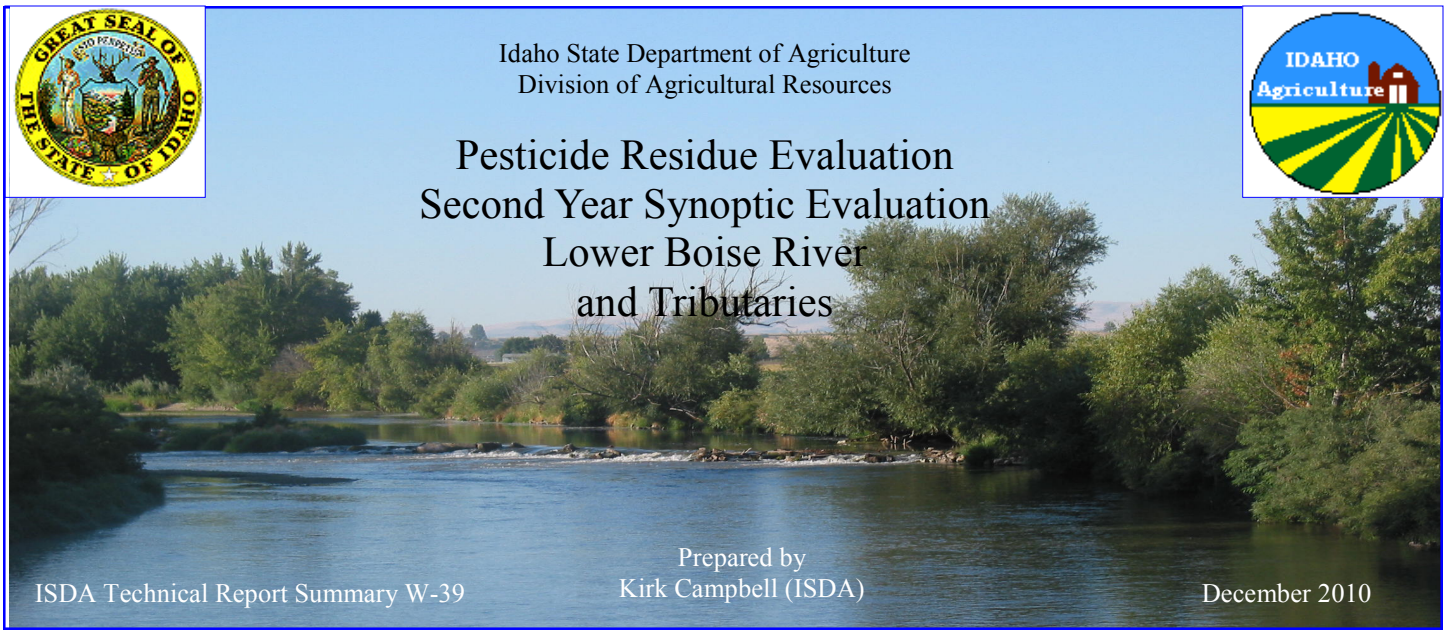

Idaho State Department of Agriculture
Division of Agricultural Resources

Pesticide Residue Evaluation
Second Year Synoptic Evaluation
Lower Boise River
and Tributaries

Prepared by
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ISDA Technical Report Summary W-39

December 2010

Introduction

The Idaho State Department of Agriculture (ISDA) conducted additional pesticide residue monitoring in 2010 on four tributaries to the Lower Boise River and one site on the Lower Boise River. This monitoring was conducted as a follow-up to the work ISDA conducted in 2009 on five tributaries to the Lower Boise River (ISDA, 2009). This additional work was conducted an attempt to determine if certain pesticide residues detected in 2009 continue to be detected in the Lower Boise River system at potentially acute or chronic levels. Partial funding for this project was provided by the U.S. Environmental Agency (EPA) Region 10.

The four tributaries that had repeat monitoring in 2010 were Dixie Slough (DS-1), Conway Gulch (CG-1), Mason Creek (MC-1), and Fifteenmile (15-1). Hartley Gulch was monitored in 2009, and was not resampled in 2010. One additional site was added for 2010 on the main stem of the Lower Boise River (LBR-1) near Parma (Figure 1).

