Quality Assurance Project Plan

Total Maximum Daily Load Technical Study: DDT Contamination and Transport in the Lower Mission Creek Basin, Chelan County, Washington

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April 2003

Publication No. 03-03-103

This report is available on the Department of Ecology home page on the World Wide Web at http://www.ecy.wa.gov/biblio/0303103.html.

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303(d) listings addressed in this study:

Waterbody	*Old Segment No.*	*New Segment No.*	*Parameter*	*Year*
Mission Creek	WA-45-1011	DQO4NW	4,4'-DDT	1996, 1998
Mission Creek	WA-45-1011	DQO4NW	4,4'-DDE	1996, 1998
Mission Creek	WA-45-1011	DQO4NW	DDT	1996, 1998

Ecology EIM Number: DSER0011

Approvals

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Background/Problem Statement

Mission Creek in central Washington was rated by the Wenatchee River Watershed Steering Committee as the most polluted waterbody in the Wenatchee River watershed due to excessive fecal coliform bacteria, elevated temperatures, low dissolved oxygen, inadequate instream flow, and pesticides (WRWSC, 1998). Pesticide monitoring conducted from 1992-1994 by the Washington State Department of Ecology (Ecology) found several chlorinated and organophosphorous insecticides at concentrations in water that are potentially harmful to aquatic life (Davis, 1993; Davis and Johnson, 1994; Davis, 1996). Ecology conducted more extensive sampling in three Mission Creek basin streams during 2000 and found elevated concentrations of pesticides in all three streams (Serdar and Era-Miller, 2002). Davis et al. (1995) also found DDT* in Mission Creek fish above levels derived to protect human health from consumption of contaminated fish tissue.

Results of analysis of water and fish tissue samples collected by Ecology exceeded the state surface water quality standards established to provide beneficial uses of surface waters, such as aquatic habitat and fish consumption. Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses are impaired by pollutants and are not expected to improve within the next two years.

Waters placed on the 303(d) list require the preparation of Total Maximum Daily Loads (TMDLs), a key tool in the work to clean up polluted waters. TMDLs identify the maximum amount of a pollutant allowed to be released into a waterbody so as not to impair uses of the water, and allocate that amount among various sources.

The current (i.e. 1998) 303(d) listings are for DDT compounds (4,4'-DDE, 4,4'-DDT, t-DDT) and azinphos-methyl in Mission Creek. However, dropping azinphos-methyl was recommended due to the lack of a formal water quality rule or standard for this chemical (Serdar and Era-Miller, 2002).

This ongoing project is an assessment of DDT contamination and transport in the Mission Creek basin and will serve as a technical basis for a TMDL. The primary focus of the study will be to investigate mechanisms by which DDT is delivered to the water columns of streams in the Mission Creek Watershed.

Basin Description

Mission Creek flows approximately 29 km from its headwaters high in the Cascades to its confluence with the Wenatchee River at the city of Cashmere in central Washington (Figure 1). The basin drains 241 km^2 mostly within the Wenatchee National Forest (WNF). Land use in the lower basin (downstream of the WNF boundary) is largely in agriculture with some rural and urban residential areas near the mouth.

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*unless stated otherwise, DDT refers to 4,4'-DDT, its primary aerobic metabolite 4,4'-DDE, and the anaerobic breakdown product 4,4'-DDD. The sum concentration of these compounds is total DDT (t-DDT).

