

Introduction

During the period from April 13, 2011 through September 28, 2011 the Idaho State Department of Agriculture (ISDA) and the University of Idaho Analytical Science Laboratory (ASL) conducted an evaluation of pesticide residues on seven tributaries to the main fork of the Clearwater River. These seven tributaries are designated as salmonid spawning waters by NOAA's National Marine Fisheries Service (NMFS) and the U.S. Fish and Wildlife Service (USFWS). Research by both NMFS, USFWS, and the U.S. Environmental Protection Agency (USEPA) continue to evaluate the overall impact that certain pesticide residues, in the water column or sediment, have on threatened or endangered salmonid species.

The Clearwater River Basin is located in north-central Idaho and covers approximately 9,645 square miles. The seven tributaries monitored during this study encompasses approximately 755,878 acres with approximately 350,529 of those acres involved in agricultural activities (Table 1).

Monitoring Sites	Total Acreage ¹	Ag. Acreage ¹	% Ag Acreage	Salmonid Spawning
Lapwai Creek	171,462	58,297	40	Yes
Catholic Creek	7,789	5,242	67	Yes
Potlatch River	380,211	156,647	41	Yes
Pine Creek	14,605	11,362	78	Yes
Big Canyon Creek	80,653	51,860	64	Yes
Little Canyon Creek	60,544	51,039	84	Yes
Cottonwood M.F. Clearwater	40,614	16,083	40	Yes
1 Acreage figures calculated using USGS Str	reamStat program			

Table 1. Tributary acreage and salmonid spawning designation.

The seven tributaries evaluated for this study were Lapwai Creek, Catholic Creek, Potlatch River, Pine Creek, Big Canyon Creek, Little Canyon Creek, and Cottonwood Creek (Figure 1). Five of the seven creeks were evaluated by ISDA for pesticide residues in 2004 (ISDA, 2004). In 2011 Big Canyon and Little Canyon Creek were sampled individually unlike in 2004 when they were sampled below the confluence and treated as one sample. In addition, Pine Creek was added for the 2011 monitoring.



Figure 1. Clearwater River's tributary monitoring sites; tributaries highlighted in red are designated for salmonid spawning.

Analytical and Field Quality Assurance

Analytical methods and techniques used for this study were as follows: EPA Method 507 modified, EPA Method 632 modified, EPA Method 508 modified, and EPA Method 515.2 (on file at ASL). All analyte spikes and surrogate standard recoveries were within acceptable ranges (70-130%) indicating that pesticide residues were accurately recovered. All submitted duplicate samples resulted in no detections (ND), of any pesticides, which made relative percent difference calculations (RPD) unnecessary. There were holding times, between extraction and instrumental analysis, issues for carbamate and phenylurea pesticides analysis. Due to instrument failure samples collected on August 3, 17, 31, and September 14, and 28, missed their holding times. The extraction solutions were frozen while the instrument was being replaced and after analysis all of the standard recoveries were within acceptable ranges.

All field monitoring techniques followed the protocols outlined in the Quality Assurance Project Plan (QAPP) for the Clearwater River Pesticide Evaluation, April 2011 (on file at ISDA). All bottle blanks and equipment blanks prepared in the field were non-detectable for pesticides indicating that both the field and laboratory activities were free from contamination.

Overall Results

In 2011 there were a total of 15 pesticides detected throughout the watershed with 12 herbicides, 2 insecticides, and 1 desethyl atrazine which is a degradate of atrazine (Table 2).

Detected Pesticides	Pesticide Type	Trade Name	Detected Pesticides	Pesticide Type	Trade Name
2,4-D	Herbicide	Curtail	Diuron	Herbicide	Karmex
2,4-Dichorobenzoic Acid	Herbicide	_	Hexazinone	Herbicide	Velpar
Bentazon	Herbicide	Basagran	Linuron	Herbicide	Lorox DF
Bromoxynil	Herbicide	Buctril	MCPA	Herbicide	Banlene
Desethyl Atrazine	Degradate ¹	—	Methomyl	Insecticide	Lannate
Dicamba	Herbicide	Brushmaster	Metribuzin	Herbicide	Sencore
Dimethoate	Insecticide	Dimethoate 4EC	Pendimethalin	Herbicide	Goal
¹ degradate of atrazine			Simazine	Herbicide	Sim-Trol 4L

Table 2. Detected pesticides, Trade Names, and type of pesticide (herbicide or insecticide).