These four tributaries drain approximately 131,140 acres which include both urban and rural land uses (IDEQ, 2003). They also make up approximately 16% of the total acreage encompassed by the Boise River drainage (836,876 acres).

Monitoring for this project was conducted on a bi-weekly schedule starting from April 20, 2010 through September 21, 2010. A total of 12 pesticide samples were collected from each monitoring site.

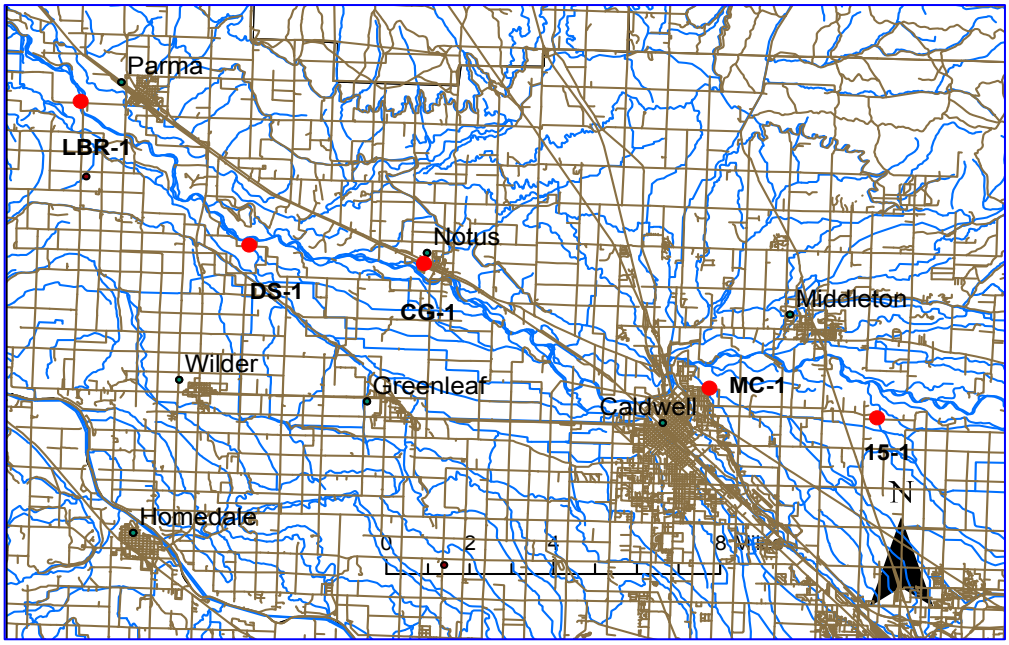

Figure 1. Lower Boise River and tributary monitoring sites.

Analytical Methods and Quality Assurance

Analytical methods and techniques used for this study by the University of Idaho's Analytical Science Laboratory (UIASL) in Moscow, Idaho are listed in Table 1.

Table 1. Analytical methods. for pesticides.

Method	Compounds	Techniques
EPA 507	Nitrogen and phosphorus	Gas Chromatography Mass Selective Detector
	containing pesticides	Gas Chromatography Flame Photmetric Detector
EPA 508	Chlorinated pesticides	GC/MSD and GC/FPD
EPA 515.2	Chlorinated Acids (Herbicides)	Gas Chormatograph Electron Capture Detector
		GC/MSD
EPA 632	Carbamates and Urea pesticides	Liquid Chromatography Mass Selective Detector

UIASL follows strict quality control guidelines that require 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 UIASL, had a range of 0-26% an overall mean of 9% and a median of 7.5%.

Sampling Methods and Quality Assurance

Samples 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 and 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 bottle and Teflon cap.

Discrete samples from each site were composited into a clean 2.5 gallon glass carboy. The resultant composite was then poured off into three laboratory cleaned, one-liter amber bottles. All sampling equipment was thoroughly cleaned between monitoring locations using the following procedure: 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 sample water into a clean 2.5 gallon glass carboy. The resultant composite was then mixed and poured off into six 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 of the QA samples were submitted to UIASL as blind samples.

All samples from each study were placed in a cooler on ice for shipment directly to the UIASL. All samples were shipped priority overnight and Chain-of-Custody protocols were followed throughout the project.

