	5.0 *U*	5.0 *U*

[a] Samples from Muck Creek were collected in 1989.
Bold—detected values.

TABLE 5. SUMMARY OF PESTICIDE DATA FOR PUGET SOUND WATERS

Compound	Concentration Range (µg/L)	
	Mayer[a]	1990 Survey
Diazinon	--	0.054 - 0.14 (5 of 14 samples)[b]
2,4-D	0.14 - 1.3 (4)	0.077 - 0.70 (10 of 14 samples)
Dicamba	10 - 170 (10)	0.11 - 0.27 (3 of 14 samples)
Bromacil	--	3.3 (1 of 16 samples)
Diuron	--	1.3 - 3.3 (5 of 16 samples)

[a] Mayer (1989).

[b] ( ) - number of samples with detectable pesticide.

TABLE 6. CONCENTRATIONS OF PESTICIDES IN SEDIMENT SAMPLES (mg/kg)

Compound	Sample					
	BGDH-S	LSAM-S	MRCR-S	SWMP-S	LACO-S	CNWY-S
Azinophos methyl	0.0086 *U*	0.0073 *U*	0.013 *U*	0.01 *U*	0.015 *U*	0.019 *U*
Chlorpyrifos	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
Diazinon	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.0088 *T*
Dichlorvos	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
Disulfoton	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
Fenamiphos	0.0086 *U*	0.0073 *U*	0.013 *U*	0.01 *U*	0.015 *U*	0.019 *U*
Malathion	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
Methyl parathion	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
Parathion	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
Phorate	0.0045 *U*	0.0038 *U*	0.0065 *U*	0.0052 *U*	0.0077 *U*	0.01 *U*
2,4-D	0.0018 *U*	0.0015 *U*	0.0026 *U*	0.002 *U*	0.003 *U*	0.0039 *U*
Dicamba	0.0018 *U*	0.0015 *U*	0.0026 *U*	0.002 *U*	0.003 *U*	0.0039 *U*
Dinoseb	0.0018 *U*	0.0015 *U*	0.0026 *U*	0.002 *U*	0.003 *U*	0.0039 *U*
Trichlopyr	0.0022 *U*	0.0019 *U*	0.0032 *U*	0.0025 *U*	0.0038 *U*	0.0049 *U*
Alachlor	0.053 *U*	0.044 *U*	0.092 *U*	0.061 *U*	0.091 *U*	0.13 *U*
Atrazine	0.053 *U*	0.044 *U*	0.092 *U*	0.061 *U*	0.091 *U*	0.13 *U*
Hexazinone	0.053 *U*	0.044 *U*	0.092 *U*	0.061 *U*	0.091 *U*	0.13 *U*
Prometon	0.053 *U*	0.044 *U*	0.092 *U*	0.061 *U*	0.091 *U*	0.13 *U*
Simazine	0.053 *U*	0.044 *U*	0.092 *U*	0.061 *U*	0.091 *U*	0.13 *U*
Methomyl	2.6 *U*	2.2 *U*	3.8 *U*	3 *U*	4.5 *U*	5.8 *U*
Tebuthiuron	0.3 *U*	0.2 *U*	0.4 *U*	0.3 *U*	0.5 *U*	0.6 *U*
Bromacil	0.3 *U*	0.2 *U*	0.4 *U*	0.3 *U*	0.5 *U*	0.6 *U*
Terbacil	0.1 *U*	0.1 *U*	0.2 *U*	0.1 *U*	0.2 *U*	0.2 *U*

TABLE 6. (Continued)

Compound	Sample					
	BGDH-S	LSAM-S	MRCR-S	SWMP-S	LACO-S	CNWY-S
Bendiocarb	0.3 *U*	0.2 *U*	0.4 *U*	0.3 *U*	0.5 *U*	0.6 *U*
Carbaryl	0.3 *U*	0.2 *U*	0.4 *U*	0.3 *U*	0.5 *U*	0.6 *U*
Diuron	0.1 *U*	0.1 *U*	0.2 *U*	0.1 *U*	0.2 *U*	0.2 *U*
Propham	1 *U*	0.9 *U*	1.5 *U*	1.2 *U*	1.8 *U*	2.3 *U*
Diphenamid	1 *U*	0.9 *U*	1.5 *U*	1.2 *U*	1.8 *U*	2.3 *U*
Pronamide	0.3 *U*	0.2 *U*	0.4 *U*	0.3 *U*	0.5 *U*	0.6 *U*
Dichlobenil	0.0022 *U*	0.0018 *U*	**0.022**	**0.0026**	**0.0021** *T*	0.0049 *U*
Trifluralin	0.0022 *U*	0.0018 *U*	0.0032 *U*	0.0025 *U*	0.0038 *U*	0.0049 *U*
Benfluralin	0.0022 *U*	0.0018 *U*	0.0032 *U*	0.0025 *U*	0.0038 *U*	0.0049 *U*
Lindane	0.0022 *U*	0.0018 *U*	0.0032 *U*	0.0025 *U*	0.0038 *U*	0.0049 *U*
4,4'-DDE	0.0022 *U*	0.0018 *U*	**0.0038**	**0.0015** *T*	**0.0052** *E*	**0.0045** *E*
4,4'-DDD	0.0032 *U*	0.0027 *U*	**0.0074**	**0.0020** *T*	**0.0066** *E*	**0.0041** *E*
4,4'-DDT	0.0032 *U*	0.0027 *U*	**0.0097**	**0.0023** *T*	**0.0029** *TE*	0.0070 *UR*
Endosulfan I	0.0022 *U*	0.0018 *U*	**0.0113**	0.0025 *U*	0.0038 *U*	0.0049 *U*
Endosulfan II	0.0032 *U*	0.0027 *U*	**0.0080** *E*	0.0036 *U*	0.0054 *U*	0.0070 *U*
Fenvalerate	0.0055 *U*	0.0047 *U*	0.0080 *U*	0.0064 *U*	0.0095 *U*	0.0120 *U*
Chlordane	0.011 *U*	0.0093 *U*	0.016 *U*	0.013 *U*	0.019 *U*	0.025 *U*
Pentachlorophenol	**0.0039** *E*	**0.0021** *E*	**0.0130** *E*	**0.0330**	**0.0038** *E*	**0.0020** *E*

U - Undetected at the detection limit shown.

T - Detected below quantification limit.

E - Estimate.

R - Rejected.

Bold - Detected values.

TABLE 7. SUMMARY OF PESTICIDE DATA FOR SEDIMENTS

Compound	Concentration Range (µg/kg)		
	Mayer[a]	1988 Survey[b]	1990 Survey
Chlorpyrifos		2.7 - 7.6 (3)[c]	
Dichlobenil		2.0 - 4.9 (4)	2.1 - 22 (3 of 6 samples)
Lindane		2.2 - 20 (9)	
Dicamba	2,100 - 17,100 (10)	1.2 - 12 (2)	
2,4-D		12 - 43 (4)	
Pentachlorophenol		6.7 - 56 (17)	2.0 - 33 (6 of 6 samples)
DDT/DDE/DDD (total)			5.8 - 20.9 (4 of 6 samples)
Endosulfan I and II			19.3 (1 of 6 samples)

[a] Mayer (1989).

[b] Crecelius et al. (1989).

[c] ( ) - number of samples with detectable pesticide.

Of the 11 pesticides detected in Puget Sound sediments and waters during the three studies mentioned above, 6 are currently used primarily for non-urban applications: pentachlorophenol, 2,4-D, diazinon, dicamba, bromacil, and diuron (Tetra Tech 1988). Historically, pentachlorophenol, detected in all samples in both the 1988 and 1990 reconnaissance studies, has been the most heavily used pesticide in the Puget Sound area (Table 8). Pentachlorophenol is used extensively as a wood preservative; thus, treated railroad ties may also serve as a long-term source for this material. The other 5 pesticides detected are among the 12 most heavily used pesticides in the area, supporting the correlation between pesticide usage and detection of these pesticides in runoff. Dicamba, 2,4-D, and mixtures of the two are used for control of broadleaf weeds in grain crops, lawns and golf courses, right of ways, and forestry applications. Diuron, at low application rates, is used to selectively control broadleaf and grass weeds in alfalfa and tree crops. Diuron, at high rates, and bromacil are nonselective herbicides that are used alone or in combination on non-cropland. Diazinon, an insecticide, is used for a wide variety of agricultural, industrial, and home uses.

Pesticides used primarily in urban areas (Tetra Tech 1988) detected in the Puget Sound area include chlorpyrifos, lindane, and dichlobenil. Chlorpyrifos, the fifth-most heavily applied pesticide in Puget Sound (Table 9), is used for insect control on lawns, vegetables, ornamental plants, and stored products. It is also used for control of mosquitoes and termites. Lindane is used as a seed treatment for soil insect control; as a foliar spray in vegetables, fruit trees, and ornamental plants and trees; and as a wood preservative. Dichlobenil is used to control herbaceous weeds in woody ornamental or food crops such as rhododendrons, grapes, and fruit trees. It is also used as a general, nonselective weed killer in nurseries, industrial areas, and parking lots.

There are several possible reasons why other heavily used pesticides listed in Tables 8 and 9 have not been detected. Sampling locations may not have been located in areas where these compounds are specifically used. However, malathion, which is used primarily in the Puget Sound on Puyallup and Nisqually/ Deschutes military bases (Tetra Tech 1988), was not detected (U 1 μg/L) in water samples from Muck Creek flowing through the Ft. Lewis military base. Pesticides may also degrade into compounds that were not on the target list, or volatilize into the atmosphere. Malathion hydrolyses in water, and trichlopyr is subject to rapid photodegradation. Methyl bromide is a gas (above 4°C) that is used as a space, stored commodity, and soil fumigant.

Endosulfan was not listed in the Tetra Tech (1988) report as currently being used in Puget Sound area; however, endosulfan is still registered for use against foliar feeding insects on a wide variety of plants, and its use in the Puget Sound area is not unlikely. The use of DDT in the United States has been prohibited since 1973 and has not been domestically available since its registration was canceled. Therefore, it is doubtful that any significant illegal use of DDT has occurred. The fact that DDT and its degradation products have been detected in Puget Sound sediments 17 years after its use has been banned is further indication

TABLE 8. ESTIMATED PESTICIDE USAGE OF PRIMARILY NON-URBAN-SPECIFIC PESTICIDES IN THE PUGET SOUND BASIN[a]

Active Ingredient	Pounds Active Ingredient Per Year
Pentachlorophenol	**720,000**
2,4,-D Species	**311,406**
Malathion	203,326
Prometon	108,744
Simazine	97,283
Diazinon	**83,127**
Dicamba	**55,446**
Triclopyr	54,633
Atrazine	44,391
Bromacil	**40,817**
Carbaryl	37,297
Diuron	**37,120**
Glyphosate	35,088
Tebuthiuron	33,043
Vernolate	16,199
Cuprous Oxide	15,745
Dichloropropene	15,330
Parathion	13,746
Sodium Metaborate	13,689
Dinoseb	12,392
Butylate	12,000
Alachlor	9,402
Phorate	8,156
Methyl Parathion	7,856
Lime Sulfur	7,417
Disulfoton	7,340
Methamidophos	5,976
Pronamide	5,850
Trifluralin	5,547
Oryzalin	5,397
Metolachlor	5,301
Boric Acid	4,995
Sulfometuron-methyl	4,992
Acrolein	4,765
Fenvalerate	4,753
Benfluralin	4,435
Diquat	4,152
Propham	4,128
Methomyl	4,013
Tributyltin	3,686
Fosamine Ammonium	3,680
Hexazinone	2,592
Diphenamid	2,400
All others (total)	79,000

[a] From Tetra Tech (1988); pesticides shown in bold were detected in the 1990 reconnaissance survey.

TABLE 9. ESTIMATED USAGE OF PRIMARILY URBAN-SPECIFIC PESTICIDES IN THE PUGET SOUND BASIN[a]

Active Ingredient	Pounds Active Ingredient Per Year
Methyl Bromide	???,???[b]
Sulfuryl Fluoride	120,900
Metaldehyde	54,200
Chlordane	49,800
Chlorpyrifos	**39,400**
Sulfur	34,800
Xylene	21,600
Acephate	19,400
Ziram	17,600
Endosulfan	14,020
MCPP	11,290
Glyphosate	11,423
Heptachlor	10,990
Amitrole	10,170
Azinphos-methyl	8,070
Propoxur	7,540
Dichlobenil	**7,070**
Benomyl	6,660
Chlorothalonil	6,150
Chloropicrin	3,810
Lindane	**2,640**
Dichlorvos	2,490
Propetamphos	2,280

[a] From Tetra Tech (1988); the pesticides shown in bold print were detected in the 1990 reconnaissance survey.

[b] Estimated usage is unknown.

of the extreme persistence of this material, or that it may be a byproduct or process residue associated with other chlorinated pesticides.

TOXICOLOGICAL RELEVANCE: REVIEW OF WATER AND SEDIMENT QUALITY DATA

The following review of water and sediment quality data for tributaries of Puget Sound is limited to a comparison of the observed site-specific chemical concentrations with available indices of toxicity. No quantitative estimates of risk were developed as part of this project. Pesticide concentrations measured in water and sediment samples were evaluated for their potential to cause adverse effects on aquatic communities based on EPA chronic water quality criteria (U.S. EPA 1987) and the lowest observed chronic effects values provided by EPA's Integrated Risk Information System (IRIS) (U.S. EPA 1990). Aquatic acute toxicity values summarized by Tetra Tech (1988) were used when chronic toxicity values were not identified by EPA. Literature searches for indices of toxicity to aquatic organisms in addition to those described above were beyond the scope of this effort.

EPA requires chronic and/or acute toxicity data from a minimum of eight families of organisms (U.S. EPA 1987) to derive water quality guidelines. This array of species should adequately represents the communities of Puget Sound and its tributaries. However, the species represented in acute toxicity test data (Tetra Tech 1988) are not necessarily found in Puget Sound (Table 10). The evaluation of the degree to which toxicity to these species may reflect similar effects on Puget Sound resources presented below is based on available information and professional judgment.

Using the results of water and sediment sampling (Tables 4, 5, and 6), potential adverse impacts on the marine environment were evaluated. The evaluation was based on the conservative assumption that contaminant concentrations found in the tributaries are maintained in the marine environment. Conditions in the water and sediments of Lake Washington were also assumed to be the same as conditions in its tributaries.

Finally, an approach to conducting screening level evaluations of water and sediment contaminant data for fresh and marine waters of the Puget Sound region is recommended.

Toxicity Test Species

The specific names of the organisms used to establish chronic water quality criteria provided by Tetra Tech (1988) and summarized in Table 11 are not available. The data were compiled from a variety of sources, and retrieval of

TABLE 10. WATER QUALITY EVALUATION DATA

Class	Pesticide	Chronic Water Quality Criteria Value (µg/L)[a]		Concentration Range/ Detection Limit[b] (µg/L)	Mean Value[c] (µg/L)	Acute Water Quality Criteria Value: Freshwater LC_{50} (µg/L)[d]		Acute Water Quality Criteria Value: Marine LC_{50} (µg/L)[d]	
		Freshwater	Marine			Bluegill[e]	Trout[f]	Shrimp[g]	Killifish[h]
Organophosphates	Acephate	--[i]	--	*/1.0	--	>1,000,000	100,000-1,100,000	3,800-10,000	85,000
	Azinophos methyl	--	--	*/0.1	--	22	3.2-20	0.03	--
	Chlorpyrifos	0.12	--	*/0.05	--	4[j]	3	2.8[j]	0.6
	Diazinon	--	--	0.054–0.14/0.05	0.105	22	380[j]	20,000[j]	1,470
	Dichlorvos	--	--	*/0.05	--	1,000[j]	187	4	2,400
	Disulfoton	--	--	*/0.05	--	300	1,850	50,000-58,000[k]	740
	Fenamiphos	--	--	*/0.1	--	--	110	--	--
	Glyphosate	--	--	*/5.0	--	--	--	--	--
	Malathion	--	--	*/0.05	--	87-122	87-310	330-1,000[k]	14
	Methamidophos	--	--	*/1.0	--	--	--	--	--
	Methyl parathion	--	--	*/0.05	--	2,000-5,700	2,750-5,300	1[j]	790
	Parathion	0.013	--	*/0.05	--	100-710	2,000[j]	430[j]	20
	Phorate	--	--	*/0.05	--	5[k]	11-16	--	0.4
Triazines	Atrazine	--	--	*/1.0	--	116,000	4,500-8,800	10,000-33,000[k]	--
	Hexazinone	--	--	*/1.0	--	370,000-420,000	320,000-420,000	<100,000	--
	Prometon	--	--	*/1.0	--	40,000	12,000	--	--
	Simazine	--	--	*/1.0	--	>100,000[k]	5,000-60,000[k]	>100,000[k]	--
Uracils	Bromacil	--	--	3.3/2.0	3.3	71,000[k]	75,000[k]	--	--
	Diuron	--	--	1.3–3.3/1.0	2.3	7,400-9,100	2,400-23,000	38-285	15
	Tebuthiuron	--	--	*/2.0	--	112,000	144,000	--	--
	Terbacil	--	--	*/2.0	--	--	--	--	--
Carbamates	Bendiocarb	--	--	*/5.0	--	1,450[j]	1,550	--	--
	Carbaryl	--	--	*/2.0	--	2,000-6,760	1,070-1,500	10-40[j]	1,750

TABLE 10 (Continued)

Class	Pesticide	Chronic Water Quality Criteria Value (μg/L)[a]		Concentration Range/ Detection Limit[b] (μg/L)	Mean Value[c] (μg/L)	Acute Water Quality Criteria Value: Freshwater LC_{50} (μg/L)[d]		Acute Water Quality Criteria Value: Marine LC_{50} (μg/L)[d]	
		Freshwater	Marine			Bluegill[e]	Trout[f]	Shrimp[g]	Killifish[h]
	Methomyl	--	--	*[i]/5.0	--	--	--	--	--
Anilines	Propham	--	--	*[i]/2.0	--	32,000[k]	4,000-14,000	--	--
Anilides	Alachlor	--	--	*[i]/1.0	--	3,200	1,400	--	--
Substituted Amides	Diphenamid	--	--	*[i]/2.0	--	--	--	58,000[k]	--
Halogenated Hydrocarbons	1,3-Dichloropropene	244	--	*[i]/0.22	--	700-1,100	110-320	--	--
Phenoxyaliphatic Acids	2,4-D	--	--	0.077-1.3/0.05	0.267	1,500-2,500[j]	1,500-2,200[k]	2,000	--
Benzoic Acids	Dicamba	--	--	0.11-170/0.05	0.19	135,000	50,000	>100,000	>180,000
Phenols	Dinoseb	--	--	*[i]/0.05	--	105,000	179,000[k]	5,100	2,300
Pyridine Carboxylic Acids	Trichlopyr	--	--	*[i]/0.17	--	148,000	117,000	895,000	--
Miscellaneous Pesticides	Chloropicrin	--	--	*[i]/0.22	--	105	17	--	--
	Pronamide	--	--	*[i]/1.0	--	--	--	--	--

[a] Source: EPA Quality Criteria for Water guidelines (U.S. EPA 1987; last update 5/90).

[b] From current survey and Mayer (1988).

[c] Value reported is a arithmetic mean of concentrations detected.

[d] Source: Tetra Tech (1988): Table 10, *Toxicity Data*, pp. 49-52. Value reported if for a a 96-hour averaging period unless otherwise noted. Reported by Tetra Tech (1988) in parts per million.

[e] Species studied: *Lepomis macrochirus*.

[f] Species studied: unknown.

[g] Species studied: unknown.

[h] Species studied: unknown.

[i] -- indicates that data is not available.

[j] 24-hour exposure period.

[k] 48-hour exposure period.

* Pesticide was not detected in any of the samples.

TABLE 11. SEDIMENT QUALITY EVALUATION DATA

Compound	Lowest Available Toxicity Value (μg/L)	Calculated K_{oc} (L/kg)	Sediment Quality Value[a] for $f_{oc}=0.01$ (mg/kg)	Sediment Quality Value[a] for $f_{oc}=0.05$ (mg/kg)	Concentration Range (of Samples with Detectable Pesticide) (mg/kg)	Detection Limit Range (mg/kg)
Azinophos methyl	0.03[b]	3,695[c]	0.001	0.006		0.0073–0.019
Chlorpyrifos	0.12[d]	14,350[e]	0.017	0.086	0.019[f,g]	0.038–0.01
Diazinon	22[h]	264[e]	0.058	0.290	0.0088[g]	0.0038–0.0077
Dichlorvos	4.00[b]	138[e]	0.006	0.028		0.0038–0.01
Disulfoton	300[h]	267[e]	0.802	4.009		0.0038–0.01
Fenamiphos	110[i]	796[e]	0.876	4.379		0.0073–0.019
Malathion	14[j]	458[e]	0.064	0.321		0.0038–0.01
Methyl parathion	1[b]	1,172[e]	0.012	0.059		0.0038–0.01
Parathion	0.013[d]	2,816[e]	--[k]	0.002	0.141[f,g]	0.0038–0.01
Phorate	0.4[b]	267[e]	0.001	0.005	0.090[f,g]	0.0038–0.01
Atrazine	4,500[i]	684[e]	30.770	153.852		0.044–0.13
Hexazinone	100,000[b]	0.096[e]	0.096	0.481		0.044–0.13
Prometon	12,000[i]	6[e]	0.758	3.789		0.044–0.13
Simazine	5,000[i]	370[e]	18.507	92.534		0.044–0.13
Bromacil	71,000[h]	292[e]	207.137	1,035.687		0.2–0.6
Diuron	15[l]	692[e]	0.104	0.519		0.0038–0.01
Tebuthiuron	112,000[h]	433[m]	484.610	2,423.048		0.2–0.6
Terbacil	--	4[e]	--	--		0.1–0.2
Bendiocarb	1,450[h]	2,733[m]	39.625	198.125		0.2–0.6
Carbaryl	10[b]	28[e]	0.003	0.014		0.2–0.6
Methomyl	428[h]	0.276[e]	0.001	0.006		2.2–5.8
Propham	4,000[i]	203[e]	8.115	40.576		0.9–2.3
Alachlor	1,400[i]	924[e]	12.930	64.651		0.044–0.13
2,4-D (acid)	1,500[i]	227[e]	3.406	17.032	0.043	0.0013–0.0039
Dicamba	50,000[i]	2,363[e]	1,181.544	5,907.721	17.1	0.0015–0.0039
Dinoseb	2,300[l]	2,423[e]	55.730	278.649		0.0015–0.0038

TABLE 11. (Continued)

Compound	Lowest Available Toxicity Value (µg/L)	Calculated K_{oc} (L/kg)	Sediment Quality Value[a] for $f_{oc}=0.01$ (mg/kg)	Sediment Quality Value[a] for $f_{oc}=0.05$ (mg/kg)	Concentration Range (of Samples with Detectable Pesticide) (mg/kg)	Detection Limit Range (mg/kg)
4,4'-DDD	--	44,862[n]	--	--	0.002-0.0074	0.0018-0.0022
4,4'-DDE	--	32,637[n]	--	--	0.0015-0.0052	0.0027-0.0032
4,4'-DDT	0.001[o]	42,777[n]	0.428	2.139	0.0023-0.0097[g]	0.0027-0.0032
Chlordane	--	1,487[e]	0.0001	0.0005		0.0093-0.025
Dichlobenil	14,700	3,479[c]	511.424	2,557.121	0.0021-0.022	0.0018-0.0022
Diphenamid	58[b]	1,035[c]	0.600	3.001		0.9-2.3
Endosulfan I	0.056[n,o]	2,033[e]	1.138	5.692	0.0113[g]	0.0018-0.0022
Endosulfan II	--	2,220[e]	--	--	0.008	0.0018-0.0022
Fenvalerate	36	18,903[e]	6.805	34.026	0.01	0.0047-0.012
Lindane	--	795[e]	--	--	0.02	0.0018-0.0049
Pentachlorophenol	13[c]	12,660[e]	1.646	8.229	0.02-0.056	U[p]
Trifluralin	--	19,141[e]	--	--		0.0018-0.0049

[a] Sediment quality values determined from current survey, Crecelius et al. (1989), and Mayer (1989), unless otherwise noted.
[b] Lowest shrimp LC_{50} reported by Tetra Tech (1988).
[c] Vershueren (1983).
[d] Freshwater criterion continuous concentration.
[e] Tetra Tech (1988).
[f] Tentatively identified compound; concentrations not confirmed.
[g] Concentration detected >0.1 times the sediment quality value for f_{oc} = 0.01.
[h] Lowest bluegill LC_{50} reported by Tetra Tech (1988).
[i] Lowest trout LC_{50} reported by Tetra Tech (1988).
[j] Lowest killifish LC_{50} reported by Tetra Tech (1988).
[k] -- indicates data were not available.
[l] Windholz (1976).
[m] Kenaga and Goring (1980).
[n] Lowest aquatic toxicity value for fresh water available in the literature. Identified through EPA's Integrated Risk Information System (U.S. EPA 1990).
[o] Chronic freshwater quality criteria for endosulfan, provided in EPA's Integrated Risk Information System (U.S. EPA 1990). Isomers endosulfan I and endosulfan II were not differentiated. Value based on a risk assessment that has not been reviewed.
[p] *Pentachlorophenol was detected in all sediment samples.*

species names was beyond the scope of this report. However, the sensitivity of each type of test organism is discussed below.

