A Department of Ecology Report

Results from Monitoring Endosulfan and Dieldrin in Wide Hollow Creek, Yakima River Drainage, 2005-06

Abstract

Endosulfan and dieldrin were monitored in Wide Hollow Creek near Yakima from July 2005 through June 2006. Wide Hollow Creek is on the federal Clean Water Act Section 303(d) list as water quality limited for historically exceeding aquatic life and/or human health water quality criteria for these pesticides.

Results showed that endosulfan no longer qualifies for 303(d) listing. Dieldrin, however, was consistently above human health criteria and should therefore remain listed.

Data were also obtained on endosulfan sulfate and aldrin.

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Background

At the request of the Washington State Department of Ecology's (Ecology's) Central Regional Office (CRO), Ecology's Environmental Assessment Program reviewed the available water quality data on endosulfan, dieldrin, and chlorpyrifos concentrations in the Yakima River drainage during 2005 (Johnson, 2005). CRO wanted to determine how to address multiple 303(d) listings for these pesticides. CRO was specifically interested in determining if any of these chemicals could be included in the *Lower Yakima River Suspended Sediment and DDT TMDL*[1] (Joy and Patterson, 1997), based on an association with total suspended solids (TSS).

One recommendation stemming from the review was to monitor endosulfan concentrations in Wide Hollow Creek. Wide Hollow enters the Yakima River at Union Gap on the right bank at river mile 107.4 (Figure 1). The review had found that recent data warranted moving the endosulfan listings for the Yakima mainstem and other tributaries out of Category 5 (TMDL Required). However, because no recent data had been collected on Wide Hollow Creek, the appropriate listing status was uncertain. CRO agreed that Wide Hollow should be monitored for endosulfan and requested that dieldrin be included to evaluate its correlation with TSS. The detection frequency for dieldrin in the historical data had been too low to assess this relationship.

The Category 5 listings at issue in Wide Hollow Creek were as follows:

Table 1. 2002/2004 303(d) Category 5 Listings for Endosulfan and Dieldrin in Wide Hollow Creek

Parameter	Media	Listing ID	Township Range Section	Basis			
				Year	N=	Location	Reference
Endosulfan	Water	8857	12N19E08	1988-89	6	Union Gap	Rinella et al. (1992)
Dieldrin	Water	8856	12N19E08	1988	5	Union Gap	Rinella et al. (1992)

[1] Total Maximum Daily Load. The TMDL process, established by Section 303(d) of the federal Clean Water Act, requires states to identify sources of pollution in waters that fail to meet water quality standards and to develop plans to address those pollutants. The TMDL establishes limits on pollutants that can be discharged to the waterbody and still allow Washington State water quality standards to be met.

