Total Maximum Daily Load Technical Study: Chlorinated Pesticides and PCBs in the Walla Walla River

Quality Assurance Project Plan

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Washington State Department of Ecology
Environmental Assessment Program
Olympia, Washington

1998 303(d) listings addressed by this project: Walla Walla River; Segment WA-32-1010; 4,4'-DDE, 4,4'-DDD, dieldrin, heptachlor epoxide, hexachlorobenzene, chlordane, and PCB-1260 in edible fish tissue.

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Abstract

The Walla Walla River has been listed by the state of Washington under Section 303(d) of the Clean Water Act for non-attainment of the U.S. Environmental Protection Agency (EPA) human health criteria for 4,4'-DDE, 4,4'-DDD, dieldrin, heptachlor epoxide, hexachlorobenzene, chlordane, and PCB-1260 in edible fish tissue. The listing is based on sampling done by the Washington State Department of Ecology (Ecology) in 1992 and 1993.

EPA requires the states to set priorities for cleaning up 303(d) listed waters and to establish a Total Maximum Daily Load (TMDL) for each. A TMDL entails an analysis of how much of a pollutant load a waterbody can assimilate without violating water quality standards. This Quality Assurance Project Plan describes the technical study that will monitor levels of the above mentioned pesticides and PCBs in the Walla Walla River and form the basis for a proposal to allocate contaminant loads to sources. The study will be conducted by the Ecology Environmental Assessment Program.

Background and Problem Statement

The Walla Walla River has been listed by the state of Washington under Section 303(d) of the Clean Water Act for non-attainment of the U.S. Environmental Protection Agency (EPA) human health criteria for 4,4'-DDE, 4,4'-DDD, dieldrin, heptachlor epoxide, hexachlorobenzene, chlordane, and PCB-1260 in edible fish tissue.* The listing is based on sampling done by the Washington State Department of Ecology (Ecology) in 1992 and 1993 (Davis and Johnson, 1994; Davis et al., 1995). These chlorinated pesticides and polychlorinated biphenyls (PCBs) are no longer used in the United States. A brief summary of their use and regulatory history is provided in Appendix A.

EPA requires the states to set priorities for cleaning up 303(d) listed waters and to establish a Total Maximum Daily Load (TMDL) for each. A TMDL entails an analysis of how much of a pollutant load a waterbody can assimilate without violating water quality standards. This Quality Assurance Project Plan (QAPP) describes the technical study that will monitor levels of the above mentioned pesticides and PCBs (hereafter referred to as chemicals of concern or COCs) in the Walla Walla River and form the basis for a proposal to allocate contaminant loads to sources. The study will be conducted by the Ecology Environmental Assessment Program (EAP).

Basin Description

The Walla Walla River is located in the southeast corner of Washington State (Figure 1). The river extends 61 river miles (r.m.) from the headwaters of its north fork in Oregon to its confluence with the Columbia River in Washington. The drainage basin covers approximately 1,760 square miles and flows through four counties: Umatilla and Wallowa counties in Oregon, and Columbia and Walla Walla counties in Washington. Two-thirds of the drainage basin lies within Washington. Major tributaries include the Touchet River, Dry Creek, Pine Creek, and Mill Creek.

The Walla Walla basin is predominantly rural with few urban areas. The major towns are Walla Walla and College Place, with a combined population of less than 40,000. Starting as early as the 1920s, the principal form of land use was production of small grains, such as wheat and alfalfa, and row crops (Mapes, 1969). By the 1970s, nearly 90% of the Washington portion of the basin had been cultivated. Currently, spring and summer wheat, alfalfa seed and hay, and peas are the largest percentage of the irrigated crops. Other crops include grapes, apples, asparagus, wheat, barley, and onions. Figures 2 and 3 show land use patterns during the mid-1970s and in the late 1980s-to-early 1990s.

Historically, cultivation was a major cause of soil erosion in the Walla Walla basin. Erosion of agricultural soils is the primary route by which chlorinated pesticides may reach surface waters. Studies conducted in the 1960s showed yields of suspended sediment were greatest in the highly cultivated Touchet River and Dry Creek drainage basins, which were contributing up to 80% of the total sediment load to the Walla Walla River (Mapes, 1969). Soils in these two drainages

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* There is a 1998 303(d) fish tissue listing for heptachlor, but that listing is an error. Also, the DDD listing is mistakenly entered as DDT on the 1998 list.

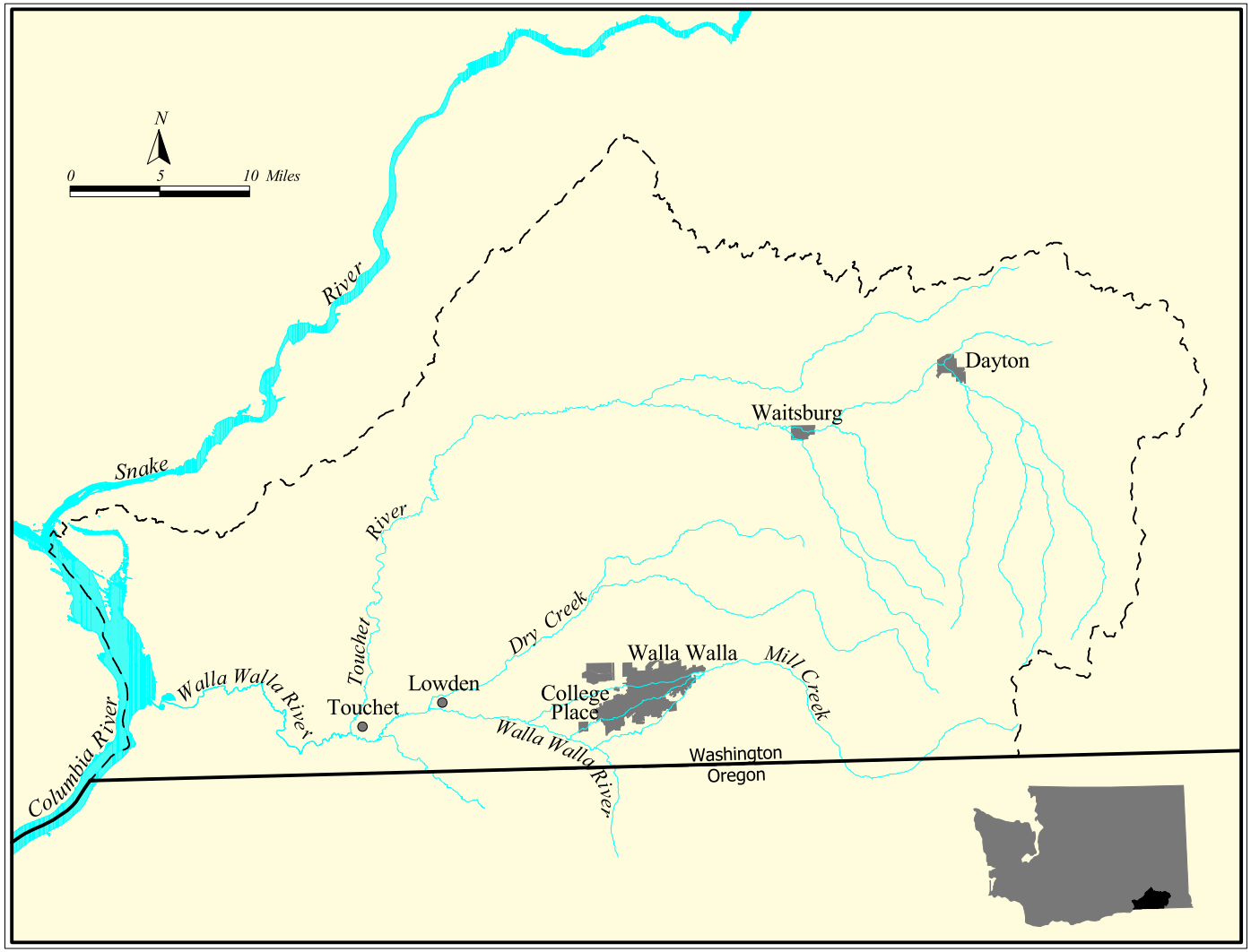

Figure 1. Walla Walla River Basin (R. Coots, EAP)

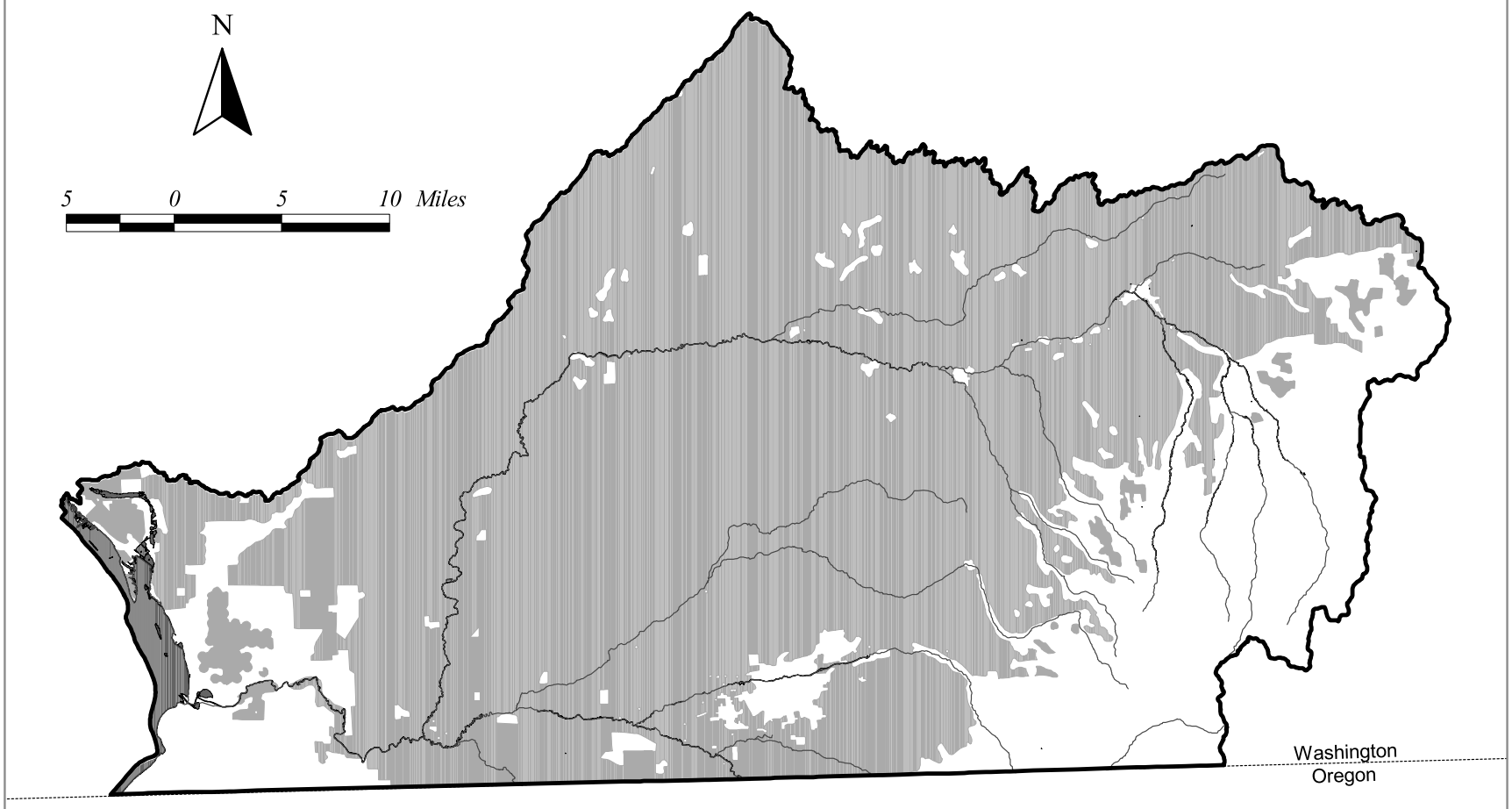

Figure 2. Land Use in the Walla Walla Basin in the Mid-1970's (99% of the shaded area is cropland or pasture)