Overall Results

The main stem of the Boise River along with the four tributaries had a total of 376 detections of 32 pesticide compounds during the 2010 study (Figure 2). That is an increase of 92 detections over the 2009 study.

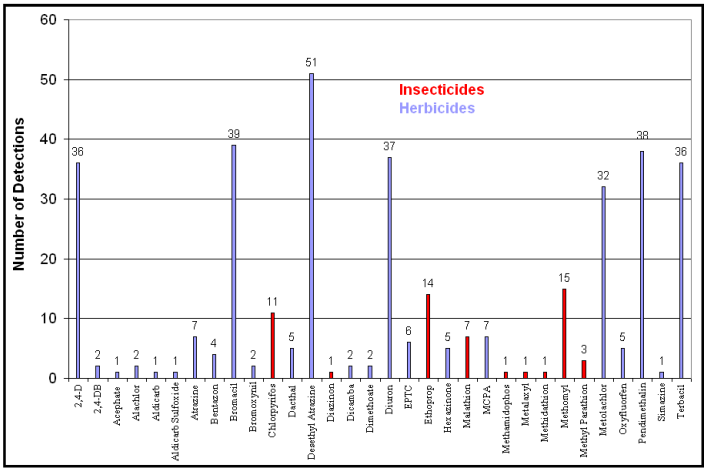

Figure 2. Total pesticide detections in 2010.

The highest number of detections included six general use (GUP) herbicides and desethyl atrazine which is a degradate of atrazine. The herbicides with the highest number of detections included: desethyl atrazine (51), bromacil (39), pendimethalin (38), diuron (37), 2,4-D (36), terbacil (36), and metolachlor (32). Desethyl atrazine, pendimethalin, diuron, 2,4-D, and metolachlor exhibit moderate to high toxicity to aquatic species when found in water at much higher concentrations than those observed during this study.

The four highest number of detections for insecticides were methomyl (15) which is a restricted use pesticide (RUP), ethoprop (14) which is a RUP, chlorpyrifos (11) which is a general use pesticide (GUP), and Malathion (7) which is a GUP.

Monitoring Results

Lower Boise River

The Lower Boise River drains an area of approximately 836,876 acres (IDEQ, 2000). Samples from the Boise River (LBR-1) were collected from the bridge on Hexon Road just southwest of the city of Parma, Idaho. There were a total of 13 different pesticides identified which included 10 herbicides and three insecticides. Overall, there were 51 detections of herbicides and seven detections of insecticides for a total of 58 detections (Table 2).

Table 2. LRB-1 pesticide detections.

LBR-1				EPA Aquatic Benchmarks (ug/L)			
Pesticides	Pesticide	Number of	Highest	Acute	Chronic	Acute	Chronic
Detected	Type	Detects	Detect ug/L	Fish	Fish	Inverts	Inverts
2,4-D	H	8	1.3	50,000	14,200	12,500	16,400
2,4-DB	H	1	0.24	1,000	—	7,500	—
Alachlor	H	1	0.058	900	187	1,250	110
Bromacil	H	8	0.1	18,000	3,000	60,500	8,200
Desethyl Atrazine	H	8	0.039	2,650	65	360	60
Diuron	H	7	0.22	200	26	80	200
Ethoprop	I	3	0.35	150	24	22	0.8
Malathion	I	1	0.22	16.4	8.6	0.3	0.035
		1	0.051	16.4	8.6	0.3	0.035
Methomyl	I	2	0.3	160	12	2.5	0.7
Metolachlor	H	6	0.1	1,600	1,000	550	1
Pendimethalin	H	5	0.036	69	6.3	140	14.5
Simazine	H	1	0.025	3,200	960	500	2,000
Terbacil	H	6	0.18	23,100	1,200	32,500	640

There were two detections of malathion at LBR-1.Both detections exceeded an established Environmental Protection Agency (EPA) aquatic benchmark. The malathion detection of 0.22 µg/L exceeded the chronic level for invertebrates and was >50% of the acute invertebrate value. ISDA considers pesticides with detections that are ≥50% of an aquatic benchmark as a potential pesticide of concern (POC). The other detection of 0.051 µg/L exceeded the benchmark for chronic invertebrates.