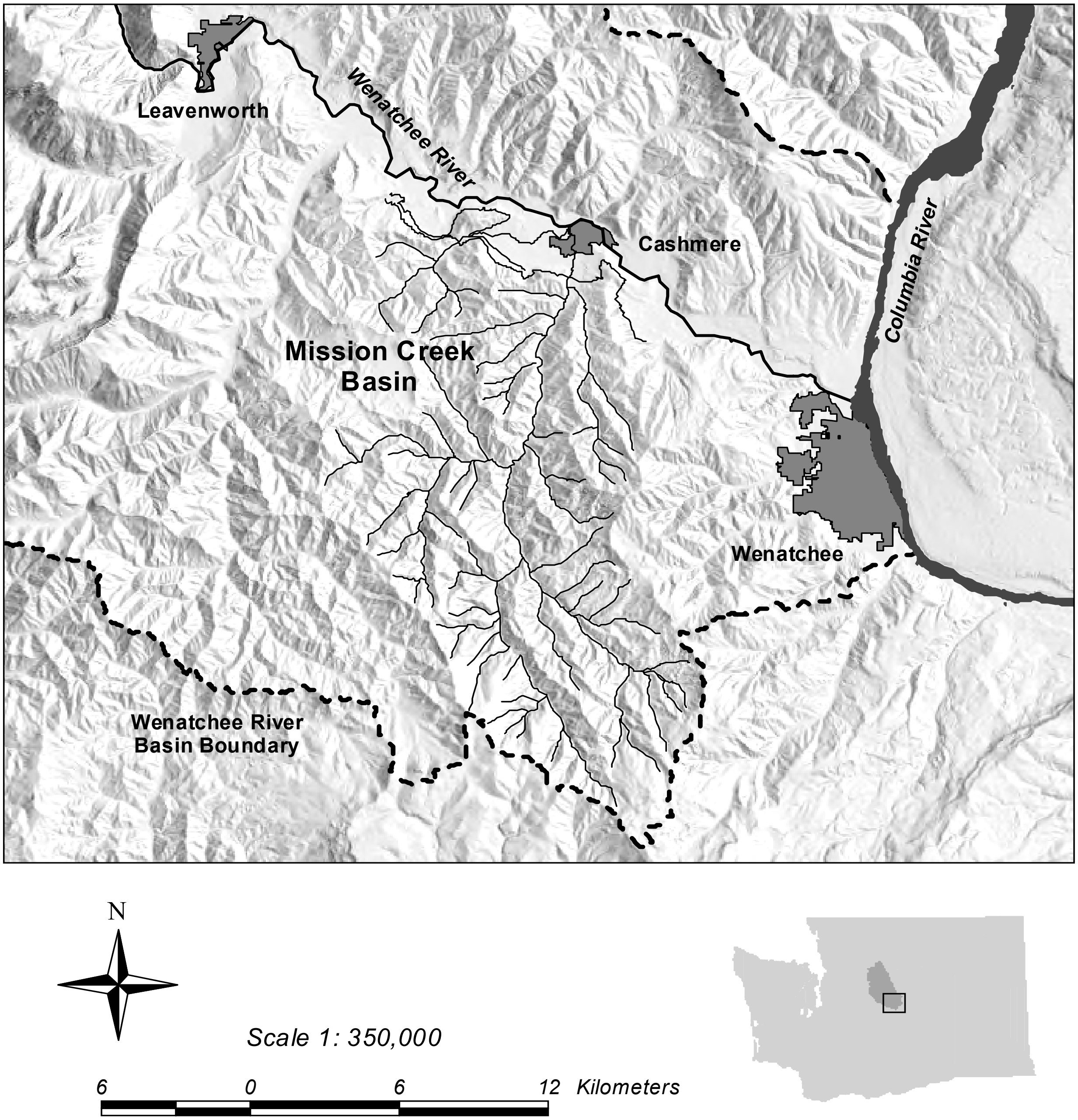

Figure 1. Mission Creek Drainage Basin

Streams in the Mission Creek basin demonstrate a seasonal flow regime typical for the east slope of the Cascades, with the highest flows following snowmelt during the spring. Flows decline to minimums in early-to-mid autumn following dry summers, although Yaksum and Brender Creek flows may actually increase during the summer possibly due to irrigation which begins in May or June and is heaviest in July and August. Other changes in stream hydrology may also occur due to irrigation withdrawals and diversions, and diversion returns from the Icicle and Peshastin Canals. Major floods occur periodically, the last one was during February, 1996. WRWSC (1998) noted that substantial riparian damage occurred as a result of this event, but the degree of scouring and bed load movement was not investigated.

The upper basin is characterized by steep slopes, deeply incised stream channels, and highly erodable soils from the Swauk and Chumstick sandstone formations. The valley becomes less confined in the lower basin, the grade shallower, and glacial and fluvial deposits have resulted in deep soils in the valley bottom. WRWSC (1998) notes that soils in the valley bottoms differ significantly among Mission (gravelly), Yaksum (loamy sand to sandy loam), and Brender Creeks (clay, silt, and sandy loams). These differences are especially important with respect to soil drainage and ability to treat on-site septage. Logs of wells constructed near Mission and Yaksum Creeks generally show the top 6-12 m as some combination of loam, sand, clay, and gravel. Although well depths vary widely (8-100 m), static water levels were almost always 3-6 m.

Pear and apple orchards constitute the primary agricultural use in the basin, with some additional alfalfa and hobby farms. Orchards flank Mission Creek in a narrow band from the urban boundary of Cashmere to near the WNF boundary (Figure 2). The lower 2 km of Yaksum Creek is in orchards where the confines of the valley are cultivatable. Orchards are also located in the Brender Creek canyon and are more extensive where the valley broadens on the west side of Cashmere.

Visual inspection of USGS topographic maps created during 1987-1989 and orthophotography from 1998 suggests that net loss of orchard land occurred in the late-1980s and 1990s, primarily from conversion to residential land use around the urban core of Cashmere. The largest converted tracts appear to be in the lower Brender Creek valley. There also appears to be limited conversion from orchards to alfalfa. New orchards have been planted since the late 1980s, primarily in the Mission Creek valley, but a rough estimate is 5-10% net loss of orchards for the entire basin.

The urban core of Cashmere (population 2,965; 2000 census) contains several kilometers of Mission Creek before it empties into the Wenatchee River. This reach has been largely channelized and its riparian area modified to accommodate the relative high density of residences. Eleven storm drains discharge directly to Mission Creek within the city limits, five in a one block area. It is not certain if stormwater drains discharge to Brender Creek which is located on the less developed west side of the city.

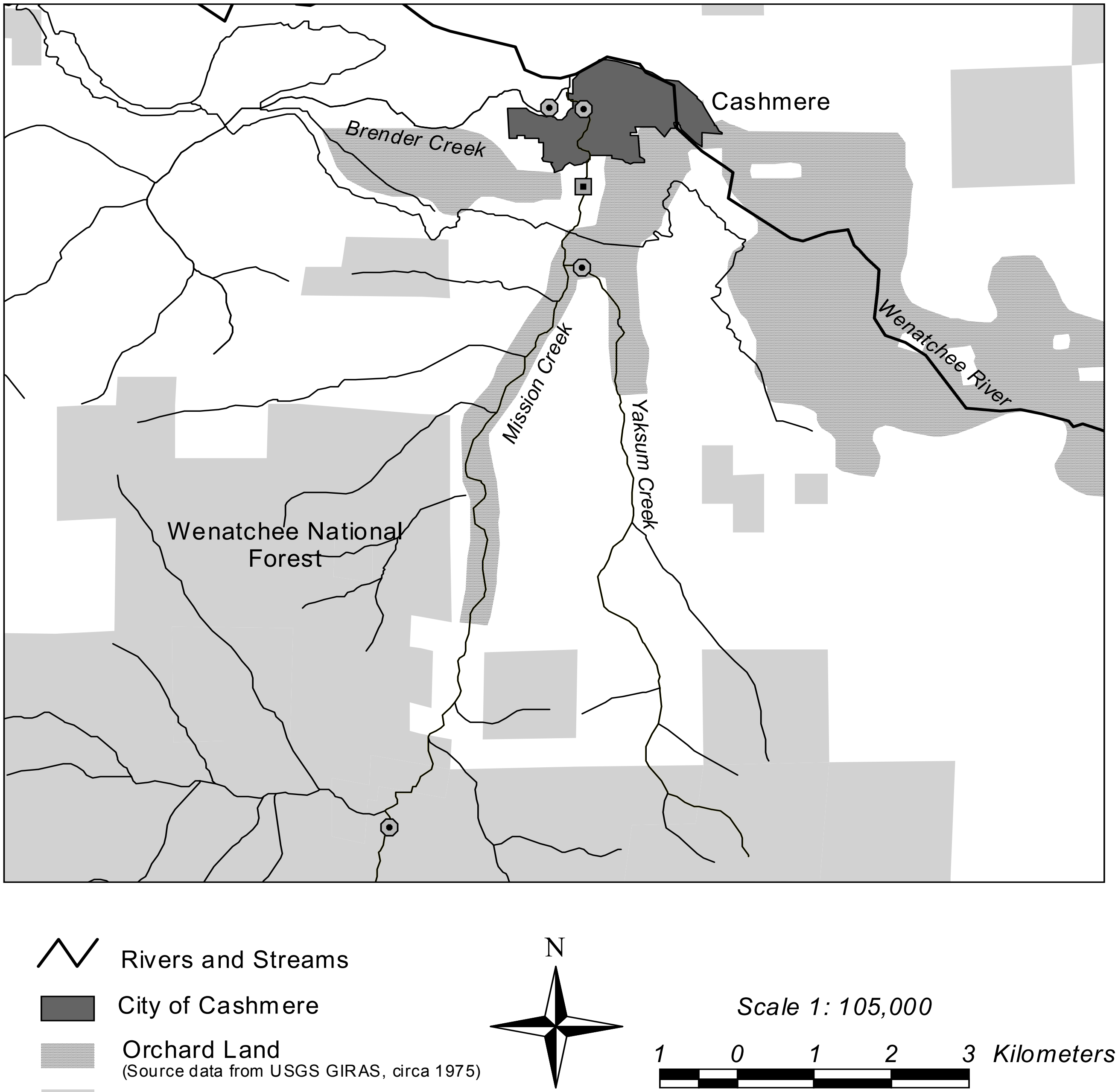

Figure 2. Lower Mission Creek Basin With Locations of Ecology's Previous DDT Sampling Sites