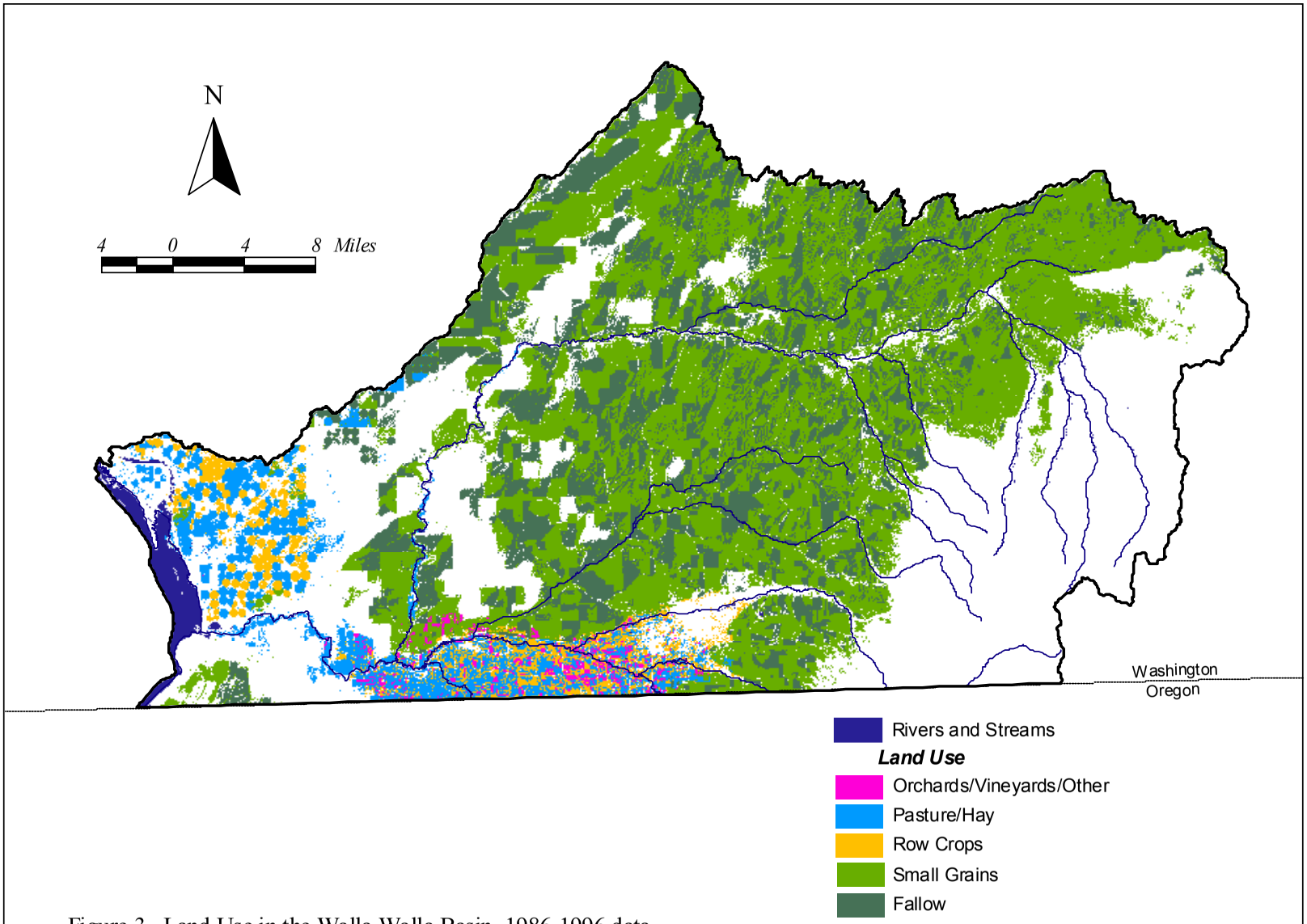

Figure 3. Land Use in the Walla Walla Basin, 1986-1996 data

consist of well-drained silty loams and very fine sandy loams that are highly susceptible to erosion from runoff.

More recently, sprinkler irrigation has replaced flood irrigation methods in much of the Washington portion of the basin (Mike Pellesier, Walla Walla Conservation District, personal communication). As a result, the majority of runoff and erosion occurs from precipitation in winter through early spring, sustained through June by snow melt. Where flood irrigation is practiced, it is primarily on fruit orchards in Oregon (Mike Pellesier, Walla Walla Conservation District, personal communication). The irrigation season in the Walla Walla basin generally extends from mid-April to mid-October.

Silt predominates in the suspended sediment transported by basin streams. Within the TMDL study area, bedload is only about 2-8 percent of the suspended load (Mapes, 1969). Sediment deposition in the mainstem occurs primarily in two areas: a five mile reach between Lowden and Touchet and in the lower ten miles of the river due to backwater effects from McNary Dam on the Columbia River. Otherwise, the river bed is mostly cobble.

The typical flow pattern in the Walla Walla and its tributaries is illustrated in Figure 4. Groundwater springs supply base-flow to surface waters year-round. Infrequent storm events during the winter months sometimes cause severe flooding from heavy rainfall and rapid snowmelt that contribute the highest concentrations of suspended sediments (Mapes, 1969). The river experiences greatly reduced flows in the summer; it has often gone dry at the border. Conditions have improved recently as a result of farmers diverting less water in response to bull trout ESA listings. Flows near the state line now range from 4-15 cubic feet per second (cfs) in the summer (Mike Pellesier, Walla Walla Conservation District, personal communication).

Pesticide/PCB Contamination

The Ecology fish tissue data that resulted in 303(d) listings for the Walla Walla River are summarized in Table 1 and compared to the listing criteria. Each of these samples was a composite formed by pooling tissues from five individual's fish. In order for data to be considered for the 1998 303(d) list, Ecology required at least two single-fish samples or one composite of at least five fish that exceeded EPA human health criteria. Ecology's 303(d) listing criteria are currently being revised.

The 303(d) human health criteria are based on EPA bioconcentration factors (BCF*) and water column criteria established under the EPA National Toxics Rule (40 CFR Part 131). For example, the 32 ug/Kg fish tissue criterion for 4,4'-DDE was calculated by multiplying the water quality criterion of 0.00059 ug/L by a BCF of 53,600 L/Kg. Units of ug/Kg and ug/L are equivalent to parts per billion.

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*BCF= C_t/C_w, where C_t is the contaminant concentration in tissue (wet weight) and C_w is the concentration in water.

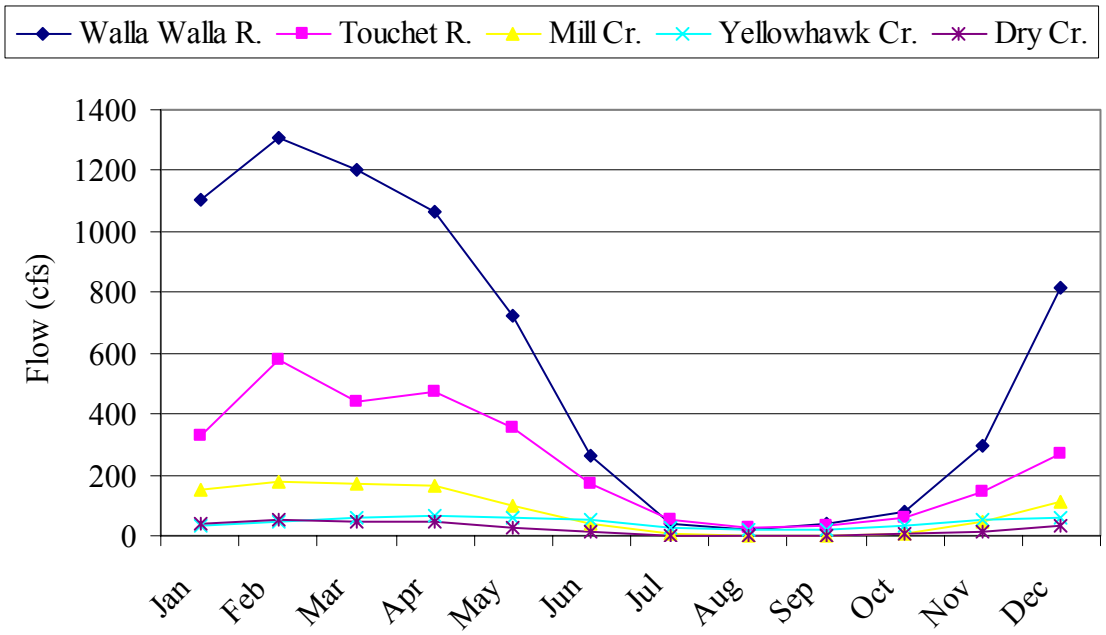


Figure 4. Mean Monthly Flow in the Walla Walla River and Major Tributaries (USGS Data)

Table 1. Summary of Ecology Data on Chlorinated Pesticides and PCBs Detected in Walla Walla River Fish (ug/Kg, wet weight; parts per billion)

Species:	Largescale sucker			White crappie	Common carp	Steelhead	303(d) Listing Criteria[a]
Tissue:	Whole Body	Eggs	Whole Body	Fillet	Fillet	Fillet	
Date:	Sep-92	Sep-92	Sep-93	Sep-92	Sep-93	Sep-93	
4,4'-DDT	26	3.6	15			4.0	32
4,4'-DDE	425	57	338	17	**600**	15	32
4,4'-DDD	51	7.2	49	1.7	**97**	15	45
2,4'-DDT						1.0	
2,4'-DDE	2.9		1.0				
2,4'-DDD	7.0				9.8	1.0	
Total DDT	512	68	403	19	**707**	**36**	32
Dieldrin	5.0		4.5		**10**	**4.0**	0.65
Heptachlor Epoxide	8.3	2.1	3.5	**3.7**	**8.2**	**4.0**	1.2
Hexachlorobenzene	6.9	2.7	8.8	2.1	**20**	4.8	6.7
Cis-Chlordane (Alpha)	4.6	0.8	3.0	0.7	8.0	2.0	
Trans-Chlordane (Gamma)	4.9	0.7	2.7	0.7	8.5	1.0	
Cis-Nonachlor	1.9		2.3		5.0	1.0	
Trans-Nonachlor	10		6.4		13	3.0	
Oxychlordane	2.0		0.8		1.0	1.0	
Total Chlordane	23	1.5	15	1.4	**36**	8.0	31
DCPA (Dacthal)						5.0	
Ethion			3.0		2.0		
DDMU	16	1.9	8.0		15		
Alpha-BHC	0.5						1.7
Gamma-BHC (Lindane)	7.9	2.3	1.0	1.3	1.0	1.0	8.2
PCB - 1254	48	10					5.3
PCB - 1260	90	22	122		300		5.3
Total PCBs	138	32	122		**300**		5.3

Note: Values in bold exceed 303(d) criteria for edible tissue

[a]Based on EPA bioconcentration factors and water column criteria established under the National Toxics Rule (40 CFR Part 131)

EPA used a default lipid (fat) value of 3% to calculate their BCFs. Because chlorinated pesticides and PCBs are preferentially soluble in lipid, the fat-content of a fish can be a major factor in determining tissue concentrations of these compounds. In the NTR, EPA suggests that states may select more appropriate lipid values and BCFs to derive human health criteria that better reflect local conditions and fish species. EPA (2000a) has new procedures for doing so.

Ecology's fish samples were collected during 1992-93 in the lower Walla Walla River. The analysis included 43 chlorinated pesticides or breakdown products and PCB mixtures; only detected compounds are shown in Table 1.

Edible tissues (fillets) were analyzed from three fish species--common carp (*Cyprinus carpio*), steelhead trout (*Oncorhynchus mykiss*), and white crappie (*Pomoxis annularis*). The highest pesticide/PCB residues were found in carp, where 303(d) listing criteria were exceeded by a factor of approximately 10 or more for DDE (a DDT breakdown product), dieldrin, heptachlor epoxide (a heptachlor breakdown product), hexachlorobenzene, and PCBs. Carp also marginally exceeded the total chlordane criterion. There were modest exceedances of the total DDT (DDT+DDE+DDD), dieldrin, and heptachlor epoxide criteria in steelhead. However, these were returning adults, so it is unknown how much contamination can be attributed to time spent in the Walla Walla River. The only criterion exceeded in crappie was for heptachlor epoxide, approximately by a factor of three. All of these chemicals were also detected in whole-body and egg samples from largescale suckers (*Catostomus macrocheilus*) collected in the same area.

Ecology has also analyzed chlorinated pesticides in a limited number of water and sediment samples from the Walla Walla mainstem and tributaries (Tables 2 and 3). PCBs, however, have only been analyzed in fish.

For the most part, the detection limits employed in past water samples have only been appropriate for observing gross contamination and few pesticides have been found. DDT and/or DDE were detected once in Dry Creek and once in Garrison Creek at 0.002 – 0.006 ug/L. A high concentration of aldrin, 0.11 ug/L, was detected once in Yellowhawk Creek. Aldrin rapidly breaks down to dieldrin. These concentrations exceed EPA human health criteria. They also exceed state aquatic life standards for chronic exposure to total DDT (0.001 ug/L) and aldrin/dieldrin (0.0019 ug/L) (Table 4).

More sensitive methods have been used to analyze sediment samples (Johnson, 1997a; White, 1998). Results showed that DDT compounds, hexachlorobenzene, and chlordane were detectable at most sites, with concentrations ranging from 0.45–46 ug/Kg. Dieldrin and heptachlor epoxide were not detected.

Monitoring programs for chemical contaminants in fish tissue routinely include these chemicals. Some perspective on the level of contamination in Walla Walla fish can be gained by comparison to state-wide and national statistics (Table 5). While it is hard to generalize because of the range of concentrations seen in various Walla Walla species, it is apparent that the levels of heptachlor epoxide, hexachlorobenzene, and total chlordane are unusually high for Washington State and for U.S. agricultural areas in general. The DDE and PCB concentrations

Table 2. Summary of Ecology Data on Chlorinated Pesticides Detected in Water Samples from the Walla Walla Drainage (ug/L; ppb)

Date	Chlor. Pesticides Detected	Yellowhawk Creek	Garrison Creek	Mill Creek	Lower Mud Creek	Dry Creek	Pine Creek	Touchet River	Walla Walla River	Reference
May-92	None	na	na	na	na	na	na	na	<0.050	1
Apr-93	None	na	na	na	na	na	na	na	<0.050	2
Jun-93	"	na	na	na	na	na	na	na	<0.050	2
Aug-93	"	<0.050	na	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	2
Oct-93	"	na	na	na	na	na	na	na	<0.050	2
Apr-96	None	<0.048	na	<0.050	<0.049	<0.049	<0.047	<0.050	<0.050	3
Jun-96	4,4'-DDT	<0.050	na	<0.049	<0.050	**0.006**	<0.052	<0.052	<0.053	3
"	Aldrin	**0.11**	na	<0.049	<0.050	<0.050	<0.052	<0.052	<0.053	3
Sep-96	4,4'-DDT	na	**0.002**	na	na	na	na	na	na	4
"	4,4'-DDE	na	**0.002**	na	na	na	na	na	na	4
Apr-97	None	<0.012	na	na	<0.011	<0.012	<0.012	na	na	5
May-97	"	<0.012	na	na	<0.012	<0.012	<0.012	na	na	5

References: 1 = Davis (1993), 2 = Davis and Johnson (1994), 3 = Johnson (1997a), 4 = White et al. (1998), 5 = Johnson (1997b),
na = not analyzed

Table 3. Summary of Ecology Data on Chlorinated Pesticides Detected in Sediment Samples from the Walla Walla Drainage (ug/Kg, dry weight; parts per billion)

