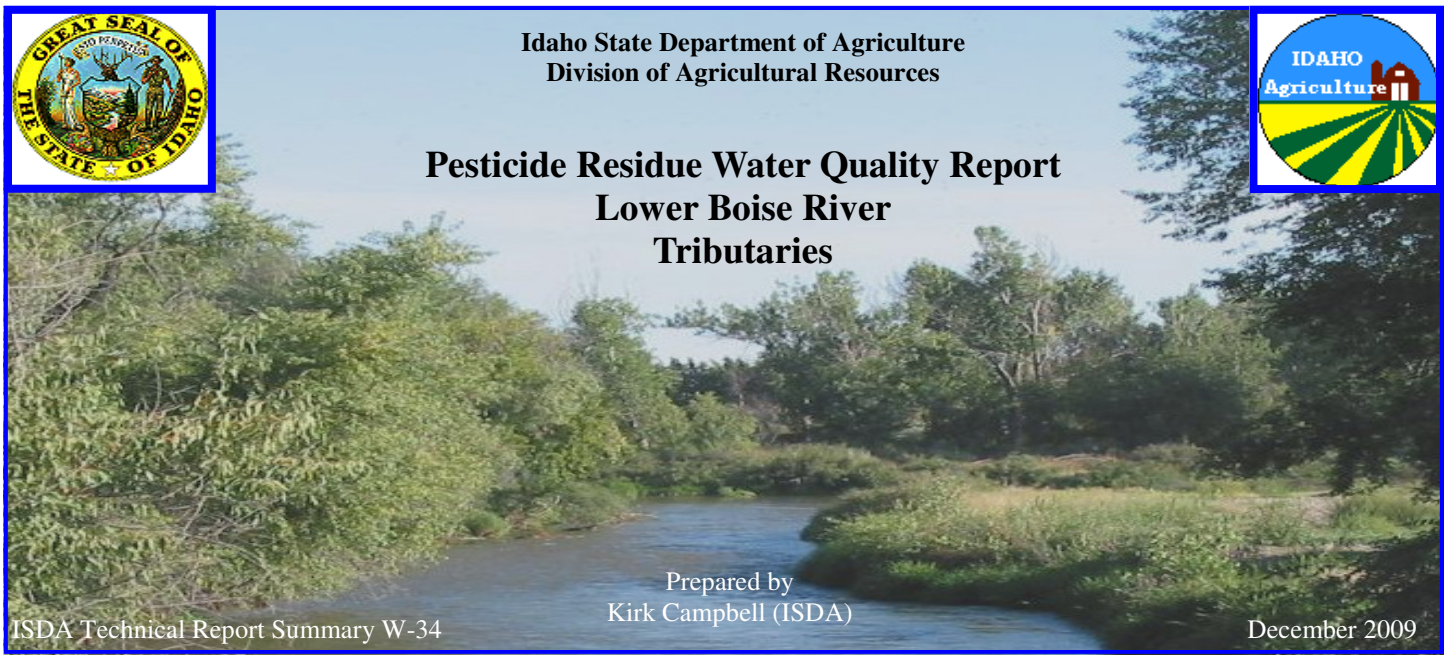

Idaho State Department of Agriculture
Division of Agricultural Resources

Pesticide Residue Water Quality Report
Lower Boise River
Tributaries

Prepared by
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ISDA Technical Report Summary W-34

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Introduction

The Idaho State Department of Agriculture (ISDA), with discretionary funding provided by the U.S. Environmental Protection Agency (EPA) Region X, conducted a surface water quality monitoring program for pesticide residues on five major tributaries to the Lower Boise River. The five tributaries monitored were Hartley Gulch (HG-1), Dixie Slough (DS-1), Conway Gulch (CG-1), Mason Creek (MC-1), and Fifteenmile (15-1). These five drainages transport irrigation return water and canal spill water back into an approximate 20 river mile section of the Lower Boise River between Middleton and Parma (Figure 1). These five tributaries have been identified, by various state and federal agencies, as major contributors of sediment and phosphorus to the Lower Boise River. During the non-irrigation season these drains return stormwater runoff and shallow ground water back to the Boise River.