Mayer and Ellerseik (1986) provide a concise summary and analysis of common aquatic bioassays and their relative sensitivity. These authors collected data from over 4,000 bioassays conducted on 66 species at the Columbia National Fisheries Research Laboratory. They report that insects are generally the most sensitive test group, followed by crustaceans, fishes, and amphibians. More specifically, Mayer and Ellerseik (1986) analyzed the standardized data from all tests to derive a sensitivity ranking. They report that species may be ranked, in descending order of sensitivity, as follows: stoneflies (*Claassenia sabulosa, Pteronarcys californica, Pteronarcella badia*), glass shrimp (*Palaemonetes kadiakensis*), daphnids (*Daphnia magna, D. pulex*), amphipods (*Gammarus fasciatus*), daphnids (*Simocephalus serrulatus*), rainbow trout (*Oncorhynchus mykiss*), bluegills (*Lepomis macrochirus*), largemouth bass (*Micropterus salmoides*), seed shrimp (*Cypridopsis vidua*), coho salmon (*O. kisutch*), cutthroat trout (*Salmo clarki*), yellow perch (*Perca flavescens*), brown trout (*S. trutta*), channel catfish (*Ictalurus punctatus*), common carp (*Cyprinus carpio*), green sunfish (*L. cyanellus*), fathead minnow (*Pimephales promelas*), goldfish (*Carassius auratus*), black bullheads (*I. melas*), western chorus frog (*Pseudacris triseriata*), and Fowler's toad (*Bufo woodhousei fowleri*). Thus, although the precise species for which toxicity values are presented by Tetra Tech (1988) are not known, it is of interest that trout, bluegill, and shrimp all appear to be among the most sensitive common aquatic test species. The relative sensitivity of killifish was not discussed by Mayer and Ellerseik (1986). However, Mayer and Ellerseik (1986) also noted that testing daphnids, gammaridae, and rainbow trout provided the lowest toxicity value 88 percent of the time. This observation, coupled with the list of species in descending order of sensitivity, indicates that toxicity data for daphnids and amphipods would have added an important measure of sensitivity to this analysis, especially with respect to evaluating ecological effects of pesticide residues.

Bluegill and several trout and char species [brook, brown, cutthroat, Dolly Vardon, and rainbow (including steelhead)] are common game fish in Washington (Wydosky and Whitney 1979). According to Bailey et al. (1960), the California killifish (*Fundulus parvipinnis*) is the only species of marine killifish that inhabits Pacific waters. The majority of *Fundulus* species are freshwater fish or live in the Atlantic. Several shrimp species of the genus *Heptacarpus* inhabit Puget Sound (Kozloff 1983). However, the specific shrimp species used in toxicity tests summarized by Tetra Tech (1988) are unknown. Thus, some species used for toxicity tests summarized by Tetra Tech (1988) are common to Puget Sound, but it cannot be said that they represent a full cross-section of Puget Sound resources.

Mayer and Ellerseik (1986) observed changes in pesticide toxicity with changing conditions in ambient water. Alteration in water temperature resulted in changes in toxicity for 40 percent of the 66 chemicals; increased temperature enhanced the toxicity of most chemicals (DDT and methoxychlor were excep-

tions). Water hardness does not generally affect toxicity of organic contaminants in water. Mixtures of chemicals used in pesticide formulations increased the toxicity of technical grade material in 32 percent of the cases and decreased it in 11 percent of the cases. Finally, sensitivities of test fish and invertebrates were reduced as these organisms progressed developmentally or increased in size. These observations suggest that the relative toxicity of pesticides may change with different ambient conditions.

Because EPA requires toxicity data from eight families to develop a criterion, it was assumed for the purposes of this report that organisms used by EPA for criteria development adequately represent species found in Western Washington waters. A critique of EPA's method and the basis for criteria is not provided here. The method used to derive ambient water quality guidelines can be found in EPA's *Gold Book* (U.S. EPA 1987).

Water Quality Evaluation

Table 10 provides a summary of water quality data from the sites sampled. The range of measured pesticide concentrations, the mean of the concentrations of those pesticides that were detected, and the detection limits are provided (a full data report of water sample analyses is given in Table 4). EPA's chronic water quality guidelines and the acute lethal concentrations from Tetra Tech (1988) are also provided in Table 10. EPA's chronic water quality criteria guidelines were selected for comparison because they provide a somewhat conservative measure of the presence of a hazard in the aquatic system. In contrast, acute lethality values do not address chronic or sublethal effects and are, therefore, less protective. Thus, these sets of toxicity indices together provide a range of potential adverse effects concentrations for contaminants in water.

Because all but three of the pesticides tested in the water analyses lack appropriate regulatory standards and criteria, several of the measured pesticide concentrations had to be compared to acute toxicity values. U.S. EPA (1985) indicates that, in the case of complex mixtures of effluents, a factor of 0.1 applied to acute toxicity values will provide a sufficient estimate of chronic toxic concentrations in water. Based on this conclusion, the following conditions are applied to measured concentrations of pesticides for this analysis:

- A concern for potential acute and chronic effects in Puget Sound exists if the pesticide concentration is equal to or greater than 0.1 of the lowest LC_{50} values. These pesticides should be included as contaminants of concern in monitoring programs for Puget Sound.
- A concern for at least potential chronic effects exists if the pesticide concentration is between 0.01 of the LC_{50} and 0.1 of the lowest LC_{50}. These pesticides are recommended for discretionary sampling in Puget Sound monitoring programs.

- There is little concern that can be documented if the pesticide concentration is below 0.01 of the lowest LC_{50}, especially if few pesticides are detected. These pesticides have a low priority for inclusion in future monitoring programs as contaminants of concern, but may warrant one additional round of sampling in Puget Sound to document this conclusion.

The potential for random error increases near the detection limit. This potential for error causes the level of uncertainty in determining whether the measured concentration exceeds a chronic value or LC_{50} to increase as the detection limit approaches these toxicity indices. Therefore, detection limits were considered to be inadequate where they exceeded the chronic criterion or 0.1 of the lowest LC_{50} value provided by Tetra Tech (1988).

Reported detection limits were inadequate for 3 of the 34 pesticides tested. The detection limit of parathion exceeds its chronic water quality criteria value by a factor of 4. Similarly, the marine shrimp LC_{50} for azinophos methyl is 0.03 parts per billion, approximately one-third of the concentration of the 0.1 μg/L detection limit. The detection limit for phorate is greater than 0.1 of its LC_{50} value for killifish. These detection limits are inadequate to identify contaminant levels that may have adverse effects on aquatic communities.

The data in Table 10 show that the majority of pesticides were undetected at the four sites. However, some pesticides warrant closer examination. Diazinon was detected in Swamp Creek, Mercer Creek, and Big Ditch Slough at concentrations ranging from 0.054 to 0.14 μg/L. Water quality criteria are not available for this pesticide. However, the highest levels detected, which were seen in three Swamp Creek samples, are within 2 orders of magnitude of the LC_{50} value for bluegill (*Lepomis macrochirus*). It is not possible to judge from the LC_{50} value the chronic effects of the lower contaminant level. However, based on the criteria for this analysis described above, there is a potential for adverse chronic effects in waters with the concentrations of diazinon observed in Swamp Creek. Thus, it is recommended that discretionary sampling for diazinon be included in Puget Sound monitoring programs. In addition, diuron was detected in two samples from Big Ditch Creek (1.2 and 1.3 μg/L) and in all three samples from Muck Creek (average 2.4 μg/L). These values are within 1 order of magnitude of the lowest LC_{50} provided by Tetra Tech (1988), 15 μg/L for killifish. Diuron should be included as a contaminant of concern in Puget Sound monitoring programs. Concentrations of the other three pesticides detected in water samples were 4-5 orders of magnitude below their respective LC_{50} values.

Sediment Quality Evaluation

A summary of results for sediment analyses is provided in Table 11. The range of measured concentrations, the mean concentrations, and the analytical detection limits are included.

No relevant sediment quality standards are available for comparison with these pesticide results. Two approaches were employed to analyze as many of the data as possible within the constraints of the project scope. The analytical approaches employed are as follows:

- A comparison was made of pesticide concentrations with sediment quality values estimated for pesticides using available chronic water quality criteria. Sediment quality values were estimated from EPA's chronic water quality standards using the equilibrium partitioning approach discussed below. Chronic water quality criteria are available for chlorpyrifos, parathion, p,p'-DDT, endosulfan, and pentachlorophenol.
- Where no standards for water or sediment have been promulgated, sediment quality data were compared with estimated acute sediment toxicity values. Sediment toxicity indices were estimated using the equilibrium partitioning approach and the lowest acute toxicity value for aquatic species provided by Tetra Tech (1988). Those toxicity values are summarized in Table 11.

Equilibrium partitioning theory was used to estimate acute and chronic indices of toxicity for sediment-associated contaminants from aquatic toxicity values. This method is based on the assumption that sediment-associated contaminants will approach a state of equilibrium with the environment and that equilibrium concentrations can be predicted from properties of the contaminants and the sediments (additional assumptions and uncertainties are discussed below, under *Uncertainties of the Evaluation*). Thus, a water quality value (e.g., a water quality criterion or toxicity level) can be employed using these assumptions to estimate a corresponding sediment quality value. Sediment quality values provided in Table 11 were calculated using the following equation:

$$C_{sed}\ (\text{mg/kg}) = [C_{water}\ (\mu\text{/L})/1{,}000\ \mu\text{g/mg} \times K_{oc}\ (\text{L/kg}) \times f_{oc}]$$

where:

C_{sed} = concentration of contaminant in sediment (mg/kg) ("Sediment Quality Value" in Table 11)

C_{water} = concentration of contaminant in water (μg/kg) ("Lowest Available Toxicity Value" in Table 11)

K_{oc} = partition coefficient normalized for organic carbon (L/kg)

f_{oc} = fraction of organic carbon in the sediments.

For this analysis, C_{water} was either a water quality criterion, the lowest freshwater chronic toxicity value found in IRIS (U.S. EPA 1990), or an acute toxicity value taken from Tetra Tech's (1988) summary (Table 10). Because of small sample sizes, it was not possible to determine the organic carbon content of the sediment collected for pesticide analysis. Instead, the f_{oc} in sediment samples was estimated to range from 0.01 to 0.05 (1 to 5 percent), based on a frequency analysis of 806 values for total organic carbon found in Puget Sound sediments. Frequency analysis of f_{oc} of Puget Sound sediments reported on EPA's Region 10 SEDQUAL database indicated that 66 percent of the sediments in Puget Sound have a f_{oc} ranging from 1 to 5 percent. Values for K_{oc} were estimated from available K_{ow} values using Equation 4.8 from Lyman et al. (1982):

$$\log K_{oc} = [0.544 \times \log K_{ow}] + 1.377$$

K_{ow} values were obtained from Tetra Tech (1988) for most compounds. If K_{OW} values were not available in either of these two sources, they were calculated from solubility data using Equation 2.14 from Lyman et al. (1982):

$$\log 1/S \text{ (mol/L)} = 1.214 \times \log K_{ow}] - 0.85.$$

where:

S = solubility.

Analysis of pesticide concentrations found in sediments and summarized in Table 11 (a full data report is provided in Table 4) is limited by the same constraints of the water quality analysis. The limited availability of sediment quality criteria and the use of LC_{50} values to evaluate the potential adverse effects of the measured pesticide levels resulted in several uncertainties, which are outlined in the *Uncertainties of the Evaluation* section. Because of these limits, the criteria used to identify potentially hazardous pesticide concentrations in water were applied to evaluate sediment-associated pesticides. These criteria are:

- A concern for potential acute and chronic effects in Puget Sound exists if the pesticide concentration is equal to or greater than 0.1 of the lowest LC_{50} values. These pesticides should be included as contaminants of concern in monitoring programs for Puget Sound.
- A concern for at least potential chronic effects exists if the pesticide concentration is between 0.01 of the LC_{50} and 0.1 of the lowest

LC_{50}. These pesticides are recommended for discretionary sampling in Puget Sound monitoring programs.

- There is little concern that can be documented if the pesticide concentration is below 0.01 of the lowest LC_{50}, especially if few pesticides are detected. These pesticides have a low priority for inclusion in future monitoring programs as contaminants of concern, but may warrant one additional round of sampling in Puget Sound to document this conclusion.

Here, LC_{50} means the sediment quality value that was derived by adjusting an aquatic LC_{50} value to account for partitioning into the organic carbon fraction of the sediments.

Detection limits were considered to be inadequate where they exceed the sediment quality value estimated from chronic criterion or where they are within 0.1 of the lowest LC_{50}-derived sediment quality value. Based on these evaluation criteria, the reported detection limits for 5 of the 39 pesticides tested in sediments were not sensitive enough to identify pesticide concentrations in sediments associated with potential adverse effects. The detection limit for parathion (0.038-0.01 mg/kg) exceeded the sediment quality value estimated from parathion's chronic water quality criterion. For both malathion and methyl parathion, the higher detection limits were within 1 order of magnitude of the more conservative sediment quality value. The range of detection limits for hexazinone was within 1 order of magnitude of the range of sediment quality values associated with 50 percent mortality of exposed organisms. Finally, the higher detection limit for phorate exceeded the higher sediment quality value derived from the aquatic LC_{50}, and the lower detection limit exceeded the lower sediment quality value derived from an aquatic LC_{50}. Therefore, in future evaluations of sediment contamination at these sites, testing for these pesticides should be repeated using larger sample sizes and detection limits that are sensitive enough to determine where potentially harmful concentrations may be present.

The detected concentration of diazinon in sediments from Big Ditch Slough is within 1 order of magnitude of its LC_{50}-derived sediment toxicity index. Similarly, the detected concentration of endosulfan I observed in Mercer Creek sediments was half the LC_{50}-derived sediment toxicity index. Both diazinon and endosulfan I appear to be present in concentrations that are potentially hazardous to aquatic life making contact with sediments. Although LC_{50}-derived sediment quality guidelines do not provide a precise definition of the presence of a hazard, these two pesticides should be monitored in future surveys. In addition, concentrations of three pesticides detected in the 1988 survey (chlorpyrifos, parathion, and phorate), although not confirmed, were above calculated sediment quality criteria. These compounds should be monitored in future sampling events.

Uncertainties of the Evaluation

Because the specific names of organisms for which toxicity data are summarized by Tetra Tech (1988) are not known, the extent to which these data predict toxicity to Puget Sound species cannot be provided with certainty. In addition, it is critical to note that an LC_{50} or an LD_{50} value is not a protective standard for environmental media. The LC_{50} bioassay measures lethality; it does not address adverse sublethal effects. Thus, the modification of LC_{50} values in this report to predict chronic toxicity levels using a factor of 0.1 is an important source of uncertainty. Also, evaluation of LC_{50}s for single chemicals does not account for possible synergistic or multiple chemical interactions. An additional uncertainty in assessing the toxicity of commercial pesticides is the effect of inert ingredients, such as surfactants or carriers.

In addition, predictions using the sediment-water equilibrium partitioning approach incorporate the uncertainties of that method as well as the uncertainty in the estimate of organic carbon content for this survey. A primary source of uncertainty in the theoretical approach is the implicit assumption that the time scale for attaining thermodynamic equilibrium is short relative to the time scale of kinetic factors (e.g., disruptions of bedded sediments, short-term changes in physicochemical conditions). Other sources of uncertainty in the approach relate to predictions in measured and estimated K_{OC} values and the assumption that organisms follow sediment-biota equilibrium partitioning and are unaffected by the route of contaminant exposure (e.g., dermal absorption vs. ingestion of sediments). In systems where flow is sufficient to suspend large amounts of sediment, ingestion of particulates may be of importance.

Recommendations

The approach to screening-level evaluations of pesticide concentrations found in site-specific samples can be conducted in phases. State and federal standards, results of toxicity tests, and extrapolation methods are useful in preliminary analyses of the potential for adverse biological effects of site-specific concentrations. The following approach is recommended for screening level analyses of site-specific data for water and sediment quality.

Water Quality—Site-specific water quality should first be evaluated for potential harm to aquatic communities using EPA's water quality criteria (U.S. EPA 1987). EPA provides freshwater and marine water quality guidelines for protection of aquatic life following acute and chronic exposure scenarios. Acute water quality criteria are expressed as a criterion maximum concentration (CMC) for a 1-hour averaging period. The criterion continuous concentration (CCC) assumes a 4-day maximum exposure period. These levels are not to be exceeded more than once every 3 years. Comparison of water quality measurements with the CCC provides a screening level estimate of potential adverse effects to aquatic

communities. When a more conservative approach is warranted, based on the presence of endangered or threatened species, it is recommended that a safety factor of 0.1 be applied to the CCC before comparison with water quality data. In this type of situation, contaminant levels should not exceed 0.1 of the CCC. It is noteworthy that the CMC and CCC values are derived for individual pesticides and do not account for potential synergistic, additive, or antagonistic effects of the pesticides, or for associated inert ingredients, surfactants, and other additives.

When water quality guidelines are not available, site-specific water bioassays are recommended. Unlike sediment quality, however, water quality conditions are frequently transient and unpredictable. This behavior reduces the reliability of water toxicity bioassays that are based on single or poorly timed sample collections. A screening-level approach is to sample water for toxicity testing or chemical analysis during peak flow and low flow events. Sample collection during a high flow event following a dry spell (i.e., a first flush event) provides a worse-case scenario: contaminants that have built up in a watershed during the dry period will be washed into the stream water during this type of event. Alternatively, continuous monitoring or very frequent sampling over extended periods (1-2 years) would provide a relatively complete profile of water contamination.

There is no standard set of water quality bioassays that can be recommended for all site evaluations. Aquatic systems vary with their geographic locations, as do the valued species that are the targets of protection. Therefore it is recommended that the design of water quality studies be determined on a site-specific basis with consideration for the species that are to be protected, food chain interactions (e.g., where loss of keystone species may lead to large impacts), the presence of endangered or threatened species, other conditions specific to the individual system, and the specific project objectives.

Sediment Quality—Sediment management standards have not yet been proposed for regulation of pesticides in marine sediments in Puget Sound (Ecology 1990). There are also no national or Washington state standards or guidelines available for freshwater sediments. However, sediment quality guidelines have been derived by several other government agencies. The Wisconsin Department of Natural Resources has derived sediment quality guidelines for some metals, pesticides, and polychlorinated biphenyls (Appendix E, Table E-1). In addition, the Ontario Ministry of the Environment has estimated sediment management guidelines (Geisy and Hoke 1990) using no effect levels, lowest effect levels, and limits of tolerance. These guidelines are based on overt effects on benthic invertebrates and do not account for indirect effects of contaminants such as food chain alteration or bioaccumulation potential (Geisy and Hoke 1990). Finally, the National Oceanic and Atmospheric Administration (Long and Morgan 1990) has recently summarized levels of concern for numerous contaminants found in both freshwater and marine sediments (Appendix E,

Table E-2). When state or federal guidelines are not available, the sources just cited should be employed where possible.

In the absence of available marine or freshwater sediment quality criteria, the preferred approach for evaluating potential sediment toxicity is to conduct a suite of site-specific sediment bioassays. As in the case of water quality evaluations, no standard set of bioassays can be recommended for sediment toxicity evaluations. Each study design should be based on site-specific resources, site uses, and program objectives.

Finally, levels of sediment contamination that are unlikely to result in adverse biological impacts can be estimated by extrapolating available water quality criteria values to sediment quality values using the equilibrium partitioning approach. As discussed previously, this method assumes that contaminants associated with the solid phase of sediments will reach a state of equilibrium with the environment and that equilibrium concentrations can be predicted from properties of the contaminant and the sediments. The approach has been developed primarily for nonionic organic compounds and is applicable to sediment-associated pesticides in both marine and fresh waters. Geisy and Hoke (1990) observe that this approach has utility in establishing general criteria, but that it should not be used to determine site-specific criteria.