Location:	Yellowhawk Creek	Garrison Creek	Mill Creek	Lower Mud Creek	Dry Creek	Pine Creek	Touchet River	Walla Walla River
Date:	Jun-96	Aug-96	Jun-96	Jun-96	Jun-96	Jun-96	Jun-96	Jun-96
4,4'-DDT	3.0	1.2	1.8	1.2	<1.1	1.9	0.69 J	1.2
4,4'-DDE	2.7	30	3.3	6.6	5.0	4.2	3.1	7.6
4,4'-DDD	0.61	12	0.76	2.5	0.99	0.77	0.83	1.8
Total DDT	6.3	43	5.9	10.3	6.0	6.9	4.6	10.6
Dieldrin	<3.7	nd	<4.5	<5.3	<4.3	<3.9	<4.2	<4.6
Heptachlor epoxide	<1.2	nd	<1.5	<1.8	<1.4	<1.3	<1.4	<1.5
Hexachlorobenzene	0.49	2.7	0.45	0.89	3.7	1.2	1.4	2.0
Chlordane (technical)	1.7	46	3.5	<18	3.0 J	1.5	<14	3.0
Gamma BHC (Lindane)	0.74	nd	0.91	0.89	3.7	0.9	0.56	0.80
Total organic carbon (%)	0.3	na	1.5	1.4	0.8	0.6	0.8	9.2

data from Johnson (1997a) and White et al. (1998)
nd = not detected
na = not analyzed

Table 4. Applicable Water Quality Criteria (ug/L; parts per billion)

	Washington State Aquatic Life Standards[a]		EPA Aquatic Life Criteria[b]		EPA Human Health Criteria[c]		EPA Biocon-centration Factor
	Acute	Chronic	Acute	Chronic	Water + Organisms	Organisms Only	
4,4'-DDT			1.1	0.001	0.00059	0.00059	53,600
4,4'-DDE					0.00059	0.00059	53,600
4,4'-DDD					0.00083	0.00084	53,600
Total DDT	1.1	0.001					- -
Dieldrin	2.5	0.0019	0.24	0.056	0.00014	0.00014	4,670
Heptachlor	0.52	0.0038	0.52	0.0038	0.00021	0.00021	11,200
Heptachlor epoxide			0.52	0.0038	0.0001	0.00011	11,200
Hexachlorobenzene					0.00075	0.00077	8,690
Total chlordane	2.4	0.0043	2.4	0.0043	0.0021	0.0022	14,100
PCBs	2.0	0.014		0.014	0.00017	0.00017	31,200

[a]Chapter 173-201A (11/18/97 update)
[b]EPA (1999)
[c]EPA National Toxics Rule

Table 5. State-wide and National Data on Chlorinated Pesticides/PCBs in Freshwater Fish Tissue (ug/Kg, wet weight; parts per billion)

	4,4'-DDE	Dieldrin	Heptachlor epoxide	Hexachloro-benzene	Total chlordane	Total PCBs
	Fillet Samples					
Washington State						
mean	266	3.9	0.6	0.9	2.2	67
85th percentile	500	10	nd	1.0	4.0	120
maximum	2,406	50	8.2*	20*	36*	720
	Fillet and Whole-Body Samples					
National U.S.						
background mean	56	14	1.6	0.6	5.2	47
industrial/urban mean	602	18	1.3	32	33	1,278
agricultural mean	1,527	44	0.6	2.1	17	97

as summarized in Davis and Serdar (1996)
*Walla Walla River
nd = not detected

measured in Walla Walla suckers and carp are at or above the 85th percentile for Washington. Dieldrin concentrations are slightly higher than the state average.

Problem Statement: The problem to be addressed in the TMDL technical study is to determine what COC loadings to the Walla Walla River will result in edible fish tissue meeting EPA human health criteria.

Project Description

The primary goals of this study are to: 1) quantify COC concentrations and loadings in the Walla Walla main stem, its major tributaries, and significant point sources; 2) recommend numerical water quality targets that will result in fish meeting EPA human health criteria; and 3) propose load allocations to meet the targets. In pursuit of these goals, sufficient data will be obtained to allow an assessment of human health risk from fish consumption, and benchmarks will be established to gauge future improvements in water quality. The Washington State Department of Health (WDOH) has tentatively agreed to review Ecology's fish tissue sampling plan and analyze the resulting data to determine if there is need for a fish advisory (Dave McBride, Office of Environmental Health Assessments, personal communication).

The study area will include the main stem Walla Walla River and its tributaries from the Oregon border (r.m. 40) to the Columbia River. Tributary sampling will be limited to sites at or near their mouths, except for upper Mill Creek and selected point sources. Field work will be conducted from May 2002 through March 2003.

The objectives of the study will be as follows:

1) Obtain representative data on water column concentrations of COCs, ancillary parameters, and flow in the main stem and major tributaries.
2) Investigate NPDES* discharges that are potential COC sources to the river.
3) Obtain a reliable estimate of mean COC concentrations and lipid content in the edible tissues of main stem fish species most frequently consumed.
4) Use the water and fish tissue data in conjunction with other information to select appropriate numerical water quality targets for the COCs.
5) Evaluate the correlation between DDT compounds, total suspended solids (TSS), and turbidity as a possible means of setting water quality targets.
6) Determine the river's loading capacity for COCs and propose load allocations for point sources, nonpoint sources, and background.
7) Incorporate the above data and analysis into a report that addresses the TMDL elements required by EPA Region 10, i.e., scope of the TMDL, applicable water quality standards, numerical targets, loading capacity, wasteload and load allocations, margin of safety, seasonal variation, and monitoring plan.

*National Pollution Discharge Elimination System

Sampling Design

Water Samples

The purpose of the water sampling is to: 1) identify sources of COCs; 2) assess compliance with aquatic life and human health criteria; 3) test for relationships between total DDT, TSS, and turbidity; and 4) calculate loadings to and within the river.

Semipermeable Membrane Devices - Water column concentrations of COCs in the Walla Walla drainage are poorly known but are expected to be low especially for those chemicals found at the lowest levels in fish samples.

EAP did some recent sampling in an effort to better quantify chemical concentrations in the water column. One sample each was collected from the lower Walla Walla River (Cummins Bridge Road) and the mouth of Mill Creek on January 16, 2002. The samples were analyzed at the Ecology Manchester Environmental Laboratory using a new large volume injection technique; the results are summarized in Table 6.

4,4'-DDE, dieldrin, and hexachlorobenzene were detected at both locations in concentrations ranging from 0.000043 to 0.00015 ug/L (43-150 parts per quadrillion). DDT and DDD peaks were observed in the samples but concentrations were below the practical quantitation limit (Myrna Mandjikov, personal communication). None of the other target pesticides were detected at detection limits of 0.000069 ug/L. PCBs were not detectable at or above 0.0017 ug/L. Judging from antecedent weather conditions, runoff from agricultural land was probably minimal at the time these samples were collected, so the results may represent a worst-case situation for detecting these chemicals.

In light of the low water column concentrations anticipated for the study area, the use of a semipermeable membrane device (SPMD) is proposed as a means of reliably detecting and quantifying the chemicals of interest. SPMDs are passive samplers that mimic the biological uptake of organic compounds. The device proposed for the present study was developed by the U.S. Geological Survey (USGS), Columbia Environmental Research Center and is now of standardized design, patented, and commercially available through Environmental Sampling Technologies (EST), St. Joseph, Missouri (http://www.spmds.com). Details of SPMD theory, construction, and application can be found at http://wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm. EAP has had limited but successful experience using SPMDs to sample PCBs in the Spokane River (EILS, 1995).

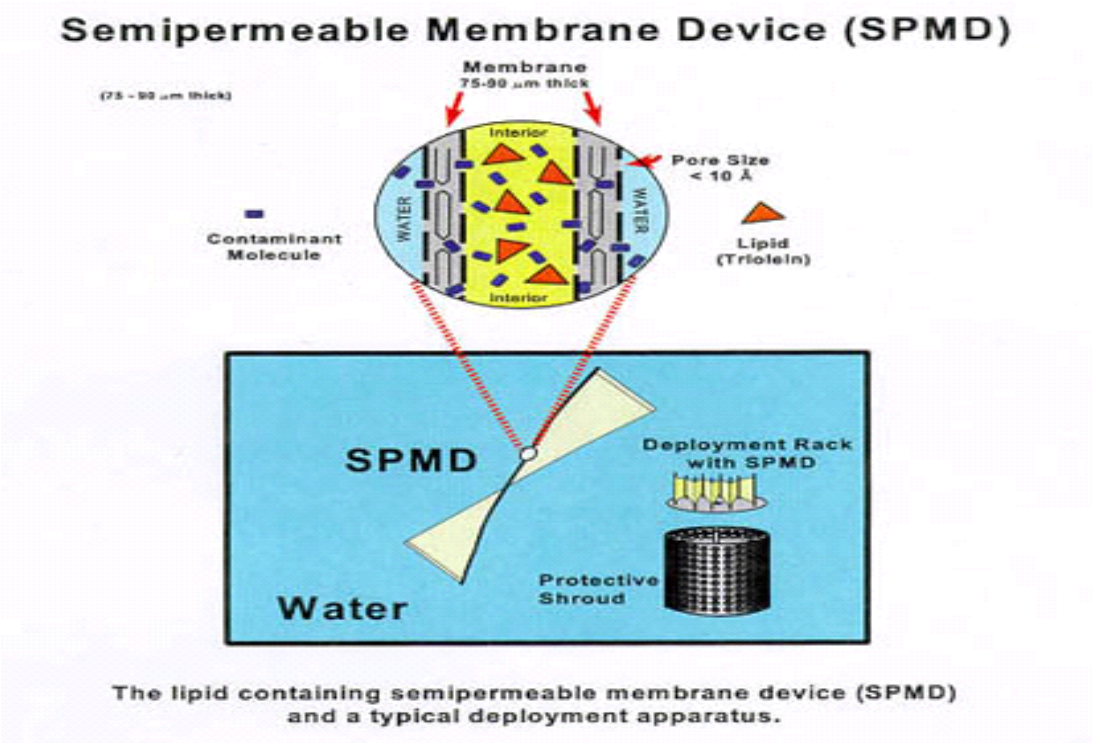
Each SPMD is composed of a thin-walled, layflat polyethylene tube (91 x 2.5 cm) filled with triolein, the major neutral lipid in fish (Figure 5). When placed in water, dissolved lipophilic organic compounds diffuse through the membrane and are concentrated over time. The typical deployment period is 20-30 days. The SPMDs are then extracted and analyzed for the chemicals of interest.

A combination of laboratory calibration data and Permeability/Performance Reference Compounds (PRCs) in deployed SPMDs is used in conjunction with field temperature to obtain

Table 6. Results of a Low-Level Analysis for Chlorinated Pesticides and PCBs in the Walla Walla River and Mill Creek (ug/L; parts per billion)

Location:	Walla Walla River	Mill Creek
Date:	16-Jan-02	16-Jan-02
4,4'-DDT	0.000069 U	0.000066 U
4,4'-DDE	**0.00015**	**0.000075**
4,4'-DDD	0.000069 U	0.000066 U
Dieldrin	**0.00013** NJ	**0.00014** NJ
Heptachlor	0.000069 U	0.000066 U
Heptachlor Epoxide	0.000069 U	0.000066 U
Hexachlorobenzene	**0.000052** NJ	**0.000043** NJ
Cis-Chlordane	0.000069 U	0.000066 U
Trans-Chlordane	0.000069 U	0.000066 U
Cis-Nonachlor	0.000069 U	0.000066 U
Trans-Nonachlor	0.000069 U	0.000066 U
Oxychlordane	0.000069 U	0.000066 U
PCB-1016	0.0017 U	0.0016 U
PCB-1221	0.0017 U	0.0016 U
PCB-1232	0.0017 U	0.0016 U
PCB-1242	0.0017 U	0.0016 U
PCB-1248	0.0017 U	0.0016 U
PCB-1254	0.0017 U	0.0016 U
PCB-1260	0.0017 U	0.0016 U

unpublished Ecology data
U = not detected at or above reported value
NJ = evidence that the analyte is present; numerical results is an estimate



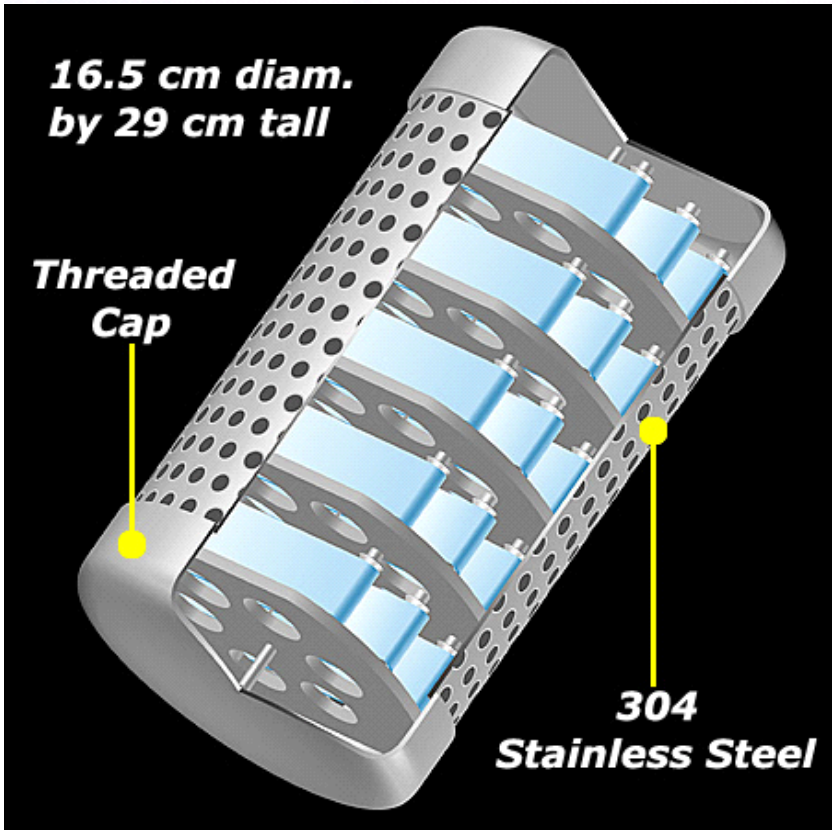


Figure 5. SPMD and Deployment Device

an estimate of average dissolved concentrations. A SPMD will effectively sample 0.5–10 liters of water per day, depending on the compound in question.