There was a combined total of 58 pesticide detections during this program. There were 54 herbicide detections, two insecticide detections, and two desethyl atrazine detections. The herbicide metribuzin had the highest number of detections (22) and the Pine Creek watershed had the highest total pesticide detections (18). Table 3 shows a breakdown of the watersheds and the overall number of detections.

Pesticides	Lapwai Ck.	Catholic Ck.	Potlatch R.	Pine Ck.	Big Canyon Ck.	Little Canyon Ck.	Cottonwood Ck.	Total
2,4-D	1	1		1	1	1	1	6
2,4-Dichorobenzoic Acid							1	1
Bentazon	1							1
Bromoxynil			1	2			1	4
Desethyl Atrazine							2	2
Dicamba				1				1
Dimethoate		1						1
Diuron			1	3				4
Hexazinone			1					1
Linuron		1	1	1				3
MCPA		1		2	1	2		6
methomyl				1				1
Metribuzin	3	6	1	5	1	3	3	22
Pendimethalin			1	2			1	4
Simazine			1					1
Total	5	10	7	18	3	6	9	58

Table 3. Pesticides detected and number of detections per watershed.

Tables 4 through 10 evaluates each watershed for pesticides detected, date of detections, and concentrations compared to the U. S. Environmental Protection Agency's Aquatic Benchmarks for pesticides.

Lapwai Creek				EPA Aquatic Benchmarks ug/L						
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular	
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute	
5/25/2011	Metribuzin	0.045	Н	21,000	3,000	2,100	1,290	8.7	130	
6/21/2011	Bentazon	0.36	Н	>50,000		>50,000	_	4,500	5,350	
	Metribuzin	0.058	Н	21,000	3,000	2,100	1,290	8.7	130	
8/17/2011	Metribuzin	0.068	Н	21,000	3,000	2,100	1,290	8.7	130	
9/28/2011	2,4-D	0.27	Н	12,075	14,200	12,500	16,050	3,880	13.1	

 Table 4. Lapwai Creek pesticide results.

ISDA considers a pesticide of concern (POC) any pesticide that is greater than or equal to fifty percent (\geq 50%) of an established EPA aquatic benchmark. Catholic Creek (Table 5) had one herbicide detection (linuron) that was \geq 50% of the chronic invertebrate benchmark and one insecticide (dimethoate) that exceeded the chronic invertebrate benchmark. Catholic Creek had the second highest number of pesticide detections (10).

 Table 5. Catholic Creek pesticide results.

Catholic Creek						EPA Aqua	tic Benchn	narks ug/L	
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute
4/13/2011	Metribuzin	0.034	Н	21,000	3,000	2,100	1,290	8.7	130
4/27/2011	Metribuzin	0.037	Н	21,000	3,000	2,100	1,290	8.7	130
5/11/2011	Metribuzin	0.57	Н	21,000	3,000	2,100	1,290	8.7	130
5/25/2011	MCPA	0.36	Н	380	I	90	_	170	20
	Metribuzin	1.2	Н	21,000	3,000	2,100	1,290	8.7	130
	Linuron	0.067	Н	1,500	5.58	60	0.09	13.7	2.5
6/8/2011	Metribuzin	0.1	Н	21,000	3,000	2,100	1,290	8.7	130
6/21/2011	2,4-D	2.6	Н	12,075	14,200	12,500	16,050	3,880	13.1
	Metribuzin	0.069	Н	21,000	3,000	2,100	1,290	8.7	130
7/20/2011	Dimethoate	1.6	I	3,100	430	21.5	0.5	84	_

The Potlatch River had one POC detection (Linuron) which exceeded both the invertebrate chronic concentration and the vascular plant acute concentration (Table 6). There were no pesticide detections on the Potlatch River after June 8, 2011.