RECOMMENDATIONS FOR FUTURE MONITORING EFFORTS

Continued monitoring of selected pesticides in waters and sediments of the Puget Sound basin is recommended. Monitoring of ambient pesticide concentrations has been limited in the past, especially when compared to monitoring efforts for other pollutants such as metals and industrial organic compounds. In addition, little is known about the potential effects of pesticides on Puget Sound biota, on transport mechanisms in estuarine and marine environments, and on specific sources of contamination. This information is necessary to determine whether pesticides are contributing to environmental degradation of the basin, and, if so, what control strategies are needed to eliminate this contamination.

Three levels of monitoring are proposed in the following sections: routine local monitoring, regional reconnaissance surveys, and in-depth research studies.

ROUTINE MONITORING

Frequent routine monitoring is needed to provide information on the spatial and temporal distribution of pesticides in the Puget Sound basin. Because detailed knowledge of the specific sampling area is important, routine sampling by county extension agents with local knowledge offers a cost-effective means of data collection. Standardized protocols for sampling, uncomplicated sampling equipment, and basic training are required to ensure that sampling results will be consistent among all areas. Sampling should occur frequently, possibly on a monthly basis, and should be performed during high runoff events and during periods immediately following pesticide applications to specific areas. Because of constantly changing conditions encountered in the field, there is likely to be high spatial and temporal variability associated with these samples. Data from Mayer (1989) indicate that sampling from the same area over time may result in several sampling episodes where high levels of a pesticide are found, while other sampling episodes produce no detectable pesticide concentrations.

Because of the frequency of sampling and potential for high analytical costs, compounds targeted for routine monitoring should be limited to those that have been recently applied to the specific areas being sampled, plus the following compounds that have been detected in this and previous reconnaissance surveys:

- Diuron, diazinon, 2,4-D, dicamba, and bromocil in water
- Pentachlorophenol, chlorpyrifos, dichlobenil, lindane, dicamba, 2,4-D, DDT and its metabolites, diazinon, parathion, phorate, and endosulfan I in sediments.

In addition, chemicals that are extensively used, such as glyphosate, malathion, and metaldehyde, should be included in the target list even though they have not been previously detected in sediment or water samples, since previous sampling may have not been conducted when maximum residue concentrations were present. The results of this and previous surveys indicate that the current EPA priority pollutant list is out of date and needs revision. Although a few of the pesticides detected in Puget Sound drainages (e.g., DDT, endosulfan) are on the current list, most of the compounds found in this and the 1988 study, as well as other heavily used pesticides, are not.

Compounds that are not detected in this routine monitoring after 1 year of repeated sampling should be deleted from future sampling events, unless changes in pesticide application suggest a need for resampling or unless the cost of analysis will not be affected by their inclusion. For three reasons, frequent collection of water samples during this routine monitoring is recommended as a higher priority than frequent collection of sediment samples. First, relatively nonpersistent pesticides discharged in storm events may nevertheless produce toxic effects in the aquatic environment and may only be detected in frequently collected water samples. Second, analyses of unfiltered water samples, including suspended particulates, over time provide the most direct evidence of the potential for and seasonal pattern of pesticide transport from freshwater basins to Puget Sound. Third, water samples are easier to routinely collect and analyze than are sediment samples, and there were no pesticides of concern detected exclusively in sediment that have not already been included in standard analyses for chlorinated pesticides (i.e., endosulfan I). Details of an easy-to-use, low-cost water sampling apparatus are given in Appendix C. Occasional collection of sediment samples (e.g., once every 1-2 years) is still recommended in depositional areas to determine if there are accumulations over time of particle-bound pesticides that may be present at undetectable levels in the more frequently collected water samples.

REGIONAL RECONNAISSANCE

The routine monitoring efforts discussed in the previous section are narrowly focused with regard to targeted pesticides and are limited to specific areas of local concern. On a broader scale, reconnaissance surveys for pesticides should continue on a regional basis as funding permits. Such surveys should include several different classes of pesticides, such as those included in the present survey. Reconnaissance surveys should also include collection of water,

sediment, and possibly biota samples (i.e., when the potential for bioaccumulation is high) so that all media of potential concern are addressed. In addition, degradation products and pesticides registered since the previous reconnaissance survey should be included in the list of compounds for analysis, provided that analytical methods exist for their determination in the media of interest.

Diazinon and diuron, found in this drainage basin survey at levels potentially associated with chronic or acute toxic effects, should be added as chemicals of concern for Puget Sound ambient monitoring programs. A link to major land sources has been documented for these pesticides, but it is unknown whether they persist at similar levels in Puget Sound proper. Therefore, analyses for these pesticides should be conducted in Puget Sound reference areas and near major drainages. Endosulfan I was also detected in sediment samples collected in the Mercer Creek drainage to Lake Washington. Previous analyses for this compound in selected Puget Sound sediments have been reported, but it has not been identified as a chemical of concern in the marine environment. Continued monitoring for endosulfan I in Puget Sound is recommended, based on the results of this reconnaissance survey.

RESEARCH STUDIES

While this reconnaissance survey has provided important information concerning the levels of pesticides found in Puget Sound drainages, it has also highlighted gaps in knowledge about the impacts of pesticides in estuarine environments. The interpretation of the data gathered in this and future surveys would be enhanced by formulating research studies that address the following general questions:

- What is the ecological significance of the different mixtures of pesticides documented in Puget Sound drainages? Are the available toxicity data representative of effects on Puget Sound estuarine species? Even if present below individual LC_{50} values, are these mixtures likely to produce effects on migrating fish or their prey organisms indigenous to Puget Sound?

- For compounds detected in Puget Sound drainages, what is their potential for further degradation, both abiotic and biotic, under marine and estuarine conditions? Are these pesticides transported primarily in the particulate or dissolved phases, and are they ultimately dispersed in the water column or accumulated in localized areas of sediment contamination?

- Is there any evidence of bioaccumulation or biomagnification of the major pesticides found in Puget Sound drainages in harvestable invertebrates (e.g., clams, mussels), fish, birds, or marine mammals of the sound?

- To what extent are safety factors applied to acute criteria protective of chronic effects for the pesticides detected in Puget Sound drainages, or for undetected pesticides that nevertheless have major sources on land? Are *routine* detection limits attained in this survey adequate for assessing the potential for chronic effects or are specialized analyses required?

- What are the major sources of persistent pesticides that were widely detected in Puget Sound drainages (e.g., pentachlorophenol in sediment)?

- How can *routine* analytical techniques be improved for pesticides that were apparently subject to substantial interferences in some media (e.g., triazines in sediment)? Are the general holding times of 1-2 weeks between collection and analysis sufficient for all classes of pesticides; can any of these holding times be extended to facilitate episodic sampling in different areas?

- What is the threat to water quality in Puget Sound drainages from inert ingredients found in pesticide formulations? What are the persistence, bioaccumulation, and toxicity characteristics of the materials?

- What is the impact of other agricultural chemicals (fertilizers, soil amendments, plant growth regulators) on Puget Sound water quality?

Finally, regional reference materials should be formulated for these pesticides to provide a means for assessing the comparability of monitoring and reconnaissance results over time.

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APPENDIX A

Sampling Reports

1990 Pesticide Reconnaissance Survey
Big Ditch Slough Sampling Report

Water samples were collected from three locations on Big Ditch Slough on June 7, 1990, by Dena Hughes and Bob Stuart of E.V.S. Consultants. Weather conditions were partly cloudy with light winds from the southwest. The temperature was estimated to be in the high 50s to the low 60s. Water turbidity, flow and depth in Big Ditch Slough appeared to be greater than on the previous day. Water was observed flowing into the slough from several drainage ditches along its length. The ditches appeared to be draining standing water from fields adjacent to the slough. According to Mr. Richard Norgaard, a farmer with cultivated fields adjacent to the slough, it had rained heavily the night before. Because of recent heavy rains, Mr. Norgaard stated that most farmers in the area had not begun applying pesticides to their crops. Mr. John Garret of the Washington Department of Wildlife, the game ranger for the Skagit Wildlife-Recreation area, also stated that farmers in the area had not yet begun pesticide application.

Station 1

The station is within the Skagit Wildlife Area and access is controlled by the Washington Department of Wildlife. It was necessary to contact John Garret to unlock the gate across the road to the site, which is located approximately one-half mile from the gate. The one-lane gravel road leads to a gravel parking lot adjacent to the site.

Station one is located approximately 75 feet north of the tide gates on the east bank of Big Ditch Slough. The west bank is ten to fifteen feet high and forms part of the dike for the south fork of the Skagit River. The slough is approximately 45 feet wide and three feet deep at this point. A drainage ditch on the east bank was observed emptying into the slough about 200 feet north of the sampling station.

Stream flow measurements were taken by measuring the traversal time of an orange over a measured distance along the slough. Three measurements were taken over a 45 foot course. The three readings were 18.74, 16.13 and 19.51 seconds for a mean time of 18.13 seconds. The mean velocity was calculated to be 2.48 feet per second. Discharge was calculated based on the cross-sectional area of the slough and the mean velocity:

Discharge = (2.48 ft./sec.) x (3 ft. x 45 ft.) = 335 cubic feet/sec.

Sampling commenced at 0942. Bob Stuart collected the samples and Dena Hughes transferred the contents of the collection bottle to sample bottles. Twelve 2.5 liter sample bottles and two 40 ml vials were collected according to protocol and were numbered 1-1 through 1-12 and VOA 1-1 and VOA 1-2, respectively. Six additional 2.5 liter bottles and two 40 ml vials were also collected as duplicates and were numbered 1-1D through 1-6D and VOA 1-3 and VOA 1-4, respectively. All samples were stored on ice. The last sample was collected at 1055 and the site was vacated at 1140.

Station 2

Station two is located 1.4 miles north of station one on the farm of Mr. Richard Norgaard. Because of heavy rains it was necessary to carry the sampling equipment about one quarter mile to the slough. Because of steep banks and thick overgrowth, it was necessary to collect samples from a wooden foot bridge spanning the slough.

The width of the slough at this point was measured at 46 feet with a mean depth of 4.3 feet. Three depth measurements were taken across the channel: 4, 5 and 4 feet. Mean velocity was calculated to be 0.4 feet/second based on two velocity measurements taken over a 20 foot course with times of 52 and 48 seconds. Discharge was calculated to be 79.1 cfs.

Sampling commenced at 1240 and ended at 1315. Twelve 2.5 liter sample bottles and two 40 ml vials were collected. The bottles were numbered 2-1 through 2-12 and the vials were numbered VOA 2-1 and VOA 2-2. The samples were stored on ice and the site vacated at 1430.

Station 3

Station three is located 2.3 miles north of station one on the west side of Highway 530 and approximately ten feet to the west of the railroad tracks on the south bank. The slough passes under the highway and the railroad tracks. A more suitable sampling location was sought, but because of inaccessible roads and steep, overgrown banks, this was the only location that was accessible.

The width of the slough appeared to be approximately 45 feet. Because of the location, it was not possible to get depth measurements or velocity measurements, but the velocity appeared to be similar to that at station two.

Sampling commenced at 1542 and ended at 1620. Twelve 2.5 liter sample bottles and two 40 ml vials were collected. The bottles were numbered 3-1 through 3-12 and the vials were numbered VOA 3-1 and VOA 3-2. The samples were stored on ice and the site was vacated at 1445.

Contacts

Mr. John Garret, Washington Department of Wildlife, Skagit Wildlife-Recreation Area. Telephone: 445-4441

Mr. Richard Norgaard. Telephone: 629-2014

PESTICIDE RECONNAISSANCE SURVEY
Mercer Creek Sampling Report
August 30, 1990

Water samples were collected from Mercer Creek on 30 August 1990 during and immediately following a major storm event. Sampling took place between 1745 and 2400 hrs. The sampling site was located on the north bank of Mercer Creek approximately 50 m below the culvert passing east-west under Interstate 405 and 118th Avenue Southeast. Access to the site was through the Bellefield Business Park. Weather conditions during the sampling period ranged from 100 percent cloud cover with heavy rain to broken clouds with no rainfall. A moderate to light wind from the southwest persisted during the entire sampling period. The temperature was estimated to be between 10-12° C. The field crew consisted of Nancy Musgrove and Dave Jansen of E.V.S. Consultants.

Samples were collected using 2.5 l bottles held in a ring at the end of a 4.5 m stainless steel pole. Samples were taken from below the water surface at a minimum of 3 m from the bank. Three series of samples were collected during the storm event. Each series consisted of 12 composite samples. Composites were made by splitting each sample among 12-2.5 l bottles. The first series was collected in the first hour of the sampling effort (1745 to 1845 hrs). Sample bottles were labelled 1-1 through 1-12. The second series of samples was collected between 1915 and 2045 hrs. and bottles were labelled 2-1 through 2-12. The final series was collected between 2115 and 2400 hrs. and bottles were labelled 3-1 through 3-12. During the sampling period, 8 pairs (duplicates) of VOA samples were collected in 40 ml vials from a sample bottle used to create the composites, at the following times:

- 1745
- 1845
- 1945
- 2045
- 2215
- 2245
- 2315
- 2345

Mercer Creek is a broad (~30 m), shallow (<3 m) slough in the vicinity of the sampling site. Changes in elevation in the area are slight. Banks on both sides of the creek are low and the creek meanders through the grounds of Bellefield Park. In most areas, the banks are over grown with dense, low-growing shrubs and blackberry brambles. During the sampling effort, stream velocity at mid-channel and changes in the level of the water were measured. Velocity measurements were taken at the sampling site, while changes in elevation were measured from the bridge entering the office park near the sampling site. The following velocity measurements were crude and represent surface velocity only:

Time	Velocity
1910	0.08 $m*sec^{-1}$
2115	0.14 $m*sec^{-1}$
2315	0.09 $m* sec^{-1}$

During the sampling event, water in the creek was extremely turbid with a lot of floating duckweed on the surface. Water color was greenish brown. A slight change in water level was noted during the sampling period. The following measurements represent changes in water depths (in meters) during the sampling event.

Time	North Bank	Mid-Channel	South Bank
1910	1.83	1.93	1.47
2010	1.80	1.88	1.37
2115	1.80	1.85	1.40
2230	1.80	1.85	1.40

Based on an approximate channel width of 30 m and the mid-channel depth, estimates of discharge rate were made as follows:

Discharge = velocity * channel area

Time	Discharge
1910	4.63 cubic m*sec^{-1}
2115	7.77 cubic m*sec^{-1}
2315	5.00 cubic m*sec^{-1}

1990 PESTICIDE RECONNAISSANCE SURVEY

Swamp Creek Sampling Report
October 4,5, 1990

Water samples were collected from Swamp Creek on October 4 and 5, 1990 during and immediately following a major storm event. Sampling took place between 2000 (Oct. 4) and 0545 (Oct. 5). The sampling site was located on the west bank of Swamp Creek immediately upstream of a bridge on NE 175th St. Access to the site was via this bridge. Weather conditions during the sampling period ranged from 100 percent cloud cover with heavy rains to broken clouds with no rainfall. Moderate to heavy rains occurred between 2000 to about 0130, after which clearing occurred with very little rain. Very little wind was observed. The temperature was estimated between 45 and 50 °F. Flow in the stream was moderate to high; water was turbid and brown. The field team consisted of Mark Munn and Jim Starkes of E.V.S. Consultants.

Samples were collected using 2.5 liter bottles held in a ring at the end of a 4.5 meter stainless steel pole. Samples were collected from below the water surface at a minimum of 2 meters from the bank. Three series of samples were collected during the storm event. Each series consisted of 12 composite samples. Composites were made by splitting each sample among 12 - 2.5 liter bottles. The first series was collected between 2000 and 2300 hours. Sample bottles were labelled 1-1 through 1-12. The second series of samples were collected between 2300 and 0200 hours. Six field duplicate samples were also collected during this time period. Bottles were labelled 2-1 through 2-18. The final series was collected between 0200 and 0545 hours and bottles were labelled 3-1 through 3-12. During the sampling periods, 8 pairs of VOA samples were collected in 40 ml vials from a sample bottle used to create the composites at the following times:

- 2050
- 2200
- 2300
- 2350
- 0030
- 0100
- 0315
- 0545

The last sample was collected at 0545 and the site was vacated at 0630. All samples were stored on ice.

Swamp Creek is a small (7 meters wide), shallow (~1 meter maximum depth) stream in the vicinity of the sampling site. Stream banks were steep and heavily vegetated with deciduous trees and shrubs. On two occasions a beaver was observed in the stream. The animal was observed entering a dense overhanging canopy of vegetation on the east bank of the stream opposite the sampling site.

During the sampling effort, stream velocity at mid channel was measured and changes in the level of water was observed. Surface velocity was measured by the traversal time of an orange placed in the middle of the stream over a measured distance (8.2 meters). Velocity was calculated twice during the sampling effort.

Time	Velocity
2240	1.37 m/sec
0615	1.03 m/sec

A slight decrease in water level was observed during the second velocity measurement. Actual measurements of changes in depth could not be made. Based on an approximate stream width of 7 meters and average depth of 0.6 meters, the following estimates of discharge were made:

Time	Discharge
2240	19.2 cubic m/sec
0615	14.4 cubic m/sec

1990 Pesticide Reconnaissance Survey
Big Ditch Slough Sampling Report
October 16, 1990

Water samples were collected from three locations on Big Ditch Slough on October 16, 1990, by Dena Hughes and Bob Stuart of E.V.S. Consultants. Weather conditions were partly cloudy with light winds from the southwest. The temperature was estimated to be in the low to mid 50s. Flow in the slough was very low and no water was observed flowing into the slough from several drainage ditches along its length as in the first sampling episode on June 7, 1990. Most of the fields near the slough appeared recently plowed with nothing growing in them, although a few fields did have corn growing. The soil in the fields and along the sides of the road appeared slightly damp but there was no standing water.

Station 1

The station is within the Skagit Wildlife Area and access is controlled by the Washington Department of Wildlife. Station one is located approximately 75 feet north of the tide gates on the east bank of Big Ditch Slough. The west bank is ten to fifteen feet high and forms part of the dike for the south fork of the Skagit River. The slough is approximately 45 feet wide and three feet deep at this point.

Stream flow measurements were taken by measuring the traversal time of an orange placed in the middle of the slough over a measured distance (37 feet) along the slough. The velocity was calculated to be 0.82 feet per second. Discharge was calculated based on the cross-sectional area of the slough and the velocity:

Discharge = (0.82 ft./sec.) x (3 ft. x 45 ft.) = 111 cubic feet/sec.

Sampling commenced at 0955. Bob Stuart collected the samples and Dena Hughes transferred the contents of the collection bottle to sample bottles. Twelve 2.5 liter sample bottles and eight 40 ml vials were collected according to protocol and were numbered 1-1 through 1-12 and V1-1 and V1-8, respectively. Six additional 2.5 liter bottles and two 40 ml vials were also collected as duplicates and were numbered 1-1D through 1-6D and V1-1D and V1-2D, respectively. All samples were stored on ice. The last sample was collected at 1100 and the site was vacated at 1130.

Station 2

Station two is located 1.4 miles north of station one on the farm of Mr. Richard Norgaard. Because of heavy rains it was necessary to carry the sampling equipment about one quarter mile to the slough. Because of steep banks and thick overgrowth, it was necessary to collect samples from a wooden foot bridge spanning the slough.

The width of the slough at this p[illegible] measured at 46 feet with a mean depth of 4.3 feet. Three depth measurements w[illegible]en across the channel: 44.5, 62.5 and 49 inches. Velocity was calculated [illegible] feet/second based on one velocity measurement taken over a 30 foot course wi[illegible] ersal time of 162 seconds. Discharge was calculated to be 36.6 cfs.

Sampling commenced at 1205 and ended at 1315. Twelve 2.5 liter sample bottles and eight 40 ml vials were collected. The bottles were numbered 2-1 through 2-12 and the vials were numbered V2-1 and V2-8. Two duplicate VOA samples were also collected and labeled V2-1D and V2-2D. The samples were stored on ice and the site vacated at 1430.

Station 3

Station three is located 2.3 miles north of station one on the west side of Highway 530 and approximately ten feet to the west of the railroad tracks on the south bank. The slough passes under the highway and the railroad tracks.

The width of the slough was measured to be 34 feet with an approximate depth of three feet. One velocity measurement was taken over a 40 foot length. Traversal time was 411 seconds for a velocity of 0.097 feet/sec. Discharge was calculted to be 9.9 cfs.

Sampling commenced at 1350 and ended at 1440. Twelve 2.5 liter sample bottles and eight 40 ml vials were collected. Two duplicate VOA samples were also collected. The bottles were numbered 3-1 through 3-12 and the vials were numbered V3-1 and V3-8 and V3-1D and V3-2D. The samples were stored on ice and the site was vacated at 1500.

Contacts

Mr. John Garret, Washington Department of Wildlife, Skagit Wildlife-Recreation Area. Telephone: 445-4441

Mr. Richard Norgaard. Telephone: 629-2014

PESTICIDE RECONNAISSANCE SURVEY
Sediment Sampling Report
October 25th & 26th, 1990

MICHAEL RYKO
EPA
553-4014

Indian Slough, Higgins Slough, and Sullivan Slough Composite Sample (INHI/SUSL):

The Indian Slough portion of this sample was obtained on October 25th at approximately 1200 hours. The sample was collected from the landward side of the southern tidegate immediately east of La Conner and Samish Road. The tidegate was closed due to an extremely high tide. Four sediment grabs were made using a hand-held Eckman dredge. Each grab was de-watered and released from the dredge onto grass on the top of the dike. Using a lab-cleaned stainless steel spatula, the top centimeter from the center of each sample* was collected into lab prepared 200 mg glass jars. Sample depth varied between 6 inches and 3 feet.

Two grabs were taken from the bottom of a small pool in an un-named creek entering Higgins Slough at about 1300 hours. Creek velocity was estimated at 1 meter/second, depth 1 foot, and width 2 feet. The grabs were collected from the east side of the northernmost culvert under La Conner and Samish Road in section 18 (T 34 N, R 3 E). The same collection procedures were followed.

The Sullivan Slough portion of this sample was also taken on October 25th at approximately 1340 hours. Two grabs were taken from the west side of the culvert at the southern crossing of La Conner and Samish Road and the un-named creek in section 30 (T 34 N, R 3 E). Flow was estimated at 1 meter second, depth 1 foot, and width 2 feet. The same collection procedures were followed.

All samples were immediately placed in coolers packed with both crushed and block ice. Samples were marked as INHI and SUSL, respectively.