SPMDs provide a time-weighted average concentration for the chemicals of interest and only measure the dissolved and, therefore, readily bioavailable fraction. Studies have shown the results are comparable to other low-level sampling methods such as liquid-liquid extraction and solid-phase extraction (Ellis et al., 1995; Rantalainen et al, 1998). Results from all of these methods are subject to uncertainty, but the other methods have the added drawbacks of being time consuming, expensive, and only providing a single point measurement. Disadvantages of SPMDs include the potential for losing them in field studies and the fact that determination of a total water concentration must rely on calculations based on theoretical partitioning between the dissolved and particulate form of a chemical.

USGS recently used SPMDs to quantify chlorinated pesticides and PCBs in the Columbia River drainage (McCarthy and Gale, 1999). To improve sensitivity, five SPMDs were deployed at each sampling site and the extracts pooled. Table 7 shows the USGS data for sites in the general vicinity of the Walla Walla River. With the exception of DDT compounds and one PCB result, all concentrations were less than 0.001 ug/L.

For the Walla Walla TMDL, SPMDs will be deployed at the ten locations listed in Table 8 and shown in Figure 6. The six tributaries being monitored--Touchet River, Pine Creek, Dry Creek, Mill Creek, Garrison Creek, and Yellowhawk Creek--represent over 85% of the river's drainage area in Washington. They include the major TSS sources (Touchet River and Dry Creek) and the two major urban streams (Mill and Garrison creeks). A sampling site will also be established on upper Mill Creek to determine COC levels in drainage from forested vs. agricultural land and to establish background water quality for Mill, Garrison, and Yellowhawk creeks. The main stem will be monitored at the Oregon border, approximately midway downstream below Mill Creek, and near the mouth. The lower Walla Walla site is an Ecology long-term water quality monitoring station.

SPMDs will be deployed quarterly for a period of approximately 28 days each as indicated in Figure 7. The deployments are timed to provide representative data over the range of flow conditions that normally occur in the drainage. There will be two deployments during the irrigation season, one each in the first and second half (summer low flow); one deployment during the rising flows of fall and early winter; and one deployment during late winter peak flows. The SPMD extracts will be analyzed for all COCs, with PCBs being analyzed as Aroclor-equivalents*.

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* In the United States, PCBs were primarily manufactured and sold under the trade name Aroclors. PCBs are typically analyzed as equivalent concentrations of commercial Aroclor mixtures (e.g., PCB-1260) or as individual compounds, referred to as PCB congeners.

Table 7. Selected USGS SPMD Data on Organochlorine Concentrations in the Columbia River Drainage (estimated dissolved concentrations in ug/L; parts per billion)

	Wenatchee River	Lower Crab Creek	Columbia River @ Vernita	Yakima River	Columbia River @ Umatilla
4,4'-DDT	nd	nd	nd	nd	nd
4,4'-DDE	0.0006	nd	0.001	0.002	0.0002
4,4'-DDD	0.0002	nd	0.001	0.0006	0.0002
Dieldrin	nd	0.00009	0.00003	0.0006	0.00003
Heptachlor	nd	nd	nd	nd	nd
Heptachlor epoxide	nd	nd	nd	0.00002	0.00001
Hexachlorobenzene	nd	nd	0.00007	0.00005	0.00007
cis-Chlordane	0.0001	0.00004	0.0002	0.0001	0.00004
trans-Chlordane	nd	nd	nd	0.00003	nd
cis-Nonachlor	nd	nd	nd	0.00003	nd
trans-Nonachlor	nd	nd	nd	0.00005	nd
Oxychlordane	nd	nd	nd	nd	nd
Total PCBs	0.003	0.00004	0.0008	0.0004	0.0001

from McCarthy and Gale (1999)
nd = not detected

Table 8. Water Quality Sampling Sites in the Walla Walla Drainage

Sampling Site	River Mile	Drainage Area (sq. miles)
Walla Walla River @ Peppers Bridge	39.6	~193
Yellowhawk Creek @ Old Milton Highway	37.9	70
Garrison Creek @ Mission Rd.	36.1	?
Mill Creek @ Mission Rd.	33.6	96
Mill Creek @ Seven Mile Rd.	- -	?
Walla Walla River @ Detour Rd.	32.9	~328
Dry Creek @ Highway 12 Bridge	27.2	246
Pine Creek @ Sand Pit Rd.	23.4	170
Touchet River @ Highway 12 Bridge	21.6	747
Walla Walla River @ Cummins Bridge Rd.[1]	15.3	1690

[1]Ecology ambient station 32A070

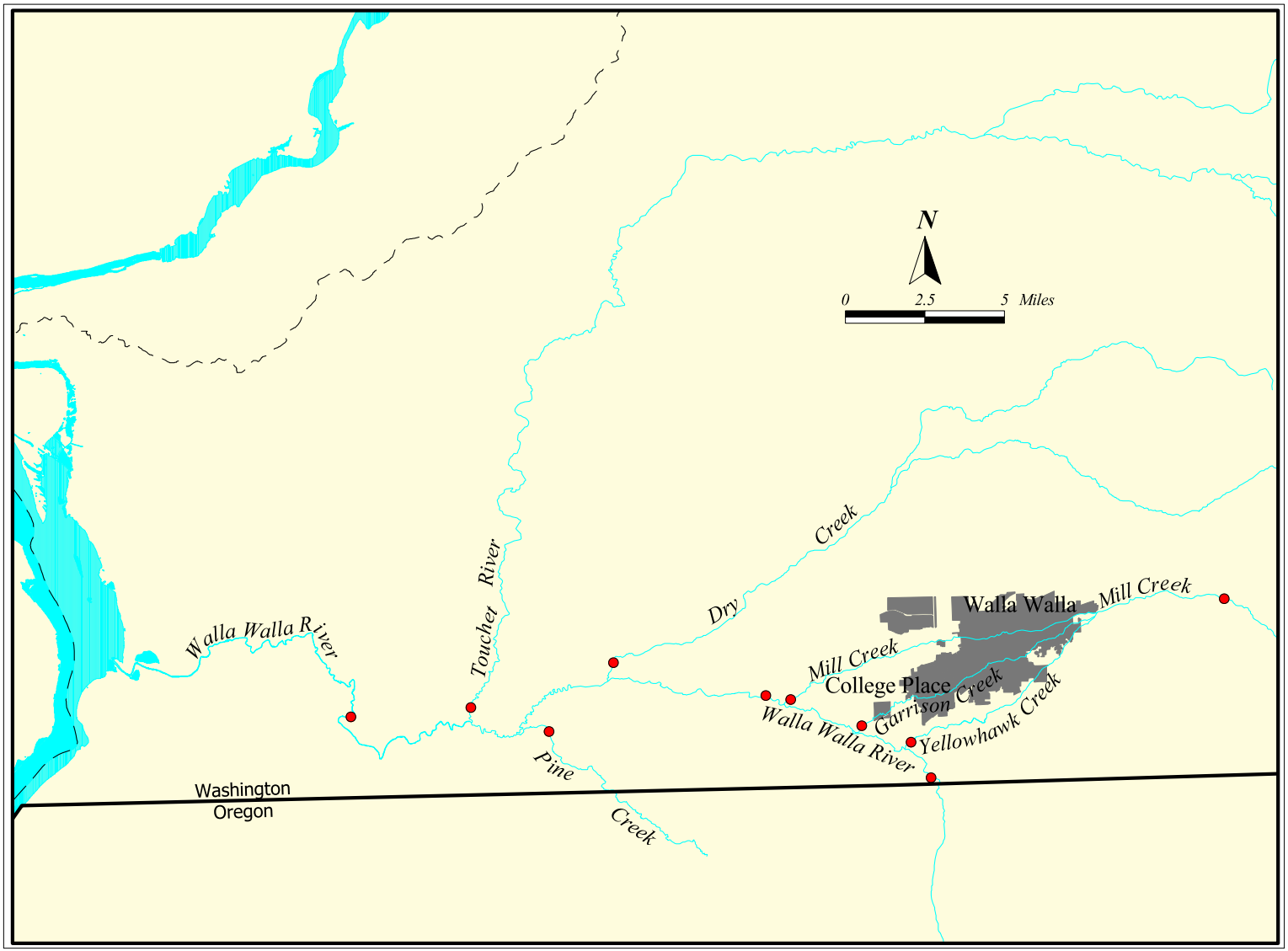

Figure 6. Location of Water Quality Monitoring Sites (R. Coots, EAP)

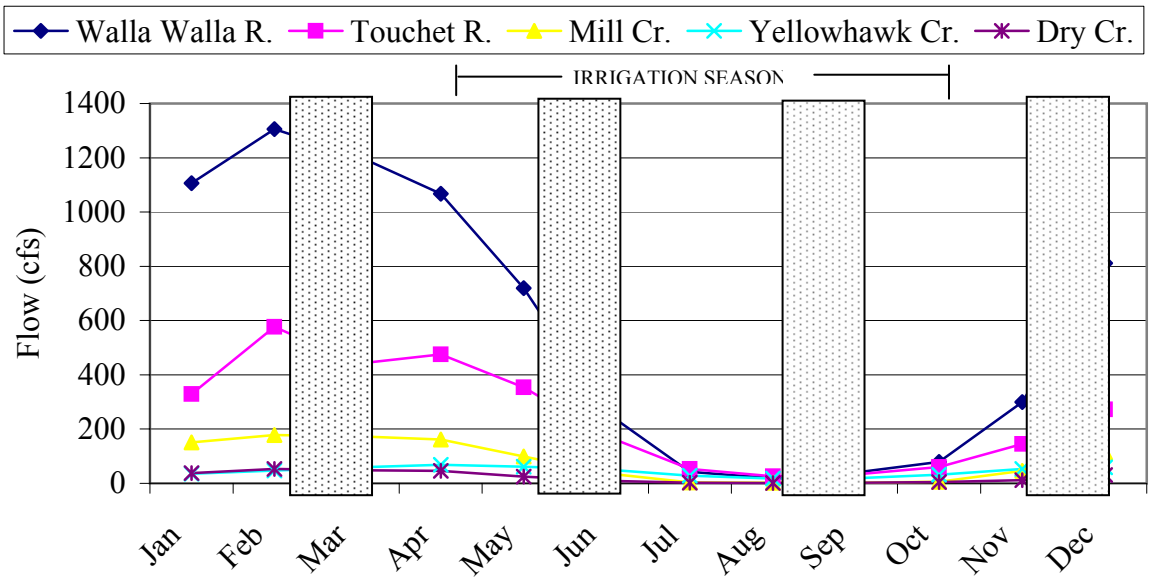

Figure 7. Average Flow Patterns in the Walla Walla Drainage, with Shaded Areas Indicating Periods When SPMD Samplers Will be Deployed (starting in May 2002)

Temperature will be monitored continuously during deployment. At the beginning, middle, and end of each deployment period, ancillary data will be obtained on TSS, turbidity, total organic carbon (TOC), and conductivity. Flow data will be obtained through the EAP Stream Hydrology Unit, USGS, or gauged in the field.

DDT/TSS/Turbidity Relationships - The National Research Council (2001) suggests using statistical regression of a water quality indicator on one or more predictor variables as a simple and potentially useful model for developing TMDLs. This approach has been used successfully in the lower Yakima River (Joy and Patterson, 1997) but more recently gave equivocal results in the upper Yakima (Joy and Dickes, 2002). For the lower river, Joy and Patterson were able to correlate total DDT with TSS (Figure 8) and set targets for TSS reduction to meet DDT water quality criteria for aquatic life. TSS was, in turn, linked to the state turbidity standard and fish habitat.

Setting water quality targets based on TSS and turbidity has the advantage of translating more directly into land use practices and being easier to measure than targets based on trace chemical concentrations. Therefore, data will be obtained to test this relationship in the Walla Walla drainage. Once each quarter, depth-width integrated samples for DDT compounds (4,4'- DDT, -DDE, and –DDD) will be collected at each of the SPMD deployment sites in conjunction with the TSS, turbidity, TOC, and conductivity samples. Low detection limits will be achieved for DDT compounds by using large volume injection. The first quarter's samples will be screened for all pesticide COCs to determine the value of analyzing these other compounds.

Since all the COCs absorb strongly to the organic carbon in particulate matter and since DDT compounds are the COCs present in the highest concentrations in the Walla Walla system, setting a water quality target linked to total DDT would also effectively reduce concentrations of other chlorinated pesticides in the drainage. PCBs would be reduced only to the extent that the sources are the same.

After the second quarter's samples have been analyzed, the data will be examined for evidence of significant correlations between DDT, TSS, and turbidity. If the correlations are weak, this part of the study would be terminated.

NPDES Discharges - The Walla Walla and College Place Wastewater Treatment Plants (WWTPs) will be evaluated as possible COC sources. The Walla Walla plant (9.6 million gallons per day--mgd) discharges to Mill Creek and the College Place plant (1.6 mgd) discharges to Garrison Creek (Figure 9).

The city of Walla Walla is authorized to discharge treated and disinfected effluent to Mill Creek from December 1 through April 30 each year, subject to the effluent limits and conditions of its NPDES permit. The city is required by a 1927 court order to deliver up to 7.9 mgd of treated and disinfected wastewater to the Gose and Blallock Irrigation Districts from May 1 through November 30. The NPDES permit allows diversion of the effluent to the irrigation districts from April 15 through December 15. The irrigation districts can choose to use the effluent or divert it to Mill Creek.