Applicable Water Quality Criteria

Washington State

Water quality standards for surface waters of Washington State are set in Chapter 173-201A of the Washington Administrative Code (WAC). Lower Mission Creek and its tributaries are designated as Class A streams under Chapter 173-201A WAC. Characteristic uses of Class A waters include, but are not limited to:

- Water supply (domestic, industrial, agricultural).
- Stock watering.
- Fish and shellfish (migration, rearing, spawning, and harvesting).
- Wildlife habitat.
- Recreation (primary contact recreation, sport fishing, boating, and aesthetic enjoyment).
- Commerce and navigation.

Chapter 173-201A WAC includes a provision that "Toxic, radioactive, or deleterious material concentrations shall be below those which have the potential either singularly or cumulatively to adversely affect characteristic water uses, cause acute or chronic conditions to the most sensitive biota dependent on those waters, or adversely affect public health as determined by the department [Ecology]." The numeric criteria to protect aquatic life from DDT exposure spelled out in Chapter 173-201A-040 WAC are driven largely by harmful effects to the most sensitive aquatic species, particularly eggshell thinning in piscivorous birds exposed to DDT (e.g. EPA, 1980). The chronic criterion for DDT is 1 ng/l, a concentration not to be exceeded as a 24-hour average (Table 1). The acute criterion is three orders of magnitude higher – 1,100 ng/l (not to be exceeded at any time).

National Toxics Rule

In 1992, the U.S. Environmental Protection Agency (EPA) promulgated the National Toxics Rule (NTR, 40 CFR 131.36) which established numeric, chemical-specific water quality criteria for all priority pollutants in order to bring states into compliance with the Clean Water Act. NTR human health criteria were derived from acceptable levels of fish tissue and water consumption, although water ingestion is considered a negligible DDT exposure pathway for humans. Acceptable fish tissue concentrations are 32 ng/g for 4,4'-DDE and 4,4'-DDT, and 45 ng/g for 4,4'DDD. The NTR uses a bioconcentration factor of 53,600 (EPA, 1980) to translate acceptable tissue concentrations to criteria for water – 0.59 ng/l for 4,4'-DDE and 4,4'-DDT, and 0.83 ng/l for 4,4'DDD.

Table 1. Water Quality Criteria for DDT to Protect Aquatic Life and Human Health.

Parameter	Aquatic Life – Chronic[a] (ng/l)	Aquatic –Life Acute[b] (ng/l)	Human Health[c] –Tissue (ng/g)	Human Health[c] – Water (ng/l)
4,4'-DDE	1	1,100	32	0.59
4,4'-DDD	1	1,100	45	0.83
4,4'-DDT	1	1,100	32	0.59
t-DDT	1	1,100	ne	ne

[a]Not to be Exceeded as a 24-Hour Average
[b]Not to be Exceeded at Any Time
[c]For Consumption of Organisms and Water
ne=Not Established

Existing Water Quality Data

The Chelan County Conservation District (CCCD) collected conventional water quality and fecal coliform data at a number of Mission Creek basin sites from 1992 to 2000 (WRWSC, 1998). In addition, Ecology has been collecting ambient monitoring data since 1997 at Mission Creek (Station 45E070) and since 1996 at Brender Creek (Station 45D070). Ecology also conducted monthly water quality and fecal coliform monitoring in Mission Creek, as well as synoptic surveys in both Mission and Brender Creeks during 2002 as part of the Wenatchee River TMDL (Bilhimer et al., 2002). A continuous-recording stream gage is currently operated by Ecology at the Mission Creek site.

The only known data on DDT in Mission Creek comes from the Ecology surveys previously mentioned (Davis, 1993; Davis and Johnson, 1994; Davis et al., 1995; Davis, 1996; Serdar and Era-Miller, 2002). These data are summarized in Table 2; complete data from these surveys are in Appendix B.

Table 2. Summary of Mission Creek Samples Analyzed for DDT by Ecology, 1992-2000.

Location	Year	Samp. Type	n	n det.	t-DDT Range
Mission Cr. @ Cashmere	1992-1994	Water	8	3	nd*– 25 ng/l
Mission Cr. @ Cashmere	1993	Tissue	1	1	363 ng/g
Mission Cr. @ Cashmere	2000	Water	5	5	1.3 – 6.9 ng/l
Mission Cr. @ WNF	2000	"	5	0	nd**
Brender Cr. @ Mouth	"	"	5	5	4 – 39 ng/l
Yaksum Cr. nr. Mouth	"	"	5	5	23 – 92 ng/l

*d.l. = 50 ng/l
**d.l. = 2 – 12 ng/l

Ecology first began sampling pesticides in Mission Creek as part of the Washington State Pesticide Monitoring Program (WSPMP). It was selected as a target water sampling site due to the high density of fruit orchards in the basin (Davis, 1993). Several pesticides were detected during the initial year of sampling and during the subsequent two years until Mission Creek was dropped from the WSPMP target site list after 1994. A total of eight water samples and one rainbow trout fillet sample were analyzed from Mission Creek during 1992-1994.

In 2000, pesticides were monitored in surface water at four locations: Mission Creek near the mouth and upstream of the WNF boundary; Brender Creek near the mouth; and Yaksum Creek near the mouth. Brender and Yaksum Creeks are Mission Creek tributaries located within the agricultural or urban areas of the basin. No DDT was detected above the WNF boundary but was prevalent at other sites, probably reflecting its historical use in agricultural areas of the basin. However, its presence is conceivably due to mosquito control efforts, mishandling, or other sources.

Conclusions Drawn from Existing Data

Although banned 30 years ago, DDT compounds continue to be present at relatively high concentrations in the major streams of the lower Mission Creek basin. Since DDT remains stable for decades when bound to orchard soils (e.g. Harris et al., 2000), DDT transport to streams in the Mission Creek basin is likely to be primarily through input of contaminated orchard soils. Ecology found a positive correlation between DDT loads and total suspended solids (TSS) in water samples collected during 2000 but transport of orchard soils appears to be a slow process in the Mission Creek basin due to the lack of significant erosion or conveyance systems such as rill irrigation returns. Current orchard practices include ground cover which virtually eliminates soil erosion from orchards.