These five major tributaries drain approximately 160,356 total acres which include both urban and rural land uses. The individual drainage area for each tributary is listed in Table 1 (IDEQ, 2003).

Table 1. Approximate drainage acreage for each tributary.

Tributaries	HG-1	DS-1	CG-1	MC-1	15-1
Acreage	29,216	39,639	7,616	41,635	42,250

Monitoring for this project was conducted on a bi-weekly schedule starting in late April through September 2009. A total of 12 pesticide samples were collected from each tributary.

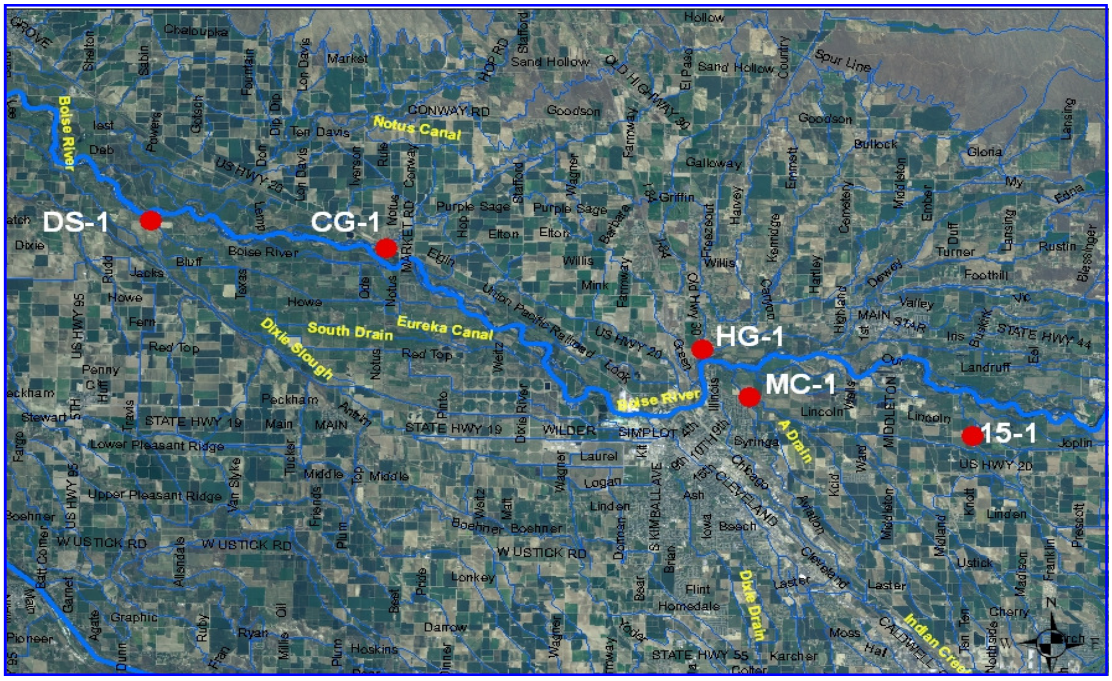

Figure 1. Lower Boise River monitoring sites.

Analytical Methods and Quality Assurance

Analytical methods and techniques used for this study consisted of the following: EPA method 507/508 Pesticides by Gas Chromatography Mass Selective Detector (GC/MSD) and Gas Chromatography Flame Photometric Detector (GC/FPD), EPA method 632 pesticides by Liquid Chromatography Mass Selective Detector (LC/MSD), and EPA method 515.2 herbicides by Gas Chromatography Electron Capture Detector (GC/ECD) and GC/MSD. Analytical testing for this study was completed by the University of Idaho's Analytical Science Laboratory (UIASL) Moscow, Idaho. UIASL follows strict quality control guidelines that requires the extraction and analysis of samples be accompanied by laboratory fortified blanks, laboratory reagent blanks, laboratory fortified sample matrix (matrix spikes), quality control samples, and performance check standards to evaluate and document data quality.

