



Pesticide Monitoring in the Mission Creek Basin, Chelan County

Abstract

The Washington State Department of Ecology monitored pesticide concentrations in streams within the Mission Creek basin on five occasions from April through October, 2000. Several chlorinated insecticides, organophosphorous insecticides, and nitrogen herbicides were found in three creeks located within or downstream of agricultural and urban areas. No pesticides were found at a site located in the Wenatchee National Forest upstream of agricultural and urban areas, except for a single detection of azinphos-methyl.

DDT (and metabolites DDE, DDD, and DDMU), endosulfan compounds, azinphos-methyl, and chlorpyrifos were detected in most samples. Methoxychlor, diazinon, dimethoate, bromacil, dichlobenil, and atrazine were detected much less frequently, generally in only one instance each. No carbamates or chlorophenoxy herbicides were found in any samples.

Concentrations of azinphos-methyl (0.001 – 0.043 $\mu\text{g/l}$), chlorpyrifos (0.001 – 0.047 $\mu\text{g/l}$), and DDT compounds (0.001 – 0.048 $\mu\text{g/l}$) were, at times, above criteria to protect aquatic life from chronic exposure. In addition, DDT was above levels derived to protect human health from consumption of contaminated fish tissue.

Azinphos-methyl and chlorpyrifos concentrations appear to closely follow seasonal use patterns. Endosulfan concentrations seem to reflect both its current seasonal use and historic use, while DDT concentrations appear to be related to delivery of contaminated soils to streams. Investigating mechanisms of pesticide transport to streams is recommended as a high priority for follow-up sampling.

Publication Information

This report is available on the Department of Ecology home page on the World Wide Web at <http://www.ecy.wa.gov/biblio/0203022.html>

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Waterbody Numbers

Lower Mission Creek – WA-45-1011 (DQ04NW)

Upper Mission Creek – WA-45-1012 (DQ04NW)

Brender Creek – WA-45-1100

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Introduction

Mission Creek flows approximately 18 miles 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 an area of 93.3 mi² mostly within the Wenatchee National Forest. Land use in the lower basin is largely orchards with some rural and urban residential areas near the mouth.

Although it contributes only 2% of the Wenatchee River flow, Mission Creek was rated as the most polluted waterbody in the Wenatchee River watershed during a ranking process for the 1998 Wenatchee River Watershed Action Plan (WRWSC, 1998). Water quality problems in the Mission Creek basin include excessive fecal coliform bacteria, elevated temperatures, low dissolved oxygen, inadequate instream flow, and pesticides.

Historic Pesticide Data

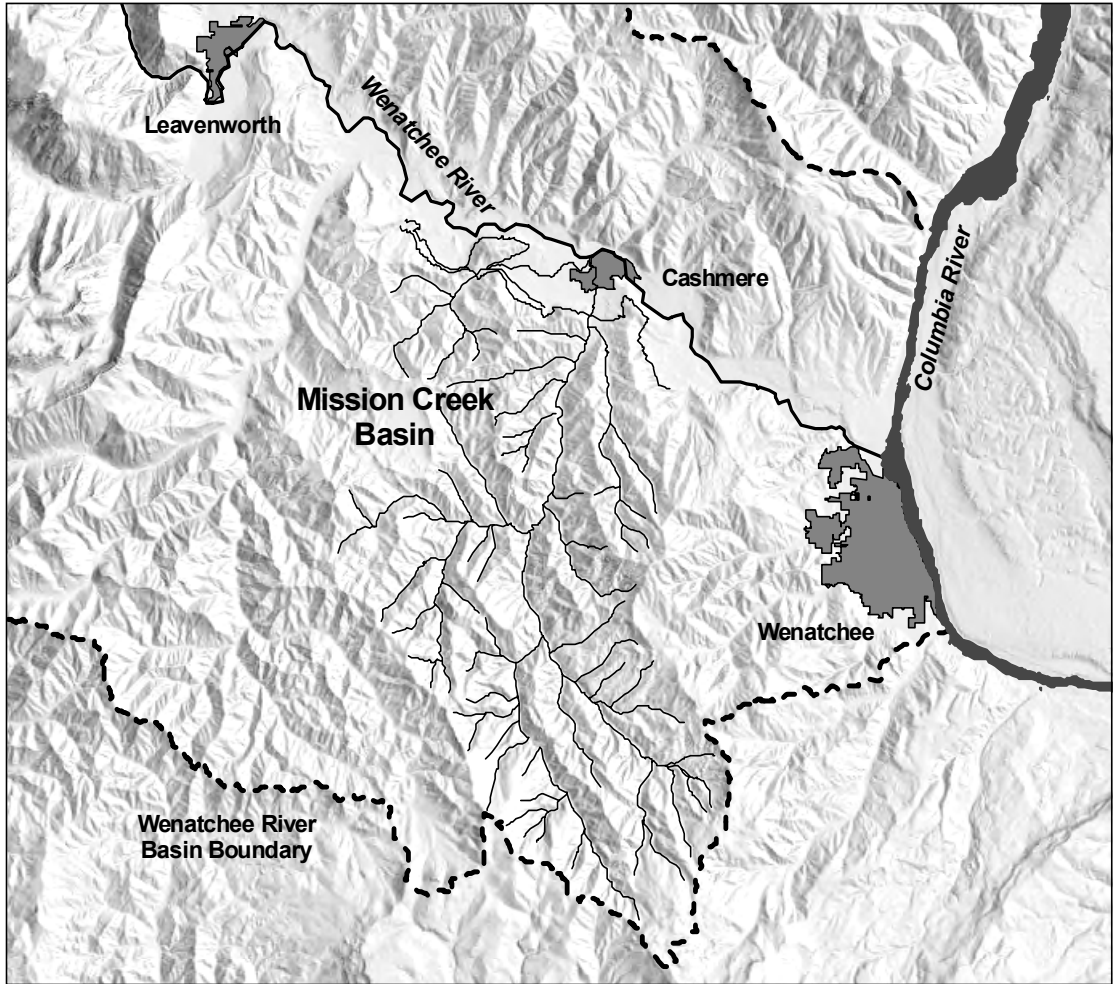
In 1992 the Washington State Pesticide Monitoring Program (WSPMP) administered by the Washington State Department of Ecology (Ecology) began including lower Mission Creek as a target water sampling site due to the high density of fruit orchards in the basin (Davis, 1993). Several pesticides were detected 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 (Davis, 1993; Davis and Johnson, 1994; Davis et al., 1995; Davis, 1996).

Tables 1 and 2 summarize pesticides detected in Mission Creek during WSPMP sampling. In all, 15 pesticides and their metabolites were detected in WSPMP samples including several above criteria to protect aquatic life or human health. As a result, Mission Creek has been included on the federal 1998 Clean Water Act Section 303(d) list of waterbodies not meeting state water quality standards (Table 3).

Concentrations of 4,4'-DDE, 4,4'-DDT, 4,4'-DDD, total DDT, and chlorpyrifos exceeded Washington State water quality criteria for surface water or edible fish tissue, but chlorpyrifos did not meet the listing requirement that a minimum of two samples exceed standards (Ecology, 1993). For Mission Creek, total DDT, 4,4'-DDE, and 4,4'-DDT have been included on the 1998 303(d) list. 4,4'-DDD meets all of the conditions for listing but appears to have been inadvertently left off the list. Azinphos-methyl was included on the 1998 303(d) list, but this appears to be a mistake since there are no state standards or federal criteria established in rule for this chemical.

Objectives

Ecology's Environmental Assessment Program conducted the present study to 1) assess the current types and concentrations of pesticides in Mission Creek and its tributaries, and 2) help determine which drainages are contributing pesticides to Mission Creek. To the extent possible, the results of this study were used to assess the relationship between the application of pesticides and their



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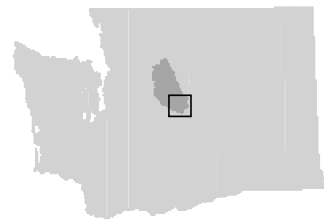


Figure 1. Mission Creek Drainage Basin

Table 1. Pesticides Detected in Mission Creek Water (µg/l) by Ecology's WSPMP, 1992-1994.

Date	4,4' - DDE	4,4' - DDT	Endosulfan I	Endosulfan II	Endosulfan sulfate	Chlorpyrifos	Azinphos-methyl	Diazinon	Bromacil	Simazine	3-Hydroxycarbofuran	Carbaryl	Glyphosate	Pentachlorophenol
May-92	0.05u	0.05u	0.05u	0.05u	0.05u	0.05u	0.033	0.07u	0.05u	0.041	2.5u	2.5u	1.13	0.002
Apr-93	0.002	0.002	0.031	0.013	0.004	0.14	0.16u	0.07u	0.05u	0.08u	0.15u	0.3u	1.0u	0.01u
Jun-93	0.05u	0.018	0.05u	0.05u	0.05u	0.05u	0.13	0.07u	0.05u	0.08u	0.15u	0.3u	1.0u	0.01u
Aug-93	0.05u	0.05u	0.05u	0.05u	0.05u	0.05u	0.16u	0.07u	0.05u	0.08u	0.15u	0.3u	na	0.01u
Oct-93	0.05u	0.05u	0.05u	0.05u	0.05u	0.05u	0.012	0.007	0.05u	0.08u	0.15u	0.3u	na	0.01u
Apr-94	0.05u	0.05u	0.05u	0.05u	0.05u	0.05u	0.004	0.07u	0.05u	0.25	0.04u	0.04u	na	0.02u
Jun-94	0.013	0.012	0.05u	0.05u	0.05u	0.05u	0.027	0.07u	0.022	0.08u	0.04u	0.059	na	0.02u
Oct-94	0.05u	0.05u	0.05u	0.05u	0.05u	0.02	0.16u	0.031	0.044	0.011	0.421	0.04u	na	0.02u
Water Quality Standards and Criteria														
AWQS	1.1	1.1	0.22	0.22	ne	0.083	ne	ne	ne	ne	ne	ne	ne	25 ^a
CWQS	0.001	0.001	0.056	0.056	ne	0.041	0.01 ^b	ne	ne	ne	ne	ne	ne	16 ^a
HH	0.00059	0.00059	2.0 ^c	2.0 ^c	2.0 ^c	ne	ne	ne	ne	ne	ne	ne	ne	8.2

Bold = detected concentrations

█ = concentrations exceed water quality standards or criteria to protect aquatic life

□ = concentrations exceed water quality standards or criteria to protect human health

u = undetected at quantitation limit shown

na = not analyzed

ne = not established

AWQS = Acute Water Quality Standards, Washington State (ch. 173-201A WAC)

CWQS = Chronic Water Quality Standards, Washington State (ch. 173-201A WAC)

HH = Human Health Criteria for consumption of organisms only, National Toxics Rule (40 CFR 131)

^a pH dependent. A pH of 8.00 was used to calculate criteria

^b Recommended Criterion (EPA, 1999)

^c EPA now recommends a criterion of 240 µg/l (EPA, 1999), but this criterion has not been promulgated in the National Toxics Rule

presence in streams. The relationships between pesticide concentrations, streamflow, and suspended solids were also examined. The study may ultimately help guide management practices designed to reduce pesticides in Mission Creek.