Conway Composite Sample (CNWY,CNWY2,CNWY3):

These samples were also taken on October 25th between 1400 and 1440 hours. Three grabs were taken from each of the two drainage ditches that enter the northernmost section of Big Ditch, just north and east of Conway. Grabs were collected from off of the railroad trestle along the west ditch, and from a one-hundred meter section of the east ditch, before it enters Big Ditch. Flow in both ditches was estimated at .1 meter per second, depth 3 feet, and width 4 feet. Sample depths were approximately 3 feet. The same collection procedures were followed. These samples were marked as CNWY, CNWY2, CNWY3.

Big Ditch Sample (BGDH):

*, that was not in contact with the grass,

This was the last sample to be collected on October 25th. Four grabs were taken from the landward side of the tidegate which is approached from the Skagit Wildlife Refuge access road. The tidegate was closed and thus no flow was observed. Samples were collected at approximately 1520 hours. Sample depth was approximately 2-3 feet. The same collection procedures were followed. This sample was marked as BGDH.

Lower Sammamish River (LSAM):

Three grabs were taken October 26th between 0630 and 0800 hours along a one hundred meter section of river immediately west of the 68th Avenue N.E. bridge at Kenmore. The flow velocity was estimated at .8 meter per second, average depth 4 feet, and width 30 feet. The depths of the grabs varied between 6 inches and 2 feet. Same collection procedures were followed.

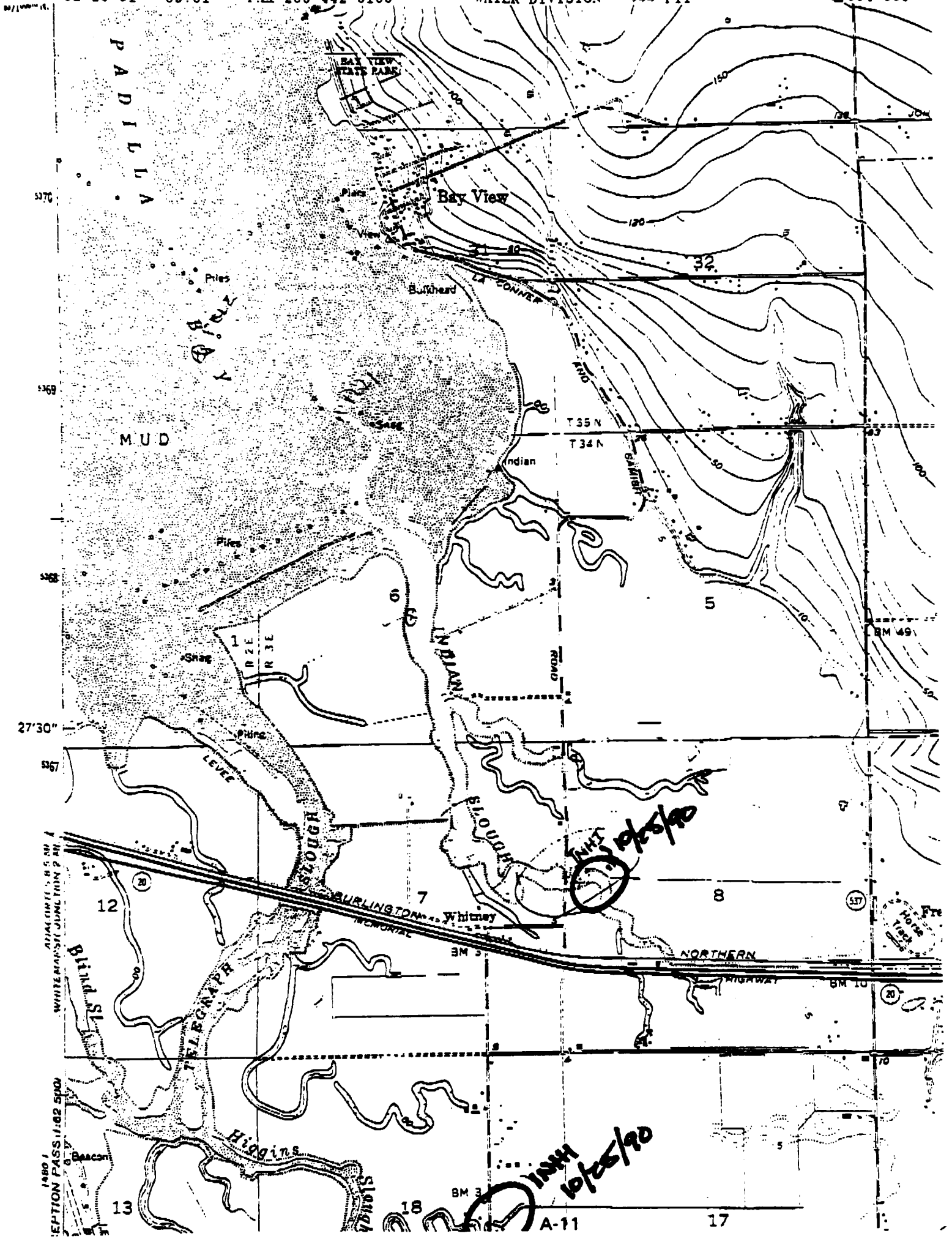
Two additional grabs for this sample were collected from underneath a private bridge which crosses the Sammamish River at about 84th Avenue N.E. Sample depth was about eighteen inches. Sample time was about 1030. Same collection procedures were followed. This sample was marked LSAM.

Swamp Creek (SWMP):

Samples were collected on October 26th between 0830 and 1000 hours. Six grabs were taken during a stream-walk along the lowermost portion of Swamp Creek, beginning at N.E. 175th Street and ending just before Swamp Creek enters the Sammamish River. Flow velocity was estimated at 1.2 meter per second, average creek depth 3 feet, and average width 20 feet. Sample depths varied between 2 and 4 feet. Same collection procedures were used. This sample was marked as SWMP.

Mercer Creek (MRCR):

Four grabs were taken from the Bellefield Business Park bridge as it crosses Mercer Creek on October 26th at 1130 hours. Samples were taken from between 3 and 6 feet. Estimated flow velocity was .1 meter per second, depth 6 feet, and width 60 feet. Again, the samples were drained and released from the dredge onto a grassy area. Only the top centimeter from the center of the sample was collected. Samples were immediately placed in ice. This sample was marked as MRCR.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Bay View
Piles
Bulkhead
LA CONNER
ROAD
T35N
T34N
Indian
Snag
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SLOUGH
LEVEE
R2E
R3E
BM 49
27'30"
BURLINGTON
NORTHERN
HIGHWAY
Whitney
BM 3
BM 10
Blind St
TELEGRAPH
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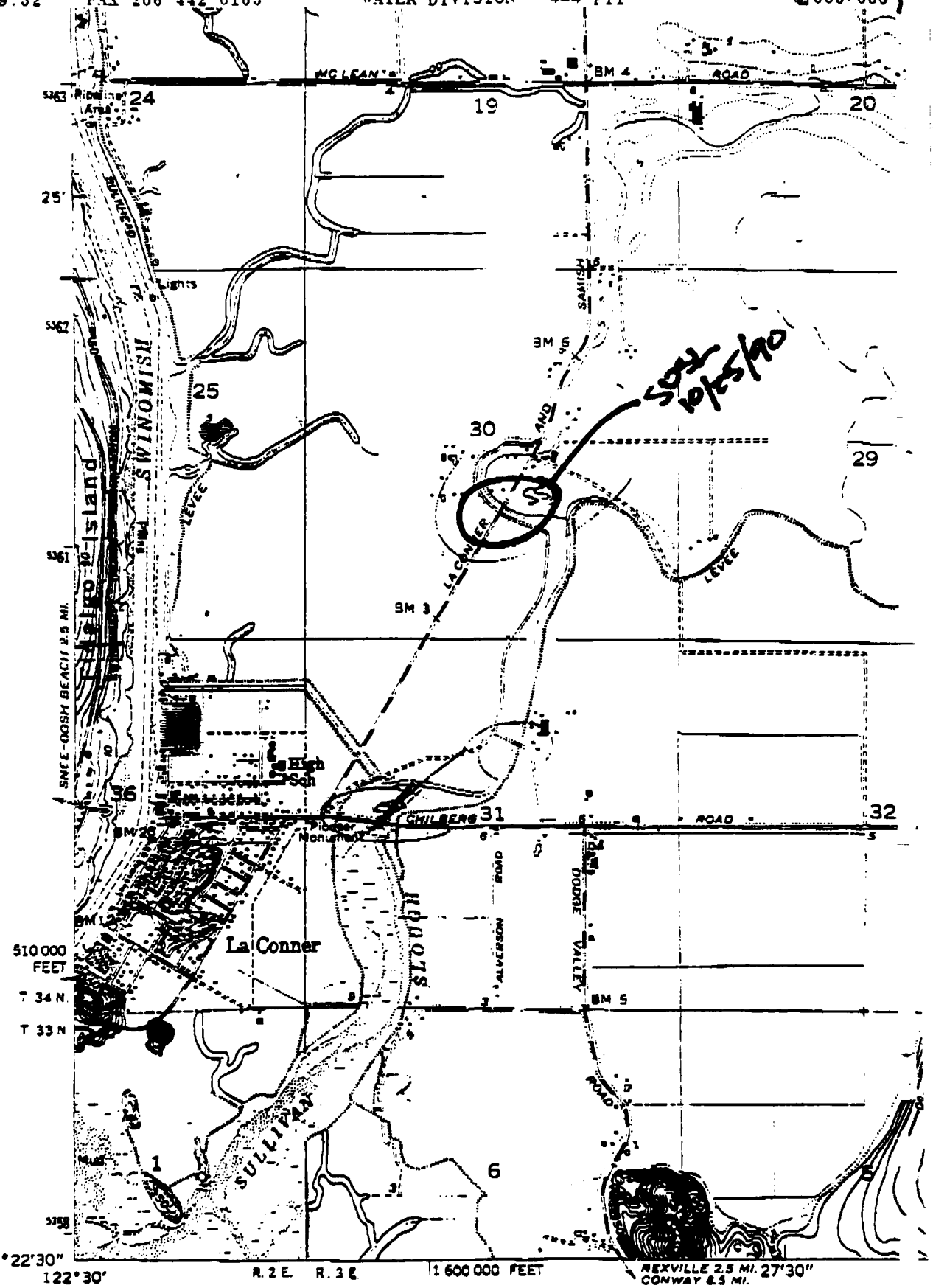


Mapped, edited, and published by the Geological Survey

Control by USGS and USC&GS

Topography from aerial photographs by Kelsh plotter and by planetable surveys 1956. Aerial photographs taken 1954

Hydrography compiled from USC&GS chart 6376 (1954)

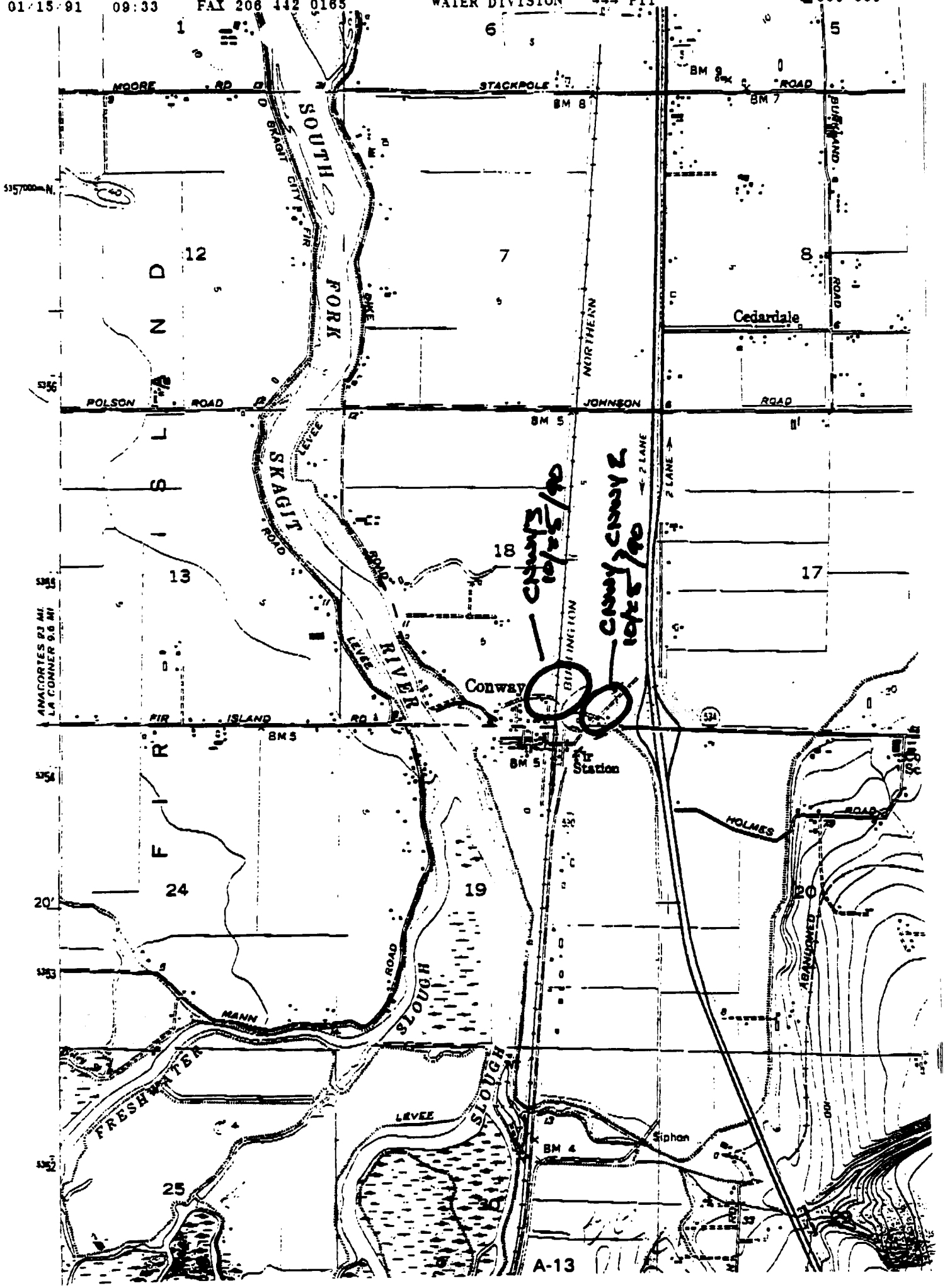
Polyconic projection. 1927 North American datum

10,000-foot grid based on Washington coordinate system, north zone

1000-meter Universal Transverse Mercator grid ticks, A-12

1400 (DECEPTION PASS) 1:62 500

GN MN 22° 391 MILS 0°29' 7 MILS 1000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STACKPOLE ROAD
BM 8
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BURLINGTON
Cedardale
POLSON ROAD
JOHNSON ROAD
BM 5
2 LANE
FIR ISLAND RD
Conway
Station
HOLMES ROAD
ABANDONED
MANN ROAD
SLOUGH
FRESHWATER
SLOUGH
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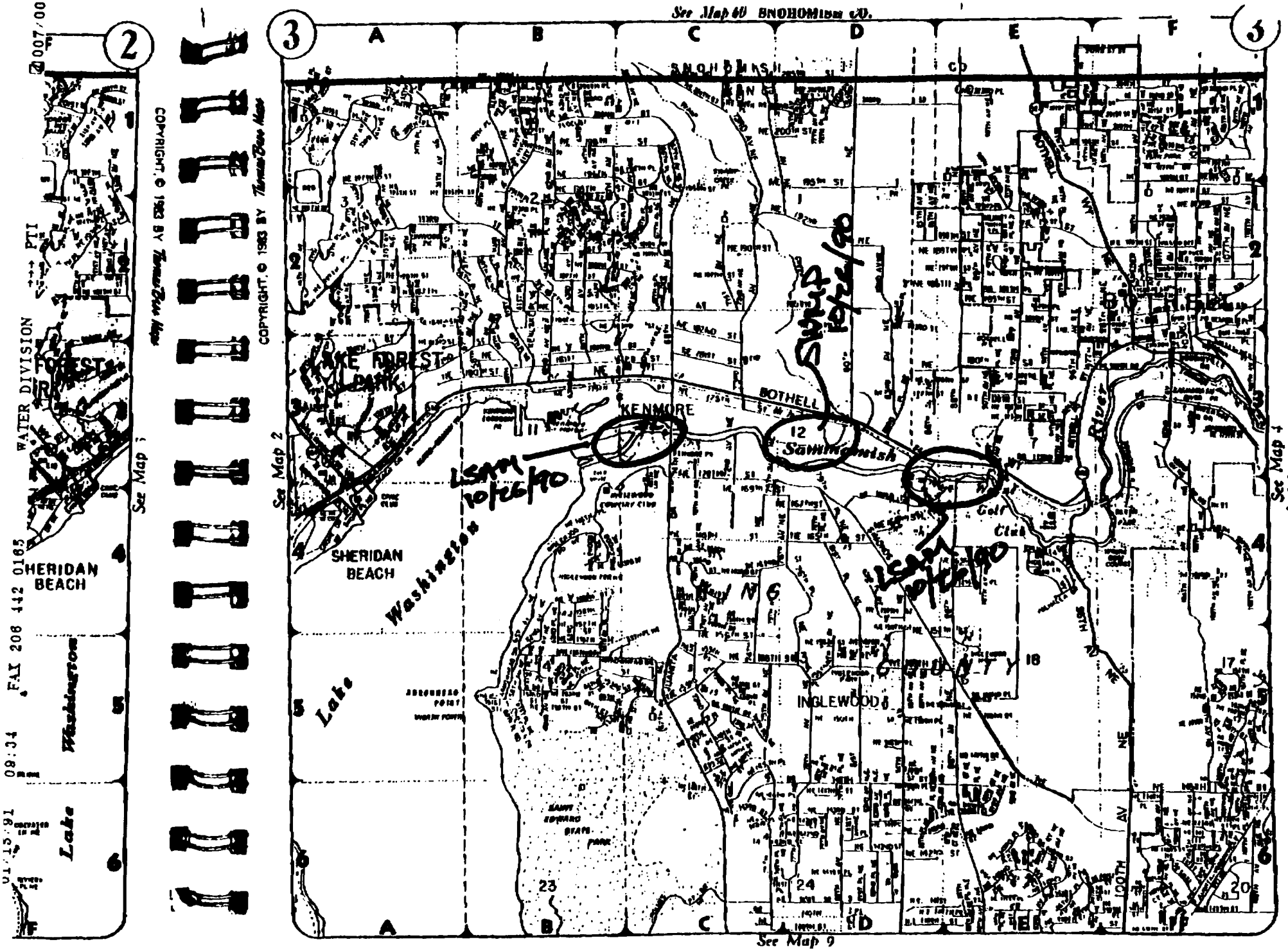
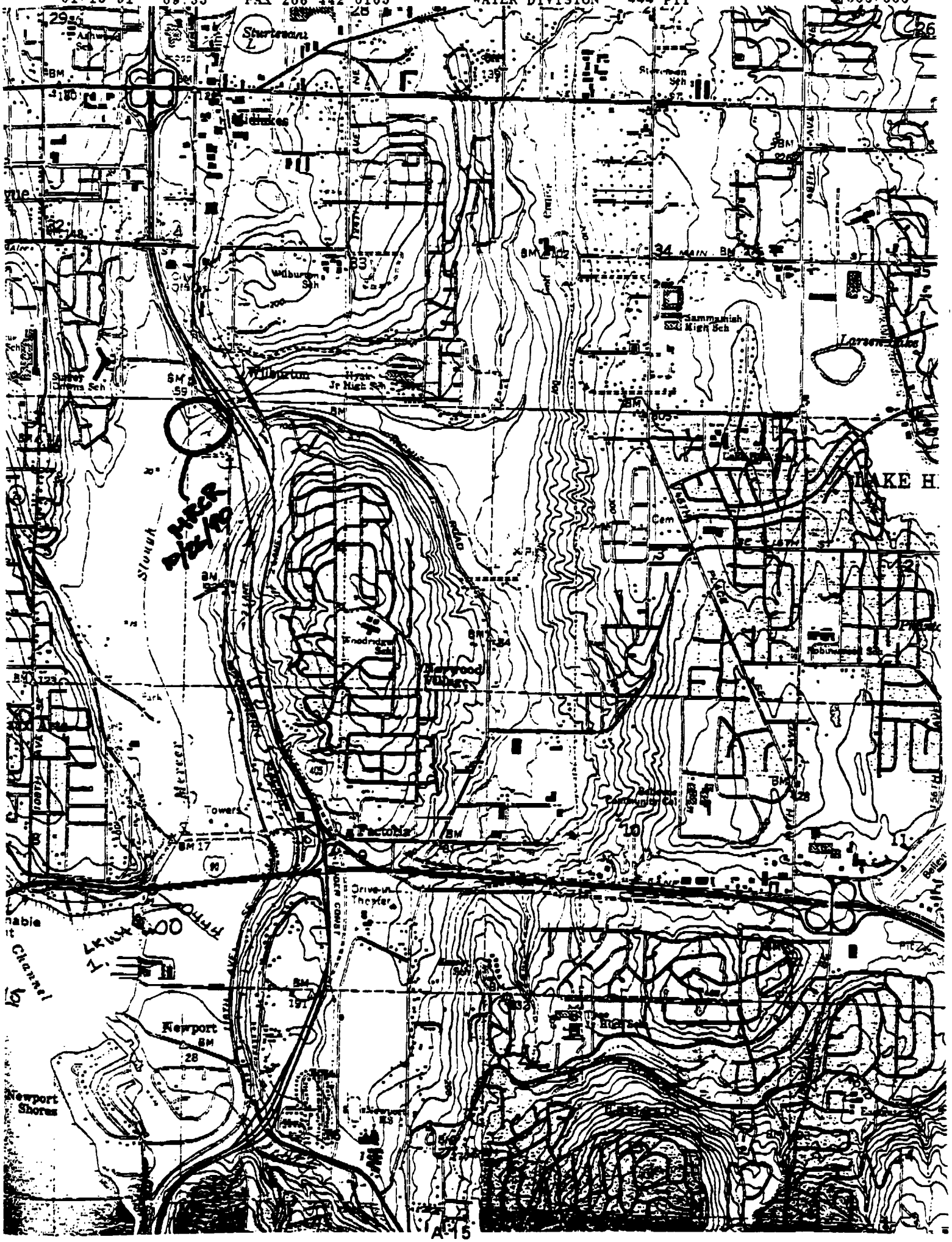



Shortesian
Midlakes
Wilburton Sch
Wilburton
Hyak Jr High Sch
Sunset Terrace Sch
Sammamish High Sch
Larsen Lake
LAKE H
Cem
Slough
Woodridge Sch
Newcastle Sch
Merwood Village
Park
Mercer
Towers
Factoria
Drive-in Theater
Newport
Newport Shores
Channel

APPENDIX B

Rainfall Runoff Model

RAINFALL RUNOFF MODEL

SELECTION OF SIGNIFICANT RAINFALL EVENT FOR WATER SAMPLING

Sampling was concentrated during precipitation events to enhance the probability of sampling pesticides possibly being flushed into Puget Sound. The following approach to sampling was developed in 1990 based on an evaluation of the specific sites and on consultation with county agents, regional hydrogeologists, and weather forecasters. Hydrographic data for each of the sites sampled in 1990 were also reviewed (see discussion in the *Rainfall Runoff Analysis* section). Application times for the pesticides of concern vary over a period of several months but are maximized during the late spring and summer growing season. A peak in pesticide concentrations is expected during or soon after rains of sufficient magnitude and duration have soaked pesticide application areas and, subsequently, produced a flush of surface runoff. Based on available information on runoff characteristics in each area and best professional judgment, estimates were made for 1) appropriate antecedent conditions to prime each area for runoff, 2) minimum rain accumulations to produce runoff in each area, and 3) the potential elapsed time between the start of precipitation and the discharge of runoff at each sampling point. These criteria, which describe the conditions that may constitute a significant precipitation event, are summarized in Table B-1.