Although the key mechanism(s) of transport to streams is unclear, we have consistently found DDT concentrations in Mission Creek and its tributaries above the Washington State water quality standard to protect aquatic life from chronic exposure. Results of the most recent monitoring also suggest that DDT levels in Mission Creek fish probably remain well above human health criteria promulgated by the NTR.

Problem Statement

The mechanism(s) by which DDT is delivered to Mission Creek and its tributaries is unclear. Likely possibilities include: 1) Transport of DDT-containing upland particles (soil) to streams, primarily through hydraulic erosion; 2) Transfer of DDT from orchard soils to streams through shallow groundwater; and 3) Transfer of DDT from contaminated aquatic sediments to the water column through sediment re-suspension or partitioning to water column components (dissolved phase, colloidal phase, non-settling particulate matter). A better understanding of these processes is needed in order to tailor efforts to control or remove DDT from these streams.

Project Description

The present project is an assessment of DDT contamination and transport in the Mission Creek basin and will provide technical information for development of a TMDL. The primary focus of this study will be to investigate mechanisms by which DDT is delivered to the water column of streams in the Mission Creek basin mentioned above in the problem statement. Quantitative loading of DDT in Mission Creek and its tributaries has previously been calculated (Serdar and Era-Miller, 2002), but these data are of limited use without more detailed information about mechanisms of transport and dynamics of DDT in streams. These details, coupled with information on quantitative loading, will yield results which will be useful in pursuing DDT control strategies to reduce loads.

The objectives are:

1) Obtain representative data on dissolved and solid-phase DDT concentrations in the water column, ancillary parameters, and flows in Mission Creek and its major tributaries.

2) Locate areas within each sub basin that may actively transport pesticides into the surface waters by erosion of upland soils. Where feasible, characterize concentrations of DDT in terrestrial soils found to be transported to streams.

3) Determine if DDT is present in shallow groundwater. If so, estimate net contributions or losses of DDT from groundwater in the Mission Creek basin.

4) Locate depositional areas within streams and obtain data on representative concentrations of DDT and ancillary parameters in sediments.

5) Use sampling data to estimate DDT loads and loading via the pathways investigated. Use with flow data to assign load allocations for specific transport mechanisms at key locations.

6) Complete a TMDL assessment report which includes all of the elements required by EPA Region 10. Include recommendations for DDT source control based on quantitative analysis and/or qualitative observations.

Responsibilities

EAP Project Lead – Dave Serdar (360-407-6772)
EAP Field Lead – Brandee Era-Miller (360-407-6771)
EAP Hydrogeology Support – Kirk Sinclair (360-407-6557)
Toxics Studies Unit Supervisor – Dale Norton (360-407-6765)
Manchester Laboratory Director – Stuart Magoon (360-871-8801)
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Manchester Laboratory Inorganics Unit Supervisor – Dean Momohara (360-871-8808)
Ecology Quality Assurance Officer – Cliff Kirchmer (360-407-6455)
EIM Data Entry – Dave Serdar

Schedule

Table 3. Schedule for Mission Creek DDT TMDL Technical Study.

	2003									**2004**	
	Apr	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**
Sampling											
Upland Soils		X									
Groundwater	X		X								
SPM	X										
Bed Sediments	X	X									
Storm Sampling	X										
Integrated Grabs	X		X								
Reporting											
Draft Report								X			
Final Report											X
EIM Data Entry		X	X	X	X	X					

Data Quality Objectives and Decision Criteria

Data quality objectives for this project are to obtain data of sufficient quality so that: 1) Uncertainties in contaminant concentration values are minimized; 2) Results are comparable to previous data and relevant criteria; and 3) Contaminant load calculations, estimates of DDT phase partitioning, or other calculations based on sample results can be made with confidence. It is especially important to have high quality data to achieve this final objective since computations may compound any errors in the data. Data quality will be enhanced through field procedures, sample handling, and laboratory quality control described in this sampling plan.

Measurement Quality Objectives

Measurement quality objectives are shown in Table 4. The laboratories are expected to meet all quality control requirements of the analytical methods selected for this project. Required reporting limits in Table 4 are the lowest achievable with the selected methods. The reporting limit for DDT analogs in water (0.16-0.47 ng/l) is low enough to measure analyte concentrations below the lowest applicable criteria (0.59 ng/l).

Table 4. Measurement Quality Objectives.

Parameter	**Accuracy** (max. % difference from true value)	**Precision** (RPD)	**Bias** (% of true value)	**Required Reporting Limits**
Soil/Sediment				
4,4’-DDE	70%*	30%	10%	1 ng/g
4,4’-DDD	70%	30%	10%	1 ng/g
4,4’-DDT	70%	30%	10%	1 ng/g
Zinc (Zn) and Boron (B)	20%	5%	10%	5 µg/g
Percent Solids	15%	5%	5%	0.1%
Grain Size	15%	5%	5%	0.1%
Total Organic Carbon (TOC)	25%	10%	5%	0.1 %
Water				
4,4’-DDE	50%	20%	10%	0.16 ng/l
4,4’-DDD	50%	20%	10%	0.34 ng/l
4,4’-DDT	50%	20%	10%	0.47 ng/l
B	20%	5%	10%	50 µg/l
Total Dissolved Solids (TDS)	15%	5%	5%	1 mg/l
Total Suspended Solids (TSS)	17%	6%	5%	1 mg/l
Settleable Solids (SS)	15%	5%	5%	1 mg/l
TOC	19%	7%	5%	1 mg/l

RPD=Relative Percent Difference

Study Design

Multiple components of the aquatic environment and influences from terrestrial soils will be sampled in order to understand the transport and in-stream dynamics of DDT. These components are linked and should reveal pathways and sinks that DDT follows as it moves from terrestrial soils to streams, and within streams. Sampling will be conducted in the Mission, Brender, and Yaksum Creek drainages to assess representative conditions in each sub-basin, although the locations of most sampling sites will not be selected until just prior to sampling.

The following is a description of each sampling component and how they can be linked to piece together an understanding of DDT in the Mission Creek basin. Table 5 shows a summary of the sampling to be conducted.

Transport of DDT to Streams

- Upland soils will be analyzed to assess whether DDT is sequestered at significant concentrations in representative orchard lands and public areas such as schools and city parks. Specific objectives of the upland soil sampling will be to obtain data on typical concentrations from orchards and compare them to soils not expected to contain significant concentrations of agricultural pesticides. Soil samples will also be analyzed for boron (B) and zinc (Zn), micronutrients vital for orchard fruit production added to boron and zinc-poor soils in the Mission Creek basin. B is quickly leached from orchard soils while Zn becomes tightly bound to soil.