Table 2. Pesticides Detected in Mission Creek Fish Tissue ($\mu\text{g}/\text{kg}$) by Ecology's WSPMP, September 1993.

4,4'-DDE	4,4'-DDT	4,4'-DDD	Endosulfan sulfate
270	42	51	8
Human Health Criteria			
32	32	45	540

Bold = detected concentrations

= concentrations exceed criteria to protect human health

Human Health Criteria for consumption of organisms only, National Toxics Rule (40 CFR 131)

Table 3. Mission Creek Pesticide Parameters on the 1998 303(d) List.

Parameter	Medium	Segment	Basis for Listing
DDT (total)	water	DQ04NW	1993 WSPMP data – Davis and Johnson, 1994 ^a
Azinphos-methyl	water	DQ04NW	WSPMP data – Davis 1993 ^b
4,4'-DDT	tissue	DQ04NW	1993 WSPMP data – Davis et al., 1995
4,4'-DDE	tissue	DQ04NW	1993 WSPMP data – Davis et al., 1995

^a The 1998 decision matrix erroneously cites Davis, 1996

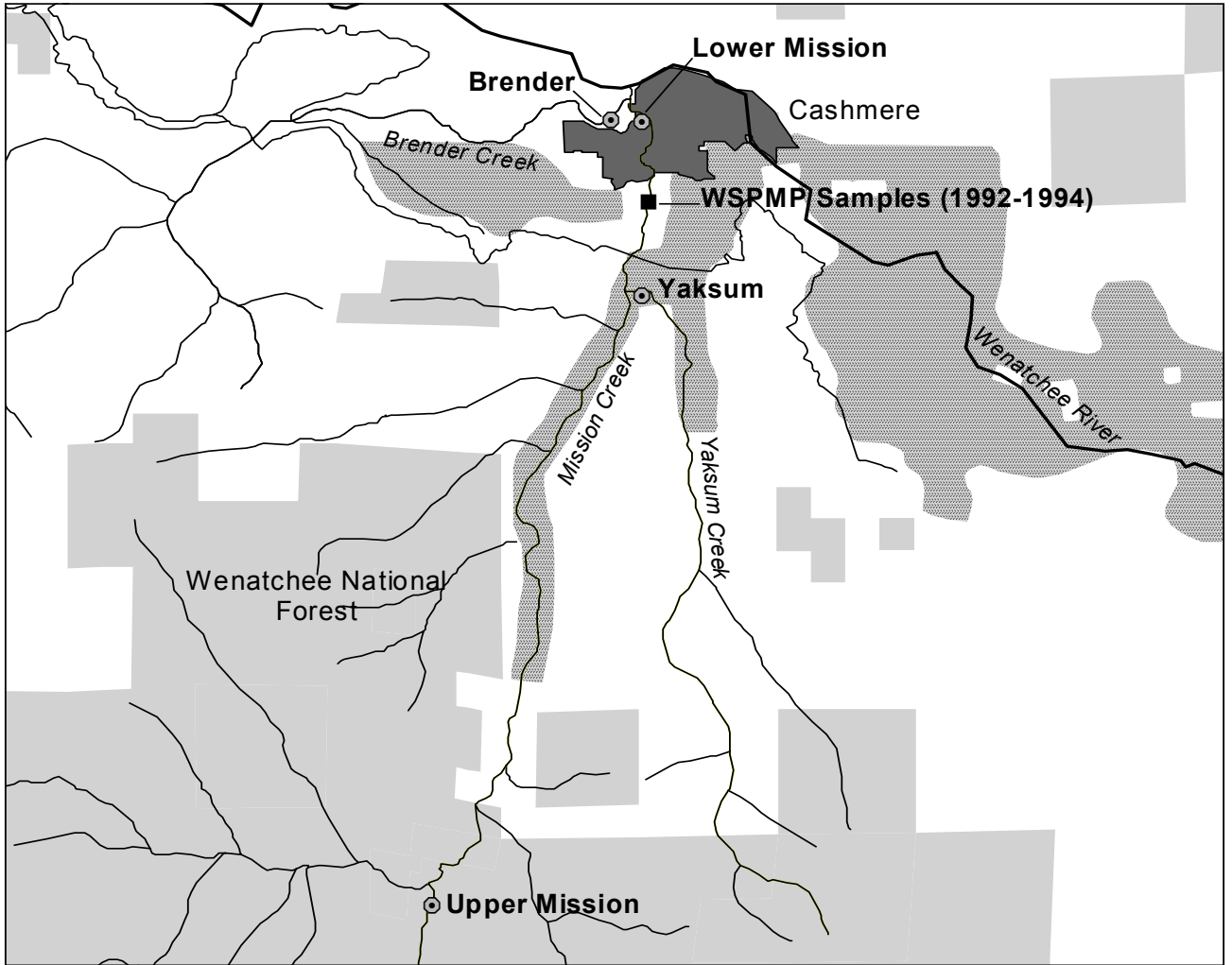
^b The 1998 decision matrix should also cite Davis and Johnson, 1994





Methods

Timing and Site Selection

Water samples were collected from two Mission Creek sites and two tributary streams on five occasions from April through October, 2000 (Figure 2). Sampling was conducted from fruit tree pre-bloom to post-harvest in order to capture the full range of pesticide use throughout the growing season. However, sampling was not timed to investigate any particular occurrence of pesticide application.

Sample site selection was based on a review of land use/land cover in the Mission Creek basin and site reconnaissance during September 1999. Brender Creek and Yaksum Creek were selected for sampling because they provide the greatest contribution to flows in the orchard lands



-  Rivers and Streams
-  City of Cashmere
-  Orchard Land
-  Wenatchee National Forest



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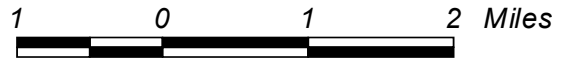


Figure 2. Sampling Locations for Mission Creek Drainage Pesticide Sampling

of the lower basin. Mission Creek was sampled near the mouth just upstream of the Brender Creek confluence. Sampling was also done at Mission Creek upstream of the Wenatchee National Forest boundary to determine pesticide concentrations before the stream flows into private lands. Stations correspond to those developed during the Wenatchee Watershed Ranking Project (WRWSC, 1998) and are described in Appendix A.

Analyte Selection

Water samples were analyzed for five classes of pesticides: chlorinated, organophosphorous, and carbamate insecticides, as well as nitrogen and chlorophenoxy herbicides. The selection of this suite was based on pesticides found in Mission Creek during WSPMP monitoring (Table 1). Although glyphosate had been previously detected in Mission Creek, it was not analyzed for this project because it requires a separate method at a relatively high cost. Glyphosate was also dropped from the WSPMP due to difficulty in obtaining low detection limits (Davis and Johnson, 1994).

Samples were also analyzed for total suspended solids (TSS) and total organic carbon (TOC). Flows, pH, temperature, and specific conductance were measured in the field.

Sample Collection and Field Procedures

Samples were 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 were 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 were split into separate containers to ensure all samples were representative of the stream cross-section. The depth-integrating samplers and jars were cleaned prior to sampling by scrubbing with Liquinox® detergent followed by sequential rinses with tap water, deionized water, pesticide-grade acetone, and spectro-grade hexane.

Sample bottles, preservatives, and holding times are listed in Table 4. All water samples were immediately put on ice and delivered to the Ecology/EPA Manchester Environmental Laboratory (MEL) within 24 hours of collection.

Stream flows were measured using USGS Stream Gaging Procedure (196) and a Swiffer Model 2100 TSR or a Marsh-McBirney, Inc. Model 201 flow meter. pH was measured using an Orion Model 250 temperature-compensating pH meter. Specific conductance was measured using a YSI Model 33 S-C-T meter. Temperature readings were done with both the pH and S-C-T meters. Sample location coordinates were recorded using a Magellan NAV 5000 global positioning receiver.

Table 4. Summary of Sample Containers, Preservation, and Analytical Methods.

Parameter	Sample Container	Preservation	Holding Time (extract./anal.)	Method
Pesticides (OP, Cl, N, Cl-phenoxy)	glass/Teflon lid liner, 1 gal.	4°C	7/14 days	GC/AED – EPA 8085
Pesticides (carbamates)	amber glass/Teflon lid liner, 4 oz.	4°C, monochloro-acetic acid	7/40 days	HPLC/FD – EPA 8318
Total Suspended Solids	polyethylene, 1 l.	4°C	7 days	Gravimetric - EPA 160.2
Total Organic Carbon	polyethylene, 60 ml.	4°C, H ₂ SO ₄ , <pH 2	28 days	Combustion IR - EPA 415.1

Laboratory Analysis and Data Quality

Table 4 shows a summary of analytical methods for pesticides and conventional parameters. Laboratory analyses were conducted at MEL. All classes of pesticides except carbamates were analyzed using gas chromatography with atomic emission detection (GC/AED). Carbamates were analyzed by high performance liquid chromatography with fluorescence detection (HPLC/FD). Practical quantitation limits for pesticides are listed in Appendix B. TSS and TOC were analyzed using standard EPA methods.