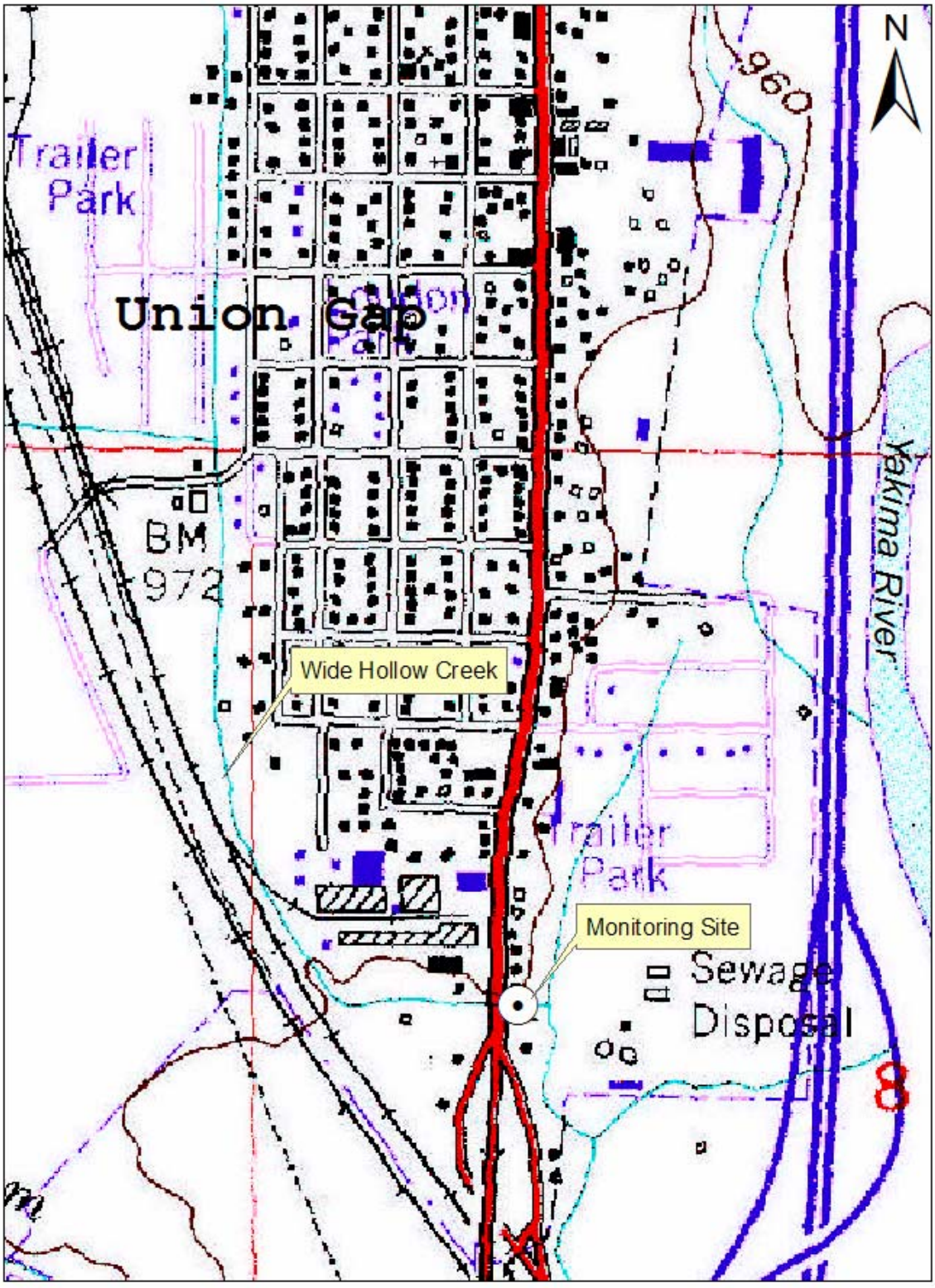


Figure 1. Location of Monitoring Site on Wide Hollow Creek

The applicable Washington State water quality criteria are shown in Table 2. Wide Hollow Creek is listed for water samples exceeding aquatic life criteria (endosulfan and dieldrin) and human health criteria (dieldrin), based on U.S. Geological Survey (USGS) data reported in Rinella et al. (1992).

Table 2. Water Quality Criteria for Endosulfan and Dieldrin (ng/L, parts per trillion)

Parameter	Aquatic Life Criteria		Human Health Criteria	
	Acute	Chronic	Fish Consumption	Fish+Water Consumption
Endosulfan I/II	220	56	2000	93
Dieldrin	2500	1.9	0.14	0.14

The Environmental Assessment Program began monitoring Wide Hollow Creek in July 2005 through the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams* project (Burke et al., 2006). The objectives were to determine (1) if a change in 303(d) listing status was appropriate for endosulfan or dieldrin, and (2) if there was a correlation between dieldrin and TSS. The data and supporting quality control information were to be provided to the CRO Water Quality Program for consideration during the next 303(d) listing cycle.

Monitoring Program

Endosulfan use is restricted to 4 quarts/acre/year (liquid; product formulation) and 3 lbs/acre/year (powder; active ingredient). It is used on pears, apples, and cherries once or twice a year. There is very little use of endosulfan outside the two-month window between March 15 and May 15. Dieldrin is no longer used, having been banned by the U.S. Environmental Protection Agency (EPA) in the 1980s.