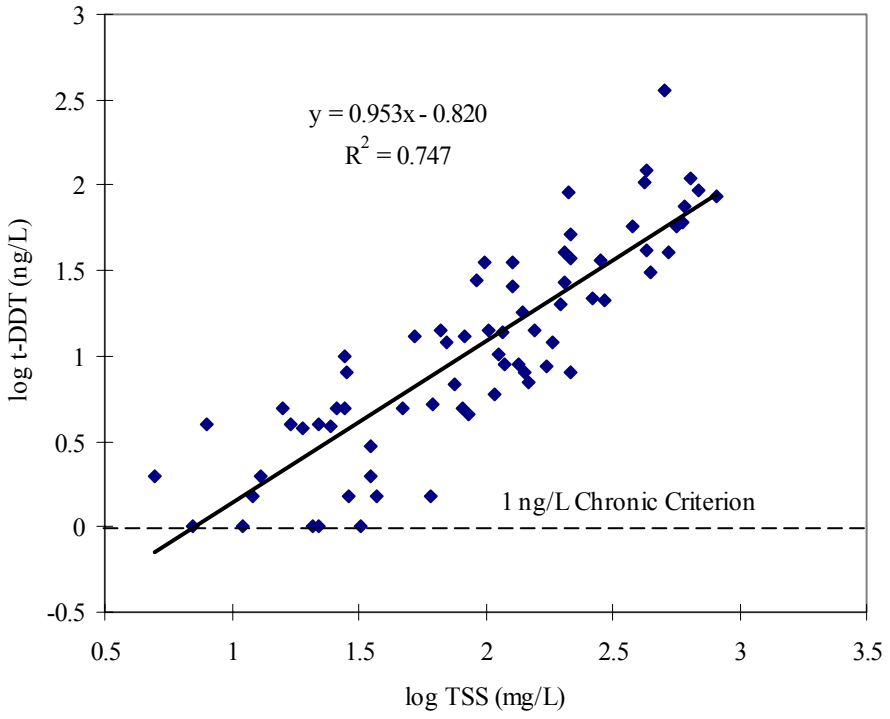

Figure 8. Total DDT:TSS Correlation for the Lower Yakima River (from Joy and Patterson, 1997; 1 ng/L = .001 ug/L)

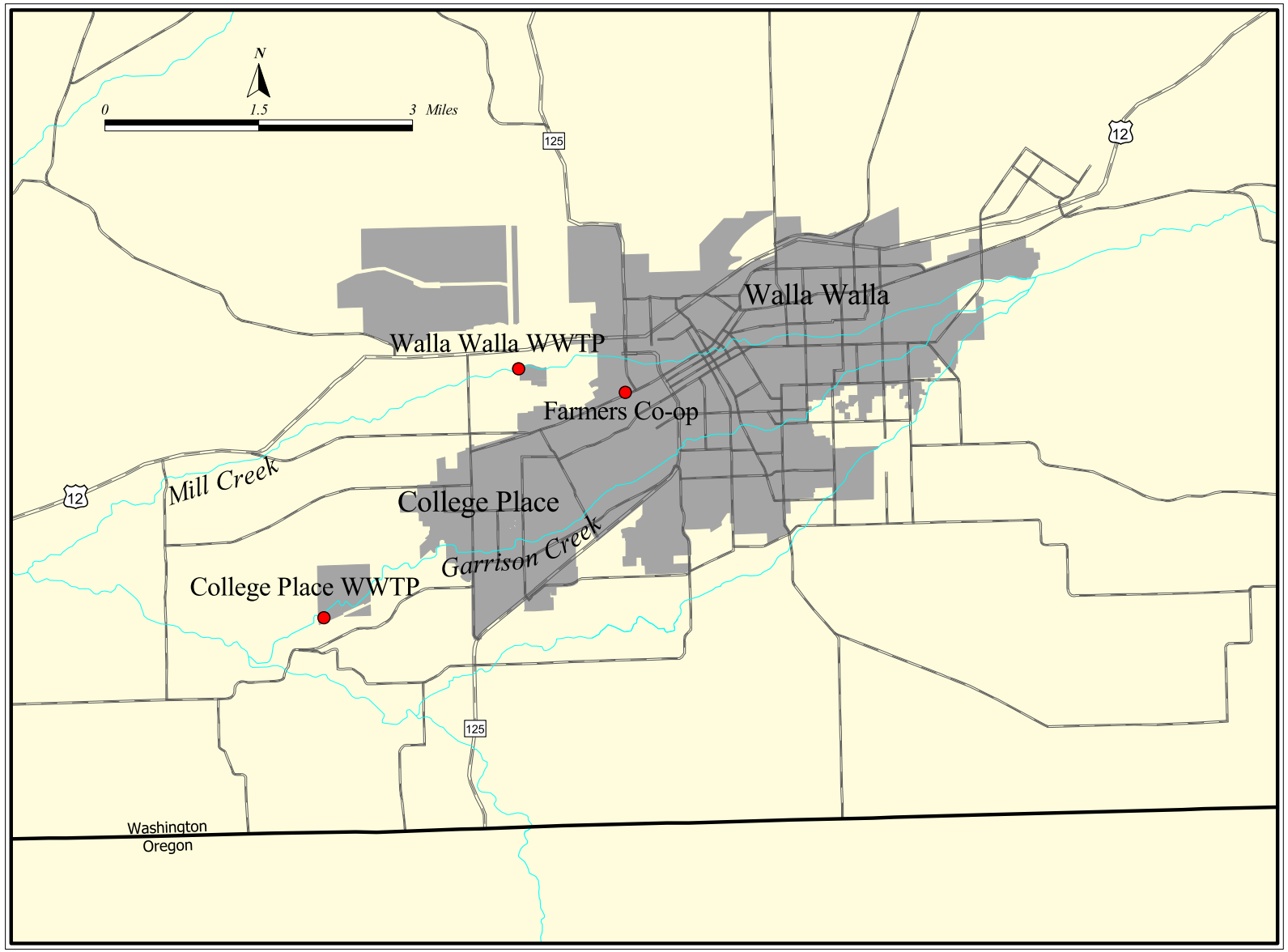

Figure 9. Locations of Walla Walla WWTP, College Place WWTP, and Walla Walla Farmer's Co-op (R. Coots, EAP)

College Place effluent is discharged during the summer period (May through October) through wetlands prior to discharge into Garrison Creek. November through April the effluent is discharged directed to Garrison Creek.

There are two other WWTPs in the basin, Dayton and Waitsburg, but these are small discharges (< 1 mgd) located over 40 miles up the Touchet River and not likely to be significant sources for the Walla Walla River. In the opinion of Ecology Eastern Regional Office (ERO), industries and other NDPES facilities in the Walla Walla basin are not COC sources (Pat Hallinan, Jerry Anderson, personal communication).

Composite effluent samples will be collected over a two-day period from the Walla Walla and College Place WWTPs. Effluent data obtained by EAP for other WWTPs has shown only minor variations in PCB concentrations over a two-day period (Golding, 2002). Sampling will be done once per quarter, near the midpoint of the SPMD deployment period. Each sample will be analyzed for COCs, TSS, and conductivity. Low detection limits will be achieved by using large volume injection for chlorinated pesticides and high-resolution GC/MS for individual PCB congeners.

Fish Tissue Samples

The purpose of the fish tissue samples is to: 1) determine which of the COCs detected in 1992-93 continue to exceed 303(d) listing criteria; 2) assess appropriateness of the EPA human health water quality criteria for the Walla Walla River; and 3) provide data to WDOH for a human health assessment.

Washington State Department of Fish & Wildlife (WDFW) biologists in the Walla Walla area were contacted for information on sport and subsistence fishing on the river. Results of these discussions are summarized in Table 9.

Table 9. Fisheries Information for Resident Walla Walla Species (notes from discussion with G. Mendel and M. Birely, WDFW)

Species	**Range**	**Season and locations fished**	**Spawn season**	**Size and bag limits**
Smallmouth bass*	Several miles downstream of Mill Creek to the Columbia and in Touchet upstream to Dayton	Fished in the late Spring/early Summer from the mouth of the Touchet to the Columbia	Spring	No min. size/ 5 per day
Common carp*	In the Walla Walla from the mouth of Mill Creek to the Columbia River and a short distance up the Touchet	Fished from April through June in the shallow delta at the mouth of the Walla Walla River (fish caught in the delta are probably resident to the lower part of the Walla Walla River delta). Local fishing places: between Burbank and Walulla (Casey pond)	Spring	No min. size or limit
Channel catfish*	From the mouth of the Touchet out to the Columbia	Fished in late Spring/early Summer (particularly night fishing in the Summer) from the mouth of the Touchet out to the Columbia. Local fishing places: at old abandoned highway bridge, below Little Goose Dam and Lion's Ferry State Park, highway 12 off of Walulla Game Department Road	Spring/early Summer	12" min. size/ 5 per day
Largescale/ Bridgelip Suckers	From the State line to the Columbia River and up the Touchet to Dayton	From the State line to the Columbia River and up the Touchet to Dayton; not really fished	Spring/early Summer	No min. size or limit
Brown/ Black bullheads*	From the mouth of the Touchet out to the Columbia, but since they are a reservoir-type fish, adult fish are probably found more often near the mouth of the Walla Walla River	Fished in Spring/early Summer (and Fall?) from the mouth of the Touchet out to the Columbia River. Fished in many of the same local places as channel catfish.	Spring/early Summer	No min. size or limit
White crappie*	From the mouth of the Touchet out to the Columbia (mainly near the mouth of the Walla Walla)	Found in low abundance, so aren't fished for much. A few are caught locally near the old abandoned highway bridge.	Spring/early Summer	No min. size or limit
Crayfish*	In Mill Creek near city of Walla Walla and in streams throughout the basin with a rocky bottom	Some immigrants have been found fishing for them in Mill Creek. Are found on rocky stream bottoms, probably not too many near the mouth of the Walla Walla (Legal fishery open from May through Summer)	unknown	2 pots per day

* = Consumption fish in the Walla Walla River, underlined species are the main non-salmonid fisheries.

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According to WDFW, the resident species most frequently consumed are smallmouth bass (*Micropterus dolomieui*), channel catfish (*Ictalurus punctatus*), and carp. The fish tissue analyses will therefore focus on these species. There is also some consumption of crayfish, but studies have demonstrated that crayfish muscle has a very low potential to accumulate chlorinated pesticides or PCBs, probably due to its low lipid content (Serdar et al., 1999; EILS, 1995).

The Confederated Tribes of the Umatilla Indian Reservation (CTUIR) were also contacted to determine if the Washington portion of the Walla Walla River is an important source of fish for tribal members. There is evidence that Tribal elders and members have eaten the above-mentioned fish species in the past. There is suspected current use by tribal members, although there is no written documentation. It is expected that use will increase once flows are restored and other traditional anadromous species are returned to the river. This is expected to bring tribal members back to the area more regularly; in which case, these other species would be harvested more frequently as well. (Terry Shepard, personal communication).

Salmonids that inhabit the Walla Walla drainage include steelhead, spring chinook, and bull trout. These species will not be sampled because they are migratory, threatened, and/or endangered. Rainbow trout and whitefish occur in the study area but legal size rainbow are rare and the whitefish density is low (Mendel et al., 2001).

Within the main stem, bass and catfish are primarily found between the mouth of the Walla Walla and the Touchet River. Carp occur from the mouth to the state line. As previously mentioned, the Touchet River and nearby Dry Creek transport most of the sediment load discharged from the basin. Inputs of sediments and associated contaminants from these two rivers have the potential to result in substantially different levels of contamination between upper and lower river fish. Therefore, separate specimens for COC analysis will be obtained from the upper and lower river, using the Touchet River-Dry Creek reach as an approximate dividing line (Figure 10).

Bass, catfish, and carp will be collected downstream of the Touchet from approximately r.m. 21 to r.m. 8. Samples closer to the confluence with the Columbia are being avoided in an effort to obtain data representative of the Walla Walla River. Carp and a second consumed species, if encountered, will be collected in the reach between Dry Creek and the Oregon border. Large-scale or bridgelip suckers, although apparently of minor importance, are the most likely second species to be analyzed from the upper river. The sampling will be done in June to correspond with the peak harvest period (Table 9).