All samples for pesticide analysis were extracted and analyzed within recommended holding times except carbamates sampled in May 2000. These samples were analyzed 11 days beyond the 40-day holding time, but the data are usable (Reimer, 2000). No target compounds were detected in laboratory blanks.

No field replicates or laboratory duplicates were analyzed for pesticides. Bias was assessed through duplicate matrix spikes. Quality control was also assessed through recovery of surrogates spiked into each sample. In general, quality of the data appeared to be excellent based on results of these analyses. Matrix spike and surrogate recoveries were within acceptable limits with the following exceptions:

- Low surrogate (2,4-dichlorophenylacetic acid and 2,4,6-tribromophenol) recoveries in the chlorophenoxy herbicide analysis for one of the April 2000 samples (Sample No. 00178040)
- Low matrix spike recoveries for prometon, aldicarb, and aldicarb sulfoxide in a May 2000 sample (00228000)
- Low matrix spike recoveries for dioxathion, carboxin, and temephos in a July 2000 sample (00298000)
- Low matrix spike recoveries for demeton-O, methiocarb and aldicarb sulfoxide, and high matrix spike recovery for lindane in a September 2000 sample (00388000)

- Low and sometimes variable matrix spikes recoveries for dinoseb, picloram, propoxur, carbofuran, methiocarb, and carbaryl in an October, 2000 sample (00438000)
- Low surrogate (BDMC) recoveries in the carbamate pesticide analysis for two of the October samples (00438000 and 00438004)

In some cases, data are qualified to indicate control limits were not met. However, none of the previously mentioned exceptions affects usability of the data.

Field replicate and laboratory duplicate analyses of TSS and TOC showed a high degree of precision and low bias. Precision measurements, as expressed in terms of relative percent difference (RPD), were generally at or near 0%. The only exception was the large difference in TSS from field replicates analyzed during the April sampling round (31 vs 16 mg/l). Matrix spike recoveries for TOC averaged 106%, with a range of 98% - 121%.

Results

Field and Conventional Parameters

Table 5 shows field and conventional parameters sampled during the five rounds of sampling. Water quality data appear to be consistent with those collected during 1995 -1996 from the same four sites as part of the Wenatchee Watershed Planning Project (WRWSC, 1998). Streamflows in Mission Creek above the National Forest boundary (Upper Mission) and near the mouth (Lower Mission) demonstrated a seasonal flow regime typical for the east slope of the Cascades: high flows during spring consistently falling off to minimums in early autumn (Figure 3).

Flows at Brender Creek increased gradually throughout the growing season, peaking in September followed by a significant decrease in October. Flows in Yaksum Creek followed a pattern similar to Brender Creek. Late-summer flow increases such as those observed in Brender and Yaksum creeks are probably indicative of irrigation influences since they are inconsistent with the natural hydrologic regime of the area.

TSS levels were low with the exception of all samples collected in April and most of the Yaksum Creek samples. In general, TSS levels mirrored flows throughout the season (Figure 4). Notable exceptions were the September samples from Brender and Yaksum creeks which showed only slight increases in TSS accompanying significantly higher flows. These data, although limited, suggest that early season high flows amplify suspended sediment loads more than irrigation-induced flow increases of late summer.

Table 5. Field and Conventional Water Quality Parameters in the Mission Creek Basin.

Station/ Date	Sample No. (00-)	TOC (mg/l)	TSS (mg/l)	Flow (l/s)	pH (s.u.)	Temp. (°C)	Spec. Cond. (µmhos/cm)
Lower Mission							
24-Apr-00	178040/1	2.9/2.9 ^a	31/16 ^a	1378	7.39	6.4	139
30-May-00	228003/4	2.2/2.2 ^a	8/8 ^a	582	8.26	11.1	149
17-Jul-00	298003/4	1.5/1.6 ^a	4/4 ^a	312	8.63	18.0	195
18-Sep-00	388002/4	1.1/1.1 ^a	4/4 ^a	82	8.55	18.0	136
23-Oct-00	438002/3	2.0/2.0 ^a	1/2 ^a	63	8.74	7.0	232
Breder							
24-Apr-00	178042	2.5	18	199	7.38	10.0	148
30-May-00	228002	1.9	9	204	7.76	12.8	237
17-Jul-00	298002	1.6	4	223	7.84	17.0	272
18-Sep-00	388003	1.4	7/7 ^b	317	7.68	16.0	220
23-Oct-00	438004	1.4	2	61	7.79	11.0	380
Yaksum							
24-Apr-00	178043	2.4	34/35 ^b	31	7.62	9.8	131
30-May-00	228001	2.2	31/32 ^b	18	8.20	12.0	139
17-Jul-00	298001	1.5	11	19	8.43	17.0	150
18-Sep-00	388001	1.3	17	34	8.20	16.5	111
23-Oct-00	438001	2.1	2	4	8.60	7.0	350
Upper Mission							
24-Apr-00	178044	2.3	22	749	7.41	7.1	114
30-May-00	228000	1.6/1.6 ^b	9	506	8.21	8.5	107
17-Jul-00	298000	1.3	2	283	8.60	14.0	148
18-Sep-00	388000	1.4/1.4 ^b	1u	44	8.56	15.0	171
23-Oct-00	438000	1.7/1.8 ^b	1u	49	8.28	3.0	130

^a Field replicates

^b Laboratory duplicates

u = undetected at detection limit shown

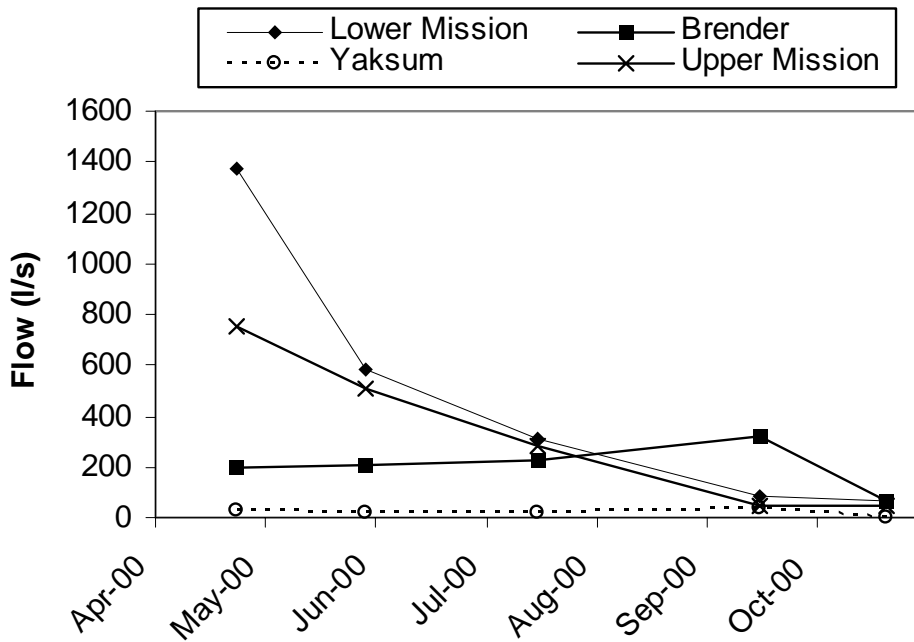


Figure 3. Flows in the Mission Creek Basin, April - October, 2000

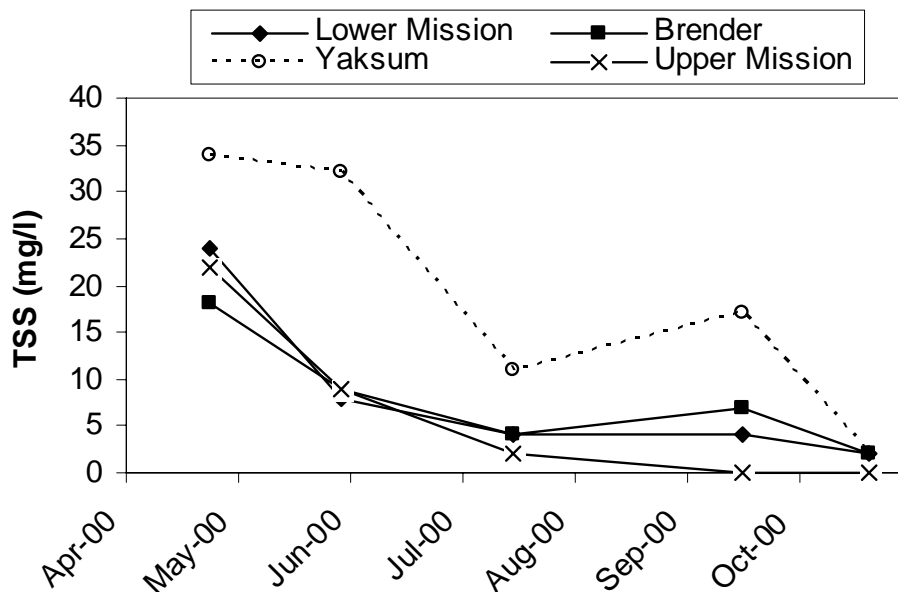


Figure 4. Total Suspended Solids in the Mission Creek Basin, April - October, 2000

Pesticide Concentrations

Sixteen pesticides and pesticide metabolites were found in water samples, with similar detection frequencies at Lower Mission, Brender, and Yaksum. Only one detectable pesticide was found at Upper Mission: azinphos-methyl at 0.0043 µg/l in the May sample.

DDT¹ and endosulfan products were the most frequently occurring pesticides, with detectable levels of 4,4'-DDE and endosulfan sulfate at Lower Mission, Brender, and Yaksum during all five sampling events (Table 6). 2,4'-DDD, a breakdown product of the DDT impurity 2,4'-DDT, and DDMU, a secondary breakdown product of DDT, were also found at Yaksum during one instance each. Methoxychlor, an insecticide structurally similar to DDT but still registered for use, was detected at low levels during the July sampling at Brender.

Concentrations of both DDT and endosulfan products were highest at Yaksum, followed by Brender, then Lower Mission (Figures 5 and 7). DDT concentrations did not appear to follow any seasonal patterns at Lower Mission and Brender, whereas endosulfan compounds decreased throughout the growing season. At Yaksum, DDT and endosulfan compounds decreased throughout the season.