During this study, all analyte spikes and surrogate standard recoveries were within acceptable ranges (70-130%) indicating that pesticide residues were accurately recovered. All field blanks submitted during this study resulted in non detectable results indicating both field and laboratory activities were free from contamination. Relative percent difference (RPD) calculated on field duplicate samples submitted to ASL had a range of 2%-20%, an overall mean of 6%, and a median of 1.5%.

Sampling Methods and Quality Assurance

All samples collected for this project were collected utilizing two types of depth integrated suspended sediment samplers (USDH-95 and USDH-81). The USDH-95 was used for samples collected from bridges using suspension equipment while the USDH-81 was used while wading. The USDH-95 sampler was equipped with a one-liter Teflon sample bottle and cap; the USDH-81 had a one-liter glass sample container and Teflon cap.

Discrete samples from each site were composited into a clean 2.5 gallon carboy. The resultant composite was then poured off into three laboratory cleaned amber one-liter bottles. All sampling equipment was thoroughly cleaned between sample locations as follows: thorough scrubbing with deionized water and Liqui-Nox detergent, deionized water rinse, acetone (high resolution chromatography grade) rinse, followed by a deionized water rinse. The equipment was then rinsed with source water just prior to collection.

For field quality assurance (QA) three types of QA samples were submitted over the duration of this project. (1) Duplicate samples were collected by compositing creek water into a clean 2.5 gallon glass carboy. The resultant composite was then mixed and poured off into 6 one-liter amber bottles. (2) Field bottle blanks were collected by transferring deionized water directly from a Nalgene carboy into three clean one-liter amber bottles. (3) Equipment blanks entail thorough cleaning of the equipment, as previously mentioned, followed by filling the sampling equipment with deionized water and transferring that water into clean one-liter amber bottles. All blanks and duplicates were submitted to UIASL as blind samples.

All of the samples from each study were placed within a cooler, on ice, for shipment directly to the UIASL in Moscow, Idaho. All samples were shipped priority overnight and Chain-of-Custody forms accompanied each sample set.

Results

During the Lower Boise River tributary assessment there were a total of 24 pesticides detected and identified for the five tributaries. There were 17 herbicides, 6 insecticides, and 1 fumigant (Table 1).

Table 1. Lower Boise toxicity class and pesticides detected.

Detected Pesticide	Pesticide Type	Trade Name	Toxicity Class
Atrazine	Herbicide	Aatrex	Class III
2,4-D	Herbicide	Curtail	Class III
2,4-DB	Herbicide	Butoxone	Class III
Bentazon	Herbicide	Basagran	Class III
Bromacil	Herbicide	Krovar	Class IV
Bromoxynil	Herbicide	Buctril	Class II
Carbofuran	Insecticide	Furadan	Class I/II
Chlorothalonil	Fungicide	Bravo	Class II
Chlorpyrifos	Insecticide	Dursban	Class II
DCPA	Herbicide	Dacthal	Class IV
Desethyl Atrazine	[1] degradate	—	Class III
Diuron	Herbicide	Karmex	Class III
Ethalfluralin	Herbicide	Sonalan	Class III/IV
Ethoprop	Insecticide	Mocap	Class I
Hexazinone	Herbicide	Velpar	Class III
MCPA	Herbicide	Banlene	Class III
Methomyl	Insecticide	Lannate	Class I
Metolachlor	Herbicide	Dual	Class III
Metribuzin	Herbicide	Sencore	Class III
Oxamyl	Insecticide	Blade	Class I
Pendimethalin	Herbicide	Prowl	Class III
Phorate	Insecticide	Agrimet	Class I
Simazine	Herbicide	Aquazine	Class IV
Terbacil	Herbicide	Sinbar	Class IV

[1] atrazine degradate

The toxicity class in Table 1 is based on human exposure and indicates the overall toxicity levels (Table 2).

Table 2. Pesticide class identification and human toxicity.