Fillets from these fish will be analyzed for COCs, percent lipids, and percent solids. Composite sampling will be used to obtain a cost efficient estimate of mean COC concentrations. The lipid data are needed to assess the bioconcentration potential of each species and may be useful for between-species or between-site comparisons. PCBs will be analyzed as Aroclor-equivalents, with one composite from each species from each location being analyzed for individual PCB

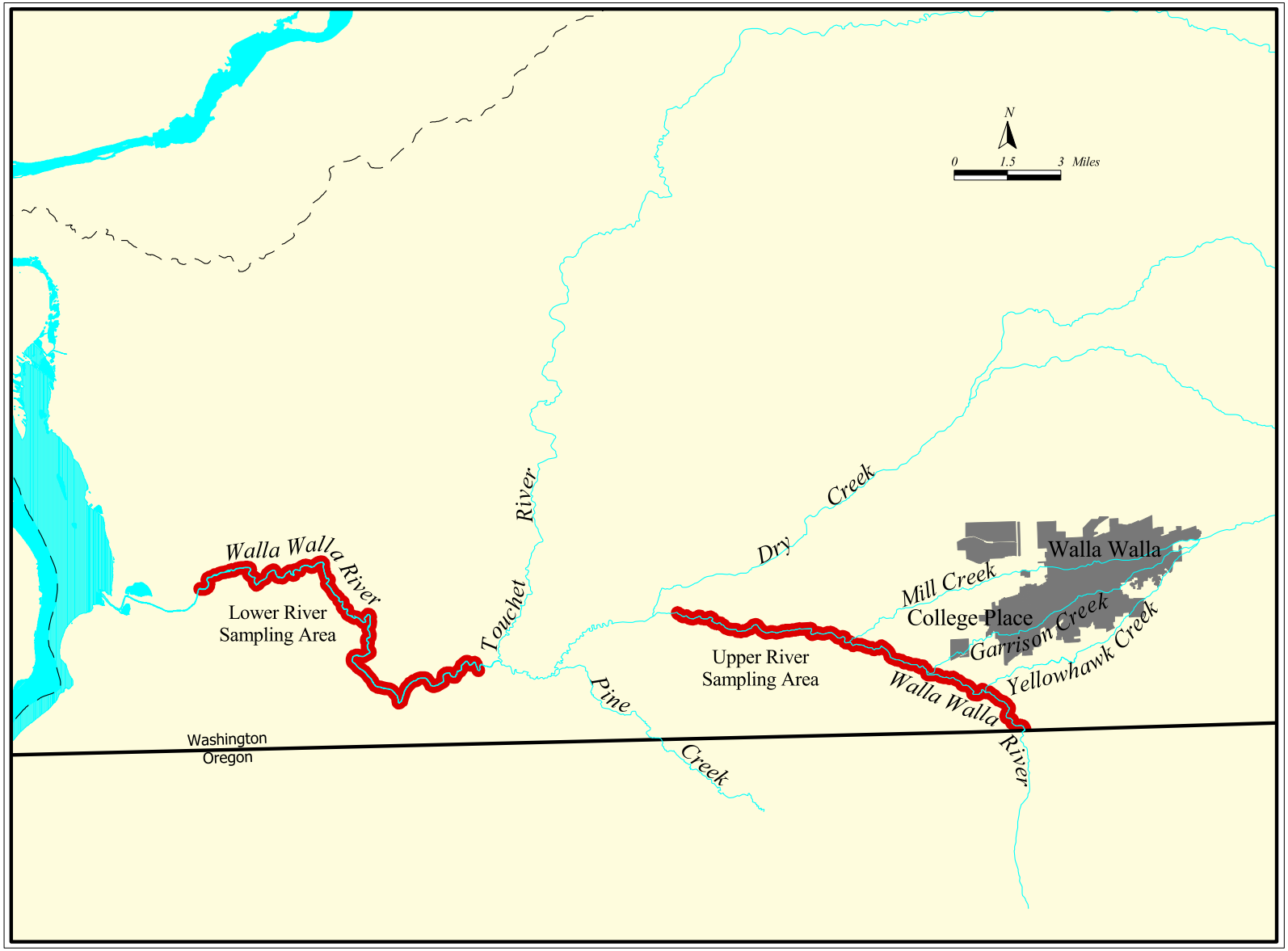

Figure 10. Location of Fish Samples (R. Coots, EAP)

congeners. The congener data will show the relative amounts of planar vs. nonplanar PCBs* in the samples, which may permit WDOH to refine their health risk estimates (EPA, 1996). However, the specific approach WDOH will use to assess health risk is not known at this time.

The sample size must be large enough to give representative data and meet whatever requirements WDOH may set for the human health assessment. Ideally, the sample size will allow for detecting small differences between the sample mean and 303(d) criteria.

For a given number of fish to be analyzed as composites, greater statistical power is achieved by increasing the number of replicate composites as opposed to increasing the number of fish per composite (EPA, 2000b). A target sample size of 20 fish is proposed for each species from each location, to be analyzed in composites of five fish each as explained below (80-100 total fish). The sample size will be modified to meet WDOH requirements, to the extent possible.

Based on EAP's experience and in consideration of the fisheries resources in the Walla Walla River, the number of individual fish per location that one might optimally expect to obtain from the river is around 20. Assuming that 20 individuals are available for analysis, a composite size of five was selected to balance the need for confidence in estimating COC concentrations against the cost of sample analysis.

Figure 11 shows the confidence intervals around the median for the case where 20 fish are analyzed in composites of five fish each. The geometric standard deviation (x-axis) is a measure of how variable the samples are: a value near 1 indicating results are relatively close and a value of 5 indicating the results are highly dispersed. In EAP surveys similar to the one proposed for the Walla Walla, this value has been around 2. A log-normal distribution of the data is assumed.

The composites will be formed with fish having similar lengths, in keeping with EPA (2000b) guidance (see Laboratory Procedures). A large overall size range could be encountered for some species. However, an EAP review of the literature found that fish length is often poorly correlated with organochlorine residues (Bill Yake, personal communication) so it is unlikely that results will be adversely affected if a somewhat disparate size range is analyzed.

In a CTUIR board meeting on April 2, 2002, the Umatilla Tribe requested that Ecology include whole fish samples in the TMDL study, as many Tribal members use the entire fish. Therefore, one whole fish composite of each species from each sampling area will be analyzed for COCs, percent lipids, and percent solids. Two of the composites will be analyzed for PCB congeners. There will be five fish per whole body composite, as with fillets.

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*PCB compounds that assume a dioxin-like planar shape due to the lateral position of substituted chlorine atoms are far more toxic than non-planar PCBs.

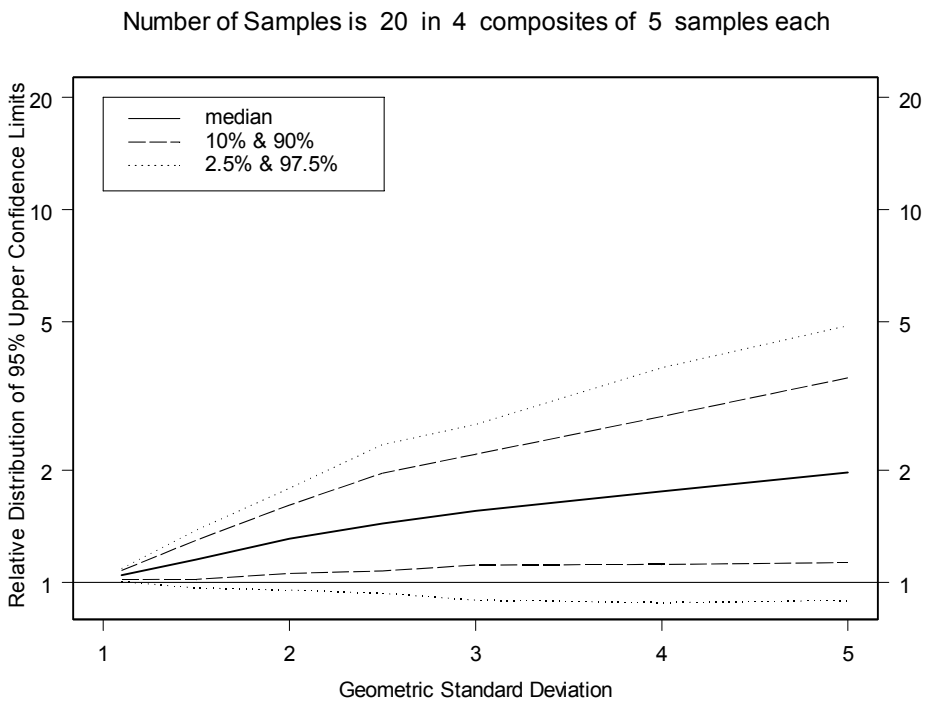

Figure 11. Confidence Intervals for 20 Fish Analyzed in Composites of 5 Fish Each (prep. by Bill Griffith, University of Washington, Dept. of Environmental Health).

Number of Samples

The number of field samples to be collected for this project is summarized below (not including QC samples, described later in this plan):

River and Tributaries - 80 water samples (40 passive samples / 40 grab samples)
WWTP's - 8 effluent samples
Fish - 25 composite tissue samples

Organization, Schedule, and Laboratory Cost Estimate

EAP Project Lead - Art Johnson (360/407-6766)
EAP Field Lead - Brandee Era (360/407-6771)
EAP Field Assistance - Steve Golding (360/407-6701), Randy Coots (360/407-6690)
EAP Toxics Studies Unit Supervisor - Dale Norton (360/407-6765)
Manchester Environmental Laboratory Director - Stuart Magoon (360/871-8813)
Manchester Laboratory Organics Unit Supervisor - John Weakland (360/871-8820)
Ecology Quality Assurance Officer - Cliff Kirchmer (360/407-6455)
Environmental Sampling Technologies - Terri Spencer (816/232-8860)
EIM Data Entry - To Be Determined

Proposed Schedule for Walla Walla River Chlorinated Pesticide/PCB TMDL Technical Study

	2002								2003							
	M	J	J	A	S	O	N	D	J	F	M	A	M	J	-	- D
Field Work																
SPMD Deployment	x	x	x	x	x	x	x	x	x	x	x					
DDT Correlation Samples		x			x			x			x					
WWTP Effluents		x			x			x			x					
Fish Tissue			x													
Reports																
Fish Tissue Data to WDOH						x										
Draft TMDL Report																x
Final Technical Report (May 2004)																

Estimate of Laboratory Costs

	FY2002	FY2003	Total
SMPD (preparation/extraction)	$5,683	$17,051	$22,734
SPMD (analysis)	$1,920	$5,760	$7,680
DDT/TSS/ tubidity correlation samples	$4,425	$26,868	$31,293
WWTP Effluents	$5,819	$9,494	$15,313
Fish Tissue samples	$9,703	$10,000	$19,703
TOTAL PROJECT LAB COSTS	$27,550	$69,173	$96,723

Data Quality Objectives

The laboratories are expected to meet all of the quality control (QC) requirements of the analytical methods selected for this project. Surrogate recoveries have been selected as significant, bottom- line measurement quality objectives (MQOs). Surrogates, or radio-labeled compounds for the PCB congener analysis, are added to every sample and their percent recovery provides an estimate of accuracy for the entire method, including sample preparation. The MQOs are shown in Table 10.

The reporting limits required for project samples are shown in Table 11. These limits are the lowest currently achievable with the selected methods. The limits shown for SPMD extracts are Manchester Laboratory's practical quantitation limits (PQLs). The water limits are lower than the EPA human health criteria by factors of approximately 2-10. A higher reported limit

Table 10. Measurement Quality Objectives

Matrix	Analysis	MQO
SPMD extracts	Chlorinated pesticides	50-150% surrogate recovery
	PCB Aroclors	50-150% surrogate recovery
Water	Chlorinated pesticides	50-150% surrogate recovery
WWTP effluent	Chlorinated pesticides	50-150% surrogate recovery
	PCB congeners	25-150% labeled congeners
	"	50-150% unlabeled congeners*
Fish Tissue	Chlorinated pesticides	50-150% surrogate recovery
	PCB Aroclors	50-150% surrogate recovery
	PCB congeners	25-150% labeled congeners
	"	50-150% unlabeled congeners*

*recovery in a standard solution of 27 congeners

Table 11. Required Reporting Limits

Analyte	SPMD Extracts*	River Water	WWTP Effluent	Fish Tissue**
Chlorinated pesticides	1-5 ng	0.00007 ug/L	0.003 ug/L	0.25 ug/Kg
PCB Aroclors	5 - 25 ng	na	na	2.5 ug/Kg
PCB congeners	na	na	1 pg/L	10-50 ng/Kg
TSS	na	1 mg/L	1 mg/L	na
Turbidity	na	1 NTU	na	na
TOC	na	1 mg/L	na	na
Conductivity	na	1 umhos/cm	1 umhos/cm	na
Percent lipid	na	na	na	0.1%
Percent solids	na	na	na	1%

*for 1 mL of extract
**wet weight basis
na = not analyzed

was set for WWTP effluent due to anticipated interferences from PCBs. For fish tissue, except for dieldrin and PCBs, the limits are lower than EPA human health criteria by a factor of at least 10. Based on the historical data, these reporting limits should be adequate to consistently quantify COC concentrations in the fish samples.

Field Procedures

SPMD Samples

Deployment and retrieval procedures for SPMDs will follow the guidance in Huckins et al., (2000).

Standard SPMDs (91 x 2.5 cm membrane containing 1 mL triolein) and the stainless steel canisters (16.5 x 29 cm) and spindle devices that hold the membranes during deployment will be obtained from EST. The SPMDs are preloaded onto the spindles by EST in a clean-room and shipped in solvent-rinsed metal cans under argon atmosphere. Five SPMDs will be used in each canister, with one canister per sampling site, not including field replicate SPMDs. The SPMDs will be kept refrigerated until deployed.

On arrival at the sampling site, the cans will be pried open, spindles slid into the canisters, and the device anchored and tethered in the stream. The SPMDs will be located out of strong currents, situated in such a way as to minimize the potential for vandalism, and placed deep enough to allow for anticipated fluctuations in water level. Because SPMDs are potent air samples, this procedure should be done as quickly as possible. Field personnel will wear nitrile gloves and not touch the membranes.

The SPMDs will be deployed for approximately 28 days, as recommended by USGS and EST. The retrieval procedure is essentially the opposite of deployment. The cans holding the SPMDs must be carefully sealed and the SPMDs must be maintained at or near freezing until they arrive at EST for extraction.

Temperature data are required to calculate dissolved COC concentrations, and TOC data are needed to calculate total COC concentrations. An Onset StowAway Tidbit will be attached to each canister to monitor temperature. The latitude and longitude of each sampling site will be recorded from a Magellan 320 global positioning receiver (GPS). Where required, stream flow will be measured using a Swoffer Model 2100 or Marsh-McBirney Model 201 meter and top-setting rod.

At the beginning, middle, and end of each deployment period, a depth-width integrated TOC, TSS, turbidity, and conductivity sample will be collected at each sampling site. A total DDT sample will be included at the midpoint of the deployment period (see DDT/TSS/Turbidity Correlation Samples below). These samples will be composites from a quarter-point transect.