Rainfall Runoff Analysis

Rainfall runoff modeling was completed for the four watersheds sampled in 1990 in order to develop guidelines for sampling. The Soil Conservation Service (SCS) TR-20 model was used to produce storm hydrographs and simulate the rainfall runoff response for each of the watersheds. The model input required for these simulations included watershed physical characteristics, hydraulic parameters developed using watershed physical characteristics and empirical relationships, and synthetic precipitation data. Watershed physical characteristics were determined using topographic maps and information contained in the soil surveys for King County (SCS 1973), Snohomish County (SCS 1978), and Skagit County (SCS 1960). A synthetic storm hyetograph, which shows the time distribution of rainfall, was developed using historical precipitation data; a dimensionless storm distribution developed by the SCS (1986); and published statistical data for depth, duration, and frequency of precipitation events for the specific watershed locations (NOAA 1973).

TABLE B-1. CRITERIA FOR SAMPLING RUNOFF FROM A 6-HOUR DURATION, 2-YEAR RETURN PERIOD PRECIPITATION EVENT[a]

Sampling Location	Antecedent Precipitation[b] (inches)	Antecedent Period (days)	Total Precipitation Depth Required to Meet Abstractions[c] and Produce Runoff (inches)	Time Between Start of Precipitation and Start of Runoff (hours)	Time of Sampling After Start of Precipitation[d] (hours)
Swamp Creek	0.8	5	0.35–0.7	2	2–5 5–7 7–12
Mercer Creek	0.8	5	≥0.7	3	3–4.5 4.5–6.5 6.5–9
Big Ditch Slough (Skagit River)	1.4	5	0.35–0.7	2.5	2.5–4.5 4.5–6.5 6.5–9

[a] These criteria were developed specifically for the 6-hour duration, 2-year return period precipitation event for the watersheds of the listed drainages. Precipitation events with different durations and frequencies will result in different storm hydrographs.

[b] Cumulative amount of precipitation necessary in the antecedent period for runoff to occur.

[c] Abstractions are differences between rainfall and runoff.

[d] Sampling times based on simulated storm hydrographs.

Model Input Development—Land use conditions in the four study watersheds range from agricultural to urban. Section *a* of Table B-2 lists physiographic data for the watersheds and streams that were sampled. Predominant soil types and land uses that exist in each watershed are also listed.

Hydraulic parameters developed from the data in Table B-2 (Section *a*) include curve number and time of concentration. The curve number is a empirically based parameter that relates rainfall, runoff, and the difference between rainfall and runoff (abstractions). Abstractions may occur as a result of interception by vegetation, infiltration into soil, and retention of water on impermeable ground surfaces (i.e., depression storage). Land use and soil hydraulic characteristics are used to determine the curve numbers that best represent hydrologic conditions in specific areas of a watershed. In general, larger curve numbers indicate that a larger volume of runoff will be produced for a given precipitation event. A single curve number was chosen for each watershed based on predominant soil types and land use characteristics in each watershed. The time of concentration for a watershed is the time required for a particle of water to travel from the most distant point in the watershed to the watershed outlet. The time of concentration for each of the watersheds was estimated using an empirical relationship that relates the curve number, hydraulic length (length of the longest watercourse), and the average watershed slope. The curve numbers and times of concentration for each of the watersheds are listed in Table B-2 (Section *b*).

Precipitation event data required for rainfall runoff modeling include precipitation intensity, duration of precipitation, and total depth of precipitation. The return period for a precipitation event is defined as the average length of time between events equaling or exceeding a certain depth. The return period is also defined as the inverse of the probability of exceeding a certain depth and duration. Therefore, if the return period of a 6-hour storm that produces 2 inches of rain is 100 years, then there is a 1 in 100 chance of a storm of equal or greater magnitude occurring in any one year.

Location-specific data for precipitation depths, durations, and return periods were determined using maps contained in the National Oceanic and Atmospheric Administration's (NOAA) *Precipitation-Frequency Atlas for Washington State* (NOAA 1973). Because the maps in the atlas were developed from historical data for the entire year, seasonal data may be somewhat different. For example, historical data from 108 storms that were analyzed for the Bellevue Urban Runoff Program indicate that the average amount of rain per storm during the months of March through September was 82 percent of the average annual amount of rain per storm (Pitt and Bissonette 1984). The average duration of storms that occurred during the months of May, June, and July was 8 hours.

The storm duration chosen for modeling was 6 hours. Precipitation depth and frequency data for this storm duration in the Seattle area and at the mouth of the Skagit River were determined using the precipitation-frequency atlas. Rainfall

TABLE B-2. DATA FOR STUDY STREAMS AND WATERSHEDS

Data	Big Ditch Slough	Swamp Creek	Mercer Creek
a. Physiographic Data			
Watershed area (mile^2)	10	22	12
Average slope (%)	1	5	10
Hydraulic length[a] (miles)	2	10	6
Predominant land use	Agriculture	Urban/suburban	Urban
Predominant soil type	Puget silty clay loam	Alderwood Gravelly sandy loam	Alderwood Gravelly sandy loam
b. Hydraulic Parameters			
Curve number	85	85	80
Time of concentration (hours)	3.0	4.8	2.6

c. Precipitation Depth, Duration, and Frequency

Return Period (years)	Depth (inches)	
	Mouth of Skagit River	Seattle
2	0.8	1.0
5	1.1	1.2
10	1.2	1.4
25	1.4	1.6
50	1.6	1.8
100	1.8	2.0

[a] Hydraulic length is defined as the length of the longest watercourse within the watershed.

depths for return periods ranging from 2 to 100 years for the 6-hour duration storm are listed for both locations in Section *c* of Table B-2. The 2-year and 25-year return periods were chosen as bounding conditions to be used in modeling. Because depths at the two locations were within 0.2 inches of one another, a mean depth was calculated. These values were adjusted for seasonal differences in precipitation depth from March through September by multiplying by 0.82. The resulting storm depths for the 6-hour duration, 2-year and 25-year storms that were used in modeling were 0.7 inches and 1.2 inches, respectively.

Two synthetic storm hyetographs were developed for the rainfall runoff analysis by applying the calculated storm depths to a dimensionless hyetograph. The dimensionless hyetograph was developed by the SCS for use in the United States for storms with 6-hour durations (SCS 1986). A graph of the resulting cumulative precipitation for the 2-year and 25-year return period storms is included in this appendix.

The amount of water contained in the soil prior to a precipitation event is termed the antecedent moisture condition. Antecedent moisture conditions were simulated using specific scenarios established for use with the model. Antecedent Condition I simulates dry soils where less than 0.5 inches of rain have fallen in the previous 5 days during the dormant season and less than 1.4 inches of rain have fallen in the previous 5 days during the dry season. Antecedent Condition II simulates average conditions where between 0.5 and 1.1 inches of rain have fallen in the previous 5 days during the dormant season and between 1.4 and 2.1 inches of rain have fallen in the previous 5 days during the growing season. Average conditions are simulated using the curve number, as determined by the methods discussed above. The model simulates the dry antecedent condition by decreasing the curve number input for average conditions. This decrease in curve number results in a prediction of less runoff occurring for a given precipitation event, which would be expected under drier antecedent conditions.

Model Results—Four simulations were completed for each watershed: dry and average antecedent conditions for both the 2-year and 25-year storms. An example model output is included in this appendix. Storm hydrographs were developed for each of the simulations. These hydrographs are also included in this appendix.

Antecedent conditions were found to strongly affect total volumes and rates of runoff. No runoff occurred in any of the watersheds for the 2-year return period storm that occurred after Antecedent Condition I. Peak flows occurring from 25-year return period storms after Antecedent Condition I constitute approximately 20 percent of the peak flows that occurred after Antecedent Condition II.

Sensitivity analyses were completed for the 2-year return period storm and average antecedent condition scenario to determine the amount of precipitation

required to satisfy abstractions and produce runoff. Each hourly rainfall increment was decreased by one-half to retain the shape of the hyetograph and to decrease total rainfall from 0.7 to 0.35 inches. No runoff occurred in any of the watersheds when the total precipitation was decreased from 0.7 to 0.35 inches, indicating that abstractions are between 0.35 and 0.7 inches. Initial abstractions vary depending on antecedent conditions, total storm depth, and the distribution of precipitation within specific storm events.

Guidelines for Sampling Events

The 6-hour duration, 2-year return period precipitation event has a high probability of occurring and was used as the basis for the sampling program design. Model results indicated that 0.5-2.1 inches of rain must occur in the 5 days preceding this precipitation event in order for runoff to occur, with the specific amount of antecedent precipitation dependent on the season. The higher range of this required antecedent precipitation will be interpreted as applying to agricultural lands where significant evapotranspirative losses occur during the growing season. Therefore, sampling at the Big Ditch Slough occurred after approximately 1.4 inches of rain had fallen during the 5-day antecedent period. It was determined that the 5-day antecedent precipitation needed at the Mill Creek and Swamp Creek watersheds was only approximately 0.8 inches due to a lower evapotranspirative demand from land highly developed with commercial or residential structures.

Sensitivity analyses indicated that between 0.35 and 0.7 inches of precipitation must occur during the 6-hour storm under average antecedent conditions for runoff to result in any of the watersheds. Because peak runoff from the Mercer Creek watershed is only 30 cubic feet per second, at least 0.7 inches of rain would have to fall for runoff to occur.

Sampling was planned according to the hydrographs shown in this appendix. Actual sampling times and conditions are recorded in Appendix A.

Model results are based on available data regarding watershed and precipitation characteristics. More accurate modeling results would be possible if the model was calibrated with actual precipitation and discharge data. It is recommended that rain gauges be established concurrent with sampling and that rainfall depth data be collected every 30 minutes. Stream discharge measurements will be made at the same time that rainfall measurements are made to calibrate the model if future simulations are anticipated. Real-time modeling using short-term precipitation forecasts and the calibrated model would result in more refined sampling guidelines for future sampling programs at these sites. For this survey, sampling personnel used best judgment in adjusting the time periods indicated based on actual conditions during each precipitation event.

REFERENCES

Pitt and Bissonnette. 1984. Bellevue urban runoff program summary report. Robert Pitt, Consulting Environmental Engineer, Mounds, WI, and Pam Bissonnette, Storm and Surface Water Utility, Bellevue, WA.

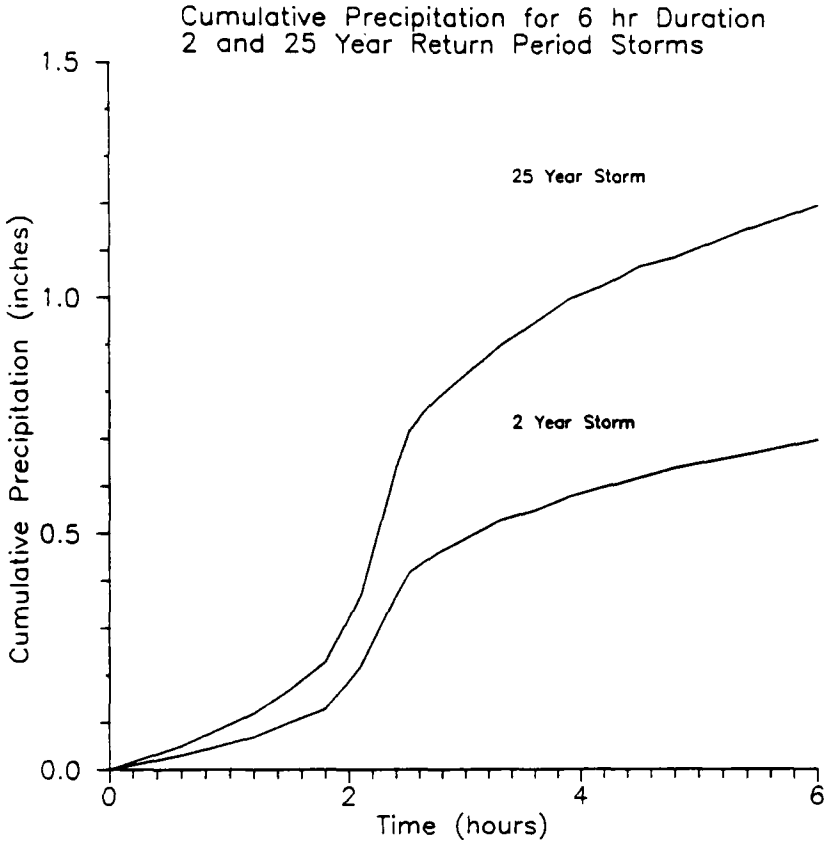
PTI. 1990. Pesticide reconnaissance survey quality assurance plan. Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA. PTI Environmental Services, Bellevue, WA.

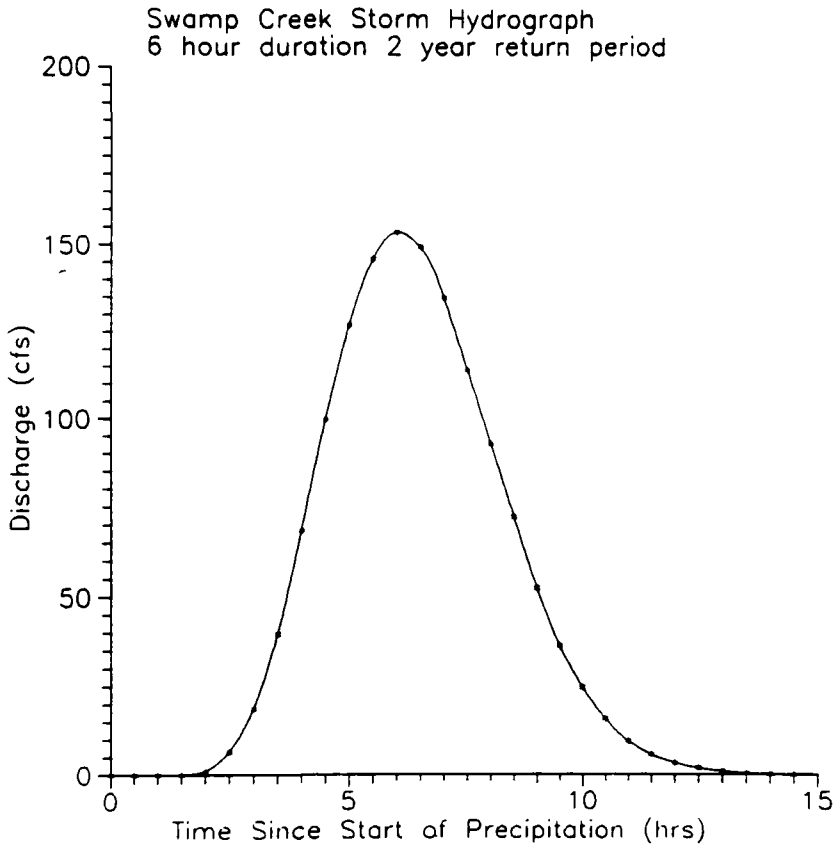
SCS. 1960. Soil survey for Skagit County Washington. U.S. Department of Agriculture Soil Conservation Service, in cooperation with Washington Agricultural Experiment Station.

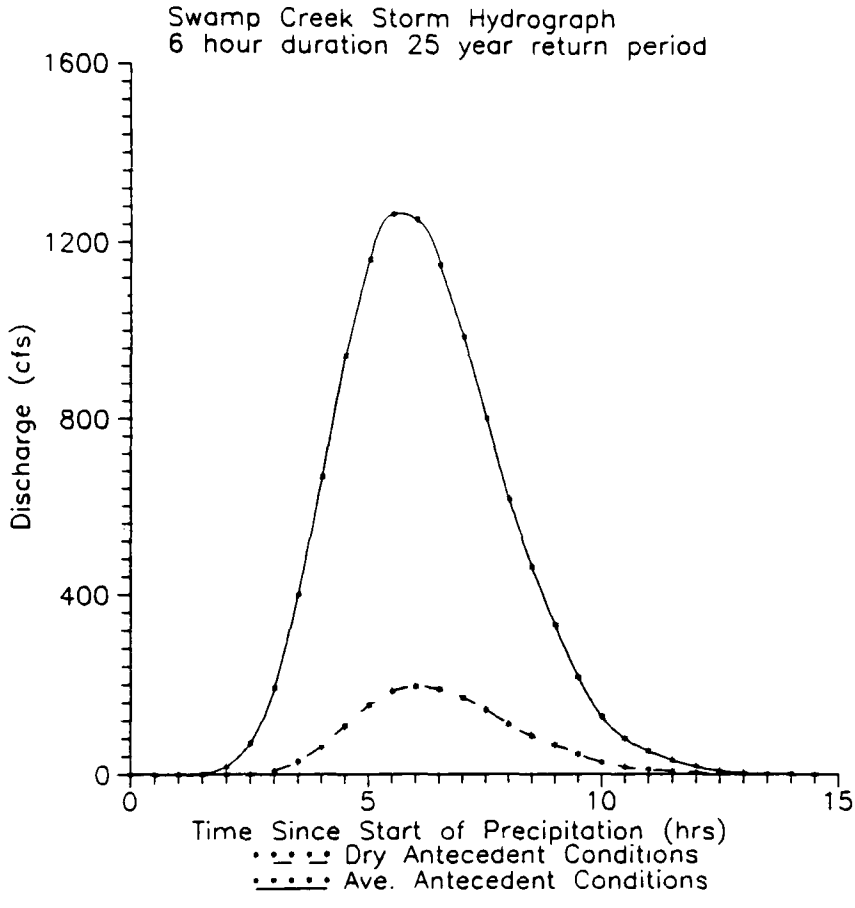
SCS. 1973. Soil survey for King County area Washington. U.S. Department of Agriculture Soil Conservation Service, in cooperation with Washington Agricultural Experiment Station.

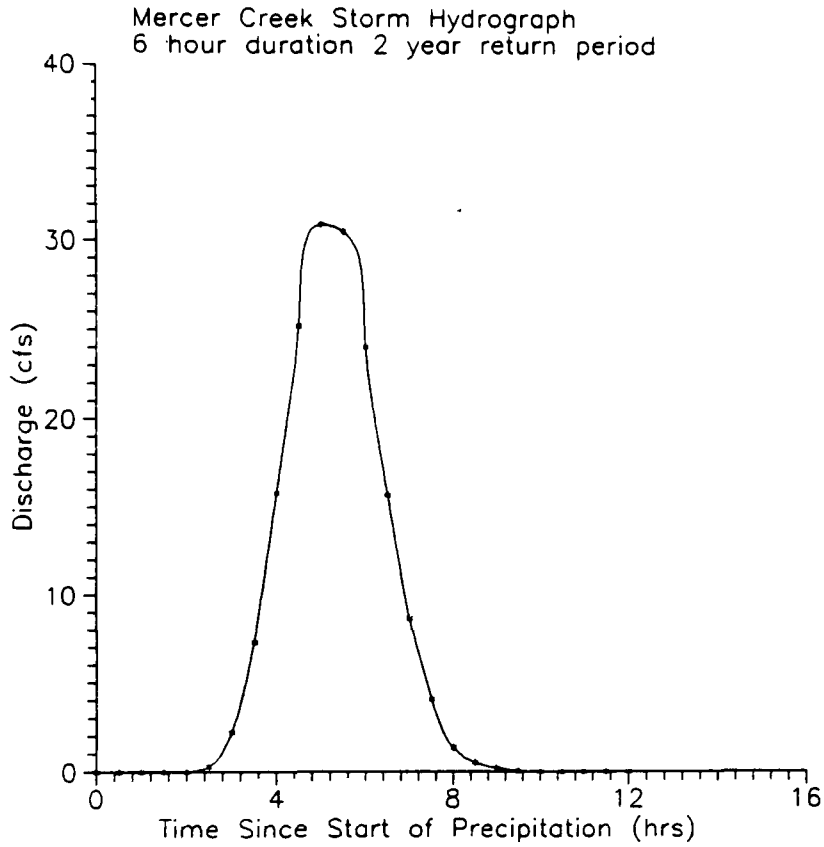
SCS. 1978. Soil survey for Snohomish County area Washington. U.S. Department of Agriculture Soil Conservation Service, in cooperation with Washington Department of Natural Resources and Washington State University Agriculture Research Center.

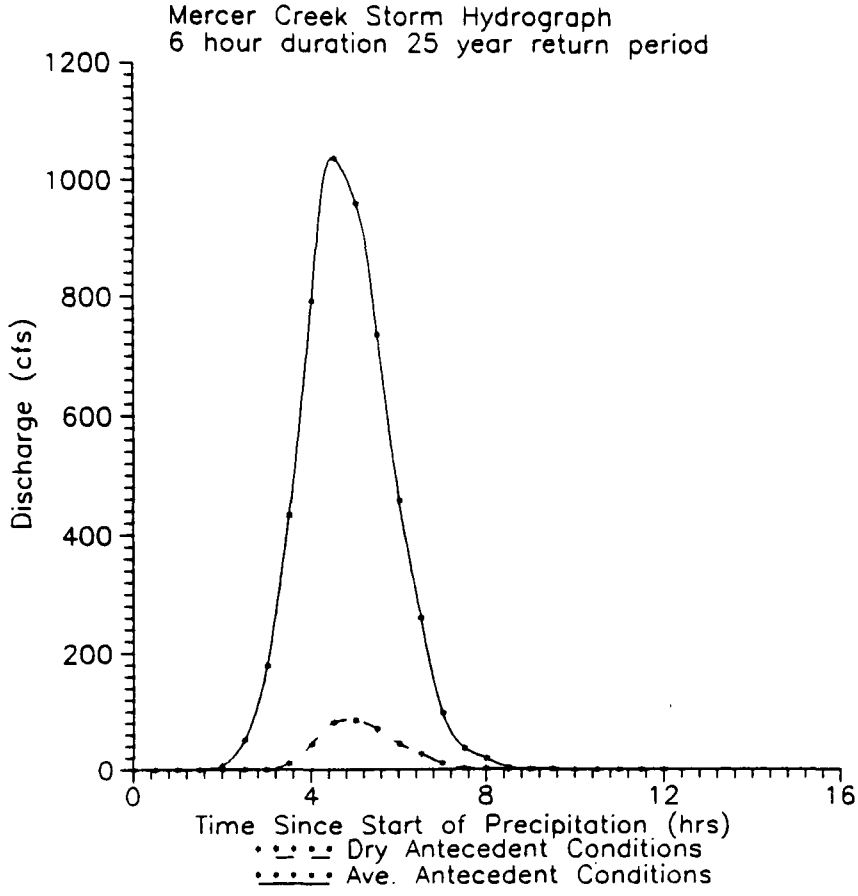
SCS. 1986. Urban hydrology for small watersheds. Technical Release No. 55. U.S. Department of Agriculture, Soil Conservation Service, Washington DC.