Class Idenfification	Label	Toxicity
Class I	Danger Poison	Highly Toxic
Class II	Warning	Moderately Toxic
Class III	Caution	Slightly Toxic
Class IV	—	Non-Toxic

The five tributaries in this study had a total of 284 detections of the 24 identified pesticide compounds (Figure 1). The six pesticides with the largest number of detections were herbicides including: bromacil (42), diuron (40), desethyl atrazine (33), terbacil (31), pendimethalin (27), and metolachlor (26). The herbicides are general use pesticides (GUP) except desethyl atrazine which is a degradate of atrazine. Extoxnet's pesticide information profiles indicate that bromacil and terbacil are primarily non-toxic to aquatic species, desethyl atrazine shows a moderate toxicity to aquatic species, and diuron exhibits a moderate toxicity to fish and a high toxic effect on aquatic invertebrates (Extoxnet, 1996).

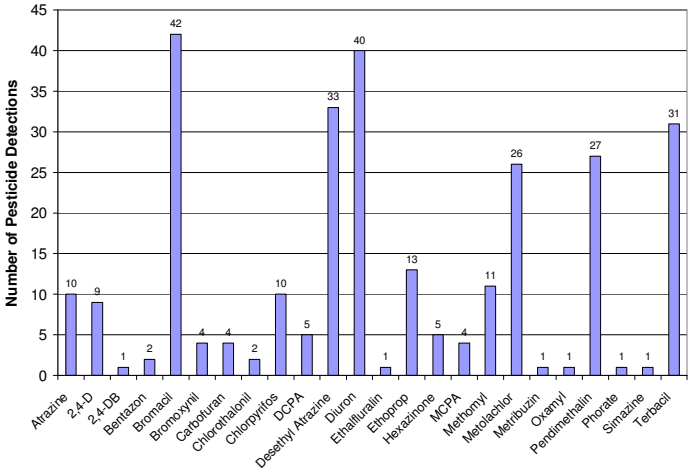

Figure 1. Pesticide detections Lower Boise tributaries.

Individual Tributary Results

Hartley Gulch

Hartley Gulch (HG-1) subwatershed encompasses approximately 29,216 acres and originates in Gem County and flows southwest toward the Lower Boise River. Hartley Gulch consists of an east and west branch that confluences prior to entering the Boise River on the north side of the river.

Hartley Gulch had ten different pesticides identified with a total of 35 detections (Table 1).

Table 1. HG-1 Aquatic Life Benchmarks for pesticides.

				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detections	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
Atrazine	H	2	0.032	2,650	62	360	62
2,4-D	H	3	0.67	50,000	14,200	12,500	16,400
Bromacil	H	7	0.076	18,000	3,000	60,500	8,200
Desethyl Atrazine	H	5	0.039	2,650	62	360	62
Diuron	H	6	0.28	355	26	80	160
Hexazinone	H	1	0.08	137,000	17,000	75,800	20,000
Metolachlor	H	4	0.13	1,950	780	12,550	—
Pendimethalin	H	2	0.064	69	6.3	140	14.5
Simazine	H	1	0.056	3,200	960	500	2,000
Terbacil	H	4	0.12	23,100	1,200	32,500	640

All of the pesticides detected at HG-1 were herbicides with the most prevalent compounds being bromacil and diuron. Diuron is an urea herbicide and is often used in combination with other pesticides such as bromacil. None of the pesticides detected exceed any established EPA aquatic life benchmarks. Aquatic life bench marks are only used as indicators and are estimates of pesticide concentration levels that are not expected to cause acute or chronic efficacy on fish or aquatic invertebrates (Table 1).

Dixie Slough

Dixie Slough (DS-1) Subwatershed consists of 39,639 acres located within the Lower Boise River watershed. DS-1 originates at the base of Lake Lowell and flows northwest towards the Boise River; DS-1 enters the Boise River from the south.

There were 14 pesticides identified within DS-1 and a total of 56 detections of those pesticides. Of the 56 detections, 51 were herbicides and five were insecticides (Table 2).

Table 2. DS-1 Aquatic Life Benchmarks for pesticides.