Dixie Slough

Dixie Slough subwatershed consists of approximately 39,639 acres located within the Lower Boise River watershed. Dixie Slough originates at the base of Lake Lowell and flows northwest towards the Boise River and confluences from the south.

Two insecticides and 11 herbicides were detected at DS-1. The two insecticides ethoprop and methomyl are restricted use pesticides (RUP). There were a total of 69 detections, which included 63 herbicides and six insecticides. The largest number of detections were atrazine's degradate desethyl atrazine (10). The two insecticides (ethoprop and methomyl) each had three detections. All detections were below any EPA aquatic benchmark and did not meet ISDA's POC criteria (Table).

Table 3. DS-1 pesticide detections.

DS-1				EPA Aquatic Benchmarks (ug/L)			
Pesticides	Pesticide	Number of	Highest	Acute	Chronic	Acute	Chronic
Detected	Type	Detects	Detect ug/L	Fish	Fish	Inverts	Inverts
2,4-D	H	8	0.43	50,000	14,200	12,500	16,400
Atrazine	H	2	0.075	2,650	65	360	60
Bentazon	H	1	0.22	>50,000	—	>50,000	—
Bromacil	H	8	0.12	18,000	3,000	60,500	8,200
Dachtal	H	5	0.2	15,000	—	13,500	—
Desethyl Atrazine	H	10	0.041	2,650	65	360	60
Diuron	H	7	0.23	200	26	80	200
EPTC	H	1	0.053	7,000	—	3,245	810
Ethoprop	I	3	0.27	150	24	22	0.8
Methomyl	I	3	0.1	160	12	2.5	0.7
Metolachlor	H	6	0.12	1,600	1,000	550	1
Pendimethalin	H	7	0.12	69	6.3	140	14.5
Terbacil	H	8	0.34	23,100	1,200	32,500	640

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. It confluences with the Boise River from the north side and has historically been a heavy contributor of sediment and phosphorus into the Boise River.

CG-1 had a total of 24 pesticides detected with a total of 85 detections. Of the 85 detections, 70 were herbicides and 15 were insecticides (Table 4).

Table 4. CG-1 pesticide detections.

CG-1				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides	Pesticide	Number of	Highest	Acute	Chronic	Acute	Chronic
Detected	Type	Detects	Detect ug/L	Fish	Fish	Inverts	Inverts
2,4-D	H	6	8.8	50,000	14,200	12,500	16,400
Aldicarb	H	1	0.12	26	0.46	10	1
Aldicarb Sulfoxide	H	1	0.11	3,570	—	21.5	—
Atrazine	H	1	0.28	2,650	65	360	60
Bentazon	H	1	0.49	>50,000	—	>50,000	—
Bromacil	H	11	0.18	18,000	3,000	60,500	8,200
Bromoxynil	H	2	0.58	100	15	96	2.5
Chlorpyrifos	I	4	0.077	0.9	0.57	0.05	0.04
	I		0.075	0.9	0.57	0.05	0.04
Desethyl Atrazine	H	12	0.046	2,650	65	360	60
Dimethoate	I	1	0.18	3100	430	21.5	0.5
Diuron	H	6	0.2	200	26	80	200
EPTC	H	3	0.14	7,000	—	3,245	810
Ethoprop	I	2	0.062	150	24	22	0.8
Hexazinone	H	1	0.056	137,000	17,000	75,800	20,000
Malathion	I	2	0.067	16.4	8.6	0.3	0.035
			0.069	16.4	8.6	0.3	0.035
MCPA	H	3	0.48	48,000	12,000	41,000	11,000
Metalaxyl	I	1	0.052	65,000	9,100	14,000	100
Methidathion	I	1	4.5	1.1	6.3	1.5	0.66
Methomyl	I	3	2.3	160	12	2.5	0.7
Methyl Parathion	I	1	0.092	925	<10	0.49	0.25
Metolachlor	H	8	0.76	1,600	1,000	550	1
Oxyfluorfen	H	4	1.4	102	1.3	40	13
Pendimethalin	H	9	0.32	69	6.3	140	14.5
Terbacil	H	1	0.059	23,100	1,200	32,500	640

There were four detections of the insecticide chlorpyrifos at CG-1 with two exceeding both the acute and chronic benchmark levels for invertebrates (Table 4). The other two detections (both at 0.028 µg/L) were ≥50 % of both the chronic and acute invertebrate concentrations.