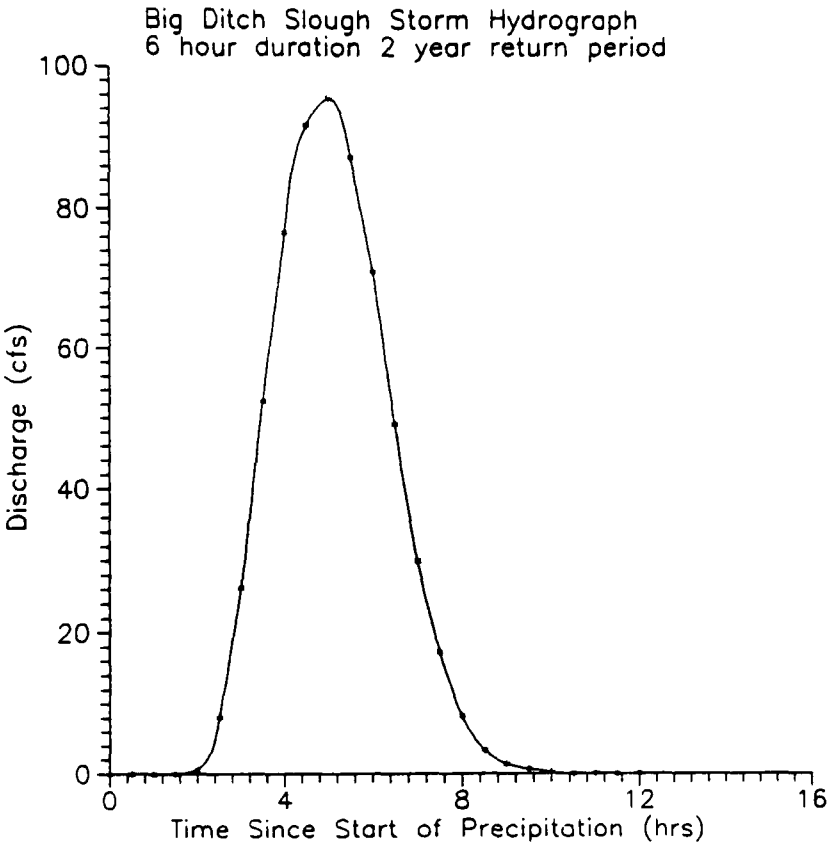

Cumulative Precipitation for 6 hr Duration
2 and 25 Year Return Period Storms
1.5
1.0
0.5
0.0
Cumulative Precipitation (inches)
25 Year Storm
2 Year Storm
0
2
4
6
Time (hours)

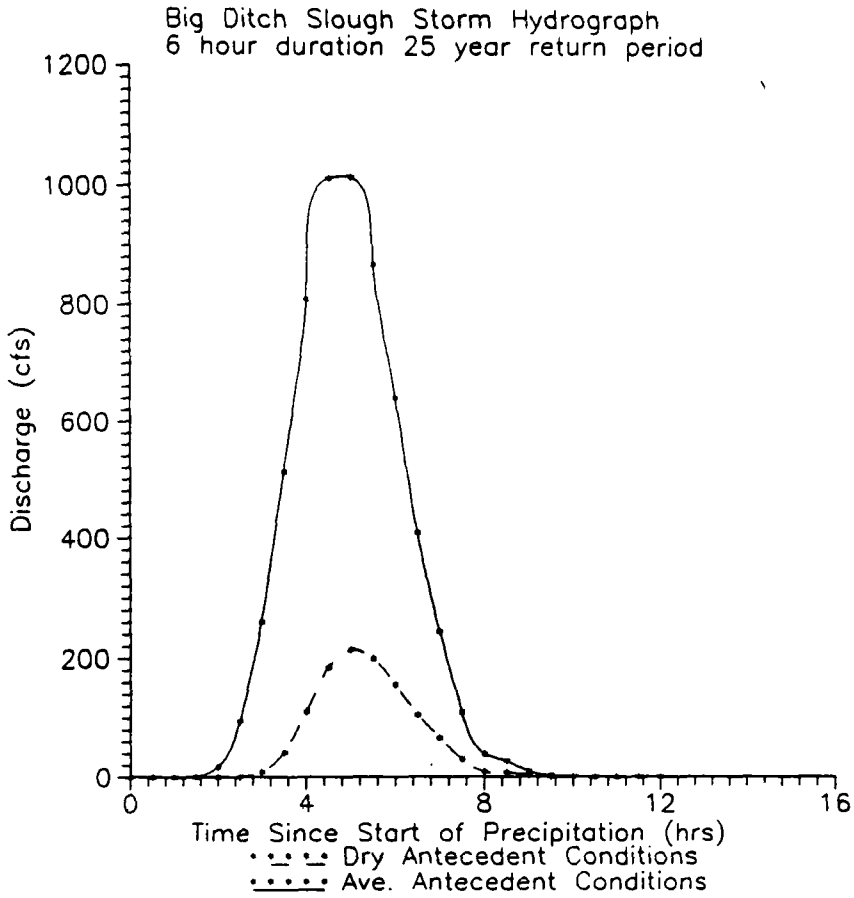

Swamp Creek Storm Hydrograph
6 hour duration 2 year return period
200
150
100
50
0
Discharge (cfs)
0
5
10
15
Time Since Start of Precipitation (hrs)


Swamp Creek Storm Hydrograph
6 hour duration 25 year return period
1600
1200
800
400
0
Discharge (cfs)
0
5
10
15
Time Since Start of Precipitation (hrs)
Dry Antecedent Conditions
Ave. Antecedent Conditions


Mercer Creek Storm Hydrograph
6 hour duration 2 year return period
Discharge (cfs)
40
30
20
10
0
0
4
8
12
16
Time Since Start of Precipitation (hrs)


Mercer Creek Storm Hydrograph
6 hour duration 25 year return period
Discharge (cfs)
1200
1000
800
600
400
200
0
0
4
8
12
16
Time Since Start of Precipitation (hrs)
Dry Antecedent Conditions
Ave. Antecedent Conditions


Big Ditch Slough Storm Hydrograph
6 hour duration 2 year return period
Discharge (cfs)
100
80
60
40
20
0
0
4
8
12
16
Time Since Start of Precipitation (hrs)


Big Ditch Slough Storm Hydrograph
6 hour duration 25 year return period
Discharge (cfs)
1200
1000
800
600
400
200
0
0
4
8
12
16
Time Since Start of Precipitation (hrs)
Dry Antecedent Conditions
Ave. Antecedent Conditions

TR-20 S/N: 32001325

DATE: 05/08/1990 TIME: 11:00:40.49

DATA FILE: MS25D.DAT

EXAMPLE RAINFALL RUNOFF MODEL OUTPUT

```
******************80-80 LIST OF INPUT DATA FOR TR-20 HYDROLOGY******************

JOB TR-20                    FULLPRINT          SUMMARY                    10
TITLE                 SIMULATION # 2:  6 HOUR, 25 YEAR STORM               20
TITLE                                 MERCER CREEK                         3
 4 DIMHYD             .02                                                  40
 8          .000      .030      .100      .190      .310                   50
 8          .470      .660      .820      .930      .990                   60
 8          1.0       .990      .930      .860      .780                   70
 8          .680      .560      .460      .390      .330                   80
 8          .280      .207      .147      .107      .007                   90
 8          .055      .040      .029      .021      .015                  100
 8          .011      .005      .000                                      110
 9 ENDTBL                                                                 115
 5 RAINFL 3           .5                                                   120
 8          .05       .1        .16       .32       .72        .84        130
 8          .93       1.1       1.6       1.11      1.15       1.2        140
 9 ENDTBL                                                                 145
 6 RUNOFF 1     1     1 12.        80.     2.6       1 1   1 1 1          150
   ENDATA                                                                 155
 7 INCREM 6           0.5                                                  160
 7 COMPUT 7     1     1 0.0     1.0       1.0       3 1      1            170
   ENDCMP 1                                                               180
   ENDJOB 2                                                               190

*********************************END OF 80-80 LIST*********************************
```

COMPUTER PROGRAM FOR PROJECT FORMULATION - HYDROLOGY USER NOTES

THE USERS MANUAL FOR THIS PROGRAM IS THE MAY 1982 DRAFT OF TR-20. CHANGES FROM THE 2/14/74 VERSION INCLUDE:

REACH ROUTING - THE MODIFIED ATT-KIN ROUTING PROCEDURE REPLACES THE CONVEX METHOD. INPUT DATA PREPARED FOR PREVIOUS PROGRAM VERSIONS USING CONVEX ROUTING COEFFICIENTS WILL NOT RUN ON THIS VERSION.

THE PREFERRED TYPE OF DATA ENTRY IS CROSS SECTION DATA REPRESENTATIVE OF A REACH. IT IS RECOMMENDED THAT THE OPTIONAL CROSS SECTION DISCHARGE-AREA PLOTS BE OBTAINED WHENEVER NEW CROSS SECTION DATA IS ENTERED. THE PLOTS SHOULD BE CHECKED FOR REASONABLENESS AND ADEQUACY OF INPUT DATA FOR THE COMPUTATION OF "M" VALUES USED IN THE ROUTING PROCEDURE.

GUIDELINES FOR DETERMINING OR ANALYZING REACH LENGTHS AND COEFFICIENTS (X,M) ARE AVAILABLE IN THE USERS MANUAL. SUMMARY TABLE 2 DISPLAYS REACH ROUTING RESULTS AND ROUTING PARAMETERS FOR COMPARISON AND CHECKING.

HYDROGRAPH GENERATION - THE PROCEDURE TO CALCULATE THE INTERNAL TIME INCREMENT AND PEAK TIME OF THE UNIT HYDROGRAPH HAVE BEEN IMPROVED. PEAK DISCHARGES AND TIMES MAY DIFFER FROM THE PREVIOUS VERSION. OUTPUT HYDROGRAPHS ARE STILL INTERPOLATED, PRINTED, AND ROUTED AT THE USER SELECTED MAIN TIME INCREMENT.

INTERMEDIATE PEAKS - METHOD ADDED TO PROVIDE DISCHARGES AT INTERMEDIATE POINTS WITHIN REACHES WITHOUT ROUTING.

OTHER - THIS VERSION CONTAINS SOME ADDITIONS TO THE INPUT AND NUMEROUS MODIFICATIONS TO THE OUTPUT. USER OPTIONS HAVE BEEN MODIFIED AND AUGMENTED ON THE JOB RECORD, RAINTABLES ADDED, ERROR AND WARNING MESSAGES EXPANDED, AND THE SUMMARY TABLES COMPLETELY REVISED. THE HOLDOUT OPTION IS NOT OPERATIONAL AT THIS TIME.

PROGRAM QUESTIONS OR PROBLEMS SHOULD BE DIRECTED TO HYDRAULIC ENGINEERS AT THE SCS NATIONAL TECHNICAL CENTERS:

CHESTER, PA (NORTHEAST) -- 215-499-3933, FORT WORTH, TX (SOUTH) -- 334-5242 (FTS)
LINCOLN, NB (MIDWEST) -- 541-5318 (FTS), PORTLAND, OR (WEST) -- 423-4099 (FTS)
OR HYDROLOGY UNIT, ENGINEERING DIVISION, LANHAM, MD -- 436-7383 (FTS).

PROGRAM CHANGES SINCE MAY 1982:

12/17/82 - CORRECT PEAK RATE FACTOR FOR USER ENTERED DIMHYD

CORRECT REACH ROUTING PEAK TRAVEL TIME PRINTED WITH FULLPRINT OPTION

5/02/83 - CORRECT COMPUTATIONS FOR ---

1. DIVISION OF BASEFLOW IN DIVERT OPERATION
2. HYDROGRAPH VOLUME SPLIT BETWEEN BASEFLOW AND ABOVE BASEFLOW
3. CROSS SECTION DATA PLOTTING POSITION
4. INTERMEDIATE PEAK WHEN "FROM" AREA IS LARGER THAN "THRU" AREA
5. STORAGE ROUTED REACH TRAVEL TIME FOR MULTIPEAK HYDROGRAPH
6. ORDERING "FLOW-FREQ" FILE FROM SUMMARY TABLE #3 DATA
7. BASEFLOW ENTERED WITH READHYD
8. LOW FLOW SPLIT DURING DIVERT PROCEDURE #2 WHEN SECTION RATINGS START AT DIFFERENT ELEVATIONS

ENHANCEMENTS ---

1. REPLACE USER MANUAL ERROR CODES (PAGE 4-9 TO 4-11) WITH MESSAGES
2. LABEL OUTPUT HYDROGRAPH FILES WITH CROSS SECTION/STRUCTURE, ALTERNATE AND STORM NO'S

09/01/83 - CORRECT INPUT AND OUTPUT ERRORS FOR INTERMEDIATE PEAKS

CORRECT COMBINATION OF RATING TABLES FOR DIVERT

CHECK REACH ROUTING PARAMETERS FOR ACCEPTABLE LIMITS

ELIMINATE MINIMUM REACH TRAVEL TIME WHEN ATT-KIN COEFFICIENT EQUALS ONE

```
EXECUTIVE CONTROL OPERATION INCREM                                                    RECORD ID      160
ME INCREMENT =  0.50 HOURS


EXECUTIVE CONTROL OPERATION COMPUT                                                    RECORD ID      170
RUCTURE  1                                                  TO STRUCTURE  1
       STARTING TIME =  0.00    RAIN DEPTH =  1.00    RAIN DURATION=  1.00    RAIN TABLE NO.= 3    ANT. MOIST. COND= 1
       ALTERNATE NO.= 0         STORM NO.=10    MAIN TIME INCREMENT =  0.50 HOURS


OPERATION RUNOFF   STRUCTURE  1
          OUTPUT HYDROGRAPH=  1
          AREA=  12.00 SQ MI   INPUT RUNOFF CURVE= 80.    TIME OF CONCENTRATION=  2.60 HOURS
          COMPUTED CURVE NO. = 63.                                    INTERNAL HYDROGRAPH TIME INCREMENT= 0.3467 HOURS

          PEAK TIME(HRS)              PEAK DISCHARGE(CFS)          PEAK ELEVATION(FEET)
              4.85                          86.44                        (RUNOFF)

TIME(HRS)        FIRST HYDROGRAPH POINT =  0.00 HOURS      TIME INCREMENT = 0.50 HOURS      DRAINAGE AREA =  12.00 SQ.MI.
   0.00    DISCHG        0.00      0.00      0.00      0.00      0.00      0.00      0.08     10.90     44.42     81.79
   5.00    DISCHG       85.59     70.42     44.65     27.00     10.47      2.47      1.77      0.46      0.00

  RUNOFF VOLUME ABOVE BASEFLOW =  0.02 WATERSHED INCHES,    191.02 CFS-HRS,    15.79 ACRE-FEET;   BASEFLOW =   0.00 CFS

                     --- HYDROGRAPH FOR STRUCTURE  1, ALTERNATE  0, STORM 10, ADDED TO OUTPUT HYDROGRAPH FILE ---


EXECUTIVE CONTROL OPERATION ENDCMP                                                    RECORD ID      180
TIONS COMPLETED FOR PASS   1


EXECUTIVE CONTROL OPERATION ENDJOB                                                    RECORD ID      190
```

APPENDIX C

Description of Water Sampling Apparatus

WATER SAMPLING APPARATUS

The apparatus used to collect water samples during this investigation can be easily made and used for routine water monitoring efforts. It consists of an all-Teflon® closure (which screws directly onto a 2.5-liter sampling bottle) that has water inlet and air outlet ports separated by a fixed vertical distance (Figure C-1). The closure is the top from a Teflon® wash bottle (Cole-Parmer Instrument Company, 7425 North Oak Park Avenue, Chicago, Illinois, 60648). The narrowed tip of the port is clipped off, leaving a constant-bore tube. A second hole is drilled in the lid, and a section of glass or Teflon® tubing is inserted into the hole. To avoid breaking the glass sample bottles, a bottle holder, which partially encases the bottle, is used. Attached to the bottle holder is a rigid handle and extension rods. These are used to control the depth of the sampler in the water column.

This sampling system had the advantage that the sample only contacts glass and Teflon® and that the number of sample transfer steps is reduced. To minimize aeration of the sample as it flows into the sample bottle, the Teflon® inlet tube can be extended to the lowest point of the sample bottle, thereby reducing splashing. Decontamination between samples is simplified because of the size and simplicity of the Teflon® closure. The primary functional difference between this ported closure and the United States Geological Survey (USGS) depth integrating samplers is that the filling rates of the USGS samplers can be controlled with the inlet nozzles of various diameters, whereas the ported Teflon® closures have a fixed diameter. Both systems allow depth integrated sampling.

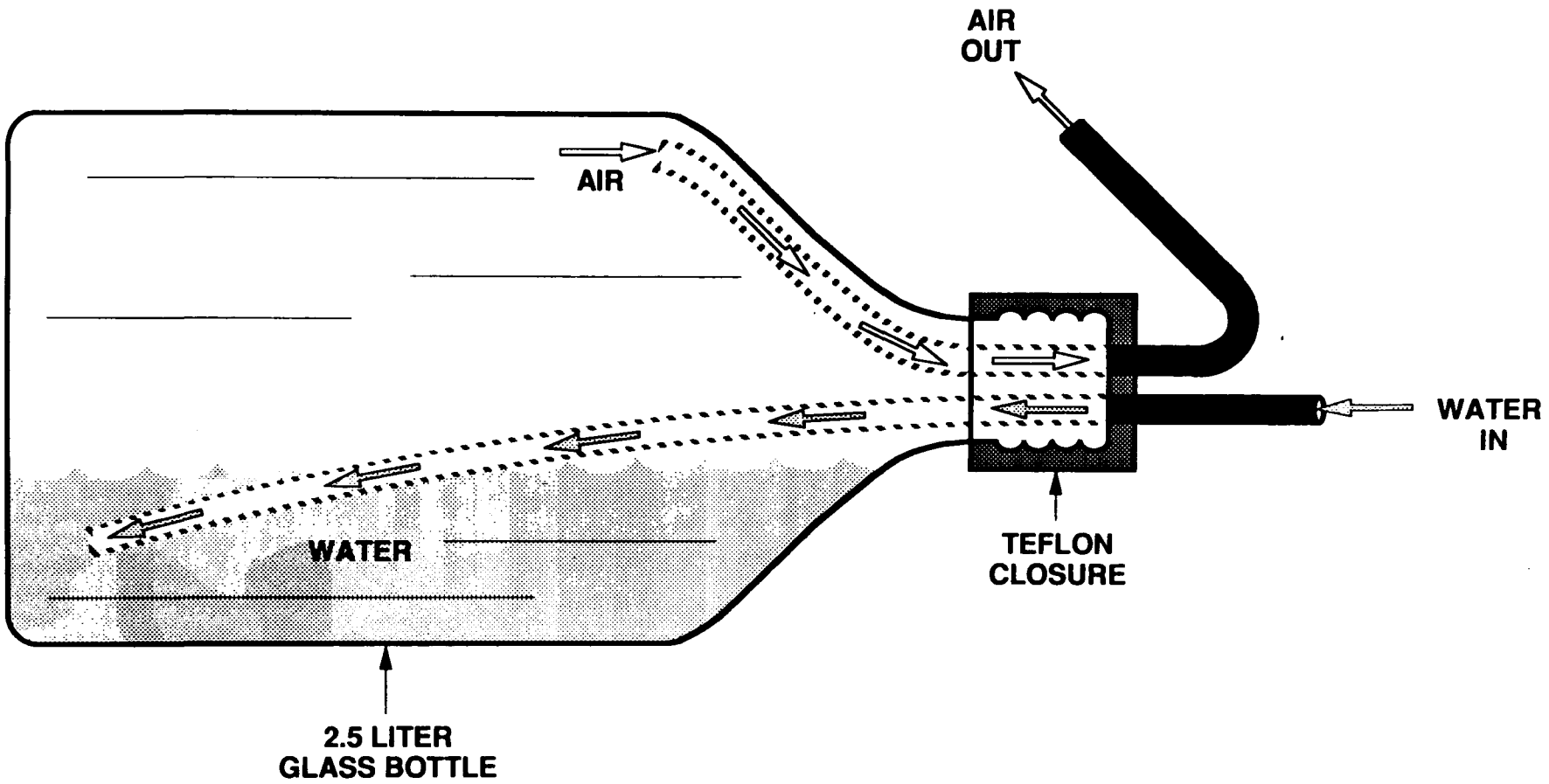


Figure C-1. Water sampling apparatus.