				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detections	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
Atrazine	H	1	0.038	2,650	62	360	62
2,4-D	H	2	0.44	50,000	14,200	12,500	16,400
Bromacil	H	9	0.22	18,000	3,000	60,500	8,200
Bromoxynil	H	1	0.11	11.5	9	5.5	2.5
Dacthal	H	5	0.17	15,000	—	13,500	—
Desethyl Atrazine	H	7	0.48	2,650	62	360	62
Diuron	H	8	0.18	355	26	80	160
Ethoprop	I	2	0.16	150	24	22	0.8
Hexazinone	H	1	0.093	137,000	17,000	75,800	20,000
MCPA	H	1	0.4	380	12,000	90	11,000
Methomyl	I	3	0.2	265	57	4.4	0.4
Metolachlor	H	4	0.11	1,950	780	12,550	—
Pendimethalin	H	5	0.04	69	6.3	140	14.5
Terbacil	H	7	0.1	23,100	1,200	32,500	640

The herbicide bromoxynil, which was only detected once, is considered to be highly toxic to moderately toxic to freshwater fish (Extoxnet, 1996). It is a restricted use pesticide (RUP) which means it must be applied by a certified applicator. The concentration detected did not exceed the EPA aquatic benchmark concentration (Table 2).

The two insecticides, methomyl (3 detects) and ethoprop (2 detects) are both considered moderate to highly toxic to fresh water fish and highly toxic to aquatic invertebrates (Extoxnet, 1996). Although neither insecticide exceeded the aquatic benchmarks the methomyl concentration (0.2 µg/L) was one-half of the chronic invertebrate level (0.4 µg/L). Methomyl and ethoprop are both restricted use pesticides.

Conway Gulch

Conway Gulch (CG-1) encompasses approximately 7,616 acres and is the smallest of the five Subwatersheds monitored during this study. CG-1 originates near the "C" Line canal in Canyon County and flows southwest toward the Boise River and enters the river from the north side. CG-1 had been identified in previous studies as a major contributor of sediment and phosphorus to the Lower Boise River.

CG-1 had a total of 16 pesticides identified and a total of 62 detections of those pesticides. Of the 62 detections 54 were herbicides, seven were insecticides, and one was a fumigant (Table 3).

Table 3. CG-1 Aquatic Life Benchmarks for pesticides.

				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detections	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
Atrazine	H	4	0.034	2,650	62	360	62
2,4-D	H	3	5.8	50,000	14,200	12,500	16,400
Bromacil	H	11	0.29	18,000	3,000	60,500	8,200
Bromoxynil	H	1	0.15	11.5	9	5.5	2.5
Chlorothalonil	F	1	0.077	11.5	3	34	39
Desethyl Atrazine	H	7	0.076	2,650	62	360	62
Diuron	H	7	0.29	355	26	80	160
Ethoprop	I	3	0.059	150	24	22	0.8
Ethalfluralin	H	1	0.067	16	0.4	30	24
MCPA	H	1	0.53	380	12,000	90	11,000
Metribuzin	H	1	0.15	21,000	3,000	2,100	1,290
Methomyl	I	3	**0.36**	265	57	4.4	**0.4**
Metolachlor	H	9	0.42	1,950	780	12,550	—
Pendimethalin	H	6	0.17	69	6.3	140	14.5
Phorate	I	1	0.078	0.5	1	0.3	0.21
Terbacil	H	3	0.075	23,100	1,200	32,500	640

Of the seven insecticides detected none exceeded the recommended EPA aquatic life benchmarks. Methomyl (0.36 µg/L) was within 10% of the chronic invertebrate (0.40 µg/L) recommendation. All of the insecticides detected are considered toxic to fish and aquatic invertebrates at higher concentrations. The one fumigant (chlorothalonil) did not exceed the aquatic life benchmarks but is still considered highly toxic to fish and aquatic invertebrates at higher doses.

Mason Creek

Mason Creek (MC-1) subwatershed contains 41,635 acres and originates near the New York canal in Ada County and flows northwest and west towards the Lower Boise River. MC-1 contains an increasing portion of urban acreage with parts of the cities of Caldwell, Nampa, and Meridian included in the subwatershed.