A hand-held bottle, cleaned to EPA (1990) QA/QC specifications, will be used to collect samples where the water depth is less than two feet. A depth-integrating sampler consisting of a DH-81

adapter with a Teflon D-77 cap or DH-76 sampler and one-liter glass jar, cleaned to EPA specifications, will be used for deeper water. The sub-samples will be split into appropriate containers (Table 12). The depth-integrating samplers will be cleaned prior to use by scrubbing with Liquinox® detergent followed by sequential rinses with tap water, deionized water, and pesticide-grade acetone. The cleaned equipment will be wrapped in aluminum foil for transport into the field.

EAP will ship the SPMDs and a chain-of-custody record to EST by overnight Federal Express, in coolers with blue ice or ice in poly bottles. The water samples will be returned to Ecology HQ and held in a secure cooler for later transport with chain-of-custody record to Manchester Laboratory.

DDT/TSS/Turbidity Correlation Samples

These will be depth-width integrated samples collected as described above. Sample containers, preservation, and holding times for DDT compounds and other pesticides are shown in Table 12. The samples will be returned to Ecology HQ and held in a secure cooler for later transport with chain-of-custody record to Manchester Laboratory.

WWTP Effluent Samples

Final effluent samples from the Walla Walla and College Place WWTPs will be composites, collected manually to avoid contamination that could occur with automatic samplers. Each composite will consist of two separate grabs per day (morning and afternoon) for two days.

The composites will be split into appropriate containers for pesticide COCs, PCB congeners, TSS, and conductivity. Sample containers, preservation, and holding times are shown in Table 12. Field personnel will wear nitrile gloves. Flow data will be obtained from WWTP records. The latitude and longitude of the effluent sampling sites will be recorded from a Magellan 320 GPS. The effluent samples will be returned to Ecology HQ and held in a secure cooler for later transport with chain-of-custody record to Manchester Laboratory.

Table 12 Field Procedures (water samples)

Parameter	Min. Sample Size	Container[a]	Preservation	Holding Time
Chlorinated pesticides	1 gallon	1 gal. glass; Teflon lid	Cool to 4^oC	7 days
PCB Congeners	1 gallon	1 L glass; Teflon lid	Cool to 4^oC	7 days
TSS	1000 mL	1 L poly bottle	Cool to 4^oC	7 days
Turbidity	100 mL	500 mL poly bottle	Cool to 4^oC	48 hours
Conductivity	300 mL	500 mL poly bottle	Cool to 4^oC	28 days
TOC	50 mL	125 mL poly bottle	HCl to pH<2, 4^oC	28 days

[a]Sample containers to be obtained from Manchester Laboratory, except PCB congener containers from contract laboratory.

Fish Tissue Samples

The lower river will be sampled by EAP using electrofishing or beach seine gear. The upper river will be sampled by WDFW as part of a previously planned salmonid distribution survey. Only legal size fish will be taken for chemical analysis (where applicable, see Table 9). For species with no size limits, those taken for analysis will be large enough to reasonably be retained for consumption. The latitude and longitude of the sampling sites will be recorded from a Magellan 320 GPS.

Fish selected for analysis will be killed by a blow to the head. Each fish will be given a unique identifying number and its length and weight recorded. The fish will be individually wrapped in aluminum foil, put in plastic bags, and placed on ice for transport to Ecology headquarters, where the samples will be frozen pending filleting.

Laboratory Procedures

Fish Tissue

Preparation of tissue samples will follow the guidance in EPA (2000b). Techniques to minimize potential for sample contamination will be used. Persons preparing the samples will wear non-talc nitrile gloves and work on heavy duty aluminum foil or a polyethylene cutting board. The gloves and foil will be changed between samples; the cutting board will be cleaned between samples as described below.

The fish will be thawed enough to remove the foil wrapper and rinsed with tap water, then deionized water to remove any adhering debris. The entire fillet from one side of each fish will be removed with stainless steel knives and homogenized in a Kitchen-Aid or Hobart commercial blender. The fillets will be skin-off for catfish and scaled with skin-on for other species. Whole fish samples will be homogenized in a Hobart blender without scaling. The sex of each fish will be recorded and structures (scales, otoliths, opercles, dorsal, and/or pectoral spines as appropriate for each species) saved for age determination.

Five individual fish will be used for each composite sample. To the extent possible, the length of the smallest fish in a composite will be no less than 75% of the length of the largest fish. The composites will be prepared using equal weights from each fish. The pooled tissues will be homogenized to uniform color and consistency, using a minimum of three passes through the blender. The homogenates will be placed in 8 oz. glass jars with Teflon lid liners, cleaned to EPA (1990) QA/QC specifications.

Cleaning of resecting instruments, cutting boards, and blender parts will be done by washing in tap water with Liquinox detergent, followed by sequential rinses with tap water, de-ionized water, and pesticide-grade acetone. The items will then be air dried on aluminum foil in a fume hood before use.

The tissue samples will be refrozen for shipment with chain-of-custody record to Manchester Laboratory. The samples will be stored frozen at Manchester until analyzed. Separate containers, with excess sample, will be stored frozen at Ecology HQ. The holding time for tissue samples being analyzed for chlorinated pesticides and PCBs is up to one year (PSWQAT, 1997; Method 1668A).

Chemical Analyses

EST will extract the SPMDs (referred to as dialysis), perform GPC cleanup on the extracts, and ship the ampoulated extracts to Manchester Laboratory. The dialysis method used by EST is a patented procedure, described in Huckins et al., (2000). EST's dialysis and GPC methods are documented in SOPs E14, E15, E19, E21, E33, E44, and E48, which are on file at EAP.

Table 13 shows the types and numbers of samples to be analyzed, expected range of results, and sample preparation and analysis methods. Other methods may by used by Manchester and their contractor after consulting with the project lead. 2,2'-Dichlorobiphenyl and 2,4,5-trichlorobiphenyl will be quantified in the pesticide/PCB analysis of SPMD extracts (see Field QC Samples). All compounds qualitatively identified by GC will be verified on a second chromatography column.

Manchester will select a contract laboratory to analyze PCB congeners in the WWTP effluent and fish tissue samples and ship the samples to the contractor. Method 1668A permits congener-specific determination of more than 150 chlorinated biphenyl congeners by isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The contractor will report total PCBs as well as individual congeners. The fish tissue samples to be analyzed for congeners will be selected in consultation with WDOH after reviewing the Aroclor data. Manchester will analyze all remaining samples for this project.

Excess sample extracts and excess fish tissue will be saved for a period of 60 days after reporting the data to the project lead. Manchester's routine turn-around times will meet the needs of this project.

Quality Control

Field QC Samples

The field QC samples to be analyzed for this project are shown in Table 14.

Field replicates will provide estimates of the total variability in the data (field + laboratory). Once each quarter a replicate SPMD will be deployed and analyzed. The site for replicate sampling will be rotated to obtain variability estimates for the upper and lower Walla Walla River, the Touchet River, and lower Mill Creek. The Touchet was selected as being the largest tributary and major source of TSS, and lower Mill Creek as being the major urban tributary. One set of field replicates of whole water samples for DDT compounds, TSS, turbidity, TOC, and conductivity will also be collected at these sites. One set of field replicates will be collected for

Table 13. Laboratory Procedures

Analysis	Sample Matrix	Number of Field Samples[a]	Expected Range of Results	Sample Prep Method	Analytical Method
Chlor. pesticides[b]	SPMD extract	12[c]	1-500 ng	dialysis/GPC[d]	SW8081
PCB Aroclors	SPMD extract	12[c]	50-500 ng	dialysis/GPC[d]	SW8082
Chlor. pesticides[b]	whole water	10[c]	<0.0001-0.01 ug/L	SW3510/3620/3665[e]	SW8081
TSS	whole water	30[c]	1 - 500 mg/L	N/A	EPA 160.2
Turbidity	whole water	26[c]	1-100 NTU	N/A	EPA180.1
TOC	whole water	26[c]	1-10 mg/L	N/A	EPA415.1
Conductivity	whole water	30[c]	1 - 500 umhos/cm	N/A	EPA 120.1
Chlor. pesticides[b]	WWTP effluent	2[c]	<0.0001-0.01 ug/L	SW3510/3620/3665[e]	SW8081
PCB congeners	WWTP effluent	2[c]	0.001-0.005 ug/L[g]	EPA 1668A	EPA 1668A
TSS	WWTP effluent	2[c]	5- 50 mg/L	N/A	EPA 160.2
Conductivity	WWTP effluent	2[c]	500-1000 umhos/cm	N/A	EPA 120.1
Chlor. pesticides[b]	fish tissue	25	1-1,000 ug/Kg, wet	SW3540/3620/3665[e]	SW8081
PCB Aroclors	fish tissue	25	50-500 ug/Kg, wet	SW3540[f]	SW8082
PCB congeners	fish tissue	6	50-500 ug/Kg, wet[f]	EPA 1668A	EPA 1668A
Percent lipid	fish tissue	25	0.1-10%	extraction	EPA608.5[f]
Percent solids	fish tissue	25	~20%	dry @ 105°C	SM2540

[a]Not including periodic blanks and replicates

[b]4,4'-DDT, 4,4'-DDE, 4,4'-DDD, dieldrin, heptachlor, heptachlor epoxide, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, hexachlorobenzene

[c]to be submitted quarterly for four quarters

[d]EST SOPs E14, E15, E19, E21, E33, E44, E48

[e]and corresponding Manchester SOPs and modifications (Appendix B)

[f]total congeners

Table 14. Field Quality Control Samples

	Replicates	Field Blanks
SPMD Deployment		
SPMDs	1/quarter	1/quarter
DDT/TSS/Turbidity Correlation		
4,4'-DDT, -DDE, -DDD	1/project	1/project
TSS	1/project	- -
Turbidity	1/project	- -
TOC	1/project	- -
Conductivity	1/project	- -
WWTP Effluents		
Chlorinated pesticides	1/project	1/project
PCB congeners	1/project	1/project
TSS	1/project	- -
conductivity	1/project	- -
Fish Tissue	- -	- -

WWTP effluent. No field replicates are specified for fish tissue since multiple composites are being analyzed.

Because SPMDs sample vapors while being exposed to air, a field blank is needed to record potential chemical accumulation during deployment, retrieval, and transport. The field blank SPMD is opened to the air for the same amount of time it takes to open and place the SPMD samplers in the water, then the blank is resealed and refrigerated. The blank is taken back into the field and opened and closed again to mimic the retrieval process. The blank is processed and analyzed the same as deployed SPMDs. There will be one SPMD field blank per quarter. The location of its exposure will be rotated over the course of the study, as described above for the field replicates.

EST will spike each SPMD with Permeability/Performance Reference Compounds (PRCs) prior to their being deployed in the field, including all SPMD blanks. PRCs are analytically non-interfering compounds with moderate to relatively high fugacity (escape tendency). The loss rate of PRCs is proportional to the uptake of target compounds. PRC loss rates during field exposure are used to adjust for the effects of temperature, water velocity, and biofouling on SPMD sampling rates determined in the laboratory (see Data Quality Assessment).

2,2'-Dichlorobiphenyl and 2,4,5-trichlorobiphenyl will be used as PRCs for the Walla Walla project as recommended by USGS (Huckins et al., 2002; Jim Huckins, personal communication). These congeners are not present in significant amounts in commercial Aroclors. It has been shown that uptake rates of compounds with a wide range of K_{ow}'s*, like the Walla Walla COCs, can be predicted by loss rates of PRCs with a much narrower K_{ow} range (Huckins, et al., 2002). The spiking level will be 0.2 ug of each congener per SPMD. Manchester will provide the PRC spiking solution.

The potential for contamination arising from the whole water and effluent sampling procedures, sample containers, preservation, or transport will be assessed with transfer blanks. Transfer blanks will be prepared in the field by pouring organic-free water, obtained from Manchester Laboratory, from one sample bottle to another and the bottle re-sealed. One transfer blank each will be analyzed for samples being collected for DDT correlation and at the WWTPs, as indicated in Table 14.

Laboratory QC Samples

The laboratory QC samples to be analyzed for this project are shown in Table 15. Manchester Laboratory's routine QC samples for TSS, turbidity, TOC, conductivity, percent lipid, and percent solids will be satisfactory for the purposes of this project.

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*octanol-water partition coefficient; a measure of a chemical's tendency to bioaccumulate

Table 15. Laboratory Quality Control Samples

Matrix	Analysis	Method Blanks	Spiked Blanks	OPR[a] Standards	Surrogate Spikes	Labelled Compounds	Matrix Spike	Std. Ref. Material	Duplicate Analyses
SPMD extracts	Chlor. pesticides	1/batch[b]	- -	- -	all samples[c]	- -	2/batch[c]	- -	- -
"	PCB Aroclors	1/batch[b]	- -	- -	all samples[c]	- -	2/batch[c]	- -	- -
Water	Chlor. pesticides	1/batch	1/batch	- -	all samples	- -	2/batch	- -	- -
"	TOC	1/batch	- -	- -	- -	- -	- -	- -	- -
WWTP effluent	Chlor. pesticides	1/batch	1/batch	- -	all samples	- -	1/batch	- -	- -
	PCB congeners	1/batch	1/batch	each batch	- -	all samples	2/batch	- -	- -
Fish Tissue	Chlor. pesticides	1/batch	- -	- -	all samples	- -	2/batch	2/batch	2/batch
"	PCB Aroclors	1/batch	- -	- -	all samples	- -	2/batch	- -	2/batch
"	PCB congeners	1/batch	- -	each batch	- -	all samples	2/batch	- -	1/batch
"	Lipid	1/batch	- -	- -	- -	- -	- -	- -	2/batch

[a]On-going precision and recovery

[b] Manchester Laboratory; see Laboratory QC discussion for additional blanks prepared by EST

[c]To be spiked at EST

EST will prepare the following method blanks for each SPMD deployment: 1) A spiking blank-SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples. 2) A day-zero SPMD blank to serve as a reference point for PRC loss. 3) A dialysis blank-SPMD from the same lot as the project batch, to represent background during dialysis and cleanup. 4) A day-zero blank SPMD, manufactured just prior to dialysis, to serve as a control. 5) A reagent blank to assess contamination independent of the SPMDs. All of these blanks will be analyzed with the first quarter's sample set. The results will be used to determine which blanks should be analyzed with subsequent sample sets.