Azinphos-methyl (Guthion®) was the most frequently detected organophosphorous pesticide, followed by chlorpyrifos, diazinon, and dimethoate (Table 7). Unlike chlorinated pesticides, no particular stream stood out with higher organophosphorous pesticide concentrations.

Chlorpyrifos concentrations followed a consistent seasonal trend with the highest concentrations occurring in April followed by a consistent decreasing trend beginning in May (Figure 9). Chlorpyrifos was undetectable in September and October except for a very low concentration (0.0009 µg/l) at Yaksum in the September sample.

Azinphos-methyl concentrations were highest in May and July and, unlike chlorpyrifos, were virtually absent in the April samples (Figure 11). This is consistent with WSPMP Mission Creek samples which showed azinphos-methyl as the most frequently detected pesticide with the highest concentration in May and June (1992-1994). As mentioned previously, azinphos-methyl was detected on one occasion (May 2000) at Upper Mission.

Diazinon and dimethoate were generally present at low concentrations in the May and July samples, except for diazinon at 0.005 µg/l in April at Yaksum. Neither of these pesticides was present at detectable concentrations in the September and October samples. Dimethoate was not detected at Brender.

Bromacil, a general-use herbicide, was detected in four of five samples from Brender but not at the other sites (Table 8). Bromacil had previously been detected in two of the eight WSPMP samples in lower Mission Creek, but was not detected at Lower Mission during the present study.

¹ Unless specified, DDT refers to 4,4'-DDT and its metabolites 4,4'-DDE and 4,4'-DDD

Table 6. Chlorinated Pesticides Detected in the Mission Creek Basin (µg/l).

	4,4' - DDE	4,4' - DDT	4,4' - DDD	2,4' - DDD	DDMU	Endosulfan I	Endosulfan II	Endosulfan sulfate	Methoxy-chlor
Lower Mission									
24-Apr-00	0.0012	0.0014	0.011u	0.011u	0.011u	0.0032	0.0024	0.0039	0.011u
30-May-00	0.0013	0.0017	0.0007	0.011u	0.011u	0.0019	0.0027	0.0057	0.011u
17-Jul-00	0.0023	0.0017	0.001	0.011u	0.011u	0.0013	0.0018	0.006	0.0016u
18-Sep-00	0.0031	0.0024	0.0014	0.011u	0.011u	0.0015u	0.0009	0.004	0.011u
23-Oct-00	0.0013	0.0016u	0.0016u	0.011u	0.011u	0.0011	0.0019	0.0034	0.011u
Brender									
24-Apr-00	0.0059	0.03	0.0028	0.011u	0.011u	0.025	0.022	0.038	0.011u
30-May-00	0.0052	0.0028	0.0027	0.012u	0.012u	0.0057	0.0084	0.022	0.012u
17-Jul-00	0.0038	0.0013	0.0024	0.011u	0.011u	0.0018	0.0035	0.013	0.0014
18-Sep-00	0.0068	0.0025	0.003	0.011u	0.011u	0.0015u	0.0022	0.0092	0.011u
23-Oct-00	0.0024	0.0015u	0.0018	0.011u	0.011u	0.0015u	0.0015u	0.003	0.011u
Yaksum									
24-Apr-00	0.048	0.03	0.011	0.0035	0.011u	0.026	0.025	0.051	0.011u
30-May-00	0.038	0.03	0.016	0.012u	0.0046	0.0046	0.0094	0.024	0.012u
17-Jul-00	0.025	0.012	0.0086	0.012u	0.012u	0.002	0.0041	0.014	0.0017u
18-Sep-00	0.02	0.013	0.0066	0.011u	0.011u	0.0006	0.0014	0.0047	0.011u
23-Oct-00	0.012	0.005	0.0059	0.011u	0.011u	0.0016u	0.0013	0.0091	0.011u
Water Quality Standards and Criteria									
AWQS	1.1	1.1	1.1	ne	ne	0.22	0.22	ne	ne
CWQS	0.001	0.001	0.001	ne	ne	0.056	0.056	ne	0.03 ^a
HH	0.00059	0.00059	0.00084	ne	ne	2.0 ^b	2.0 ^b	2.0 ^b	100 ^{a,c}

Bold = detected concentrations

= concentrations exceed water quality standards or criteria to protect aquatic life

= concentrations exceed water quality standards or criteria to protect human health

u = undetected at quantitation limit shown

ne = not established

AWQS = Acute Water Quality Standards, Washington State (ch. 173-201A WAC)

CWQS = Chronic Water Quality Standards, Washington State (ch. 173-201A WAC)

HH = Human Health Criteria for consumption of organisms only, National Toxics Rule (40 CFR 131)

^a Recommended criterion (EPA, 1999)

^b EPA now recommends a criterion of 240 µg/l (EPA, 1999), but this criterion has not been promulgated in the National Toxics Rule

^c For consumption of water and organisms

Table 7. Organophosphorous Pesticides Detected in the Mission Creek Basin (µg/l).

	Chlorpyrifos	Azinphos-methyl	Diazinon	Dimethoate
Lower Mission				
24-Apr-00	0.004	0.031u	0.015u	0.015u
30-May-00	0.0016	0.0085	0.0009	0.0005
17-Jul-00	0.002	0.043	0.017u	0.003
18-Sep-00	0.015u	0.0015	0.015u	0.015u
23-Oct-00	0.016u	0.0050	0.016u	0.016u
Brender				
24-Apr-00	0.047	0.005	0.016u	0.016u
30-May-00	0.0047	0.02	0.001	0.017u
17-Jul-00	0.003	0.011	0.002	0.016u
18-Sep-00	0.015u	0.0012	0.015u	0.015u
23-Oct-00	0.015u	0.031u	0.015u	0.015u
Yaksum				
24-Apr-00	0.033	0.032u	0.005	0.016u
30-May-00	0.0063	0.01	0.001	0.017u
17-Jul-00	0.002	0.025	0.017u	0.009
18-Sep-00	0.0009	0.0022	0.016u	0.016u
23-Oct-00	0.016u	0.013	0.016u	0.016u
Water Quality Standards and Criteria				
AWQS	0.083	ne	ne	ne
CWQS	0.041	0.01 ^a	ne	ne

Bold = detected concentrations

█ = concentrations exceed water quality standards or criteria to protect aquatic life

u = undetected at quantitation limit shown

ne = not established

AWQS = Acute Water Quality Standards, Washington State (ch. 173-201A WAC)

CWQS = Chronic Water Quality Standards, Washington State (ch. 173-201A WAC)

^aRecommended Criterion (EPA, 1999)

Table 8. Nitrogen Pesticides Detected in the Mission Creek Basin ($\mu\text{g/l}$).

	Bromacil	Dichlobenil	Atrazine
Lower Mission			
24-Apr-00	0.077u	0.039u	0.019u
30-May-00	0.082u	0.041u	0.020u
17-Jul-00	0.081u	0.040u	0.003
18-Sep-00	0.076u	0.038u	0.019u
23-Oct-00	0.078u	0.039u	0.019u
Brender			
24-Apr-00	0.05	0.039u	0.020u
30-May-00	0.037	0.042u	0.021u
17-Jul-00	0.081u	0.041u	0.020u
18-Sep-00	0.012	0.038u	0.019u
23-Oct-00	0.019	0.038u	0.019u
Yaksum			
24-Apr-00	0.080u	0.040u	0.020u
30-May-00	0.083u	0.0043	0.021u
17-Jul-00	0.083u	0.042u	0.021u
18-Sep-00	0.079u	0.039u	0.020u
23-Oct-00	0.078u	0.039u	0.020u

Bold = detected concentrations
u = undetected at quantitation limit shown

Dichlobenil and atrazine were found at low concentrations during single occurrences at Yaksum and Lower Mission, respectively. These herbicides were not detected in historic WSPMP samples from Mission Creek, possibly due to higher detection limits than achieved in the present study.

No carbamates or chlorophenoxy herbicides were detected in any samples. This may indicate the discontinued use or further attenuation of pesticide residues found in earlier WSPMP monitoring (pentachlorophenol, simazine, 3-hydroxycarbofuran, and carbaryl).

Pesticide Loads

Daily pesticide loads were calculated for each sampling event at each site based on detectable pesticide concentrations and measured flows. Loads were generally highest at Brender and lowest at Yaksum. The relatively small loads at Yaksum were due primarily to the low flows at this site.

Total DDT loads ranged from 250 – 660 mg/day during the high April flows, to 7 – 22 mg/day during low flows in October (Figure 6). DDT loads generally decreased throughout the season at

Lower Mission and Yaksum due to a combination of decreasing DDT concentrations and decreasing flows. Brender Creek DDT loads spiked to a relatively high level (340 mg/day) in September due to a coincidental increase in DDT concentrations and flows.

DDT loads at the mouth of Yaksum Creek were similar to Lower Mission. Since Yaksum Creek is a tributary to Mission Creek, it probably accounts for the bulk of DDT loads at Lower Mission, assuming minimum attenuation of DDT in the two stream miles between sites. A substantial addition of DDT loads are delivered to Mission Creek via Brender Creek, just downstream of the Lower Mission site.

Loads of other pesticides such as endosulfan (Figure 8), chlorpyrifos (Figure 10), and azinphos-methyl (Figure 12) were generally an order of magnitude lower in Yaksum Creek, suggesting Mission Creek receives significant loading from other inputs. For instance, the July azinphos-methyl loads peaked at 1,200 mg/day at Lower Mission compared to 40 mg/day in Yaksum Creek, although concentrations were similar (0.043 µg/l and 0.025 µg/l, respectively).