There were a total of 17 pesticides detected at MC-1 and a total of 71 detections of those pesticides. Of the 71 detections 52 were herbicides, 18 were insecticides and one was a fumigant. The 18 insecticide detections was the highest number of detections of all five tributary sampling sites (Table 4).

Table 4. MC-1 Aquatic Life Benchmarks for pesticides.

				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detections	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
Atrazine	H	2	0.025	2,650	62	360	62
Bentazon	H	1	0.2	50,000	—	50,000	—
Bromacil	H	8	0.85	18,000	3,000	60,500	8,200
Bromoxynil	H	1	0.65	11.5	9	5.5	2.5
Carbofuran	I	2	0.61	44	5.7	1.115	0.75
Chlorothalonil	F	1	0.1	11.5	3	34	39
Chlorpyrifos	I	8	0.062	0.9	0.57	0.05	0.04
Desethyl Atrazine	H	7	0.082	2,650	62	360	62
Diuron	H	9	1.1	355	26	80	160
Ethoprop	I	4	1.3	150	24	22	0.8
Hexazinone	H	1	0.21	137,000	17,000	75,800	20,000
MCPA	H	1	2.4	380	12,000	90	11,000
Methomyl	I	3	0.21	265	57	4.4	0.4
Metolachlor	H	7	0.27	1,950	780	12,550	—
Oxamyl	I	1	0.12	2,100	770	90	180
Pendimethalin	H	7	0.15	69	6.3	140	14.5
Terbacil	H	8	0.3	23,100	1,200	32,500	640

There were eight detections of chlorpyrifos with two of the detections (0.062 µg/L and 0.052 µg/L) exceeding the acute and chronic benchmarks for invertebrates. Ethoprop had a detection of 1.3 µg/L (Table 4) which exceeded the chronic invertebrate benchmark and a detection of 0.74 µg/L which was within 8% of the chronic invertebrate benchmark. Carbofuran had two detections with one at 0.61 µg/L which was within 20% of the chronic benchmark for invertebrates. There was only one detection of the fumigant chlorothalonil and the concentration was below any acute or chronic benchmark levels.

Fifteenmile

The Fifteenmile Creek (15-1) subwatershed encompasses 45,250 acres and includes the lower portions of both Fivemile and Tenmile Creeks. Both creeks flow in a northwesterly direction from the New York Canal in Ada County toward the Boise River before combining to form Fifteenmile. Fifteenmile continues for about four miles before it merges with the Boise River near the city of Middleton.

There were 17 pesticides identified at 15-1 with a total of 60 detections of those pesticides. The 60 detections consisted of 50 herbicides and 10 insecticides (Table 5).

Table 5. Aquatic Life Benchmarks for pesticides.

				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detections	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
Atrazine	H	1	0.026	2,650	62	360	62
Desethyl Atrazine	H	7	0.057	2,650	62	360	62
Carbofuran	I	2	0.061	44	5.7	1.115	0.75
2,4-DB	H	1	0.23	1,000	—	7,500	—
2,4-D	H	1	0.34	50,000	14,200	12,500	16,400
Chlorpyrifos	I	2	0.053	0.9	0.57	0.05	0.04
Bentazon	H	1	0.27	50,000	—	50,000	—
Bromacil	H	7	0.21	18,000	3,000	60,500	8,200
Bromoxynil	H	1	0.12	11.5	9	5.5	2.5
Diuron	H	10	1.7	355	26	80	160
Ethoprop	F	4	1.4	150	24	22	0.8
Hexazinone	H	2	0.49	137,000	17,000	75,800	20,000
MCPA	H	1	0.7	380	12,000	90	11,000
Methomyl	I	2	**0.31**	265	57	4.4	**0.4**
Metolachlor	H	2	0.095	1,950	780	12,550	—
Pendimethalin	H	7	0.17	69	6.3	140	14.5
Terbacil	H	9	0.3	23,100	1,200	32,500	640

Of the 10 insecticide, four detections were of ethoprop with two of them (1.4 µg/L and 1.3 µg/L) exceeding the EPA aquatic benchmark for chronic invertebrates (Table 5). The highest detection of chlorpyrifos exceeded both the acute and chronic benchmark for invertebrates (Table 5). Chlorpyrifos also had a detection of 0.044 µg/L, which exceeded the chronic invertebrate benchmark.