Water samples were collected near the mouth of Wide Hollow Creek from July 2005 through June 2006 at Ecology's ambient monitoring station, Wide Hollow Creek @ Main Street (37E050). The samples were analyzed for endosulfan I, endosulfan II, endosulfan sulfate, dieldrin, and TSS. Endosulfan I and II are stereo isomers. Endosulfan sulfate is a toxic degradation product. Data were also obtained on pH, temperature, dissolved oxygen, conductivity, and discharge, which are routine parameters for the *Pesticides in Salmonid-Bearing Streams* program. Because traces of aldrin appeared in some of the early samples, aldrin was analyzed beginning in March. Aldrin is rapidly transformed into dieldrin through biotransformation and photo-oxidation.

In light of the use pattern for endosulfan, samples were collected weekly during March and April; every other week during May, June, July, August, and September; and monthly from October through February (Table 3). Sampling was initiated on July 13, 2005, and the final samples were collected on June 27, 2006.

Table 3. Sampling Frequency for Endosulfan and Dieldrin in Wide Hollow Creek

Year	Month	Frequency	N=
2005	July	twice	2
2005	Aug	twice	2
2005	Sept	twice	2
2005	Oct	once	1
2005	Nov	once	1
2005	Dec	once	1
2006	Jan	once	1
2006	Feb	once	1
2006	March	weekly	4
2006	April	weekly	4
2006	May	twice	2
2006	June	twice	2
			23

Pesticide samples were collected in one-gallon glass jars with Teflon lid-liners, cleaned to EPA quality assurance/quality control specifications. TSS samples were collected in 1-liter polyethylene bottles. Sampling methods followed routine procedures described in Burke et al. (2006).

The samples were analyzed by Ecology's Manchester Environmental Laboratory. Pesticides were extracted with methylene chloride following EPA Method 3510. The extracts were analyzed by GC/ECD according to EPA Method 8081, modified for large volume injection. TSS was analyzed by Standard Methods 2540D.

Data Quality

Manchester Laboratory prepared written case narratives assessing the quality of the data collected for this project. The reviews include a description of analytical methods and an assessment of holding times, tuning, calibration, method blanks, spike recoveries, and laboratory control samples. No significant problems were encountered in the analyses, and the data are usable as qualified. The reviews and the complete Manchester data reports are available on request.

Field quality control samples for this project include one transfer blank and two replicate samples (Appendix A). No target compounds were detected in the transfer blank. Concentrations of endosulfan compounds, dieldrin, and aldrin in the replicates agreed within 15% or better.

Results and Discussion

Concentrations Observed

Summary statistics on the pesticides monitored in Wide Hollow Creek are shown Table 4.

Table 4. Summary Statistics for Endosulfan Compounds, Dieldrin, and Aldrin in Wide Hollow Creek During 2005-06 (ng/L; parts per trillion)

Pesticide Compound	N=	Minimum	Median	Mean	90th Percentile	Maximum
Endosulfan I	23	0.39	1.5	3.2	4.5	24
Endosulfan II	23	0.61	1.2	2.0	4.2	8.3
Endosulfan I+II	23	1.0	2.7	5.2	8.1	31
Endosulfan sulfate	23	2.8	4.8	5.8	8.1	16
Dieldrin	23	0.22	0.49	0.64	0.94	2.2
Aldrin	11	<0.032	ND	ND	0.27	0.38

ND = not detected

Endosulfan compounds and dieldrin were detected in all samples analyzed. Total endosulfan concentrations (I + II) ranged from 1.0 – 31 ng/L, averaging 5.2 ng/L. The breakdown product endosulfan sulfate was detected at 2.8 – 16 ng/L.

The range in dieldrin concentrations was 0.22 – 2.2 ng/L, with an average of 0.64 ng/L. Aldrin was added as an analyte in March. It was detected in May and June at concentrations ranging from 0.25 – 0.38 ng/L.