- Storm sampling will be conducted to assess transport of upland soils to streams by analyzing eroding soils and water in rivulets or storm drains entering streams. DDT concentrations and particle size in eroding soils can then be compared to those in upland soils to assess the degree to which soil erosion is a major transport pathway for DDT. Zn in eroding soils elevated substantially above background concentrations will be an indication that soils originated from orchards.

- Shallow groundwater will be sampled to assess this as another possible DDT conveyance mechanism. Characteristics of soils and leachate measured in the field and in the laboratory will be examined to determine their relationship with DDT leaching rates and soil/water partitioning factors. Elevated B concentrations in shallow groundwater will be an indication that the groundwater has leached through orchard soils.

In-Stream DDT Dynamics

- Bed sediments will be collected from depositional areas to assess the degree to which sediments act as an aquatic sink. Only sediments appearing to be composed primarily of fine particles (i.e. ≤ 62 µm) will be analyzed since this is probably characteristic of the particle size eroding from upland soils. DDT and Zn in sediments will be compared to concentrations in upland and eroding soils to assess the contribution of orchard soils to streambed sediments. DDT and Zn will be analyzed in both surficial and buried sediments to gain insight into concentration fluxes due to bedload formation, mixing, and scouring.

- Suspended particulate matter (SPM) will be analyzed for DDT to assess the proportion of water column concentrations and loads attributable to the solid phase. Characteristics of SPM (DDT, Zn, and TOC concentrations) shared with either upland soils or bed sediments may indicate the degree to which particulate matter is re-suspended from bottom sediments as compared to introduction from exogenous sources.

- Integrated water column grab samples will be collected during sampling of stormwater and eroding soils, groundwater, and SPM to assess the influence of each component on DDT concentrations in the water column. Both whole and filtered grab samples will be analyzed for DDT to assess whether DDT remains in the phase (solid or dissolved) in which it was transported to the stream. Core stations will be established at the four previously established sites (Upper Mission, Lower Mission, Brender, and Yaksum) so that DDT concentrations and loads from 2003 can be compared to those measured during 2000.

Table 5. Proposed DDT Sampling in the Mission Creek Basin, 2003.

Type of Sampling	**No. of Sites**	**Samp. Freq. Per Site**
Upland Soils	8	1 X
Storm Sampling	8	1 X
Groundwater	5	2 X
Bed Sediments-Suficial	7	2 X
Bed Sediments-Subsurface	7	1 X
Suspended Particulate Matter	3	1 X
Integrated Water Column Grabs – Core Stations	4	4 X
Integrated Water Column Grabs – Downstream of Groundwater Stations	2	2 X
Integrated Water Column Grabs – Upstream of Urban Cashmere	1	1 X

Field Procedures

Upland Soils

Upland soils will be sampled using a site selection procedure similar to those described by Golding (2001). Sites will be selected by first compiling a list of orchard land owners for each sub-basin (Mission Creek above Yaksum Creek, Yaksum Creek, and Brender Creek) or a list of five public properties. Five land owners will be randomly selected from each sub-basin and contacted for permission to collect samples. If a landowner refuses permission, a replacement will be randomly selected from the remaining pool. Due to the low number of orchardists in the Yaksum Creek basin, sampling will likely occur at fewer than five orchards in this sub-basin. Only orchards that were in production during the 1960s will be used for sampling.

Two composite samples will be obtained from each sub-basin or land-use category. Composite samples will be formed by collecting two sub-samples – “A” and “B” – from each property. Sub-samples will be collected in a manner similar to that described by Rogowski et al. (1999). Soils for collection will be located by finding the approximate center of the largest orchard, yard, or open space for each property. “A” sub-samples will be collected by pacing off a distance at a 0˚ compass bearing. “B” sub-samples will be collected by pacing off a distance at a 90˚ compass bearing. Distances from the origin will be 50 m for orchards and 10 or 25 m for public open spaces.

Soils will be collected from 10-cm diameter holes excavated to a depth of 5 cm using a stainless steel trowel. Overlying vegetative matter will be removed prior to excavation. The 0-5 cm depth was chosen because this is the horizon most likely to be eroded in the near future and sampling work by Harris et al. (2000) showed the top 5 cm of soils contains the highest concentrations of DDT in orchards. "A" and "B" sub-samples will be placed into separate stainless steel bowls and covered with aluminum foil. Corresponding sub-samples from each property will be thoroughly mixed together to form "A" and "B" composites, then placed in appropriate sample containers.

Storm Sampling

Water discharged to streams from rivulets, road runoff, stormwater pipes, or other conveyances will be sampled during a rainstorm event. To the extent possible, sampling locations will be determined prior to the storm event through information provided by the CCCD and the city of Cashmere. Eight locations will be sampled, with high sediment loads as the primary criterion. However, an effort will also be made to select sites representing all three major streams (Mission, Brender, and Yaksum Creeks).

Water samples collected during storm events will be collected directly from the rivulet or drain using a hand-held bottle. In cases where sediment input is heavy, an attempt will be made to collect solids by placing grab samples in one gallon glass jars to allow for settling. Overlying water will be decanted once substantial settling has occurred, and the process will be repeated until an adequate volume of solid material is available for analysis. If excess moisture cannot be removed from the samples through settling and decanting, samples will be centrifuged for 20 minutes at approximately 1,000 RPM (225 x g using the floor model centrifuge available at Ecology HQ).

Groundwater

Shallow groundwater discharged to Mission, Brender, and Yaksum Creeks will be analyzed for DDT. Three groundwater sampling locations will be established in the smaller Yaksum Creek basin to assess the reason for the high DDT concentrations in this stream. One groundwater collection site each will be established along Mission and Brender Creeks.

1.25-cm (i.d.) piezometers will be driven into the stream bed to a depth of approximately 3.5 m. Upland piezometers will be installed near the streambed piezometers to determine the hydraulic gradient. Water levels will be determined using a calibrated electric well probe. Once installed, piezometers will be developed by continual pumping until a sand or gravel pack is formed and solids and turbidity are substantially reduced. Piezometers will be capped following development. Samples will be collected by purging three well volumes using a peristaltic pump fitted with Teflon® tubing, except for Silastic® tubing used at the pump head. Clean tubing will be installed on the pump following purging, and the piezometer contents will be pumped into appropriate water sample containers.

Bed Sediments

Bed sediments will be collected from six depositional areas located by visual observation; two each in lower Mission, Brender, and Yaksum Creeks. Sites will be selected based on the depth of fine (silt-clay fraction) material; sites with ≥ 10 cm are preferred but sediments ≥ 5 cm will be sampled if deeper sediments cannot be found. One surface sediment will also be collected from Mission Creek above the WNF boundary.