EST will ampoulize and ship the SPMD extracts to Manchester Laboratory. Manchester will analyze their own method blank with each batch of extracts. Manchester and their contractor will also analyze one method blank for each batch of whole water, effluent, and fish tissue samples analyzed for chlorinated pesticides, PCB Aroclors, PCB congeners, and TOC.

Manchester will analyze one spiked blank with each batch of water samples analyzed for chlorinated pesticides and PCBs. Results from these samples will be used to verify that analytical precision is in control and that the level of bias due to calibration is acceptable.

EST will add surrogate compounds to each SPMD prior to dialysis. This will provide an estimate of accuracy for the entire analytical procedure. The surrogates will be dibromooctafluorobiphenyl, decachlorobiphenyl, and dibutylchlorendate. The spiking level will be 40 ng per SPMD. Manchester will supply the surrogate spiking solution to EST.

Manchester will follow their routine practice of adding surrogates (tetrachloro-m-xylene, dibutylchlorendate, decachlorobiphenyl) to the water, effluent, and fish tissue samples prior to analyzing chlorinated pesticides and PCBs. The PCB congener analysis is being done by an isotopic dilution method and each sample is spiked with labeled PCB congeners.

For each dialysis batch, EST will do a matrix spike and matrix spike duplicate (MS/MSD) of field quality SPMDs using COC target compounds. The spiking level will be approximately 40 ng for each of the pesticides and 200 ng of Aroclor-1260. Manchester will supply the matrix spiking solution to EST.

Manchester will do an MS/MSD with each batch of water, effluent, and fish tissue samples. The PCB congener analysis will include a matrix spike and matrix spike duplicate with each batch as specified in the method. Matrix spikes may provide an indication of bias due to interference from components in the sample and an estimate of precision of results. The project lead will indicate which samples are to be spiked.

A standard reference material (SRM) will be analyzed to determine the accuracy the chlorinated pesticide data on fish tissue. Manchester will analyze National Institute of Standards & Technology (NIST) SRM 2978 - Mussel Tissue: Organic Contaminants--Raritan Bay, New Jersey. The NIST certified values are shown in Table 16. The SRM will be analyzed in duplicate. There are no appropriate SRMs for PCB aroclors or for any of the COCs in a surface water or WWTP effluent matrix.

Table 16. Certified Pesticide Concentrations in SRM 2978: Mussel Tissue, Organic Contaminants (ug/Kg, dry weight)

Pesticide	Certified Concentration
4,4'-DDT	3.84 +/- 0.28
4,4'-DDE	37.5 +/- 1.5
4,4'-DDD	38.8 +/- 2.3
2,4'-DDT	9.2 +/- 1.6
2,4'-DDE	4.41 +/- 0.56
2,4'-DDD	10.5 +/- 1.0
Dieldrin	6.30 +/- 0.67
Heptachlor	- -
Heptachlor Epoxide	- -
Hexachlorobenzene	- -
cis-Chlordane	15.56 +/- 0.83
trans-Chlordane	11.38 +/- 0.56
cis-Nonachlor	8.23 +/- 0.56
trans-Nonachlor	11.5 +/- 1.0
Oxychlordane	2.13 +/- 0.27

Precision of the fish tissue data will be assessed through duplicate analyses. One skin-on composite and one skin-off composite will be split in the laboratory and analyzed separately. One of the five composites being analyzed for PCB congeners will be split at the contract laboratory. The project lead will indicate which samples are for duplicate analysis.

The laboratories will re-mix all of the fish tissue samples by stirring prior to sub-sampling for analysis.

Data Review, Verification, and Validation

Manchester will conduct a review of all laboratory data and case narratives. Manchester will verify that methods and protocols specified in the QAPP were followed: that all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, standard reference materials analyses, and appropriateness of data qualifiers assigned. Manchester will prepare written reports on the results of their data review.

To determine if project MQOs have been met, results for surrogate spikes and labeled PCB congeners will be compared to QC limits. To evaluate whether the targets for reporting limits have been met, the results will be examined for "non-detects" to determine if any values exceed the required reporting limits.

The project lead will review the laboratory data packages and Manchester's data validation report. The project lead will check the data and reports for completeness and reasonableness. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

Data Quality Assessment

Once the data have been reviewed, verified, and validated, the project lead will make a determination if the data can be used to make the calculations, determinations, and decisions for which the project was conducted. If the results are satisfactory, the following will be done:

1) Dissolved COC concentrations will be derived from the SPMD and ancillary data using an Excel spreadsheet calculator developed by USGS and published values for laboratory determined SPMD sampling rates. For high K_{ow} compounds (i.e., $\geq$5.0) such as most of the Walla Walla COCs, uptake is usually linear over 28 days and the pertinent equations are as follows:

$$C_w = C_{SPMD}\, M_{SPMD} / R_s\, t = C_{SPMD} / k_u$$

where C_w is the analyte concentration in water, C_{SPMD} is the analyte concentration in the SPMD, M_{SPMD} is the mass of the SPMD (g), R_s is the sampling rate of a standard SPMD (L/d), t is exposure time, and k_u is the linear uptake rate constant (L/d·g).

PRC data are used to calculate a field exposure adjustment factor (EAF) to the laboratory determined sampling rates

$$EAF = k_{e\text{-}PRC} / k_{e\text{-}cal}$$

where

$$k_{e\text{-}PRC} = \ln (C_{SPMD\text{-}0} / C_{SPMD}) / t$$

where $C_{SPMD\text{-}0}$ is the PRC concentration at day-zero, C_{SPMD} is the final PRC concentration, and t is exposure time.

2) Total COC concentrations will be estimated using the following equation developed by Meadows et al. (1998):

$$C_{w\text{-}tot} = (1+TOC\ K_{oc} / M_w)\ C_w$$

where K_{oc} is the organic carbon-water equilibrium partition coefficient, M_w is the mass of water, and C_w is the dissolved concentration.

3) The DDT/TSS/turbidity data will be examined graphically and statistically for significant correlations.

4) COC loads to and within the river will be calculated for dissolved and total concentrations. A determination will be made as to whether the WWTPs are significant COC sources to Mill and Garrison creeks.

5) The appropriateness of EPA NTR lipid values and BCFs for the Walla Walla River will be assessed following new EPA procedures for assessing bioaccumulation (EPA, 2000a).

6) Numerical water quality targets for the COCs will be proposed for the Walla Walla River, following the steps outlined in Figure 12.

7) Based on the final list of COCs, water quality target(s) selected, sources identified, loads measured, flows and other seasonal considerations, the loading capacity for the river will be determined.

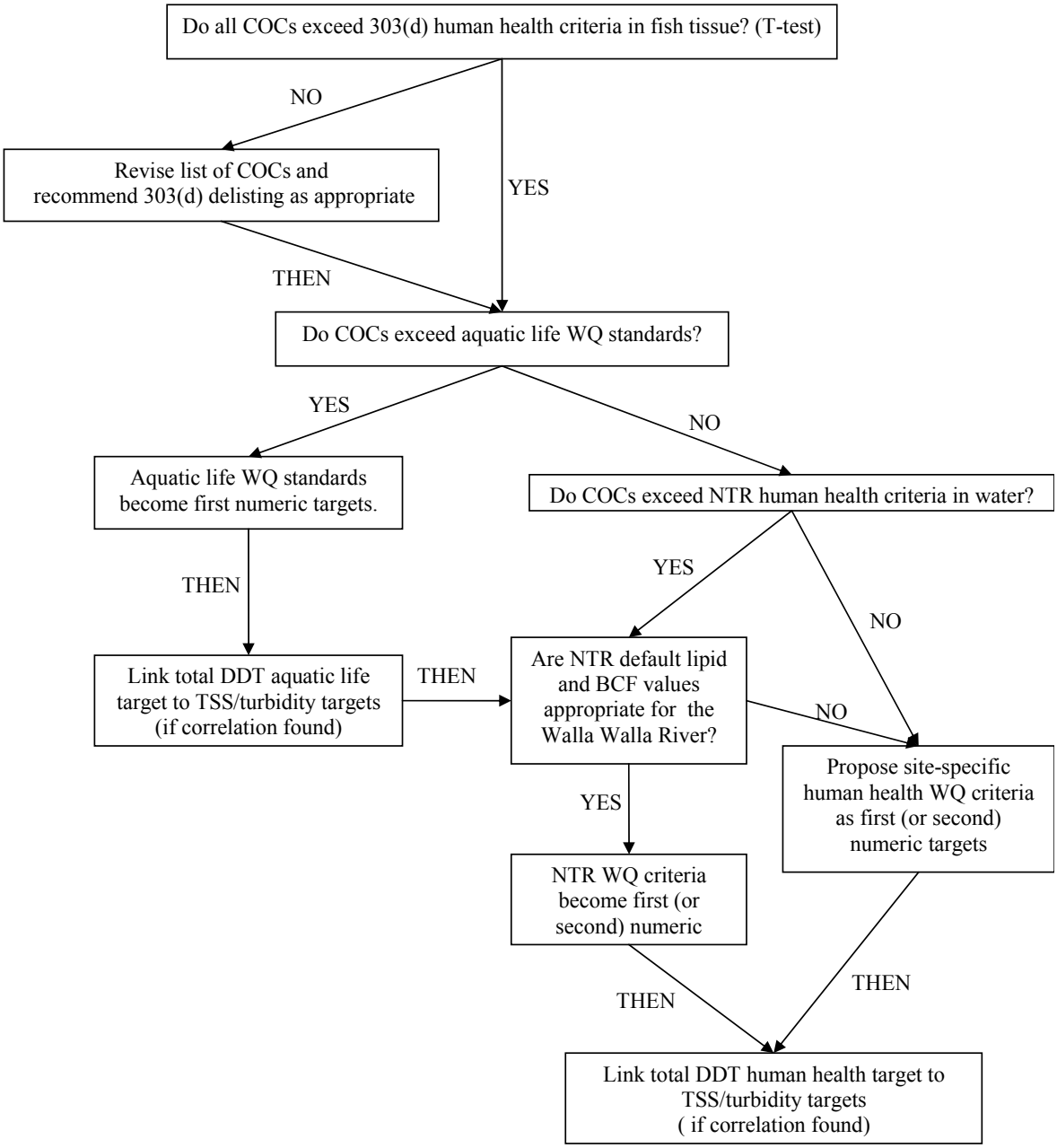

Figure 12. General Approach for Selecting Numeric Water Quality Targets for Chorinated Pesticides and PCBs (COCs)) in the Walla Walla River.

Reports

The following reports are planned for this project:

1) A fish tissue data report will be prepared for WDOH to conduct their human health assessment. The tentative date for this report is October 2002. The report will include all chemical and QC data, case narratives, Manchester's data reviews, and ancillary biological data.

2) A draft TMDL technical report will be prepared for review by ERO, EPA, and other interested parties. The tentative date for this report is December 2003.

3) A final technical report is anticipated on or about May 2004.

4) The project data will be entered into Ecology's Environmental Information Management System. The date for data entry has yet to be determined.

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Appendix A

Background Information on Walla Walla River 303(d) Pesticides and PCBs*

DDT – Insecticide on a variety of crops and for control of insect borne diseases. DDT was banned in 1972. DDE and DDD are toxic breakdown products. DDD also had some use as the insecticide Rothane.

Dieldrin – Broad spectrum insecticide primarily used on termites, other soil-dwelling insects, and on corn, cotton, and citrus. Production and most major uses of dieldrin were banned in 1974. All uses were voluntarily cancelled by industry in 1987.

Heptachlor epoxide – A breakdown product of heptachlor and a contaminant in heptachlor and chlordane formulations. Heptachlor was used to control soil insects and as a seed protectant and household insecticide. Major uses of heptachlor were suspended in 1978.

Hexachlorobenzene – Primary use was as a fungicide to protect seeds of grain crops, particularly wheat. Commercial production of hexachlorobenzene in the U.S. was discontinued in 1976 and none has been imported since 1981. Hexachlorobenzene can also be produced from incineration processes.

Chlordane – Multipurpose insecticide extensively used in home and agriculture. Its use was phased out beginning in 1975. Cis and trans isomers of chlordane, and cis and trans isomers of nonachlor are primary constituents of technical grade chlordane; oxychlordane is a major metabolite. The term total chlordane refers to the sum of these compounds.

PCBs – Widely used in industrial applications as insulating fluids, plasticizers, in inks and carbonless paper, and as heat transfer and hydraulic fluids, but had a variety of other uses. EPA restricted manufacture of PCBs to sealed systems in 1977. In 1979, EPA banned PCB manufacture, processing, and distribution but allowed continued use in closed electrical systems. EPA phased out use of electrical equipment containing PCBs through regulations in 1982 and 1985.

*Summarized from information in EPA (1992, 2000)

Appendix B

Manchester Laboratory SOPs for EPA Methods

Manchester SOP Number	EPA Method SW-846 Number
Pest/PCB Water extraction	
730084	3510(modified*)
Pest/PCB sediment extraction by Soxhlet extraction	
730012	3540
Pest/PCB tissue extraction	
730072	3540 (modified)
Pest/PCB sediment extraction by accelerated solvent extraction (ASE)	
730081	3545
Macro Florisil Clean-up procedure (waters and sediments)	
730018	3620
Macro Florisil Clean-up procedure and acetonitrile back extraction for tissue	
730073	3620 (modified)
Micro Florisil Clean-up procedure for PCBs and some Pesticides	
in process	3620
Concentrated Sulfuric acid clean-up	
part of 730002	3665
Mercury clean-up	
part of 730002	3660 (modified)
Pesticide analysis by GC-ECD / PCB analysis by GC-ECD	
730002	8081/8082
Determination of Percent Lipids	
730009	[Reference EPA 608.5 method]

"modified" indicates the SOP incorporates substantial changes to the EPA method