The total endosulfan and dieldrin concentrations measured over the course of the monitoring program are plotted in Figure 2. Endosulfan remained below approximately 5 ng/L for most of the year. Concentrations increased slightly during the winter months. Peak concentrations of 25 and 31 ng/L were observed during the March – May period when endosulfan was applied to local orchards. A maximum of two applications were used, both of which appear to be reflected in the samples.

Dieldrin concentrations were generally at or below 1 ng/L. Concentrations gradually increased from September to December and then decreased from December to April. Maximum concentrations of 1.3 and 2.2 ng/L were recorded in November and December.

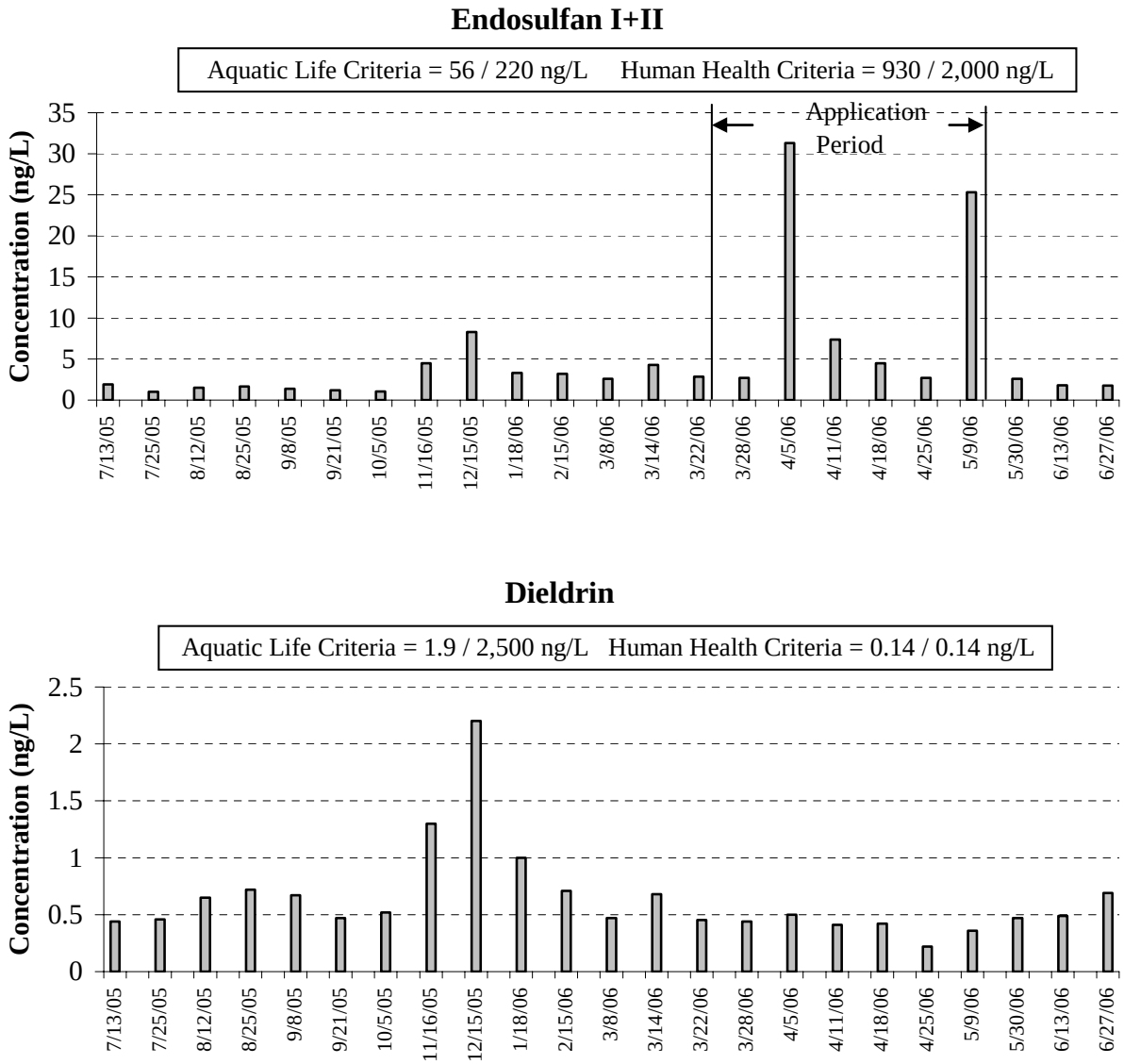


Figure 2. Total Endosulfan (I+II) and Dieldrin Concentrations in Wide Hollow Creek, 2005-06.

Comparison with Criteria

Table 5 shows the water quality criteria that apply to endosulfan compounds, dieldrin, and aldrin. The lower half of the table shows the frequency with which they were exceeded in Wide Hollow Creek during 2005-06.