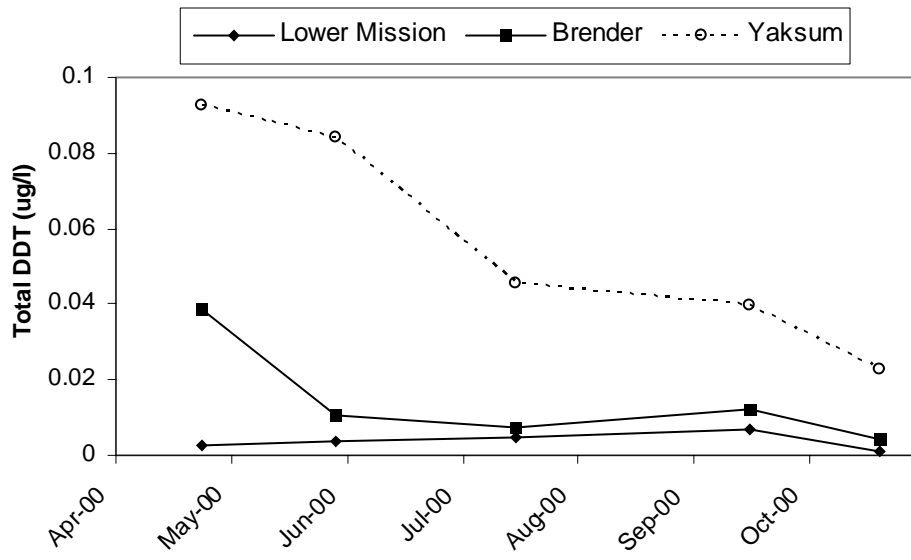


Figure 5. Total DDT Concentrations in the Mission Creek Basin, April - October 2000

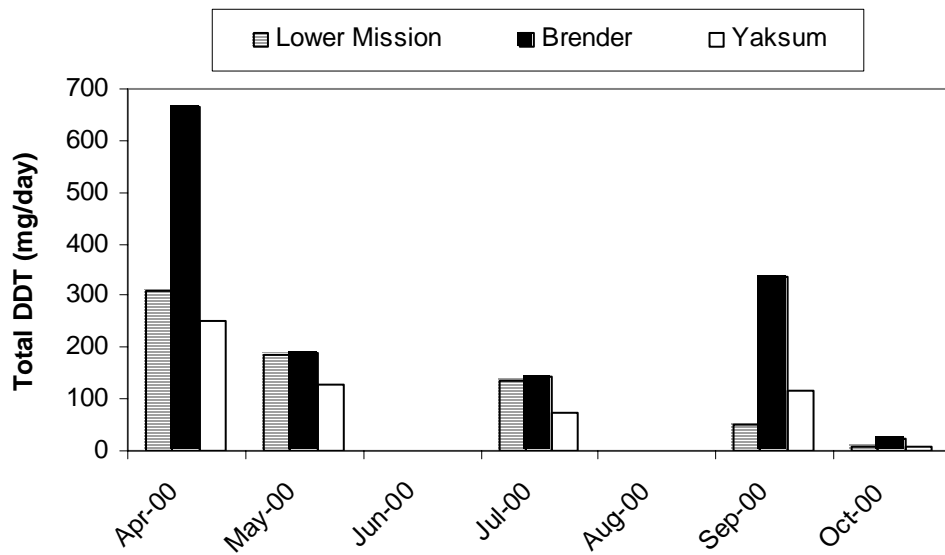


Figure 6. Total DDT Loads in the Mission Creek Basin, April - October 2000

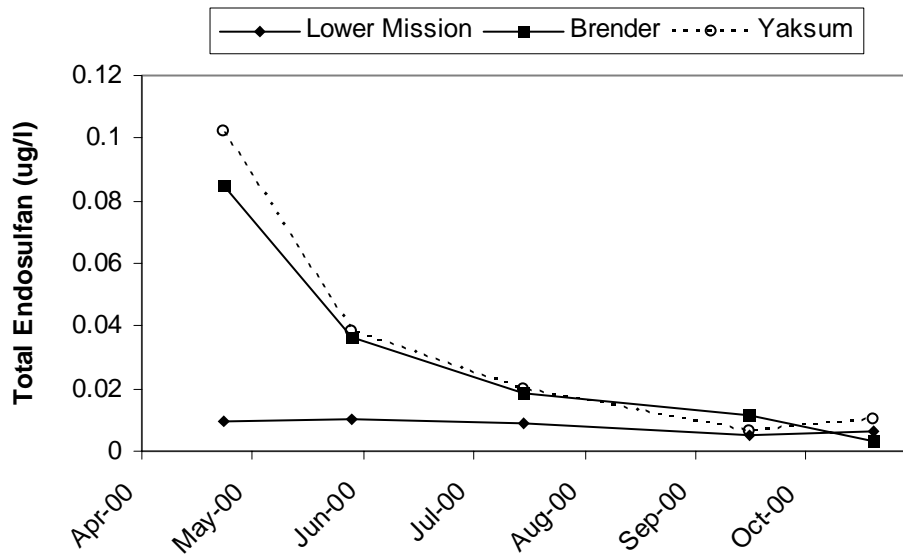


Figure 7. Total Endosulfan Concentrations in the Mission Creek Basin, April - October 2000

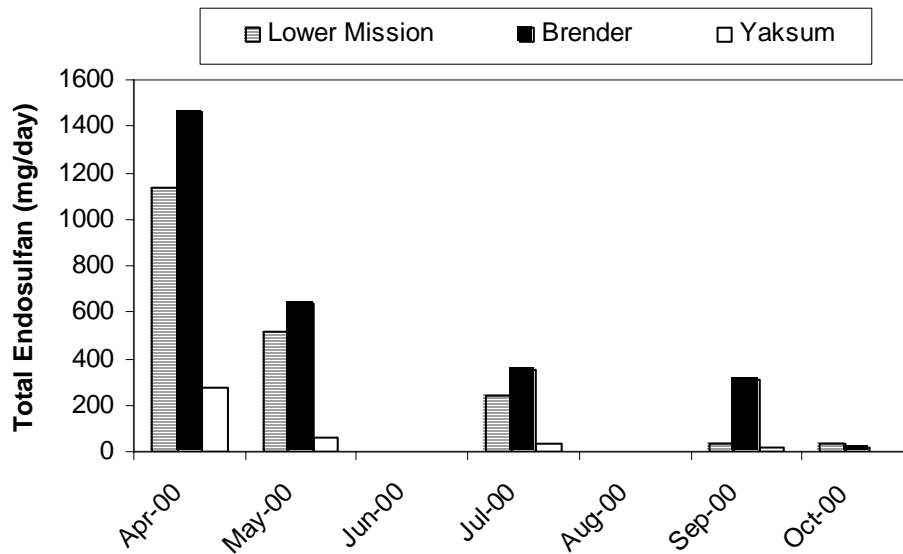


Figure 8. Total Endosulfan Loads in the Mission Creek Basin, April - October 2000

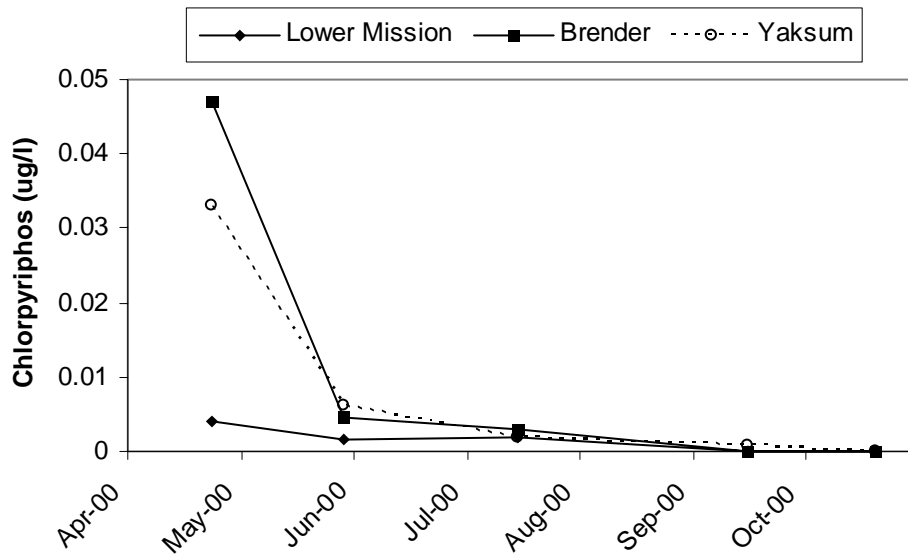


Figure 9. Chlorpyrifos Concentrations in the Mission Creek Basin, April - October 2000

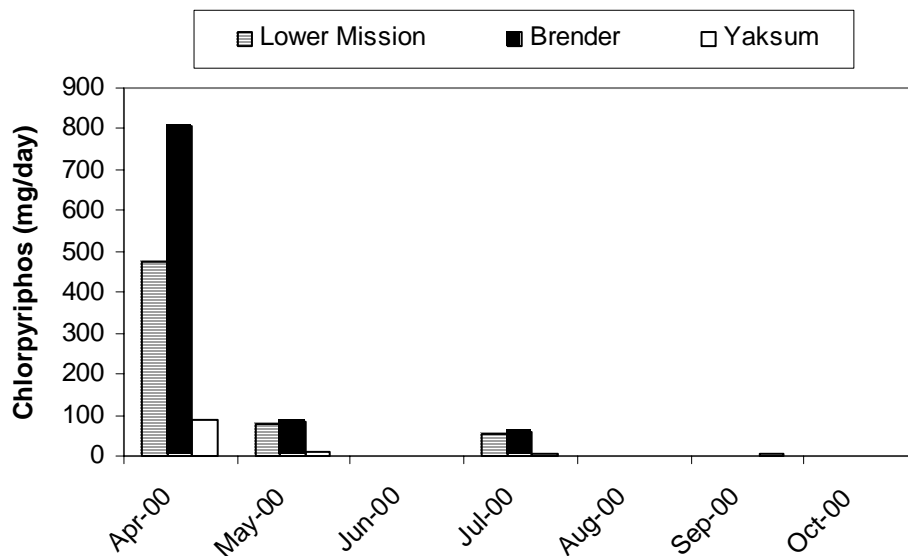


Figure 10. Chlorpyrifos Loads in the Mission Creek Basin, April - October 2000

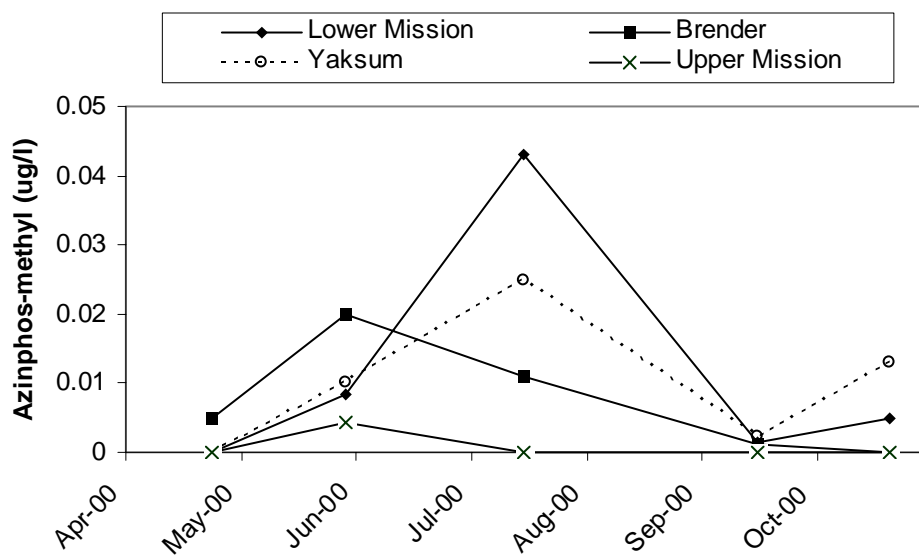


Figure 11. Azinphos-methyl Concentrations in the Mission Creek Basin, April - October 2000