The insecticide malathion (GUP) was detected twice at CG-1 and both detections exceeded the EPA aquatic benchmark for chronic invertebrates (Table 4).

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There was one detection of methidathion which is a RUP and a highly toxic organophosphorus insecticide (Extoxnet, 1996). Methidathion is very highly toxic to aquatic organisms (Extoxnet, 1996). The concentration found at CG-1 exceeded both acute and chronic levels for invertebrates and the acute level for fish (Table 4). A cancellation order for this product occurs as of December 31, 2012.

The insecticide methomyl (RUP) is considered to be moderately to highly toxic to fish and invertebrates (Extoxnet, 1996). There were three detections at CG-1 but only one (2.3 µg/L) exceeded the chronic invertebrate benchmark while also exceeding 50% of the acute invertebrate benchmark (Table 4).

Oxyfluorfen is a GUP pre and post emergent herbicide and is considered highly toxic to fish and aquatic invertebrates (Extoxnet, 1996). CG-1 had four detections with just one exceeding the chronic fish EPA aquatic benchmark (Table 4). Another herbicide metolachlor also exceeded ISDA's POC for chronic invertebrates.

Mason Creek

The Mason Creek drainage is composed of approximately 41,635 acres. Mason Creek originates near the New York canal in Ada County and flows northwest and west to join the Lower Boise River near Caldwell, Idaho.

A total of 20 different pesticides were identified at MC-1 including 13 herbicides and 7 insecticides. There was a total of 89 detections with 72 consisting of herbicides and 17 insecticides (Table 5).

Table 5. MC-1 pesticide detections.

MC-1				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detects	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
2,4-D	H	9	0.63	50,000	14,200	12,500	16,400
Atrazine	H	3	0.027	2,650	65	360	60
Bentazon	H	2	0.35	>50,000	—	>50,000	—
Bromacil	H	7	0.13	18,000	3,000	60,500	8,200
Chlorpyrifos	I	5	0.049	0.9	0.57	0.05	0.04
Desethyl Atrazine	H	12	0.046	2,650	65	360	60
Diazinon	I	1	0.034	45	<0.55	0.11	0.17
Dicamba	H	1	0.083	14,000	—	17,300	—
Dimethoate	I	1	0.057	3100	430	21.5	0.5
Diuron	H	9	0.5	200	26	80	200
EPTC	H	1	0.15	7000	—	3245	810
Ethoprop	I	2	1.2	150	24	22	0.8
Hexazinone	H	2	0.2	137,000	17,000	75,800	20,000
Malathion	I	1	0.51	16.4	8.6	0.3	0.035
		1	0.26	16.4	8.6	0.3	0.035
MCPA	H	2	0.3	48,000	12,000	41,000	11,000
Methomyl	I	5	0.61	160	12	2.5	0.7
Methyl Parathion	I	1	0.073	925	<10	0.49	0.25
Metolachlor	H	6	0.2	1,600	1,000	550	1
Pendimethalin	H	8	0.066	69	6.3	140	14.5
Terbacil	H	10	0.21	23,100	1,200	32,500	640

MC-1 had five chlorpyrifos detections with the highest (0.049 µg/L) exceeding the chronic invertebrate level and nearing the acute invertebrate level (Table 5). The other four detections were ≥50% of both the chronic and acute invertebrate concentrations. Based on these detections chlorpyrifos meets the ISDA POC criteria.

There were two ethoprop detections at MC-1 with one detection (1.2 µg/L) exceeding the chronic invertebrate bench mark concentration (Table 5).

Malathion was detected twice at MC-1with one exceeding both acute and chronic invertebrate benchmarks. The other detection (0.26 ug/L) exceed chronic invertebrate levels and exceeded ISDA's criteria for POC. (Table 5).

There were five detections of methomyl at MC-1 but only one was ≥50% of the chronic invertebrate benchmark (Table 5).

Fifteenmile

Fifteenmile subwatershed encompasses approximately 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, combining to form Fifteenmile Creek. Fifteenmile then continues north approximately four miles prior to entering the Boise River.