Samples will be divided into 0-2 cm and 2-10 cm (or 2-5 cm) layers. The surficial layer should provide an indication of DDT concentrations in recently deposited material, while the sub-surface sample will indicate levels of sequestered DDT that may serve as a reservoir in bed sediments.

It is recognized that large storm events may cause regular scouring of fine streambed sediments. Therefore, approximately two months after initial sampling, surficial sediments will be re-sampled in order to assess the effects of bedload formation, mixing, and scouring.

Samples will be collected using a Petite Ponar® grab sampler to ensure integrity of the sample. Three grab samples will be collected and homogenized together at each site to form separate surface and sub-surface samples. Aliquots will be collected from the grab sampler by gently siphoning or decanting overlying water, then scooping out the appropriate layer using a stainless steel spoon while avoiding contact with the sides of the sampler. Sediments will be homogenized in a stainless steel bowl then placed in appropriate jars for analysis.

Suspended Particulate Matter

Suspended particulate matter (SPM) will be collected from the mouths of Brender and Yaksum Creeks, and from Mission Creek just upstream of the Brender Creek confluence. A Sedisamp II continuous-flow centrifuge (model 101IL) will be used to collect the SPM in a manner described by Serdar et al. (1997). Water will be pumped from an intake situated in the middle of the water column. All tubing will be composed of Teflon® unless a peristaltic pump is required, in which case Silastic® tubing will be used on the pump head. Centrifuge bowl parts are constructed of high quality stainless steel.

Collection from each stream will occur over a period of several hours to several days, depending on TSS concentrations. Sampling will be done in April or May when TSS levels are at or near their annual peaks, typically in the range of 10 – 50 mg/l. TSS levels of 10, 30, and 50 mg/l will yield respective dry sample weights of 1.8, 5.4, and 9.0 g/h at a pump rate of 180 l/h. SPM accumulated by the centrifuge will be scraped from the centrifuge bowl and placed into appropriate sample containers.

Water samples will be collected from centrifuge intake and outlet water to measure SPM removal efficiency, which has been measured at nearly 100% using this model centrifuge in previous work (Serdar et al., 1997). Assuming nearly 100% removal of particulate matter, centrifuge discharge will be treated as filtrate and collected periodically over the course of the centrifugation to yield a composite sample of the dissolved fraction of the water column. Whole intake water will also be collected during the course of centrifugation to yield a composite whole water sample. The whole water sample will be analyzed to test agreement between DDT water concentrations calculated from the dissolved and particulate fractions.

Integrated Water Column Grabs

Integrated water column grabs samples will be collected during collection of storm samples, groundwater samples, and SPM to assess representative water column concentrations and provide supporting data for other sample results. Integrated water column grabs will be analyzed both as whole and dissolved (filtered) fractions.

Locations for water column grabs collected in conjunction with storm sampling will be at the four core stations established during 2000 (Figure 2; Upper Mission, Lower Mission, Brender, and Yaksum). One water column sample will also be collected in Mission Creek near the upstream margin of Cashmere's urban core to assess differences in chemistry and water quality variables in rural and urban reaches of Mission Creek.

Water column grabs collected in conjunction with groundwater sampling will be from core stations as well as two sites located just downstream of the Yaksum Creek piezometers to assess any effect of groundwater discharges to the water column DDT concentrations.

Samples will be collected using a hand-held bottle for water less than one foot deep or a U.S. Geological Survey (USGS) depth-integrating sampler for deeper water. The depth-integrating sampler consists of a DH-81 adapter with a D-77 cap and 1-liter jar assembled so that water contacts only Teflon® or glass. Samples will be collected by slowly lowering the sampler to the bottom then immediately raising the sampler at the same rate at three points (quarter point transect) across each stream. Samples will be split into separate containers to ensure all samples are representative of the stream cross-section. Samples for dissolved DDT analysis will be passed through a 0.45 µm pore filter in the field and placed in appropriate sample jars for analysis.

Centrifuge intake and discharge water will provide integrated water column samples at locations described in the previous description of SPM sampling.

General

All samples will be analyzed for 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, and TOC. Sediment samples will also be analyzed for Zn, percent solids, and grain size. Upland soils will be analyzed for B as well. Water samples will also be analyzed for B, TDS, TSS, and SS.

Field measurements of stream flow, pH, specific conductance (SC), and temperature will be recorded during all sampling events. Flows will be measured using USGS Stream Gaging Procedure (196) and a Swoffer Model 2100 TSR or a Marsh-McBirney, Inc. Model 201 flow meter. pH will be measured using an Orion Model 250 temperature-compensating pH meter. SC will be measured using a YSI Model 33 S-C-T meter. Temperature readings will be done with both the pH and S-C-T meters. Geographical positions will be recorded at all sampling locations using a Magellan NAV 5000 global positioning receiver.

To avoid sample contamination, all surfaces coming in contact with the samples will be pre-cleaned by scrubbing with Liquinox® detergent, followed by sequential rinses with hot tap water, de-ionized water, acetone, and hexane. Sample containers and preservation methods shown in Table 6 are those detailed by EPA (1990) and recommended by MEL (2002).

While in the field, all samples for laboratory analysis will be kept on ice in a clean cooler. Upon returning from the field, samples will be refrigerated in the Ecology headquarters chain-of-custody room then transported to the Manchester Environmental Laboratory (MEL) via lab courier the following business day.

The project lead will review all sampling and laboratory data to ensure completeness. The field lead will report any circumstances which may lead to incomplete sample collection so alternative plans can be considered. The MEL staff will also notify the project lead of problems that could lead to incomplete result production so that acceptable alternatives can be considered.

Table 6. Sample Containers, Preservation, and Holding Times.

Parameter	**Container**	**Preservation**	**Holding Time**
Soil/Sediment			
DDT Analogs, Percent Solids	4-oz glass jar w/certificate of analysis, Teflon® lid liner	cool to 4° C	7 d extraction 14 d analysis (1 yr if frozen)
Zn, B	4-oz glass jar	cool to 4° C	6 mo (2 yr if frozen)
Grain Size	8-oz plastic jar	cool to 4° C	6 mo
TOC	2-oz glass jar	cool to 4° C	14 d (6 mo if frozen)
Water			
DDT Analogs	1-gallon glass jar w/certificate of analysis, Teflon® lid liner	cool to 4° C	7 d extraction 40 d analysis
B	500 ml HDPE bottle	HNO_3 to pH<2	6 mo
TDS	500 ml w/m poly bottle	cool to 4° C	7 d
TSS, SS	1-liter widemouth poly bottle	cool to 4° C	7 d
TOC	60 ml narrowmouth poly bottle	cool to 4° C, HCl to pH<2	28 d

Laboratory Procedures

Table 7. Analytical Methods.