Table 5. Criteria Exceedance Frequencies for Pesticides Monitored in Wide Hollow Creek during 2005-06

Parameter	Aquatic Life Criteria		Human Health Criteria	
	Acute	Chronic	Fish Consumption	Fish+Water Consumption
Criteria Values (ng/L)				
Endosulfan I/II	220	56	2,000	930
Endosulfan sulfate	no criteria		2,000	930
Dieldrin	2,500	1.9	0.14	0.14
Aldrin	2,500	1.9	0.14	0.13
Exceedance Frequencies				
Endosulfan I/II	0%	0%	0%	0%
Endosulfan sulfate	0%	0%	0%	0%
Dieldrin	0%	4%	100%	100%
Aldrin	0%	0%	28%	28%

Endosulfan and endosulfan sulfate never exceeded aquatic life or human health criteria. This finding is consistent with endosulfan data collected by USGS and Ecology on other Yakima River tributaries between 1995 and 2004 (Johnson, 2005).

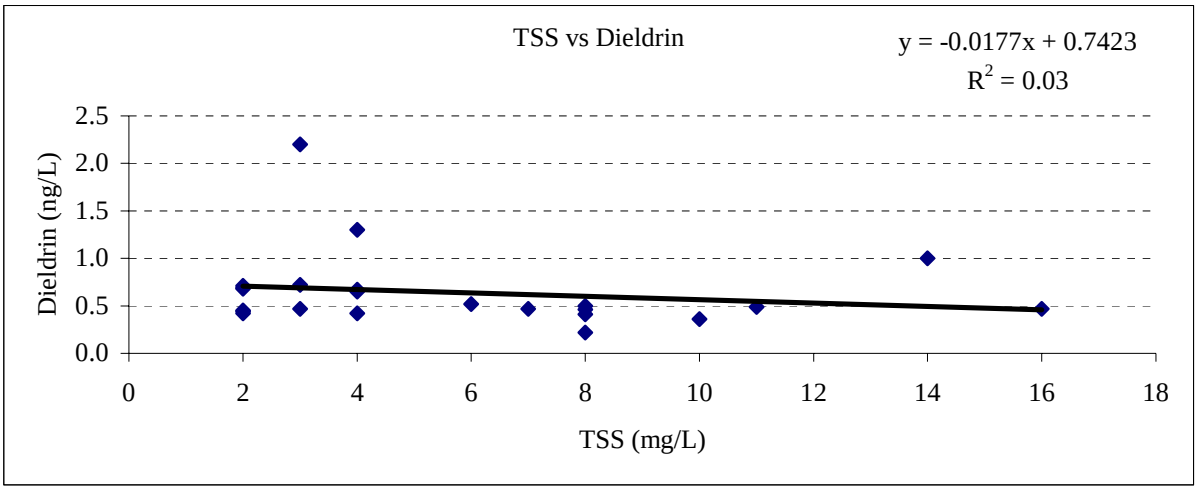
Dieldrin exceeded human health criteria in all samples analyzed, approximately by factors of 2 – 15. The dieldrin chronic aquatic life criterion of 1.9 ng/L was slightly exceeded in one sample collected in December (2.2 ng/L). Quality control data indicate this result may be biased high. Aldrin exceeded human health criteria in 3 of the 11 samples analyzed.