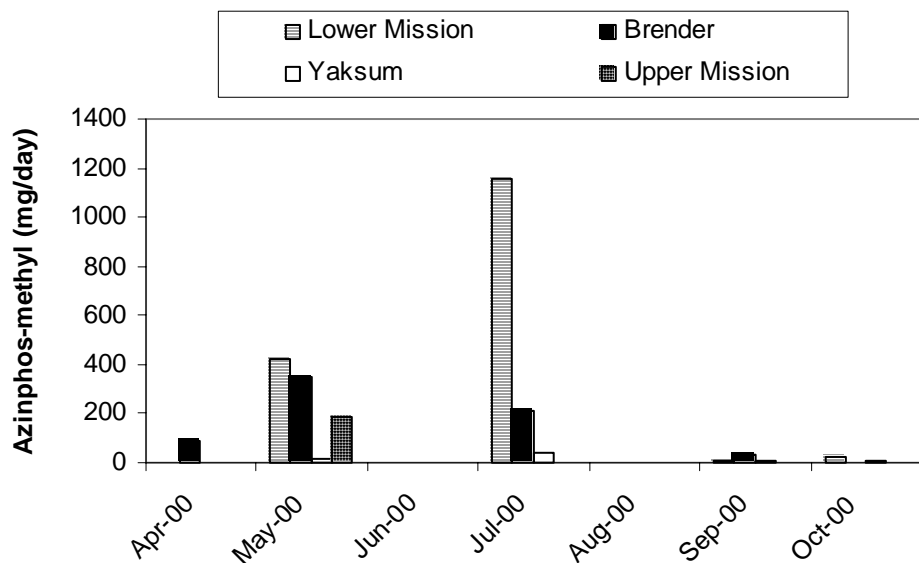


Figure 12. Azinphos-methyl Loads in the Mission Creek Basin, April - October 2000

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Discussion

Presence of Currently Used Pesticides

Pesticide use in orchard lands is most likely the source of the high concentrations found in three streams of the lower Mission Creek basin (Lower Mission, Brender, and Yaksum). However, home and garden use in residential areas cannot be ruled out as a possible source of certain pesticides. Virtually no detectable levels of pesticides are present upstream of the Wenatchee National Forest boundary (Upper Mission), indicating that any current or historic uses in the upper basin is not a source of pesticide contamination downstream.

Chlorpyrifos, one of the most widely used domestic and agricultural insecticides, was found in most of the samples collected from Lower Mission and Yaksum. Commonly formulated as Dursban® for home and garden use, chlorpyrifos is used as a termiticide, for treatment of lawns and ornamentals, and on pet collars. Sale of chlorpyrifos for domestic use was banned in 2001 except for limited use by certified and licensed applicators (EPA, 2000).

The commercial formulation of chlorpyrifos used in pear orchards (Lorsban®) is recommended for control of grape mealybug and cutworm (WSU Cooperative Extension, 2000). Timing of application is early in the season (pre-bloom) which probably explains the pattern of high concentrations seen in samples collected in April, followed by a sharp decline in the May samples, then virtual disappearance during subsequent sampling events. Recent restrictions on chlorpyrifos for agriculture include limiting its use to pre-bloom periods and lowering the tolerance for residues on apples (EPA, 2000).

The Washington State water quality standard to protect aquatic life from chronic exposure to chlorpyrifos (0.041 µg/l, Ch. 173-201A WAC) was exceeded in only one sample from Brender Creek at 0.047 µg/l. However, a minimum of two excursions above the standards is required as evidence of impairment according to the Water Quality Program's policy for assessing data for the 303(d) list (Policy 1-11; Ecology, 1993).

Azinphos-methyl, another insecticide recommended for use on pear orchards (WSU Cooperative Extension, 2000), was also found in most samples collected at Lower Mission, Brender, and Yaksum. Like chlorpyrifos, azinphos-methyl (commonly formulated as Guthion®) is used to control grape mealybugs and cutworms during pre-bloom conditions. However, higher rates of application are also recommended during post-bloom periods for grape mealybugs as well as pear psylla, codling moth, San Jose scale, and green apple aphids. Peak concentrations of azinphos-methyl in water during the May and July sampling events probably reflect the timing of its seasonal use in orchards.

The presence of azinphos-methyl in Upper Mission during the May sampling is puzzling since there has been no known use of this pesticide in the Wenatchee National Forest (Mick Mueller, personal communication). Aerial drift from lower parts of the basin is one possible explanation

for its presence in Upper Mission since it was found around the time of peak recommended application in orchards. Unfortunately, assessing aerial drift during pesticide application was beyond the scope of this study, and there is no direct evidence for this explanation. Sample contamination cannot be ruled out completely, although samples from Upper Mission were collected before others during each sampling round in an effort to avoid such an incident.

It is uncertain if azinphos-methyl will continue to be used in the Mission Creek basin. Registration for 35 crop uses is being cancelled or phased-out and another eight crop uses, including apples and pears, are being allowed to continue until EPA conducts a comprehensive review of the scientific information to see if their use should continue (EPA, 2001). EPA plans to have decisions on these “time-limited” crop uses in the year 2005.

Washington State currently has no water quality standard for azinphos-methyl in surface water. The National Academies of Sciences and Engineering recommend a maximum concentration of 0.001 µg/l to protect aquatic life (NAS/NAE, 1973), while the EPA criterion is 0.01 µg/l (EPA, 1986). At least one sample each from Lower Mission, Brender, and Yaksum exceeded the EPA criterion, and all detectable concentrations of azinphos-methyl exceeded the NAS/NAE recommended maximum concentration. However, neither criterion has regulatory standing. Although the EPA 1986 “Goldbook” criterion has been used to make decisions about inclusions on the 303(d) list of impaired waterbodies, it is only applicable where the criterion have been formally adopted in state standards or the National Toxics Rule (NTR, 40 CFR Part 131). This is not the case for azinphos-methyl, and therefore its inclusion on the 1998 303(d) list is an error.

Endosulfan is among the few chlorinated pesticides which continue to be recommended for most orchard pests (WSU Cooperative Extension, 2000). Suggested timing of application, depending on the particular pest, spans the entire season from pre-bloom to post-harvest. Common formulations of endosulfan, including Thiodan®, contain the stereoisomers endosulfan I and II. Both of these compounds were detected in nearly all samples from the lower Mission Creek basin. Endosulfan-sulfate, the microbial metabolite of endosulfan I and II, was detected in every sample collected in the lower basin during 2000.

The presence of endosulfan compounds in the Mission Creek basin probably represents a combination of its historical and current use as an orchard insecticide. Samples collected in April showed endosulfan sulfate making up 50% or less of total endosulfan (endosulfan I and II plus endosulfan sulfate). As the season progressed, endosulfan sulfate made up an increasingly higher proportion of total endosulfan (up to 100%) suggesting the commercial formulation was breaking down faster than it was being replaced. Concentrations and loads of total endosulfan in the Mission Creek basin indicate much higher use in the early growing season than in summer and fall.

The Washington State water quality standards to protect aquatic life from acute and chronic exposure to endosulfan are 0.22 µg/l and 0.056 µg/l, respectively. As written in Ch. 173-201A WAC, these criteria are somewhat ambiguous, because they are for endosulfan but fail to distinguish among the two isomers (I and II) and endosulfan sulfate. EPA has written separate criteria for endosulfan I and II in the NTR, which are the same as the state standards for

endosulfan, although EPA suggests the sum of endosulfan I and II are most appropriate for comparison to the aquatic life criteria (EPA, 1999). None of the endosulfan concentrations found during the present survey exceed these standards, whether taken individually or as the sum of endosulfan I and II.

The NTR criterion to protect human health from exposure to endosulfan I, endosulfan II, and endosulfan sulfate is 2.0 µg/l, and a new criterion of 240 µg/l is recommended based on a recent review of endosulfan reference doses (EPA, 1999). These criteria are orders of magnitude above any endosulfan levels in the Mission Creek basin.

Other insecticides recommended by WSU Cooperative Extension (2000) and detected in the present survey are diazinon and dimethoate. Diazinon is recommended throughout the season while dimethoate is used on post-bloom pests only. They were mainly present in the May and July samples, although they were detected too infrequently to assess a seasonal concentration pattern.

Bromacil was the only other pesticide detected on a regular basis, at least in the Brender Creek drainage. Concentrations were highest in April followed by declining concentrations during subsequent sampling events. As mentioned previously, bromacil is an herbicide used to control weeds and brush in non-crop areas, and the absence of bromacil in Mission and Yaksum creeks suggests it is not being used in areas adjacent to orchards.