Parameter	Expected Range of Results	Sample Prep Method	Analysis Method
Soil/Sediment			
DDT Analogs	<1 – 500 ng/g	SW3540/3545	GC/ECD (SW8081)
Total Zn	40 – 200 µg/g	SW3050B	ICP/MS (EPA 200.8)
Total B	<5 – 200 µg/g	SW3050B	ICP (EPA 200.7)
Percent Solids	10 – 50%	na	Gravimetric (SM 2540G)
Grain Size	> 50% fines	na	Sieve-pipet (PSEP, 1986)
TOC	1 – 2 µg/g	na	Combust./NDIR (PSEP, 1986)
Whole/Dissolved water			
DDT Analogs	<0.3 – 50 ng/l	SW3510	GC/ECD (SW8081)
Total B	<50 – 3,000 µg/l	EPA 200.7	ICP (EPA 200.7)
TDS	<1 – 200 mg/l	Filtration	Gravimetric (SM 2540C)
TSS	<1 – 500 mg/l	na	Gravimetric (SM 2540D)
SS	<1 – 500 mg/l	na	Gravimetric (SM 2540F)
TOC	<0.1 – 3 mg/l	na	Combust./NDIR (EPA 415.1)

na=Not Applicable

Table 8. Analytical Cost Breakdown by Parameter and Month.

Parameter	April	May	June	No. Analyses*	Unit Cost**	Cost Per Parameter
Soil/Sediment						
DDT Analogs (8081)	30	18		48	$203	$9,744
Total Zn (ICP/MS)	28	17		45	$44	$1,980
Total B (ICP)		8		8	$44	$352
Percent Solids	26	15		41	$10	$410
Grain Size	22	15		37	$100	$3,700
TOC	26	15		41	$39	$1,599
Whole/Dissolved Water						
DDT Analogs (8081)	53		21	74	$159	$11,766
Total B (ICP)	53		21	74	$36	$2,664
TDS	21		12	33	$10	$330
TSS	30		12	42	$10	$420
SS	23		6	29	$10	$290
TOC	44		18	62	$31	$1,922
Cost Per Month =	$23,235	$6,989	$4,953		**Total=**	**$35,177**

*Including QA

**Costs Include 50% Discount for Manchester Lab

Quality Control Procedures

Field Quality Control

All sampling will be done in a manner to increase reproducibility of results and reduce variability due to sampling. Duplicate samples of sediment/soil and water will be collected during each sampling event to provide an estimate of overall sampling variability. Duplicates are samples collected by repeating sampling in an identical manner.

All reasonable efforts will be made to prevent cross-contamination of samples. Nitrile gloves will be worn during sampling. Equipment blanks will be collected by and analyzed during each sampling event where samples are filtered in the field. Equipment blanks will be prepared by filtering laboratory prepared deionized water in the field and will indicate any contamination due to sample handling. All sampling equipment will be cleaned prior to use (see discussion of general procedures under field procedures section).

Lab Quality Control

The quality control procedures routinely followed by MEL for the chemical analyses requested will be satisfactory for purposes of this project. MEL will analyze at least one each of the following quality control samples per DDT and metals analysis batch:

- Method blank.
- Matrix spike.
- Laboratory duplicate.
- Surrogate spike (DDT only).
- Laboratory control sample.
- Standard reference material (DDT in sediment only).

Method blanks are used to identify contamination stemming from the laboratory environment. Matrix spikes are valuable in assessing bias due to matrix interferences. The project lead will identify the sample to be used for the matrix spikes.

Laboratory duplicates will provide an indication of analytical precision. Surrogate recoveries will provide a useful indication of overall accuracy at the concentrations used and is standard SW8081 practice at MEL. Accuracy of the metals data will also be assessed through analysis of laboratory control samples with every batch. MEL will conduct all analyses within the recommended holding times.

One Standard Reference Material sample (SRM) will also be analyzed with each batch of sediment samples to assess overall accuracy of the DDT results. The choice of reference material will be decided by the project lead's anticipation of relative low (< 20 ng/g) or high (>20 ng/g) dry weight DDT concentrations in sediments. SRM 1941b will be used for low level DDT analysis (NIST Organics in Marine Sediment; certified values for 4,4'-DDE = 3.22 ± 0.28 ng/g; 4,4'-DDD = 4.66 ± 0.46 ng/g). SRM 1944 will be used for high level DDT analysis (NIST New York/New Jersey Waterway Sediment; certified values for 4,4'-DDT = 119 ± 11 ng/g).

Table 9. Laboratory Quality Control Limits.

Parameter	Method Blanks	Matrix Spikes	Lab Duplicates	Surrogates	Lab Control Samples	Standard Reference Material
DDT Analogs	<20% of result	50%-150% recov.	NA	50%-150% recov.	50%-150% recov.	NA
B, Zn	<½RL or <10% of all samples in batch	75%-125% recov	≤20% RPD	NA	85%-115% recov	NA
TOC	NA	75%-125% recov.	≤20% RPD	NA	NA	NA
Solids	NA	NA	≤20% RPD	NA	NA	NA

NA=Not Applicable
RPD=Relative Percent Difference
RL=Reporting Limit

Data Review, Verification, and Validation

Data Review and Verification

MEL will review the Quality Assurance Project Plan (QA Project Plan) and all of the sample and quality control data. Reviews will be sent to the project lead in the form of case narratives and will include an assessment of MEL's performance in meeting the conditions and requirements set for in this sampling plan. Case narratives will also include a comparison of quality control results with method acceptance criteria, such as precision data, surrogate and spike recoveries, laboratory control sample analysis, and procedural blanks. Quality control checks on instrument performance such as initial and continuing calibrations will also be noted. Results of standard reference material analysis will be reported along with certified values in the case narratives. MEL will explain flags or qualifiers assigned to sample results.

Data Validation

The project lead will examine the complete data package in detail to determine whether the procedures in the methods, SOPs, and QA Project Plan were followed.

Precision will be assessed by calculating RPDs for the following data:

- Laboratory duplicates.
- Field duplicates.

Laboratory duplicates will yield estimates of precision obtained at the laboratory. Field duplicates will indicate overall variability (environmental + sampling + laboratory).

Bias will be calculated as deviations of mean percent recoveries of surrogate spike and laboratory control sample analyses. Consistently low or high recoveries may indicate the data are biased in that direction. Wide ranges in recovery values may indicate data are of questionable accuracy but do not indicate bias in any particular direction. Matrix spike recoveries will indicate if bias is present due to matrix effects.