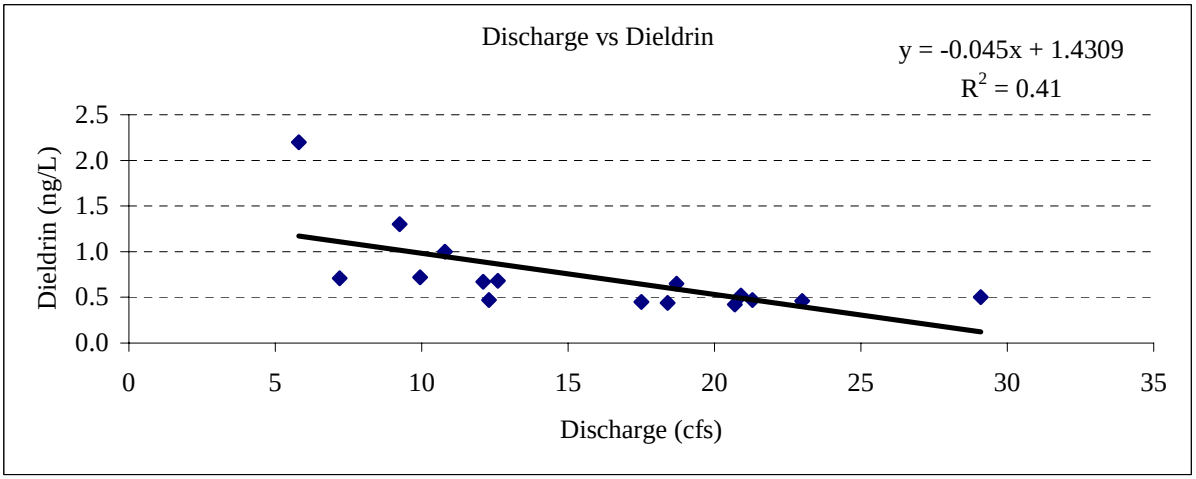
Relationships with Other Parameters

A series of scatterplots were prepared to determine if dieldrin or endosulfan were correlated with TSS or flow.

Figure 3 has the dieldrin graphs. There was no correlation between dieldrin and TSS (R^2 = 0.07). Dieldrin was, however, inversely correlated with discharge and weakly correlated with conductivity. This suggests that subsurface flow is a major source of dieldrin to Wide Hollow Creek. The groundwater in this area is close to the surface, and tile drains are likely numerous (Greg Bohn, CRO, 12/29/05 email).

Endosulfan was not correlated with TSS (R^2 = 0.04) or other parameters.