Potlatch River	Potlatch River			EPA Aquatic Benchmarks ug/L					
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute
4/27/2011	Hexazinone	0.054	Н	137,000	17,000	75,800	20,000	7	37.4
5/25/2011	Metribuzin	0.22	Н	21,000	3,000	2,100	1,290	8.7	130
6/8/2011	Bromoxynil	0.13	Н	26.5	18	48	2.5	51	
	Pendimethalin	0.34	Н	69	6.3	140	14.5	5.2	12.5
	Simazine	0.15	Н	3,200	960	500	2,000	36	140
	Diuron	0.048	Н	200	26	80	200	2.4	15
	Linuron	6.6	Н	1,500	5.58	60	0.09	13.7	2.5

 Table 6.
 Potlatch River pesticide results.

Pine Creek had the largest number of pesticide detections (18) of any tributary. Half of those detections occurred in the month of May which averaged more than twice the rainfall for 2011 than normally recorded in May (NOAA, Agrimet). Pine Creek has the highest percentage of agricultural lands (Table 1) with the majority occurring at higher elevations within the watershed. The herbicide linuron was the only POC detected in Pine Creek; the concentration exceeded the chronic invertebrate benchmark (Table 7).

 Table 7. Pine Creek pesticide results.

Pine Creek				EPA Aqua	tic Benchn	narks ug/L			
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute
4/13/2011	Metribuzin	0.048	Н	21,000	3,000	2,100	1,290	8.7	130
4/27/2011	Metribuzin	0.043	Н	21,000	3,000	2,100	1,290	8.7	130
5/11/2011	Methomyl	0.061	Ι	160	12	2.5	0.7	—	_
	Diuron	0.055	Н	200	26	80	200	2.4	15
5/25/2011	2,4-D	0.81	Н	12,075	14,200	12,500	16,050	3,880	13.1
	Bromoxynil	0.19	Н	26.5	18	48	2.5	51	_
	Dicamba	0.28	Н	14,000		>50,000		61	>3,250
	MCPA	0.58	Н	380	Ι	90		170	20
	Metribuzin	0.29	Н	21,000	3,000	2,100	1,290	8.7	130
	Pendimethalin	0.034	Н	69	6.3	140	14.5	5.2	12.5
	Diuron	0.062	Н	200	26	80	200	2.4	15
6/8/2011	Bromoxynil	0.19	Н	26.5	18	48	2.5	51	_
	MCPA	0.5	Н	380		90		170	20
	Metribuzin	0.22	Н	21,000	3,000	2,100	1,290	8.7	130
	Pendimethalin	0.1	Н	69	6.3	140	14.5	5.2	12.5
	Diuron	0.052	Н	200	26	80	200	2.4	15
	Linuron	0.2	Н	1,500	5.58	60	0.09	13.7	2.5
6/21/2011	Metribuzin	0.049	Н	21,000	3,000	2,100	1,290	8.7	130

Big Canyon Creek had the fewest pesticide detections of any tributary monitored (Table 8). Again there were no pesticide detections for Big Canyon Creek after June 8, 2011.

Table 8.	Big Canyon	Creek pesticide	results.
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Big Canyon Creek						EPA Aqua	tic Benchn	narks ug/L	
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute
5/25/2011	Metribuzin	0.078	Н	21,000	3,000	2,100	1,290	8.7	130
6/8/2011	2,4-D	0.25	Н	12,075	14,200	12,500	16,050	3,880	13.1
	MCPA	0.32	Н	380		90		170	20

Little Canyon Creek only had three different herbicides identified, no concentrations were near any aquatic benchmarks, and there were no detections after June 8, 2011 (Table 9).

Little Canyon Creek				EPA Aquatic Benchmarks ug/L					
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute
4/13/2011	Metribuzin	0.033	Н	21,000	3,000	2,100	1,290	8.7	130
5/25/2011	2,4-D	0.22	Н	12,075	14,200	12,500	16,050	3,880	13.1
	MCPA	1.1	Н	380	1	90		170	20
	Metribuzin	0.099	Н	21,000	3,000	2,100	1,290	8.7	130
6/8/2011	MCPA	0.99	Н	380	1	90		170	20
	Metribuzin	0.33	Н	21,000	3,000	2,100	1,290	8.7	130

 Table 9. Little Canyon Creek pesticide results.