APPENDIX D

Chain-of-Custody Forms

Analytical Technologies, Inc.
560 Naches Avenue SW, Suite 101 Renton, WA 98055

Chain of Custody

9006-056

DATE 6/8/90 PAGE 1 OF 1

PROJECT MANAGER: Bob Barrick
COMPANY: PTI
ADDRESS: 15375 SE 30th PL Ste 250
Bellevue, WA 98007
PHONE: 643-9803 SAMPLED BY: Bob Stuart

LABORATORY NUMBER:

SAMPLE DISPOSAL INSTRUCTIONS

☒ ATI Disposal @ $5.00 each ☐ Return ☐ Pickup (will call)

ANALYSIS REQUEST

SAMPLE ID	DATE	TIME	MATRIX	LAB ID	8010 Halogenated Volatiles	8020 Aromatic Volatiles	BETX ONLY	8240 GCMS Volatiles	8270 GCMS BNA	8310 HPLC PNA	8080 Pesticides & PCBs	PCBs ONLY	8140 Phosphate Pesticides See list	8150 Herbicides see list	WDOE PAH/HH (WAC 173)	418.1 (TPH)	413.2 Grease & Oil	8015 (Modified)	TOC 9060	TOX 9020	% Moisture	TCLP	Priority Pollutant Metals (13)	EPTOX Metals (8) Total	EP TOX Metals (8) EP EXT	8010 1,3-Dichloropropene	Alachlor (WIS)	Acetate + Methamidophos	632	619	Glyphosate	Total Solids	NUMBER OF CONTAINERS
1-1 thru 1-12	6/7/90	0947	Water	-1									X	X												X	X	X	X	X	X	X	12
1-1D thru 1-6D	"	1044	"	-2 1-1D									X	X												X	X	X	X	X	X		6
2-1 thru 2-12	"	1240	"	-3 2-1									X	X												X	X	X	X	X	X	X	12
3-1 thru 3-12	"	1542	"	-4 3-1									X	X										SX		X	X	X	X	X	X	X	12
VOA 1-1 thru VOA 1-4	"	0947	"	-5 1-1																						X							5
VOA 2-1 + VOA 2-2	"	1240	"	-6 2-1																						X							2
VOA 3-1 + VOA 3-2	"	1542	"	-7 3-1																						X							2

PROJECT INFORMATION

PROJECT NUMBER:
PROJECT NAME: Pesticide Recon
PURCHASE ORDER NUMBER:
QA:

SAMPLE RECEIPT

TOTAL NUMBER OF CONTAINERS	50
CHAIN OF CUSTODY SEALS Y/N/NA	NA
INTACT? Y/N/NA	NA
RECEIVED GOOD COND./COLD	Y/Y

TAT: ☐ 24HR ☐ 48 HRS ☐ 72 HRS ☐ 1 WK ☐ 2 WKS (Normal)

AUTHORIZATION IS REQUIRED FOR RUSH DATA

4 Week T.A.T. as Per Mike Vogel

SPECIAL INSTRUCTIONS:

RELINQUISHED BY: 1.	RELINQUISHED BY: 2.	RELINQUISHED BY: 3.
Signature: Bob Stuart Time: 1140	Signature: Time:	Signature: Time:
Printed Name: Date:	Printed Name: Date:	Printed Name: Date:
Company:	Company:	Company:
RECEIVED BY: 1.	**RECEIVED BY: 2.**	**RECEIVED BY: (LAB) 3.**
Signature: Keith Stevens Time: 1040	Signature: Time:	Signature: Time:
Printed Name: Keith Stevens Date: 6/8/90	Printed Name: Date:	Printed Name: Date:
Company: ATI	Company:	Analytical Technologies, Inc.

ATI LABORATORIES: San Diego (619) 458-9141 • Phoenix (602) 438-1530 • Seattle (206) 228-8335 • Fort Collins (303) 490-1511 DISTRIBUTION: White, Canary - ANALYTICAL TECHNOLOGIES, INC. • Pink- ORIGINATOR

Biological and Chemical Services
for the Environment

CHAIN OF CUSTODY RECORD

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS. (Signature): M. A. Musgrove

STA. NO.	Start DATE	TIME	COMP	Bottle GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS
Mercer	8/30	1745	1	1		1							
			1	2		1							
			1	3		1							
			1	4		1							
			1	5		1							
			1	6									
			1	7		1							
			1	8									
			1	9									
			1	10									
			1	11		1							
			1	12									

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
M. A. Musgrove	8/31/95 930	Robert M. Wright	Robert M. Wright	8/31 1030	[illegible]
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment

Biological and Chemical Services
for the Environment

CHAIN OF CUSTODY RECORD

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS: (Signature) M. A. Musgrove

STA. NO.	DATE	Start TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS
Mercer	8/30	1915	2	1									
			2	2		1							
			2	3		1							
			2	4		1							
			2	5		1							
			2	6									
			2	7		1							
			2	8		1							
			2	9									
			2	10									
			2	11		1							
			2	12		1							

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
M. A. Musgrove	8/31/90 930	Robert J. Clark	Robert J. Clark	8/31 1030	Kent Stevens
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment

Biological and Chemical Services for the Environment

CHAIN OF CUSTODY RECORD

Proc. 250

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS: (Signature) N. A. Musgrove

TA. NO.	DATE	Start TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS
[illegible]	8/30	2115	3	1		1							
			3	2		1							
			3	3		1							
			3	4		1							
			3	5		1							
			3	6	-3	1							
			3	7		1							
			3	8		1							
			3	9									
			3	10		1							
			3	11		1							
			3	12									

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
N. A. Musgrove	8/31/90 930	Robert McIntosh	Robert McIntosh	8/31 1030	Lloyd Stevens
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)

Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks

ibuti igina mpar ipme

E.V.S. Consultants
Biological and Chemical Services
for the Environment

CHAIN OF CUSTODY RECORD

9008-250

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS: (Signature) W. A. Musgrove

TA. NO.	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS		REMARKS
Heron	8/30	1745		X	1st series pH, DO, temp from EVS 8-31-93 to AM	2	-1	
		1845		X		2		
		1945		X	2nd series	2	-2	
		2045		X		2		
		2215		X		2		
		2245		X	3rd series	2	-3	
		2315		X		2		
		2345		X		2		

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
W. A. Musgrove	8/31 9:30	[illegible]	[illegible]	8/31 1030	[illegible]
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment

Biological and Chemical Services for the Environment

9010-058

CHAIN OF CUSTODY RECORD

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS: (Signature) Mark D. Munn

STA. NO.	DATE	(SI) TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS								REMARKS
SWAMP	10-4-90	2000	1	1		1								
			1	2		1								
			1	3		1								
			1	4		1								
			1	5		1								
			1	6		1								
			1	7	-1	1								
			1	8		1								
			1	9		1								
			1	10		1								
			1	11		1								
			1	12		1								

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Mark D. Munn	10/5/90 0948	Keith Stenson ATI			
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment

E.V.S. Consultants
Biological and Chemical Services
for the Environment

CHAIN OF CUSTODY RECORD

9010·058

PROJ NO.	PROJECT NAME
	Pestiride Monitoring

SAMPLERS: (Signature) Mark D. Nunn

STA. NO.	DATE	(24) TIME	COMP	~~GRAB~~	STATION LOCATION	NO. OF CONTAINERS							REMARKS
SWAMP	10-4-90	2300	1	1		1							
			1	2		1							
			1	3		1							
			1	4		1							
			1	5		1							
			1	6		1							
			1	7		1							
			1	8		1							
			1	9	-2	1							
			1	10		1							
			1	11		1							
			1	12		1							
			1	13		1							
			1	14		1							
			1	15		1							

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Mark D. Nunn	10/5/90 0945	Keith Stevens ATI			
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment

E.V.S. Consultants
Biological and Chemical Services
for the Environment

CHAIN OF CUSTODY RECORD

9010-058

PROJ. NO.	PROJECT NAME
	Pesticide Monitoring

SAMPLERS: (Signature) Mark D. Nelson

TA. NO.	DATE	(S2) TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS
AMP	10-4-90	2300	1	16		1							
↓		↓	1	17		1							
			1	18		1							

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Mark D. Nelson	10/5/90 0948	ATI Kent Stevenson			
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution. Original Accompanies Shipment

E.V.S. Consultants
Biological and Chemical Services for the Environment

CHAIN OF CUSTODY RECORD

9010-058

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS: (Signature) Mark D. Munn

STA. NO.	DATE	TIME	COMP.	~~GRAB~~	STATION LOCATION	NO. OF CONTAINERS							REMARKS
SwAmP	10-5-90	0200	1	1		1							
			1	2		1							
			1	3		1							
			1	4		1							
			1	5		1							
			1	6	-3	1							
			1	7		1							
			1	8		1							
			1	9		1							
			1	10		1							
			1	11		1							
			1	12		1							

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Mark D. Munn	10/5/90 0945	ATI Keith Stevenson			
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment

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Biological and Chemical Services
for the Environment

CHAIN OF CUSTODY RECORD

9010-058

PROJ. NO.

PROJECT NAME: Pesticide Monitoring

SAMPLERS: (Signature) Mark D. Munn

TA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	REMARKS
inAnP	10-4-90	2050		1	3-1	2	
	10-4-90	2200		1		2	
	10-4-90	2300		1		2	
	10-4-90	2350		1	-2	2	
	10-5-90	0030		1		2	
	10-5-90	0100		1		2	
	10-5-90	0315		1	-3	2	
	10-5-90	0545		1		2	

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Mark D. Munn	10/5/90 0948	AFT1 Scott Stevens			
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribut Origin Compa Shipme

EPA
EPA Region 10
1200 Sixth Avenue
Seattle WA 98101

FIELD SAMPLE DATA AND CHAIN OF CUSTODY SHEET

9010-040

Project Code: _____ Account: _____

Name/Location Pesticides - Puget Sound

Proj. Off.: Michael Ryko EPA Tel.# 442-4014
Rob Fabrick PTI 645-9803

☐ Enforcement/Custody
☒ Possible Toxic/Hazardous
☐ Data Confidential
☒ Date for Storet

Miscellaneous: _____

Sampling Crew: Michael Ryko

Recorder: _____ (Signatures Required)

SOURCE CODE	MATRIX: Oil	Water	Sediment	Tissue	Prsvd(Y/N)	# CONTAINERS: Qt. Cubnt	Gal. Cubnt	16 oz.	8 oz.	120 ml.	40 ml	Other	LAB NUMBER (Lab Use Only) Yr	Wk	Seq	STORET STATION NUMBER	SAMPLING DATE & TIME: Yr	Mo	Dy	Time	TRAFFIC REPORT NUMBERS: Org.	Inorg.	SAMPLER'S INITIALS	STATION DESCRIPTION (ID)	
1 2			X										9010-040				90	10	25				MSR	INHI	-1 (10) COMPOSITE
			X																				MSR	SUSL	-2
			X														90	10	25				MSR	CNWY	3 (11) COMPOSITE
			X																				MSR	CNWY 2	4
			X																				MSR	CNWY 3	5
			X																						
1 2			X														90	10	25				MSR	BGDH	6
1 2			X														90	10	26				MSR	LSAM	7
1 2			X														90	10	26				MSR	MRCR	8
1 2			X														90	10	26				MSR	SWMF	9

LAB NUMBER Yr	Wk	Seq	DEPTH	Units	Type	COL MTD CD	QA CODE	TEMP DEG C	pH	CNDCTVTY umho/cm	COMPOSITE ONLY: ENDING DATE Mo	Dy	Time	Type	Freq

CONDITION OF SAMPLES UPON RECEIPT AT LAB: _____

CUSTODY SEALS INTACT: ☒ Yes ☐ No

CHAIN OF CUSTODY RECORD

RELINQUISHED BY: (Signature)	RECEIVED BY (Signature)	DATE/TIME
Michael Ryko	[signature]	10/26/90 1350
RELINQUISHED BY: (Signature)	RECEIVED BY (Signature)	DATE/TIME
RELINQUISHED BY: (Signature)	RECEIVED BY (Signature)	DATE/TIME
RELINQUISHED BY: (Signature)	RECEIVED BY MOBILE LAB FOR FIELD ANALYSIS (Signature)	DATE/TIME
DISPATCHED BY (Signature) DATE/TIME	RECEIVED FOR LAB BY (Signature)	DATE/TIME

METHOD OF SHIPMENT

Laboratory Copy White — Project Officer Copy Yellow — Field or Office Copy Pink

APPENDIX E

Sediment Quality Criteria

TABLE E-1. SEDIMENT QUALITY CRITERIA (μg/g DRY WEIGHT FOR METALS AND NUTRIENTS) PROPOSED BY THE ONTARIO MINISTRY OF ENVIRONMENT

	No Effect Level	Lowest Effect Level	Limit of Tolerance Level
Metals			
Arsenic	4.0	5.5	33.0
Cadmium	0.6	1.0	10.0
Chronium	22.0	31.0	111.0
Copper	15.0	25.0	114.0
Iron (%)	2.0	3.0	4.0
Lead	23.0	31.0	250.0
Manganese	400.0	457.0	1,100.0
Mercury	0.1	0.12	2.0
Nickel	15.0	31.0	90.0
Zinc	65.0	110.0	800.0
			μg Contaminants/g Carbon (TOC)
Organic Compounds[a]			
δ-Chlordane	0.001	0.005	6.6
Heptachlor	0.001	0.002	0.5
Endrin	0.002	0.003	33.1
Aldrin	0.001	0.007	128.4
Mirex	0.001	0.002	9.1
Chlordane	0.001	0.008	6.2
p,p-DDT	0.005	0.009	13.6
p,p-DDD	0.002	0.008	9.0
p,p-DDE	0.003	0.005	21.3
o,p-DDT	0.001	0.006	11.3
PCB 1254	--	0.058	34.4
PCB 1248	--	0.034	150.5
PCB 1016	--	0.007	53.3
PCB (Total)	0.020	0.041	69.8
Dieldrin	0.006	0.019	59.0

TABLE E-1. (Continued)

	No Effect Level	Lowest Effect Level	μg Contaminants/g Carbon (TOC)
BHC	--	0.003	11.8
δ-BHC	0.002	0.003	25.0
ß-BHC	0.001	0.005	21.0
α-BHC	0.001	0.006	10.4
HCB	0.001	0.020	47.6
Heptachlor epoxide	0.001	0.005	5.5
Nutrients			
Total organic carbon (TOC) (%)		1.0	10.0
Total Kjeldahl nitrogen		545.0	4,800.0
Total phosphorus		600.0	2,050.0
Solvent extractables (oils and greases)		2,400.0	--

Source: Persaud et al. (1989)

[a] Values in this column are multiplied by the actual TOC content of the sediments, e.g., at TOC of 5 percent, the total PCB value is 70 × 0.05 or 3.5 ppm.

TABLE E-2. SUMMARY OF ER-L, ER-M, AND OVERALL APPARENT EFFECTS THRESHOLD CONCENTRATIONS FOR SELECTED CHEMICALS IN SEDIMENT (DRY WEIGHT)

Chemical Analyte	ER-L Concentration	ER-M Concentration	ER-L:ER-M Ratio	Overall Apparent Effects Threshold	Subjective Degree of Confidence in ER-L/ER-M Values
Trace Elements (mg/kg)					
Antimony	2	25	12.5	25	Moderate/moderate
Arsenic	33	85	2.6	50	Low/moderate
Cadmium	5	9	1.8	5	High/high
Chromium	80	145	1.8	No	Moderate/moderate
Copper	70	390	5.6	300	High/high
Lead	35	110	3.1	300	Moderate/high
Mercury	0.15	1.3	8.7	1	Moderate/high
Nickel	30	50	1.7	NSD[a]	Moderate/moderate
Silver	1	2.2	2.2	1.7	Moderate/moderate
Tin	NA[b]	NA	NA	NA	NA
Zinc	120	270	2.2	260	High/high
Polychlorinated Biphenyls (µg/kg)					
Total PCBs	50	400	7.6	370	Moderate/moderate
DDT and Metabolites (µg/kg)					
DDT	1	7	7	8	Low/low
DDD	2	20	10	NSD	Moderate/low
DDE	2	15	7.5	NSD	Low/low
Total DDT	3	350	117	No	Moderate/moderate
Other Pesticides (µg/kg)					
Lindane	NA	NA	NA	NSD	NA
Chlordane	0.5	6	12	2	Low/low
Heptachlor	NA	NA	NA	NSD	NA
Dieldrin	0.02	8	400	No	Low/low
Aldrin	NA	NA	NA	NSD	NA

TABLE E-2. (Continued)

Chemical Analyte	ER-L Concentration	ER-M Concentration	ER-L:ER-M Ratio	Overall Apparent Effects Threshold	Subjective Degree of Confidence in ER-L/ER-M Values
Endrin	0.02	45	2,250	NSD	Low/low
Mirex	NA	NA	NA	NSD	NA
Polycyclic Aromatic Hydrocarbons (µg/kg)					
Acenaphthene	150	650	4.3	150	Low/low
Anthracene	85	960	11.3	300	Low/moderate
Benz(a)anthracene	230	1,600	7	550	Low/moderate
Benzo(a)pyrene	400	2,500	6.2	700	Moderate/moderate
Benzo(e)pyrene	NA	NA	NA	NSD	NA
Biphenyl	NA	NA	NA	NSD	NA
Chrysene	400	2,800	7	900	Moderate/moderate
Dibenz(a,h)anthracene	60	260	4.3	100	Moderate/moderate
2,6-Dimethylnaphthylene	NA	NA	NA	NSD	NA
Fluoranthene	600	3,600	6	1,000	High/high
Fluorene	35	640	18.3	350	Low/low
1-Methylnaphthalene	NA	NA	NA	NSD	NA
2-Methylnaphthalene	65	670	10.3	300	Low/moderate
1-Methylphenanthrene	NA	NA	NA	NSD	NA
Naphthalene	340	2,100	6.2	500	Moderate/high
Perylene	NA	NA	NA	NSD	NA
Phenanthrene	225	1,380	6.1	260	Moderate/moderate
Pyrene	350	2,200	6.3	1,000	Moderate/moderate
2,3,5-Trimethylnaphthalene	NA	NA	NA	NSD	NA
Total PAH	4,000	35,000	8.8	22,000	Low/low

Source: Long and Morgan (1990)

[a] NSD - not sufficient data.

[b] NA - not available.

APPENDIX F

Quality Assurance Report for Chemical Analyses

CONTENTS

LIST OF TABLES

LIST OF ACRONYMS

MS	matrix spike
MSD	matrix spike duplicate
QAPP	quality assurance project plan
PSEP	Puget Sound Estuary Program
RPD	relative percent difference
RRF	relative response factor
RSD	relative standard deviation
TBA	tributyl ammonium agent

INTRODUCTION

This report documents the results of a quality assurance review of analytical data for pesticides in water and sediment samples from Puget Sound drainages and deltas. This quality assurance report is provided in support of the quality assurance project plan (QAPP) for 1990 Pesticide Reconnaissance Survey (PTI 1990).

Pesticide analyses were performed by Analytical Technologies Incorporated in Renton, Washington; San Diego, California; and Fort Collins, Colorado.

The quality assurance review included examination and validation of the following laboratory data:

- Sample preparation and extraction logs and laboratory worksheets
- All instrument printouts
- Instrument calibration and calibration verification procedures and results
- Sample holding times and custody records
- Manual data transcriptions and computer algorithms.

Data qualifiers were assigned as necessary during the quality assurance review. Following the validation procedures, data quality was assessed with respect to accuracy, precision, and completeness. All qualifier codes used in this report are defined in Table F-1.

OVERALL CASE ASSESSMENT

All data for pesticides, with one exception, are acceptable as qualified in this review. Data qualified E (estimated) are acceptable, but a greater degree of uncertainty is associated with these values than with unqualified data.

The DDT result for Sample CNWY-S was rejected because DDT degradation in the associated continuing calibration standard was greater than 20 percent and DDT was not found in the sample. Results for DDE and DDD for Sample

TABLE F-1. DATA QUALIFIER CODES

Qualifier Code	Description
E	Estimate
R	Rejected
T	Detected below quantification limit
U	Undetected at the detection limit shown

CNWY-S and for DDT, DDE, and DDD for Sample LACO-S were qualified as estimated.

The detection limits for chloropicrin and 1,3-dichloropropene for Sample BGDHJC were qualified as estimated because the holding time between sample collection and extraction was exceeded.

Results for pentachlorophenol for samples BGDH-S, LSAM-S, MRCR-S, LACO-S and CNWY-S were qualified as estimated because the percent difference in the associated continuing calibration standard exceeded control limits.

A T qualifier was assigned to several results for dichlobenil, DDT, DDE, and DDD to indicate that the compound was detected, but at a concentration less than the calibrated quantification limit.

COMPLETENESS

Complete data packages were submitted by Analytical Technologies Incorporated for 12 water and 6 sediment samples. The samples were divided into five extraction groups, as indicated in Table F-2, and analyzed for the pesticides listed in Table F-3. Method blanks, matrix spikes (MSs), matrix spike duplicates (MSDs), and standard reference material samples (chlorinated herbicides, triazines, and chloropicrin/1,3-dichloropropene only) were analyzed with the samples. For sample group BGDH-J, the laboratory analyzed for carbamates, glyphosate, acephate, and methamidophos on a composite of samples BGDHJ1, BGDHJ2, and BGDHJ3.

During the quality assurance review, 12 results (2 percent) were qualified E as discussed above. One result was rejected. Data completeness was 99.8 percent of the total requested analysis.

HOLDING TIMES

Holding times specified in the project QAPP (7 days from sampling to extraction for water samples, 1 month for frozen sediment samples) were met for all analyses, with two exceptions. For sample group BGDH-J, the holding time between sampling and extraction for the chloropicrin and 1,3-dichloropropene analyses was 8 days. Chloropicrin and 1,3-dichloropropene were not detected in the samples. The detection limits for chloropicrin and 1,3-dichloropropene in Sample BGDHJC were qualified as estimated (E). Samples for triazine analyses in sample group BGDH-J were extracted 7 days after sampling. Concern over spike recoveries led to another extraction 11 days after sampling. Because the results of the two extractions were the same, no data were qualified. All samples were analyzed within 40 days of extraction.

TABLE F-2. SAMPLE EXTRACTION GROUPS FOR PESTICIDE ANALYSES

BGDH-J	MERCER	SWAMP	BGDH-O	SEDMNT
BGDHJ1	MRCR-1	SWMP- 1	BGDH01	BGDH-S
BGDHJ2	MRCR-2	SWMP- 2	BGDH02	LSAM-S
BGDHJ3	MRCR-3	SWMP-3	BGDH03	MRCR-S
BGDHJC[a]				SWMP-S
				LACO-S
				CNWY-S

[a] BGDHJC - composite of BGDHJ1, BGDHJ2, and BGDHJ3.

TABLE F-3. PESTICIDES ANALYZED FOR IN PUGET SOUND WATERS AND SEDIMENTS

Organophosphate Pesticides	Chlorinated Pesticides[a]	Chlorinated Herbicides	Triazine Herbicides
Diazinon	Trifluralin	2,4-D	Alachlor
Malathion	Chlordane	Dicamba	Atrazine
Dichlorvos	Endosulfan	Dinoseb	Amitrole
Fenamiphos	Lindane	Triclopyr	Hexazinone
Chlorpyrifos	Dichlobenil		Prometon
Parathion (ethyl)	DDT		Simazine
Disulfoton	DDE		
Methyl parathion	DDD		
Azinphos-methyl			
Phorate			

Polar Phosphorous Pesticides[b]	Carbamates and Urea Pesticides	Miscellaneous
Acephate	Bromacil	1,3-Dichloropropene[b] and Chloropicrin[b]
Methamidophos	Carbaryl	Glyphosate
	Propham	Benfluralin
	Methomyl	Pentachlorophenol[a]
	Diphenamid	Fenvalerate[b]
	Tebuthiuron	
	Diuron	
	Pronamide	
	Bendiocarb	
	Terbacil	

[a] Sediment samples only.