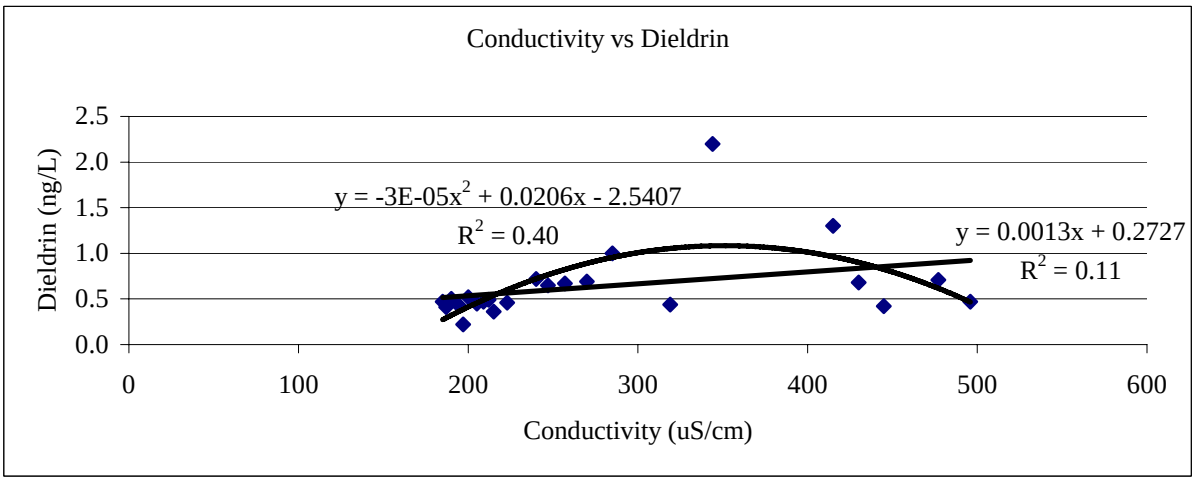


Figure 3. Correlations Between Dieldrin, TSS, Discharge, and Conductivity

Conclusions and Recommendations

1. The Category 5 listing for endosulfan in Wide Hollow Creek should be changed to Category 1 (Meets Tested Criteria).

2. The Category 5 listing for dieldrin in Wide Hollow Creek is appropriate in view of it chronically exceeding human health criteria.

3. There does not appear to be any basis for including dieldrin under the existing Suspended Sediment and DDT TMDL.

4. Both dieldrin and aldrin should be included as target compounds in the upcoming human health TMDL for the Yakima River.

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Appendix A. Results on Field Quality Control Samples for Wide Hollow Creek

Field Replicates									
Date:	7/13/2005		Replicate		RPD	3/22/2006		Replicate		RPD
TSS	NA		NA		- -	2		6	J	100%
Endosulfan I	1.0	J	0.98	J	2.0%	1.6		1.8		12%
Endosulfan II	0.95	J	0.9	J	5.4%	1.1		1.2		8.7%
Endosulfan Sulfate	3.7	J	4	J	7.8%	3.8	J	3.8	J	0%
Dieldrin	0.45	J	0.43	J	4.5%	0.42	J	0.49	J	15%
Aldrin	NA		NA		- -	ND at 0.033		ND at 0.033		0%

Field Blanks				
Date:	7/13/2005		3/28/2006	
TSS	NA		1	U
Endosulfan I	0.063	UJ	0.066	UJ
Endosulfan II	0.063	UJ	0.066	UJ
Endosulfan Sulfate	0.063	UJ	0.066	UJ
Dieldrin	0.063	UJ	0.066	UJ
Aldrin	NA		0.066	UJ

RPD = Relative Percent Difference (range as percent of mean)
NA = Not analyzed.
ND = Not detected.
U = The analyte was not detected at or above the reported result
J = The analyte was positively identified. The associated numerical result is an estimate.
UJ = The analyte was not detected at or above the reported estimated result.

Appendix B. Monitoring Data for Wide Hollow Creek

Parameter	Units	7/13/05	7/13/05 replicate	7/25/05	8/12/05	8/25/05	9/8/05	9/21/05	10/5/05	11/16/05
pH	pH	8.06		8.32	8.51	8.3	8.01	7.96	7.69	8.11
Temperature	°C	17.9		20.6	20.3	19.1	18.5	14.6	14.2	10.3
DO mg/L	mg/L				11.4	10.3	10.2	9.7	10.2	10.8
DO %	%				126.2	111.1	188.8	95.1	99.4	106
Conductivity	uS/cm	205		223	247	240	257	209	200	415
ORP	mV									
Discharge	cfs	17.5		23.0	18.7	10.0	12.1	21.3	20.9	9.3
Stage	m	3.06		3.24	3.06	2.86	2.94	3.2	3.17	--
TSS	mg/L	2		8	4	3	4	7	6	4
Aldrin	ng/L	NA		NA	NA	NA	NA	NA	NA	NA
Endosulfan I	ng/L	1.0J	0.98J	0.4NJ	0.71	0.69J	0.59	0.45J	0.39J	2
Endosulfan II	ng/L	0.95J	0.9J	0.61	0.8	0.97J	0.8	0.77J	0.67J	2.5J
Endosulfan sulfate	ng/L	3.7J	4J	2.8J	3.3	4.2J	4.4J	3.2J	3	8.3J
Dieldrin	ng/L	0.45J	0.43J	0.46	0.65	0.72J	0.67	0.47J	0.52J	1.3J