Completeness will be assessed through the following accounting:

- Number of samples collected compared to sampling plan.
- Number of samples shipped and received at MEL in good condition.
- Ability of MEL to produce usable results for each sample.
- Acceptability of sample results by project lead.

Data Quality Assessment

Data quality will be assessed to determine whether the project objectives can be met. The project lead will make this determination by examining the data and all of the associated quality control information. The project lead will be guided in this determination by the methods and procedures in this project plan. Chemists and other scientists familiar with this field may also be consulted.

Audits and Reports

Audits

The project lead and field lead will periodically assess the field sampling procedures to ensure consistency with this sampling plan or make modifications if necessary. The project lead will review all field notes to ensure quality of the field data. Laboratory results will be reviewed by the project lead to check for reasonableness and consistency with performance and completeness expectations. Any problems with the data will be discussed with chemists at MEL.

Reports

The project lead will provide a draft report of the study results to the client by November 2003. At a minimum, the report will contain the following:

- A description of the study area, the contamination problem, and applicable criteria.
- A summary of the project objectives and work performed.
- A map of the study area showing sampling sites.
- Descriptions of field and laboratory methods used in the study.
- A discussion of data quality and the significance of any problems encountered in the analyses.
- Data collected in the field including location information for each sampling site.
- Summary tables of the chemistry data.
- Comparisons between DDT concentrations in the water column and applicable criteria.
- Calculations of assimilative capacities for DDT in all stream reaches and compared to measured loads.
- An evaluation of DDT transport due to soil erosion or via shallow groundwater.
- An assessment of in-stream DDT contamination relative to upland sources.
- An evaluation of DDT compartmentalization among various matrices in streams and implications for persistence and bioavailability.
- A discussion of factors affecting DDT transport and dynamics including, but not limited to, season, stream flow, land-use, organic carbon, and particle size and concentrations.
- A discussion of correlations among the micronutrients Zn and B, presence of in-stream particles and groundwater originating from orchards, and DDT concentrations in various media.
- An assessment of possible source control options and, where feasible, a discussion of possible load allocations for DDT.
- Recommendations for follow-up work.
- Appendices showing all relevant quality assurance and sample data.

A final report will be prepared after receiving comments from the Water Quality Program's Central Regional Office, EPA, and any other reviewers they have selected. The goal is to have the revised final report completed by February, 2004.

Station data and field data will be entered into the Environmental Information Management (EIM) system. After laboratory data is reviewed, it will also be entered into EIM.

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Appendices

Appendix A
Glossary of Acronyms and Symbols

Glossary

303(d)	Section 303(d) of the Federal Clean Water Act
B	Boron
CCCD	Chelan County Conservation District
DDD	1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (a.k.a. 4,4'-DDD)
DDE	1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (a.k.a. 4,4'-DDE)
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (a.k.a. 4,4'-DDT)
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
LIMS	Laboratory Information Management System
MEL	Manchester Environmental Laboratory
ng/g	Nanograms Per Gram (Parts Per Billion)
ng/l	Nanograms Per Liter (Parts Per Trillion)
NIST	National Institute of Standards and Technology
NTR	National Toxics Rule
QC	Quality Control
RPD	Relative Percent Difference
SPM	Suspended Particulate Matter
SRM	Standard Reference Material
SS	Settleable Solids
t-DDT	Total DDT (Sum of 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in this Report)
TDS	Total Dissolved Solids
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TSS	Total Suspended Solids
µm	Micron (Micrometer, One Millionth of a Meter)
WAC	Washington Administrative Code
WNF	Wenatchee National Forest
WRWSC	Wenatchee River Watershed Steering Committee
WSPMP	Washington State Pesticide Monitoring Program
Zn	Zinc

Appendix B
Historic DDT Data from the Mission Creek Basin

Date	Location	Flow (l/s)	4,4'-DDT (ng/l)	4,4'-DDE (ng/l)	4,4'-DDD (ng/l)	t-DDT (ng/l)	t-DDT Load (mg/d)
Mission Creek							
May-92	@ Mission Cr. Road	190	u(50)	u(50)	u(50)	nd	nd
Apr-93	"	1,034	**2**	**2**	u(50)	**4**	**360**
Jun-93	"	432	**18**	u(50)	u(50)	**18**	**670**
Aug-93	"	87	u(50)	u(50)	u(50)	nd	nd
Oct-93	"	33	u(50)	u(50)	u(50)	nd	nd
Apr-94	"	1,215	u(50)	u(50)	u(50)	nd	nd
Jun-94	"	362	**12**	**13**	u(50)	**25**	**780**
Oct-94	"	51	u(50)	u(50)	u(50)	nd	nd
Apr-00	abv. Brender Cr. confl.	1,378	**1.4**	**1.2**	u(11)	**2.6**	**310**
May-00	"	582	**1.7**	**1.3**	**0.7**	**3.7**	**186**
Jul-00	"	312	**1.7**	**2.3**	**1**	**5**	**135**
Sep-00	"	82	**2.4**	**3.1**	**1.4**	**6.9**	**49**
Oct-00	"	63	u(1.6)	**1.3**	u(1.6)	**1.3**	**7**
Apr-00	abv. WNF boundary	749	u(12)	u(12)	u(12)	nd	nd
May-00	"	506	u(3.3)	u(3.3)	u(3.3)	nd	nd
Jul-00	"	283	u(1.6)	u(1.6)	u(1.6)	nd	nd
Sep-00	"	44	u(1.6)	u(1.6)	u(1.6)	nd	nd
Oct-00	"	49	u(1.6)	u(1.6)	u(1.6)	nd	nd
Brender Creek							
Apr-00	abv. Mission Cr. confl.	199	**30**	**5.9**	**2.8**	**39**	**671**
May-00	"	204	**2.8**	**5.2**	**2.7**	**11**	**194**
Jul-00	"	223	**1.3**	**3.8**	**2.4**	**7.5**	**145**
Sep-00	"	317	**2.5**	**6.8**	**3**	**12**	**329**
Oct-00	"	61	u(1.5)	**2.4**	**1.8**	**4.2**	**22**
Yaksum Creek							
Apr-00	near mouth	31	**30**	**48**	**11**	**89**	**238**
May-00	"	18	**30**	**38**	**16**	**84**	**131**
Jul-00	"	19	**12**	**25**	**8.6**	**46**	**76**
Sep-00	"	34	**13**	**20**	**6.6**	**40**	**118**
Oct-00	"	4	**5**	**12**	**5.9**	**23**	**8**

u=undetected at Concentration in Parentheses