Other pesticides detected only on a single occasion include the insecticide methoxychlor and the herbicides atrazine and dichlobenil. Their rare presence probably does not indicate widespread regular use in the Mission Creek basin.

Washington State does not currently have regulatory surface water standards for these infrequently detected pesticides. Criteria or guidelines from other agencies suggest the levels reported here do not pose a serious threat to aquatic life. The organophosphorous insecticide diazinon is probably the most toxic among them; Norris and Dost (1991) proposed a maximum permissible concentration of 0.009 µg/l to protect aquatic organisms. The EPA (1986) criterion for the insecticide methoxychlor is 0.03 µg/l. Concentrations of diazinon and methoxychlor in the Mission Creek basin were generally well below these threshold values.

Criteria or recommended permissible concentrations for atrazine (7 µg/l; Norris and Dost, 1991) and dichlobenil (37 µg/l; EPA, 1986) are at least three orders of magnitude higher than concentrations found in the present survey. Canadian water quality guidelines for bromacil and dimethoate (5.0 µg/l and 6.2 µg/l, respectively; Environment Canada, 1999) are also well above concentrations in the Mission Creek basin.

DDT

DDT compounds (DDT, DDE, DDD, and DDMU) continue to be present at relatively high concentrations in the major streams of the lower Mission Creek basin. Although banned 30 years

ago, DDT continues to be found in streams throughout Washington, especially in the orchard areas of eastern Washington. DDT remains stable for decades when bound to orchard soils (Harris et al., 2000). Therefore, DDT delivery to streams in the Mission Creek basin is likely to be primarily through erosion of orchard soils, although the presence of DDT due to mosquito control efforts in the 1950s and 1960s can not be ruled out. DDT loads are positively correlated² with total suspended solids concentrations at Lower Mission ($r^2=0.49$), Brender ($r^2=0.32$), and Yaksum ($r^2=0.36$). However, this appears to be a slow process in the Mission Creek basin due to the lack of significant erosion or conveyance systems for eroded soils such as rill irrigation returns.

Since legitimate use of DDT has not occurred for at least 30 years in the Mission Creek basin, seasonal concentration patterns are tied to other factors such as the hydrologic regimes and irrigation practices in each basin. Soil disturbance caused by orchard operations may play an important role in DDT delivery to streams. These factors will require close examination to understand DDT loading, due to the lack of obvious major delivery mechanisms in the Mission Creek basin.

The Washington State water quality standards to protect aquatic life from DDT exposure are 1.1 $\mu\text{g/l}$ (acute) and 0.001 $\mu\text{g/l}$ (chronic). The large difference between the standards is due to the bioaccumulative nature of DDT and its effect on eggshell-thinning in piscivorous birds resulting from very low levels in water (EPA, 1980). Nearly all samples had concentrations of DDT and its metabolites in excess of the chronic criterion. None of the concentrations approached the acute criterion.

Water quality criteria to protect human health from 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD have also been promulgated under the NTR. These criteria are 0.00059 $\mu\text{g/l}$ for DDT and DDE, and 0.00084 $\mu\text{g/l}$ for DDD. They are based on probable carcinogenic effects in humans, the rate of fish consumption, and the capacity of fish to bioconcentrate these chemicals. Translated to edible fish tissue using a bioconcentration factor of 53,600 (EPA, 1980), the NTR criteria are 32 $\mu\text{g/kg}$ for DDT and DDE, and 45 $\mu\text{g/kg}$ for DDD. Edible tissue from Mission Creek rainbow trout analyzed in 1993 had DDT and DDD concentrations slightly above these criteria, while DDE levels were an order of magnitude higher than the NTR criterion (Table 2; Davis et al., 1995).

It is impossible to assess relationships between water concentrations and edible tissue concentrations found in earlier sampling (1992-1994) due to the infrequency of measurable DDT concentrations in water during this period. However, a gross estimate of tissue concentrations can be calculated from the present data using average DDT concentrations and the bioconcentration factor in fish. Based on these factors, fish from Lower Mission would be expected to contain approximately 100 $\mu\text{g/kg}$ DDE, 80 $\mu\text{g/kg}$ DDT, and 30 $\mu\text{g/kg}$ DDD.

² Spearman ranked correlation, Systat, Inc.

Pesticide Loading to the Wenatchee River

The sums of pesticide loads from Lower Mission and Brender creeks provide a reasonable estimate of total loads to the Wenatchee River, since both sites are a few hundred feet upstream of the Wenatchee river confluence. In addition, the Mission Creek reach downstream of Brender Creek is swift-moving (particle deposition is unlikely), and there is no reason to suspect additional pesticide sources in this reach.

Loads of DDT, endosulfan, chlorpyrifos, azinphos-methyl, and bromacil are substantial, reaching one or more grams per day during their peak (Table 9). Notable is the pattern of decreasing loads throughout the season, except for azinphos-methyl which peaked at 1.4 grams per day in the July sample. Loads of the less frequently detected pesticides (methoxychlor, dimethoate, and atrazine) also peaked in July, while diazinon loads peaked in May.

Table 9. Estimated Pesticide Loads Delivered to the Wenatchee River from Mission Creek (mg/day).

Date	Total DDT	Total Endosulfan	Chlorpyrifos	Azinphos-methyl	Methoxychlor	Diazinon	Dimethoate	Bromacil	Atrazine
24-Apr-00	974	2,591	1,284	86	0	0	0	859	0
30-May-00	375	1,155	163	781	0	68	25	654	0
17-Jul-00	279	598	112	1,369	27	39	81	0	81
18-Sep-00	386	347	0	44	0	0	0	329	0
23-Oct-00	29	51	0	27	0	0	0	101	0

Conclusions

Streams in the lower Mission Creek basin contain a mixture of pesticides which are a result of current use and historic use over several decades. The major pesticides occurring at detectable levels in the agricultural (primarily orchard) and urban areas of the lower valley are the chlorinated insecticides DDT and endosulfan, and the organophosphorous insecticides chlorpyrifos and azinphos-methyl. During the growing season (April-October), one or more of these pesticides is consistently present at levels that exceed criteria developed to protect aquatic life.

Other pesticides present in streams of the lower basin include DDMU (a secondary DDT metabolite), the insecticides methoxychlor, diazinon, and dimethoate, as well as the herbicides bromacil, dichlobenil, and atrazine. These pesticides are not found with any regularity among streams and are below levels likely to harm aquatic organisms. There is no indication that any carbamate and chlorophenoxy pesticides used in the basin find their way into the streams sampled for this survey.

Orchard use is probably the primary source of currently registered pesticides, although domestic use could account for the presence of some chemicals. Virtually none of the measurable quantities of pesticides are from the upper Mission Creek basin which is primarily forested. The occurrence and concentrations of azinphos-methyl and chlorpyrifos, major organophosphorous insecticides currently used on orchards, appears to be closely tied to seasonal use. For endosulfan compounds, concentrations probably reflect both its current seasonal use and historic use, since it is less susceptible to degradation than the organophosphorous insecticides. For DDT, which was banned in 1972 but remains persistent for decades, concentrations appear to be related to delivery of contaminated soils to streams.

Concentrations of the major pesticides are highest in Brender and Yaksum creeks. However, loads are generally low in Yaksum Creek due to comparatively low flows. One notable exception is the high DDT loads in Yaksum Creek which probably account for most of the loading in Mission Creek upstream of the Brender Creek confluence.

DDT remains the most problematic pesticide contaminant in the Mission Creek basin. Although it does not possess the acute toxicity of many organophosphorous insecticides, DDT remains at chronically harmful levels in streams of the lower basin. There are not sufficient data to verify any trends since pesticide data were first collected a decade ago, but data reported in this current study indicate that DDT levels in fish probably remain above acceptable human health criteria.

Recommendations

Data reported in this current study, coupled with WSPMP data from 1992-1994, document pesticide contamination in the major streams of the lower Mission Creek basin. However, little is known about how these pesticides find their way into the streams. For pesticides currently being used in orchards, an investigation should focus on application methods and techniques. This probably will require water sampling during pesticide applications.

Investigations also should be conducted to assess the degree and mechanisms by which DDT bound to soils is delivered to streams. This may require detailed analysis of DDT concentrations and profiles in orchard and other soils, as well as irrigation and orchard management practices which result in soil disturbance. Results of such an analysis would be applicable to other contaminants and may have practical value in understanding pesticide dynamics in other areas with historic DDT contamination.

For the more persistent pesticides (i.e., DDT and endosulfan), investigation of instream sediment levels should be conducted to assess possible contribution of sediments to contamination of the water column.

These types of investigations will provide information useful in developing a total maximum daily load (TMDL) and implementation plan for pesticides in Mission Creek. A TMDL investigation began in July 2002.

At some point, DDT levels in Mission Creek fish should be re-examined. Current DDT concentrations in water suggest that levels in edible fish tissue have probably not changed significantly since 1994. However, using DDT concentrations in the water column to predict edible tissue concentrations is notoriously unreliable. Analysis of a composite rainbow trout sample similar to the 1994 WSPMP sample would be preferable.

The potential toxicity of pesticides to aquatic organisms should be evaluated if azinphos-methyl and chlorpyrifos continue to be used in the Mission Creek basin. Toxicity of aquatic invertebrates would probably be best assessed by using *in situ* bioassays. Caged *Daphnia* have successfully been used to reveal toxicity in other streams contaminated with organophosphorous insecticides (e.g., Davis et al., 1997).

The 303(d) list should retain entries for 4,4'-DDT and 4,4'-DDE in Mission Creek based on the data reported in this current study and previous fish tissue data. Mission Creek should also be listed for 4,4'-DDD based on these sources of data. Azinphos-methyl should be dropped from the 303(d) list, because criteria for this toxicant have not been formalized in Washington water quality standards (Ch. 173-201A WAC) or EPA's National Toxics Rule (40 CFR Part 131).