Appendix B. (continued)

Parameter	Units	12/15/05	1/18/06	2/15/06	3/8/06	3/14/06	3/22/06	3/22/06 replicate	3/28/06	3/28/06 duplicate	4/5/06
pH	pH	8	7.99	7.97	8.84	8.52	8.22		8.57		7.08
Temperature	°C	7.96	7.7	8.3	10.3	9.9	9.4		11.1		11.14
DO mg/L	mg/L	11.9	12.0	--	14.7	13.8	11.1		13.8		11.1
DO %	%	100.9	101.2	--	126	122.5	96.6		125.9		101.1
Conductivity	uS/cm	344	285	477	495.8	430	445		319		190
ORP	mV					145.4	180.8		180		152.6
Discharge	cfs	5.8	10.8	7.2	12.3	12.6	20.7		18.4		29.1
Stage	m	2.66	2.84	2.7	--	2.9	3.22		3.18		3.26
TSS	mg/L	3	14	2	3	2	2	6 J	2	1 U	8
Aldrin	ng/L	NA	NA	NA	NA	0.033 U	0.033 U	0.033 U	0.063 U		0.063 U
Endosulfan I	ng/L	3.7	1.3	1.7	1.5 J	2.6 J	1.6	1.8	1.6 J		24
Endosulfan II	ng/L	4.6	2	1.5	1.1 J	1.7 J	1.1	1.2	1.1 J		7.3
Endosulfan sulfate	ng/L	16 J	6.7	5.9 J	4.3 J	6	3.8 J	3.8 J	4.7 J		13
Dieldrin	ng/L	2.2 J	1	0.71	0.47 J	0.68 J	0.42 J	0.49 J	0.44 J		0.5

Appendix B. (continued)

Parameter	Units	4/11/06	4/18/06	4/18/06 duplicate	4/25/06	5/9/06	5/30/06	6/13/06	6/27/06
pH	pH	8.19	8.44		8.4	8.43	7.86	7.68	8.42
Temperature	°C	9.03	9.4		10.6	13.2	13.8	14.5	19.3
DO mg/L	mg/L	13.2	13.1		13.0	12.7	9.5	9.0	11.7
DO %	%	114.3	114.8		116.8	121.3	92.2	87.7	127.4
Conductivity	uS/cm	187	195		197	215	185	212	270
ORP	mV	Unstable	Unstable		Unstable	Unstable	Unstable	210.8	276.3
Discharge	cfs	28.8	21.3		25.1	18.8	27.6	28.2	21.3
Stage	m	3.42	3.18		3.3	3.1	3.38	3.4	3.18
TSS	mg/L	8	4	5	8	10	16	11	2
Aldrin	ng/L	0.032 U	0.032 U		0.032 U	0.062 U	0.38	0.27 J	0.25 J
Endosulfan I	ng/L	4.7	2.6		1.5	17 J	0.99	0.71	0.83
Endosulfan II	ng/L	2.7	1.9		1.2	8.3 J	1.6	1.1	0.95 J
Endosulfan sulfate	ng/L	7.4	7.4		4.4	5.3 J	4.8	4.8	5.4
Dieldrin	ng/L	0.41	0.42		0.22	0.36 J	0.47 J	0.49 J	0.69 J

DO = Dissolved oxygen
ORP = Oxidation-reduction potential
TSS = Total suspended solids
U = The analyte was not detected at or above the reported result
J = The analyte was positively identified. The associated numerical result is an estimate.
NJ = There is evidence the analyte is present. The associated numerical result is an estimate.
ND = Not detected.
NA = Not analyzed.