Conclusions/Observations

There were a total of 24 pesticides detected during this study and there were 284 detections. Of the 284 detections 242 were herbicides, 40 were insecticides and 2 were a fumigant.

Bromacil and diuron were the most detected herbicides with 42 and 40, detections respectively. Bromacil is slightly to practically nontoxic to fish while diuron is considered moderately toxic to fish but at very high concentrations (Extoxnet,1996). Of the herbicides found pendimethalin, which was detected 27 times, is considered highly toxic to fish and aquatic invertebrates and has some of the lower aquatic benchmarks for fish and invertebrates. All of the pendimethalin detections were low and did not exceed any of the EPA aquatic benchmarks; but its consistent presence in the environment should be viewed with some concern.

Ethoprop is a restricted use pesticide and the environmental risks are related to its acute toxicity in conjunction with its extreme persistence in the environment, especially in aquatic systems (Pesticide Profile, 2007). Based on ecological risk assessments the EPA has both acute and chronic ecological risk concerns regarding ethoprop exposures to both freshwater fish and invertebrates. Laboratory data for freshwater fish showed variable results indicating that ethoprop is slightly to highly toxic in acute tests, with most data showing moderately toxic effects. For freshwater invertebrates, ethoprop is very highly toxic in acute tests and effects growth and reproduction in chronic tests (IRED, 2006).

Ethoprop detections were present for the final four sampling dates (8/18/09, 9/01/09, 9/15/09 and 9/29/09) for both Mason Creek and Fifteenmile. Conway Gulch had three detections in September (9/01/09, 9/15/09, and 9/29/09), and Dixie Slough had two (9/01/09, and 9/15/09). Mason Creek had one detection over the chronic invertebrate benchmark and one within 8% of the chronic invertebrate benchmark. Fifteenmile had two detections over the EPA chronic benchmark for invertebrates. The reason for these detections of ethoprop at this late stage of the season has not yet been determined. The concern with so many detections of ethoprop over an extended period of time, is that these repeated frequent detections may indicate chronic conditions for aquatic invertebrates, especially within Mason and Fifteenmile creeks.

Chlorpyrifos is a general use pesticide but is considered highly toxic to freshwater fish and aquatic invertebrates. This compound has some of the lower acute and chronic EPA benchmark concentrations of the organophosphate insecticides. There were a total of 10 detection of chlorpyrifos; Mason Creek had eight detections and Fifteenmile had two detections. Of the eight detections on Mason Creek, only two exceeded both the acute and chronic aquatic invertebrate benchmark concentrations. Fifteenmile had one detection that exceeded both acute and chronic invertebrates and one detection that exceeded the chronic invertebrate benchmark. The presence of chlorpyrifos within Mason Creek on eight occasions may indicate potential chronic effects on aquatic invertebrates.

Methomyl is a restricted use pesticide and is a highly toxic compound in EPA toxicity class I. Methomyl is moderately to highly toxic to fish and highly toxic to aquatic invertebrates (Extoxnet, 1996). There were a total of 11 detections of Methomyl with three each at Dixie Slough, Conway Gulch, and Mason Creek, and two at Fifteenmile Creek. Although none of the methomyl detections exceeded any EPA benchmarks several detections were very close to the chronic invertebrate concentration.

The large number of pesticide detections indicate that the use of pesticides within the Lower Boise River Subwatersheds may be having an impact on water quality. At this time, the EPA only assesses the risk of pesticides on an individual basis. This type of assessment fails to consider the combinations of certain pesticides and their cumulative and synergistic effects on aquatic species.

In the Lower Boise River Watershed Best Management Practices (BMPs) may not be in-place for proper pesticide residue reductions or application techniques may not be following proper label instructions. Insecticides within these water bodies is cause for concern due to their potential lethal effects on aquatic species. Overall, a thorough evaluation must be conducted to determine the source of these compounds and if additional efforts need to be taken to educate applicators and install BMPs within the Lower Boise River Watershed.

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