Acknowledgements

The authors would like to thank the following people for their contributions to this study:

- Mike Rickel, Chelan County Conservation District, for helpful suggestions and sharing his knowledge of the Mission Creek watershed.
- Tim Smith, Washington State University Cooperative Extension, for providing information on pesticides used in orchards.
- Katina Kapantais for help with field work.
- Will White and Pam Covey for sample handling and tracking.
- Norm Olson, Bob Carrell, Steve Reimer (EPA), Meredith Osborn, and Catherine Bickle of the EPA/Ecology Manchester Environmental Laboratory for their excellent work.
- Dale Norton, Art Johnson, Greg Bohn, David Schneider, Mike Rickel, Laurence Gadbois (EPA), and Bridget Moran (Washington State Department of Agriculture) for their review of the final report.
- Joan LeTourneau for editing and formatting the final report.

References

- Davis, D., 1993. Washington State Pesticide Monitoring Program - Reconnaissance Sampling of Surface Waters (1992). Washington State Department of Ecology, Olympia, WA.
- Davis, D., 1996. Washington State Pesticide Monitoring Program - 1994 Surface Water Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication No. 96-305.
- Davis, D. and A. Johnson, 1994. Washington State Pesticide Monitoring Program - 1993 Surface Water Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication No. 94-164.
- Davis, D., A. Johnson, and D. Serdar, 1995. Washington State Pesticide Monitoring Program - 1993 Fish Tissue Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication No. 95-356.
- Davis, D., D. Serdar, and A. Johnson, 1997. Assessment of Cranberry Bog Drainage Pesticide Contamination. Washington State Department of Ecology, Olympia, WA. Publication No. 97-329.
- Ecology, 1993 (Revised 1997). Assessment of Water Quality for the Section 303(d) List. WQP Policy 1-11, Washington State Department of Ecology Water Quality Program, Olympia, WA.
- Environment Canada, 1999. Canadian Water Quality Guidelines. Guidelines and Standards Division. Hull, Quebec.
- EPA, 1980. Ambient Water Quality Criteria for DDT. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Criteria and Standards Division, Washington, D.C. EPA 440/5-80-038.
- EPA, 1986. Quality Criteria for Water. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC. EPA 440/5-86-001.
- EPA, 1999. National Recommended Water Quality Criteria – Correction. U.S. Environmental Protection Agency, Office of Water. EPA 822-Z-99-001.
- EPA, 2000. Chlorpyrifos Revised Risk Assessment and Agreement with Registrants. U.S. Environmental Protection Agency.
- EPA, 2001. Organophosphate Pesticides; Availability of Azinphos-Methyl and Phosmet Interim Risk Management Decision Documents. Federal Register Notice November 28, 2001. Volume 66, Number 229, pp. 59419-59421.

- Harris, M.J., L.K. Wilson, J.E. Elliott, C.A. Bishop, A.D. Tomlin, and K.V. Henning, 2000. Transfer of DDT and Metabolites from Fruit Orchard Soils to American Robins (*Turdus migratorius*) Twenty Years After Agricultural Use of DDT in Canada. *Archives of Environmental Contamination and Toxicology* 39: 205-220.
- Mueller, Mick, 2002. Personal communication. Entomologist, U.S. Forest Service, Wenatchee National Forest, Leavenworth Ranger District. January 25.
- NAS/NAE, 1973. Water Quality Criteria, 1972. Prepared by National Academy of Sciences and National Academy of Engineering for U.S. Environmental Protection Agency. EPA R3-73-033.
- Norris, L. and F. Dost, 1991. Proposed Surface Water Quality Criteria for Selected Pesticides Used for Forest Management and Management of Forest Tree Seedling and Christmas Tree Plantations in Oregon and Washington. Oregon State University, Corvallis, OR.
- Reimer, S., 2000. Unpublished data. Ecology/EPA Manchester Environmental Laboratory, Manchester, WA.
- WRWSC, 1998. Wenatchee River Watershed Action Plan. Wenatchee River Watershed Steering Committee.
- WSU Cooperative Extension, 2000. 2000 Protection Guide for Tree Fruits in Washington. Cooperative Extension, Washington State University College of Agriculture and Home Economics.

Appendix A – Sampling Locations

Lower Mission: Mission Creek near mouth

Located just above the Brender Creek confluence and approximately 750 feet from Wenatchee River entry. This station corresponds to Wenatchee Watershed Ranking Project Station 2MC.

Latitude = 47°31.281' N

Longitude = 120°28.625' W

Brender: Brender Creek near mouth

Located just above the Mission Creek confluence and approximately 700 feet from Wenatchee River entry. This station corresponds to Wenatchee Watershed Ranking Project Station 3MC.

Latitude = 47°31.272' N

Longitude = 120°28.640' W

Yaksum: Yaxon Canyon (Yaksum Creek) near mouth

Located just above the Mission Creek confluence at Coates Road crossing. This station corresponds to Wenatchee Watershed Ranking Project Station 7MC.

Latitude = 47°29.986' N

Longitude = 120°28.479' W

Upper Mission: Mission Creek on USFS land

Located just inside U.S. Forest Service boundary off FSR 2204. This station corresponds to Wenatchee Watershed Ranking Project Station 11MC.

Latitude = 47°25.573' N

Longitude = 120°30.635' W

Appendix B – Practical Quantitation Limits for Pesticide Analysis

Nitrogen Pesticides (ugl)					
Alachlor	0.071	Diuron	0.12	Pendimethalin	0.03
Ametryn	0.02	Eptam	0.039	Profluralin	0.047
Atraton	0.03	Ethalfuralin (Sonalan)	0.03	Prometon (Pramitol 5p)	0.02
Atrazine	0.02	Fenarimol	0.059	Prometryn	0.02
Benefin	0.03	Fluridone	0.12	Pronamide (Kerb)	0.079
Bromacil	0.079	Hexazinone	0.03	Propachlor (Ramrod)	0.047
Butachlor	0.12	Metalaxyl	0.12	Propazine	0.02
Butylate	0.039	Metolachlor	0.079	Simazine	0.02
Carboxin	0.12	Metribuzin	0.02	Tebuthiuron	0.03
Chlorothalonil (Daconil)	0.047	MGK-264	0.16	Terbacil	0.059
Chlorpropham	0.079	Molinate	0.039	Terbutryn Igran)	0.02
Cyanazine	0.03	Napropamide	0.059	Triadimefon	0.051
Cycloate	0.039	Norflurazon	0.039	Triallate	0.059
Diallate (Avadex)	0.14	Oxyfluorfen	0.079	Trifluralin (Treflan)	0.03
Dichlobenil	0.039	Pebulate	0.039	Vernolate	0.039
Diphenamid	0.059				

Organophosphorous Pesticides (ug/l)					
Azinphos-ethyl	0.031	EPN	0.02	Paraoxon-methyl	0.035
Azinphos-methyl (Guthion)	0.031	Ethion	0.014	Parathion	0.016
Carbophenothion	0.02	Ethoprop	0.016	Parathion-Methyl	0.014
Chlorpyrifos	0.016	Fenamiphos	0.03	Phorate	0.014
Chlorpyrifos-methyl	0.016	Fenitrothion	0.014	Phosphamidan	0.047
Coumaphos	0.024	Fensulfothion	0.02	Propetamphos	0.039
Demeton-O	0.014	Fenthion	0.014	Ronnel	0.014
Demeton-S	0.014	Fonophos	0.012	Sulfotepp	0.012
Diazinon	0.016	Imidan	0.022	Sulprofos (Bolstar)	0.014
Dichlorvos (DDVP)	0.016	Malathion	0.016	Temephos (Abate)	0.12
Dimethoate	0.016	Merphos (1 & 2)	0.024	Tetrachlorvinphos (Gardona)	0.039
Dioxathion	0.033	Mevinphos	0.02	Tribufos (DEF)	0.028
Disulfoton (Di-Syston)	0.012				

Chlorinated Pesticides (ug/l)					
2,4'-DDT	0.011	captan	0.029	Endosulfan II	0.0015-0.012
2,4'-DDE	0.011	captafol	0.054	Endosulfan Sulfate	0.0015-0.012
2,4'-DDD	0.011	Cis-Chlordane	0.011	Endrin	0.011
4,4'-DDT	0.0015-0.012	Trans-Chlordane	0.011	Endrin Aldehyde	0.011
4,4'-DDE	0.0015-0.012	Alpha-Chlordene	0.011	Endrin Ketone	0.011
4,4'-DDD	0.0015-0.012	Gamma-Chlordene	0.011	Heptachlor	0.011
DDMU	0.011	Cis-Nonachlor	0.011	Heptachlor Epoxide	0.011
Aldrin	0.011	Trans-Nonachlor	0.011	Methoxychlor	0.011
Alpha-BHC	0.011	Oxychlordane	0.011	Mirex	0.011
Beta-BHC	0.011	Dicofol (Kelthane)	0.043	Pentachloroanisole	0.011
Delta-BHC	0.011	Dieldrin	0.0015-0.012	Toxaphene	0.092
Gamma-BHC (Lindane)	0.011	Endosulfan I	0.0015-0.012		

Appendix B (cont'd) – Practical Quantitation Limits for Pesticide Analysis

Chlorophenoxy Herbicides (ug/l)					
2,3,4,5-Tetrachlorophenol	0.055	3,5-Dichlorobenzoic acid	0.10	Diclofop-methyl	0.15
2,3,4,6-Tetrachlorophenol	0.055	4-Nitrophenol	0.18	Dinoseb	0.15
2,4,5-T	0.080	Acifluorfen (Blazer)	0.40	loxynil	0.10
2,4,5-TB	0.090	Bentazon	0.15	MCPA	0.20
2,4,5-TP (Silvex)	0.080	Bromoxynil	0.10	MCPP (Mecoprop)	0.20
2,4,5-Trichlorophenol	0.060	DCPA (Dacthal)	0.080	Pentachlorophenol	0.050
2,4,6-Trichlorophenol	0.060	Dicamba	0.10	Picloram	0.10
2,4-D	0.10	Dichlorprop	0.11	Triclopyr	0.084
2,4-DB	0.12				

Carbamate Pesticides (ug/l)					
3-Hydroxycarbofuran	0.12	Carbaryl	0.12	Methomyl	0.12
Aldicarb	0.12	Carbofuran	0.12	Oxamyl (Vydate)	0.12
Aldicarb Sulfone	0.12	Methiocarb	0.12	Propoxur (Baygon)	0.12
Aldicarb Sulfoxide	0.12				