Cottonwood Creek had the third highest number of detections (9) with six different herbicides. All of the detections were well below any EPA aquatic benchmark (Table 10).

 Table 10.
 Cottonwood Creek pesticide results.

Cottonwood Cre	Cottonwood Creek M.F. Clearwater River				EPA Aquatic Benchmarks ug/L				
Collection	Pesticide	Concentration	Pesticide	Fish	Fish	Inverts	Inverts	NonVascular	Vascular
Date	Detected	ug/L	Туре	Acute	Chronic	Acute	Chronic	Acute	Acute
4/13/2011	Metribuzin	0.033	Н	21,000	3,000	2,100	1,290	8.7	130
5/25/2011	Bromoxynil	0.11	Н	26.5	18	48	2.5	51	_
	Metribuzin	0.053	Н	21,000	3,000	2,100	1,290	8.7	130
6/8/2011	Metribuzin	0.14	Н	21,000	3,000	2,100	1,290	8.7	130
	Pendimethalin	0.046	Н	69	6.3	140	14.5	5.2	12.5
6/21/2011	2,4-Dichlorobenzoic acid	0.12	Н	425	95	650	260	21	4,828
8/3/2011	2,4-D	0.27	Н	12,075	14,200	12,500	16,050	3,880	13.1
	Desethyl Atrazine	0.039	D	2,650	65	360	60	1	37
9/28/2011	Desethyl Atrazine	0.031	D	2,650	65	360	60	1	37

Conclusions

During this study there were 15 pesticides identified which consisted of 12 herbicides, two insecticides, and one degradates of atrazine (desethyl atrazine). Of these 15 pesticides there were a total of 58 detections with 54 herbicides, 2 insecticides, and 2 desethyl atrazine detections. There were two detections at Catholic Creek which exceeded ISDA's criteria for a pesticide of concern (POC). Catholic Creek had one detection of the herbicide linuron (5/25/2011) that was \geq 50% of the chronic benchmark concentration for invertebrates and the other detection was the insecticide dimethoate (7/20/2011) that exceeded the chronic invertebrate benchmark concentration. There was one detection of linuron on the Potlatch River (6/8/2011) that is a POC and exceeded the chronic invertebrate and vascular plant acute concentrations. Pine Creek had one POC of the herbicide linuron (6/8/11) which exceeded the chronic invertebrate benchmark.

The majority of pesticide detections (75%) occurred in the months of May and June. Depending on which rainfall information used (Agrimet or NOAA) May's monthly rainfall was over twice the normal and June was either at normal or twice the normal (Table 11). It appears that the number of pesticide detections correlate well with precipitation levels. The lack of detections in July, August, and September could be a result of the below normal precipitation (Table 11) or the fact that there may be less pesticide usage during those months.

 Table 11. Average monthly precipitation levels.

Month	Dworshak Agrimet	Lewiston NOAA	Normal
April	3.79	1.6	1.31
May	3.62	3.57	1.56
June	1.62	0.64	0.64
July	0.55	0.15	0.66
August	0	0.05	0.69
September	0.3	0.14	0.67

Overall the results indicate that pesticides are present, to a certain extent, in all of the seven tributaries evaluated during this study. Herbicide detections made up 93% of the detections and only linuron exceeded ISDA's POC criteria. The majority of the herbicide detections were well below any EPA established aquatic benchmarks. Insecticides only had one detection (dimethoate) that was considered a POC.

Recommendations

- Read and follow pesticide labels especially the precautionary statements environmental and water quality warnings.
- Incorporate pesticides to reduce the amount vulnerable to runoff.
- Delay applications when the soil is saturated or wet weather is expected.
- Establish buffer zones to reduce sediment and pesticide runoff.
- Mix load and dispose of pesticides properly.
- ♦ Avoid windy conditions to limit drift
- Use integrated pest management strategies.
- Pay extra attention to the use of the Pesticides of Concern, identified in this report, for the herbicide linuron, the insecticide dimethoate and the most commonly detected herbicide metribuzin.

References

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