A total of 22 pesticides including 15 herbicides and seven insecticides were detected at 15-1. There was a total of 75 total detections with 63 being herbicides and 12 insecticides (Table 6).

Table 6. 15-1 pesticide detections.

15-1				EPA Aquatic Life Benchmarks (ug/L)			
Pesticides Detected	Pesticide Type	Number of Detects	Highest Detect ug/L	Acute Fish	Chronic Fish	Acute Inverts	Chronic Inverts
2,4-D	H	5	1.3	50,000	14,200	12,500	16,400
2,4-DB	H	1	0.1	1,000	—	7,500	—
Acephate	I	1	0.72	416,000	5,760	550	150
Alachlor	H	1	0.12	900	187	1,250	110
Atrazine	H	1	0.026	2,650	65	360	60
Bromacil	H	5	0.094	18,000	3,000	60,500	8,200
Chlorpyrifos	I	1	0.095	0.9	0.57	0.05	0.04
		1	0.04	0.9	0.57	0.05	0.04
Desethyl Atrazine	H	9	0.041	2,650	65	360	60
Dicamba	H	1	0.18	14,000	—	17,300	—
Diuron	H	8	0.84	200	26	80	200
EPTC	H	1	0.24	7,000	—	3,245	810
Ethoprop	I	4	3.2	150	24	22	0.8
			2.2	150	24	22	0.8
			3.1	150	24	22	0.8
Hexazinone	H	2	0.073	137,000	17,000	75,800	20,000
Malathion	I	1	0.49	16.4	8.6	0.3	0.035
MCPA	H	2	0.26	48,000	12,000	41,000	11,000
Methamidophos	I	1	0.079	12500	48.9	13	4.5
Methomyl	I	2	0.13	160	12	2.5	0.7
Methyl Parathion	I	1	0.082	925	<10	0.49	0.25
Metolachlor	H	6	0.41	1,600	1,000	550	1
Oxyfluorfen	H	1	0.066	102	1.3	40	13
Pendimethalin	H	9	0.071	69	6.3	140	14.5
Terbacil	H	11	0.4	23,100	1,200	32,500	640

There were two detections of chlorpyrifos at 15-1 with one (0.095 µg/L) exceeding both the acute and chronic invertebrate concentration and the other (0.04 µg/L) was equal to the invertebrate chronic level and was ≥ 50% of the acute invertebrate benchmark.

There were four ethoprop detections at 15-1 with three of those exceeding the chronic invertebrate water quality benchmark.

15-1 had one detection of the insecticide malathion and it exceeded both the chronic and acute invertebrate benchmark concentration (Table 6).

Pesticides of Concern (POC)

ISDA defines a POC as any pesticide that is detected at a concentration equal to or greater than an EPA established water quality benchmark or is ≥ 50% of the established EPA acute and chronic level for fish and aquatic invertebrates.

Herbicides had approximately six times the detections of insecticides but insecticides exhibit a greater toxicity to fish and aquatic invertebrates. ISDA identifies four insecticides as POCs (ethoprop, chlorpyrifos, malathion, and methomyl) for the Lower Boise River watershed. Ethoprop, Chlorpyrifos, and Malathion are organophosphate pesticides while methomyl is a carbamate. All four insecticides function as cholinesterase inhibitors. Cholinesterase is one of many important enzymes needed for proper functioning of the nervous systems in humans, other vertebrates, and insects (Extoxnet, 1993).

Ethoprop has a high solubility in water and does not bond well with soils. It does not degrade for extended periods of time with a half life ranging from 40-100 days. Based on ecological risk assessments, the level of concern (LOC) is high for both acute and chronic ecological risk concerns for ethoprop exposure to both fish and aquatic invertebrates (Pesticide Profile, 2007). There were 14 detections of ethoprop during this study with the highest detections occurring at MC-1 and 15-1 (Figure 3).