[b] Water samples only.

ANALYTICAL METHODS

All sample extraction and analysis procedures, instrument calibration procedures, and quality control checks conformed to PSEP (1989) and QAPP requirements, except as noted below.

Sample Preparation and Analysis

Water and sediment samples were extracted according to requirements specified in the project QAPP. The extraction of the triazine blank spike and MS for sample extraction group BGDH-J was done twice. The laboratory originally extracted the sample, blank, and spikes on 13 June 1990. Because of concern over inconsistent spike recoveries, a second extraction of the MS and blank spike was done on 5 July 1990. In sample extraction group SEDMNT, sample CNWY-S, the MS and MSD were analyzed before and after a tributyl ammonium agent (TBA) cleanup. TBA is used to remove sulfur in the sample extracts. The laboratory reported that a large interference was observed in the original extract of Sample CNWY-S and the MS and MSD. The interference was present in the area where phorate, diazinon, and disulfoton elute. The laboratory performed a TBA cleanup on the three extracts. Results for the post-cleanup analyses were only used for phorate, diazinon, and disulfoton.

Sample extracts were analyzed by gas chromatography/flame photometric detection (organophosphorus pesticides), gas chromatography/nitrogen-phosphorus detection (triazine herbicides and alachlor), gas chromatography/electron capture detection (organochlorine pesticides, chlorinated herbicides, trichlopyr, chloropicrin, 1,3-dichloropropene, benfluralin, pentachlorophenol, and fenvalerate), and high performance liquid chromatography (carbamates, urea, terbacil, and glyphosate). Two columns were used for all gas chromatography analyses, one for compound quantification and a second for compound confirmation.

Calibration

Initial calibration for all analyses was performed in accordance with Puget Sound Estuary Program (PSEP) guidelines (PSEP 1989) for each sample extraction group. Calibration of chlorpyrifos was calculated from the total response factor for chlorpyrifos plus methyl parathion, since chlorpyrifos coeluted with methyl parathion on one column and parathion on the second column. A 5-point calibration was performed for each analyses as recommended by PSEP (1989). Initial calibration criteria [relative response factor (RRF) relative standard deviation (RSD) of less 30 percent] were met for all analyses with the following exceptions:

- 25 May 1990—The RSDs for methyl-parathion and fenamiphos were 42 and 39 percent, respectively. These compounds were not detected in the samples and no data were qualified.
- 28 November 1990—The laboratory performed a 5-point calibration for the organochlorine pesticides, but only used 4 points, dropping the low end standard out. The low end standard was dropped to meet the criteria of less than 30 percent RSD for DDE and endosulfan II. The low end standard could have been used for the other organochlorine pesticides, thus providing lower detection limits. For lindane, the laboratory dropped two standards on the low end of the calibration to obtain an RSD of less than 30 percent. This still meets the PSEP (1989) requirement of a minimum of three initial calibration standards.

Continuing calibrations were performed during all analyses to verify instrument calibration. In the course of each analytical sequence, RRFs of several compounds for one or more continuing calibrations failed to meet the contract-required criteria of ± 15 percent difference from the initial calibration RRF. Results for endosulfan II in sediment Sample MRCR-S, DDT in sediment Sample LACO-S, and pentachlorophenol in sediment samples BGDH-S, LSAM-S, MRCR-S, LACO-S, and CNWY-S were qualified as estimated because the associated continuing calibration standard exceeded the control limit. For all other continuing calibration standards where control limits were exceeded, no compounds were detected in the associated samples.

DDT degradation was determined during continuing calibration of organochlorine pesticides. DDT degradation was less than 20 percent in all cases except for the continuing calibration standard associated with samples LACO-S and CNWY-S. DDT degradation in this standard was 33 percent. DDT was detected in Sample LACO-S, and the result was qualified a estimated (E). DDT was not detected in Sample CNWY-S; this result was rejected (R). DDE and DDD were found in both samples. Results were qualified as estimated (E).

Detection Limits

Detection limits for all water analyses met the levels specified in the project QAPP (Table F-4). Detection limits for sediment samples were within project guidelines with the exception of the carbamates. The laboratory reported high levels of interferences in the samples during carbamate analysis, necessitating extra cleanup and dilution of the samples. This resulted in higher than expected detection limits for the sediment carbamate results.

TABLE F-4. DETECTION LIMITS FOR PESTICIDES

Compound	Water (μg/L)	Sediment (Range)[a] (mg/kg)
Azinophos methyl	0.1	0.0073 - 0.019
Chlorpyrifos	0.05	0.0038 - 0.010
Diazinon	0.05	0.0038 - 0.010
Dichlorvos	0.05	0.0038 - 0.010
Disulfoton	0.05	0.0038 - 0.010
Fenamiphos	0.1	0.0073 - 0.019
Malathion	0.05	0.0038 - 0.010
Methyl parathion	0.05	0.0038 - 0.010
Parathion	0.05	0.0038 - 0.010
Phorate	0.05	0.0038 - 0.010
Chloropicrin	0.22	NR[b]
1,3-Dichloropropene	0.22	NR
2,4-D	0.05	0.0015 - 0.0039
Dicamba	0.05	0.0015 - 0.0039
Dinoseb	0.05	0.0015 - 0.0039
Trichlopyr	0.17	0.0019 - 0.0049
Alachlor	1.0	0.044 - 0.13
Atrazine	1.0	0.044 0.13
Hexazinone	1.0	0.044 - 0.13
Prometon	1.0	0.044 - 0.13
Simazine	1.0	0.044 - 0.13
Methomyl	5.0	2.2 - 5.8
Tebuthiuron	2.0	0.2 - 0.6
Bromacil	2.0	0.2 - 0.6
Terbacil	2.0	0.1 - 0.2
Bendiocarb	5.0	0.2 - 0.6
Carbaryl	2.0	0.2 - 0.6
Ciuron	1.0	0.1 - 0.2
Propham	2.0	0.9 - 2.3
Diphenamid	2.0	0.9 - 2.3

TABLE F-4. (Continued)

Compound	Water (μg/L)	Sediment (Range)[a] (mg/kg)
Pronamide	1.0	0.2 - 0.6
Acephate	1.0	NR[b]
Methamidophos	1.0	NR
Gyphosate	5.0	NR
Dichlobenil	NR	0.0018 - 0.0049
Trifluralin	NR	0.0018 - 0.0049
Benfluralin	NR	0.0018 - 0.0049
Lindane	NR	0.0018 - 0.0049
4,4'-DDE	NR	0.0018 - 0.0047
4,4'-DDD	NR	0.0027 - 0.0070
4,4'-DDT	NR	0.0027 - 0.0070
Endosulfan I	NR	0.0018 - 0.0049
Endosulfan II	NR	0.0027 - 0.0070
Fenvalerate	NR	0.0047 - 0.012
Chlordane	NR	0.0093 - 0.025
Pentachlorophenol	NR	0.0008 - 0.0019

[a] Detection limit reported on dry weight basis. Detection limits for sediment samples were adjusted on a sample-by-sample basis to account for percent moisture.

[b] Analysis not required.

ACCURACY

Accuracy was assessed by evaluating recoveries of surrogate compounds. blank spikes, MSs, and MSDs and by the analysis of a standard reference material.

Surrogate Recoveries

To asses the accuracy of organophosphorus pesticide and organochlorine pesticide analyses, surrogate compounds were added to all samples and blanks prior to extraction. Ethyl azinophos was used as a surrogate for the organophosphorus pesticide analysis, and decachlorobiphenyl and dibutylchlorendate were added as surrogates to samples analyzed for organochlorine pesticides. Surrogate recoveries for all samples were within the QAPP guidelines of 50-125 percent, with the exception of the recovery for ethyl azinophos in the 4 September 1990 blank (189 percent) (Table F-5). The laboratory reported that this blank was double-spiked, so the true recovery of ethyl azinophos is 89 percent.

Blank Spike and Matrix Spike Recoveries

Blank spike, MS, and MSD samples were analyzed for all analyses, with the following exceptions. The laboratory did not add phorate to the MS for sample group BGDH-J. An MSD was not analyzed for sample group BGDH-J for organophosphorus pesticides, chlorinated herbicides, triazines, chloropicrin, or 1,3-dichloropropene. No blank spikes were analyzed for glyphosate for any sample group. The recovery of chlorpyrifos was calculated from the total recoveries for chlorpyrifos plus methyl parathion, since chlorpyrifos coeluted with methyl parathion on one column and parathion on the second column.

Percent recoveries for MSs or blank spike for several compounds in each sample group were outside of the QAPP-specified control limits of 50–125 percent (Table F-6). Pentachlorophenol was spiked at a level below the concentration found in the unspiked sample; therefore, the QAPP-specified control limits are not applicable for the MS recovery. No data were qualified because 1) pesticides were not detected in samples for which the associated MS or blank spike had a recovery outside of the control limit, 2) surrogate recoveries were all within PSEP (1989) control limits (organophosphorus pesticides), and 3) results for standard reference material analysis were acceptable (chloropicrin, 1,3-dichloropropene, chlorinated herbicides, and triazines).

TABLE F-5. PERCENT RECOVERY FOR SURROGATE COMPOUNDS FOR ORGANOPHOSPHORUS AND ORGANOCHLORINE PESTICIDES

Sample	Surrogate[a]		
	EAP	DCB	DBC
Blank 6/13	90	--[b]	--
BGDHOC	76	--	--
Blank 9/04	189	--	--
MRCR-1	100	--	--
MRCR-2	115	--	--
MRCR-3	107	--	--
Blank 10/10	70	--	--
SWMP-1	72	--	--
SWMP-2	66	--	--
SWMP-3	70	--	--
Blank 10/22	96	--	--
BGDH01	83	--	--
BGDH02	87	--	--
BGDH03	86	--	--
Blank 11/08	100	89	94
BGDH-S	79	65	64
LSAM-S	63	63	59
MRCR-S	55	86	68
SWMP-S	71	63	61
LACO-S	73	76	62
CNWY-S	80	83	70

[a] EAP - Ethyl azinophos
DCB - Decachlorobiphenyl
DBC - Dibutylchlordendate.

[b] Not required.

TABLE F-6. MATRIX SPIKE RECOVERY DATA FOR PESTICIDES[a]

	Sample Extraction Group																		
	BGDH-J			BGDH-J Re-extract		MERCER			SWAMP			BGDH-0			SEDMNT			SEDMNT with Cleanup	
Compound	MS[b]	MSD[c]	BS[d]	MS	BS	MS	MSD	BS	MS	MSD	BS	MS	MSD	BS	MS	MSD	BS	MS	MSD
Azinophos methyl	90	ND[e]	93	NR[f]	NR	46[g]	52	85	80	67	94	92	80	96	68	68	92	5[g]	4[g]
Chlorpyrifos	ND	ND	ND	NR	NR	83	92	83	94	89	87	105	97	83	71	60	92	49[g]	40[g]
Diazinon	119	ND	93	NR	NR	87	89	83	117	101	90	108	97	95	88	101	84	85	77
Dichlorvos	41[g]	ND	62	NR	NR	36[g]	43[g]	74	76	63	75	48[g]	41[g]	72	38[g]	31	50	13[g]	0[g]
Disulfoton	66	ND	72	NR	NR	60	66	66	85	78	78	71	71	0[g]	100	41[g]	42[g]	61	62
Fenamiphos	89	ND	91	NR	NR	55	53	65	70	64	51	89	86	68	75	69	89	60	48[g]
Malathion	82	ND	90	NR	NR	75	84	90	90	81	88	90	87	100	57	68	92	39[g]	33[g]
Methyl parathion	83	ND	70	NR	NR	78	92	83	88	88	70	94	90	80	53	55	84	28[g]	21[g]
Parathion	93	ND	72	NR	NR	81	91	89	89[g]	88	88	93	93	80	66	59	92	51	54
Phorate	ND	ND	ND	NR	NR	66	66	65	81	66	72	64	68	51	67	63	61	58	50
Chloropicrin	79	ND	70	NR	NR	45[g]	66	66	46[g]	49[g]	49[g]	53	42[g]	25[g]	NR	NR	NR	NR	NR
1,3-Dichloropropene	58	ND	54	NR	NR	61	84	79	30[g]	37[g]	46[g]	33[g]	26[g]	23[g]	NR	NR	NR	NR	NR
2,4-D	82	ND	104	NR	NR	85	83	85	88	106	118	95	86	92	548[g]	1,667[g]	86	NR	NR
Dicamba	89	ND	96	NR	NR	103	108	89	101	120	82	96	89	86	81	81	90	NR	NR
Dinoseb	48[g]	ND	67	NR	NR	56	69	94	96	82	135[g]	163[g]	149[g]	151[g]	38[g]	0[g]	0[g]	NR	NR
Trichlopyr	85	ND	106	NR	NR	93	99	113	40[g]	44[g]	35[g]	84	80	64	49[g]	0[g]	50	NR	NR
Alachlor	87	ND	140[g]	90	90	92	95	100	65	70	70	75	71	71	43[g]	75	107	NR	NR
Atrazine	68	ND	180[g]	69	60	92	94	102	67	67	65	80	85	77	51	67	77	NR	NR
Hexazinone	79	ND	120	88	97	93	101	144[g]	53	53	62	93	90	93	35[g]	45[g]	100	NR	NR
Prometon	82	ND	120	98	100	98	99	120	83	84	110	99	94	83	64	80	88	NR	NR
Simazine	20[g]	ND	53	88	70	84	84	100	73	86	81	124	127[g]	108	121	133[g]	85	NR	NR
Methomyl	76	84	88	NR	NR	102	120	117	76	69	76	92	82	94	104	77	115	NR	NR
Tebuthiuron	75	85	85	NR	NR	115	111	121	96	69	93	70	71	73	91	69	82	NR	NR
Bromacil	77	97	90	NR	NR	113	129[g]	135[g]	113	87	93	81	80	77	75	55	104	NR	NR
Terbacil	80	90	85	NR	NR	108	127[g]	131[g]	103	80	85	98	86	97	62	46[g]	91	NR	NR
Bendiocarb	70	84	84	NR	NR	37[g]	48[g]	10[g]	70	48[g]	5[g]	19[g]	4[g]	35[g]	64	57	13[g]	NR	NR
Carbaryl	80	90	90	NR	NR	74	93	35[g]	87	59	21[g]	38[g]	18[g]	50	62	43[g]	32[g]	NR	NR

TABLE F-6. (Continued)

	Sample Extraction Group																		
	BGDH-J			BGDH-J Re-extract		MERCER			SWAMP			BGDH-0			SEDMNT			SEDMNT with Cleanup	
Compound	MS[b]	MSD[c]	BS[d]	MS	BS	MS	MSD	BS	MS	MSD	BS	MS	MSD	BS	MS	MSD	BS	MS	MSD
Diuron	74	94	80	NR	NR	112	111	136[g]	96	82	93	121	122	98	63	42	97	NR	NR
Propham	70	80	80	NR	NR	81	89	93	60	75	79	74	81	94	66	29	74	NR	NR
Diphenamid	80	85	85	NR	NR	92	112	121	72	69	79	108	110	94	51	44	109	NR	NR
Pronamide	75	90	70	NR	NR	118	123	115	88	76	68	71	86	60	59	0	89	NR	NR
Acephate	120	ND	90	NR	NR	36[g]	4[g]	117	104	106	107	125	107	124	NR	NR	NR	NR	NR
Methamidophos	40[c]	ND	40[c]	NR	NR	81	27	121	95	96	94	97	75	78	NR	NR	NR	NR	NR
Gyphosate	113	ND	ND	NR	NR	102	107	ND	94	86	ND	101	101	ND	NR	NR	NR	NR	NR
Pentachlorphenol	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	156[g]	570[g]	135[g]	NR	NR
Dichlobenil	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	56	54	47[g]	NR	NR
Trifluralin	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	95	91	61	NR	NR
Benfluralin	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	105	99	76	NR	NR
Lindane	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	50	45[g]	73	NR	NR
4,4'-DDE	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	86	80	81	NR	NR
4,4'-DDD	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	80	79	76	NR	NR
4,4'-DDT	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	107	102	109	NR	NR
Endosulfan I	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	77	74	77	NR	NR
Endosulfan II	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	68	62	88	NR	NR
Fenvalerate	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	91	96	122	NR	NR
Chlordane	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	1,046[h]	975[h]	1,128[h]	NR	NR

[a] All values are percent recovery. Percent recovery = $\frac{\text{(measured value - sample concentration)}}{\text{spike added}} \times 100$.

[b] MS - matrix spike.

[c] MSD - matrix spike duplicate.

[d] BS - blank spike.

[e] ND - analysis not performed.

[f] NR - analysis not required.

[g] Results exceeded Puget Sound Estuary Program control limits.

[h] Sample spiked at 10 times reported spike added.

Standard Reference Material

Standard reference samples were extracted and analyzed for chloropicrin and 1,3-dichloropropene (water samples only), chlorinated herbicides, and triazine herbicides (water and sediment samples). Results of all analyses were within 25 percent of the true value (Table F-7).

PRECISION

Precision for pesticides was assessed using the duplicate MS results (Table F-8). The PSEP (1989) control limit of ±50 percent relative percent difference (RPD) between spiked results was not exceeded for pesticides, with the following exceptions. The RPDs for 2,4-D (51 percent), dinoseb (100 percent), trichlopyr (100 percent), pronamide (100 percent), and pentachlorophenol (57 percent) in sample group SEDMNT; for acephate (80 percent) in sample group MERCER; and for bendiocarb (65 percent) in sample group BGDH-0 exceeded PSEP (1989) control limits. Pentachlorophenol was spiked at a level below the concentration found in the unspiked sample; therefore, the QAPP-specified control limits for precision are not applicable. No other pesticides whose RPD exceeded PSEP (1989) control limits were detected in the associated samples, and no data were qualified.

BLANKS

A method blank was prepared and analyzed for each extraction group as required by PSEP (1989). No contaminant was found in any blank.

COMPOUND CONFIRMATION

Chromatograms for all analyses were examined during the quality assurance review to confirm the presence or absence of target compounds. Pesticides detected at concentrations below the detection limit were assigned T qualifiers to indicate that the concentrations are less than the calibrated quantification limit.

TABLE F-7. ANALYTICAL RESULTS FOR PESTICIDES IN STANDARD REFERENCE MATERIALS[a]

Compound	Sample Group			
	BGDH-J	MERCER	BGDH-0/ SWAMP	SEDMNT
Chloropicrin	10.7	-10	--[b]	NR[c]
1,3-Dichloropropene	1.8	-1.7	--	NR
2,4-D	1.5	8	0	0.8
Dicamba	-1	12	5.6	14
Dinoseb	0.8	-10.3	0	8
Trichlopyr	3.5	-14.5	8.7	8.9
Prometon	7	-1	-9.2	10
Atrazine	-13	-1	-5.6	3.5
Simazine	-12	4.1	-10.5	4
Alachlor	8	15	11.4	20
Hexazinone	4	1.3	-3.3	4.5
Pentachlorophenol	NR	NR	NR	8.9

[a] Percent difference from true value.

[b] -- Analysis not performed.

[c] NR - not required.

TABLE F-8. MATRIX SPIKE DUPLICATE ANALYSIS FOR PESTICIDES[a]

	Sample Extraction Group					
Compound	BGDH-J	MERCER	SWAMP	BGDH-0	SEDMNT	SEDMNT with Cleanup
Azinophos methyl	ND[b]	6	9	7	0	11
Chlorpyrifos	ND	5	3	4	8	10
Diazinon	ND	1	7	5	7	5
Dichlorvos	ND	9	9	8	10	100
Disulfoton	ND	5	4	0	42	1
Fenamiphos	ND	2	4	2	4	11
Malathion	ND	6	5	2	9	8
Methyl parathion	ND	8	0	2	2	14
Parathion	ND	6	1	0	6	3
Phorate	ND	0	10	3	3	7
Chloropicrin	ND	19	3	12	NR[c]	NR
1,3-Dichloropropene	ND	16	10	12	NR	NR
2,4-D	ND	1	9	5	51[d]	NR
Dicamba	ND	2	9	4	0	NR
Dinoseb	ND	10	8	4	100[d]	NR
Trichlopyr	ND	3	5	2	100[d]	NR
Alachlor	ND	2	4	3	27	NR
Atrazine	ND	1	0	3	14	NR
Hexazinone	ND	4	0	2	13	NR
Prometon	ND	1	1	3	11	NR
Simazine	ND	0	8	1	5	NR
Methomyl	5	8	5	6	15	NR
Tebuthiuron	6	2	16	1	14	NR
Bromacil	11	7	13	1	15	NR
Terbacil	6	8	13	7	15	NR
Bendiocarb	9	13	19	65[d]	6	NR
Carbaryl	6	11	19	36	18	NR
Diuron	12	0	8	0	20	NR
Propham	7	5	11	5	39	NR
Diphenamid	3	10	2	1	7	NR
Pronamide	9	2	7	10	100[d]	NR
Acephate	NR	80[d]	1	8	NR	NR
Methamidophos	NR	50	1	13	NR	NR
Gyphosate	NR	2	4	0	NR	NR
Pentachlorphenol	NR	NR	NR	NR	57[d]	NR
Dichlobenil	NR	NR	NR	NR	2	NR
Trifluralin	NR	NR	NR	NR	2	NR

TABLE F-8. (Continued)

Compound	Sample Extraction Group					
	BGDH-J	MERCER	SWAMP	BGDH-0	SEDMNT	SEDMNT with Cleanup
Benfluralin	NR	NR	NR	NR	3	NR
Lindane	NR	NR	NR	NR	5	NR
4,4'-DDE	NR	NR	NR	NR	4	NR
4,4'-DDD	NR	NR	NR	NR	1	NR
4,4'-DDT	NR	NR	NR	NR	2	NR
Endosulfan I	NR	NR	NR	NR	2	NR
Endosulfan II	NR	NR	NR	NR	5	NR
Fenvalerate	NR	NR	NR	NR	3	NR
Chlordane	NR	NR	NR	NR	4	NR

[a] All values are relative percent difference.

$$\text{Relative percent difference} = \frac{|\text{matrix spike} - \text{matrix spike duplicate}|}{(\text{matrix spike duplicate})/2} \times 100.$$

[b] ND - analysis not performed.

[c] NR - analysis not required.

[d] Results exceeded Puget Sound Estuary Program control limits.

REFERENCES

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