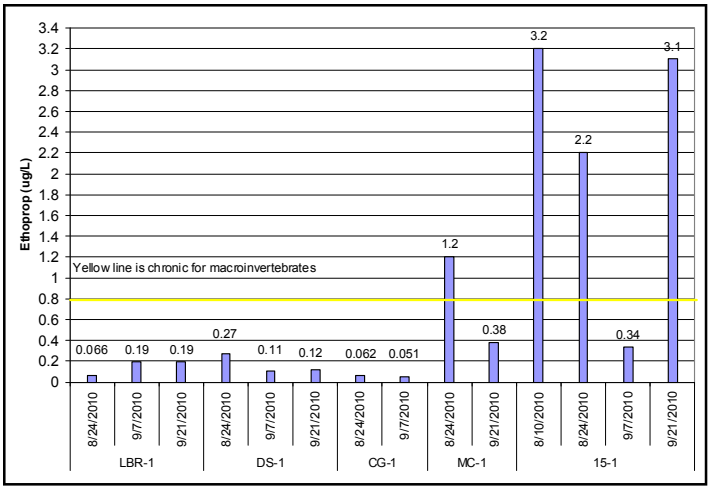

Figure 3. Ethoprop detections per station.

Similar to findings from the ISDA study in 2009, most of the detections of ethoprop occur in early fall (August and September). These late season detections are likely due to post harvest applications, on mint, to control Nematodes. After fall application the label requires application of 1 to 2 inches of water. This late irrigation could account for the transport of ethoprop in early fall to surface waters.

Chlorpyrifos is considered highly toxic to freshwater fish and aquatic invertebrates. It adsorbs strongly to soils and observed half-life in soil ranges from 60-120 days. Some testing has detected chlorpyrifos in soils for over one year (Extoxnet, 1996). There were 11 detections of chlorpyrifos during this study with all of the detections exceeding ISDA's criteria for POC. (Figure 4).

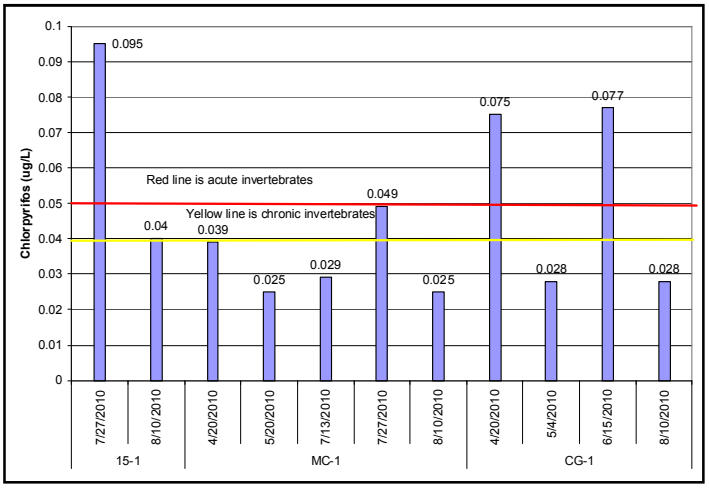

Figure 4. Chlorpyrifos detections per station.

Malathion moderately bonds to soil and is soluble in water, so it may pose a risk to surface water. The half-life in water is 1-3 weeks and soils 1-25 days. The toxicity for fish ranges from very highly toxic to moderately toxic. Malathion is highly toxic to aquatic invertebrates (Extoxnet, 1969). There were seven detections during this study with all detections exceeding the chronic invertebrate concentration (0.035 µg/L) and four exceeding or ≥ 50% of the acute invertebrate benchmark (Figure 5).

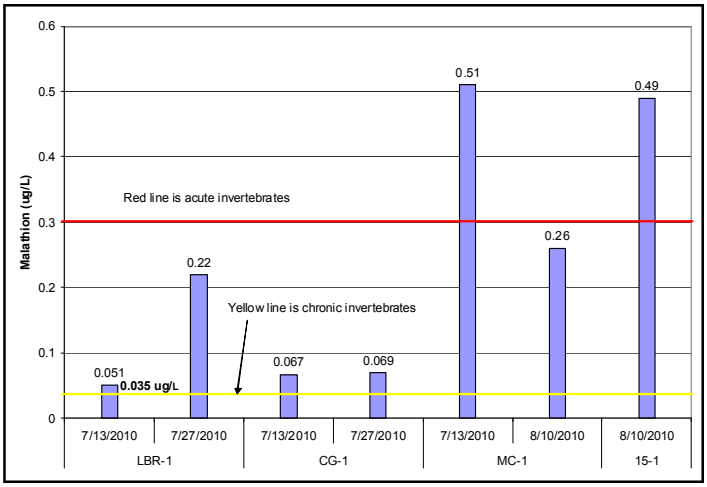

Figure 5. Malathion detections per stations.

Methomyl has a high solubility in water with poor soil bonding abilities. Soil half-life is approximately 14 days and water half-life is estimated at six days. It is rated moderate to highly toxic to fish and highly toxic to aquatic invertebrates (Extoxnet, 1969). There was only one detection that exceeded the chronic invertebrate benchmark and one that was ≥50% of the acute invertebrate (Figure 6). The concern is that methomyl had the greatest number of detections (15) of all the insecticides; which means it is quite prevalent in the Lower Boise River watershed.

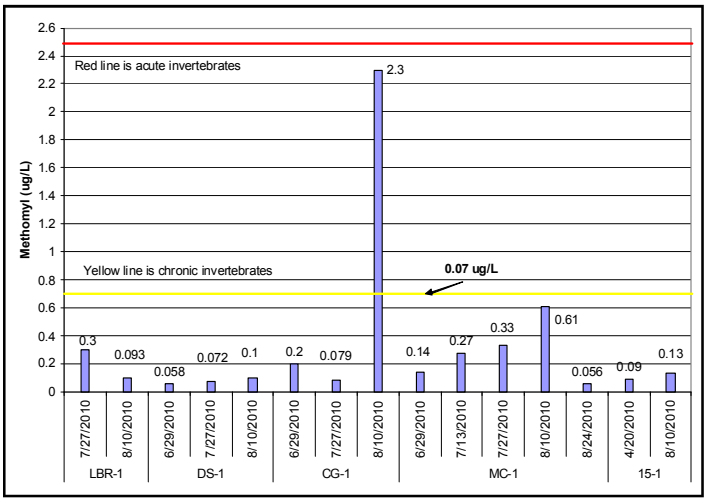

Figure 6. Methomyl detections per station.

Conclusions/Observations

There were a total of 32 pesticides detected during this study with a total of 376 detections. Of the 376 detections 322 were herbicides and 54 were insecticides.

The two herbicides with the largest number of detections were atrazine's degredate desethyl atrazine (51) and Bromacil (39). Other herbicides with 30 or more detections were pendimethalin (38), diuron (37), 2,4-D (36), terbacil (36), and metolachlor (32). The three herbicides with some of the lowest aquatic benchmark concentrations are pendimethalin, metolachlor, and oxyfluorfen. Metolachlor had one detection that was ≥50% of the chronic invertebrate benchmark and oxyfluorfen exceeded the chronic fish concentration at CG-1. Pendimethalin did not exceed any EPA aquatic benchmark concentrations.

The large number of insecticide detections (54) are of concern due to their level of toxicity, at very low concentrations, for fish and aquatic invertebrates. Of the insecticides detected, 87% were pesticides that ISDA considers a POC for the Lower Boise River drainage. These insecticides and their detections are as follows: methomyl (15), Ethoprop (14), chlorpyrifos (11), and Malathion (7).

The numerous detections of both herbicides and insecticides could indicate a significant acute or chronic condition in these systems, for both fish and aquatic invertebrates. Research is ongoing to determine the effects of pesticide mixtures and whether mixture toxicology is additive or synergistic. It is important to understand whether mixtures of certain insecticides or herbicides and insecticides increase the toxic effects of these compounds on aquatic species. One research paper suggests that in aquatic systems, a concentration of 200 µg/L of atrazine increased the toxicity of chlorpyrifos up to a factor of four (Belden and Lydy 2000). This research is still somewhat in its infancy and further studies are needed to determine the overall toxicity of these types of pesticide mixtures.

The number of pesticide detections observed during both the 2009 and 2010 studies conducted by ISDA would indicate a problem with pesticide use within the Lower Boise watershed. Proper Best Management Practices (BMPs) may not be in place or if they are they may be malfunctioning. It is imperative that applicators follow proper protocols and label directions to limit pesticide contact with live waters. Additional training or education may be needed for applicators that are active within the watershed. Additional monitoring efforts may be required to help determine or delineate areas of pesticide impacts to waterways.

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