Groundwater, Surface Water, and Sediment Monitoring for Pesticides and Nitrate in Billings, Montana

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1.0 INTRODUCTION

A pesticide is any substance used to destroy, repel, control, or reduce unwanted pests. Common types of pesticides include herbicides, insecticides, fungicides and rodenticides. Although commonly associated with agriculture, approximately 20-25% of all pesticide use is in non-agricultural areas including lawns, gardens, commercial and industrial sites, aquatic areas for mosquito control, rights-of-ways, etc. (Kiely et al, 2004). Because many of these chemicals are mobile in the environment, impacts to groundwater and surface water have become a concern worldwide. Concerns include human health as well as ecological impacts.

In 1989, the Montana Agricultural Chemical Groundwater Protection Act was passed (MCA Title 80, Chapter 15, Sections 80-15-101 through 80-15-414). Section 80-15-103 states that it is the policy of the state to: protect groundwater and the environment from impairment or degradation due to the use of agricultural chemicals including all pesticides and fertilizers, allow for the proper and correct use of agricultural chemicals, provide for the management of agricultural chemicals to prevent, minimize, and mitigate their presence in groundwater, and provide for education and training of agricultural chemical applicators and the general public on groundwater protection, agricultural chemical use, and the use of alternative agricultural chemicals. Under this Act, it is the directive of the Groundwater Protection Program (GWPP) of the Montana Department of Agriculture (MDA) to monitor the occurrence and concentration of agricultural chemicals in the waters of the State of Montana.

During the summer of 2010, the GWPP conducted a monitoring project in residential and urban areas of Billings, Montana. The project included the collection of 32 groundwater samples, 31 surface water samples, and 31 sediment samples. The study was performed in order to determine potential impacts to groundwater and surface water from the use of pesticides and contributions from nitrogen sources (i.e. fertilizer, manure, septic effluent). This was the first large scale monitoring effort to determine impacts from the use of agricultural chemicals to water resources in urban and residential areas of Montana.

2.0 HYDROGEOLOGY OF BILLINGS

The City of Billings is situated on the alluvial valley of the Yellowstone River. The geology underneath the city consists of relatively shallow alluvial (river) deposits from the Yellowstone River underlain by shale bedrock of the late Cretaceous Colorado Group (Olsen, 2005). Since the shale bedrock yields insufficient water, or water of poor quality, the overlying alluvial deposits are generally the sole source of groundwater under Billings.

The alluvial deposits are contained in seven distinct terrace surfaces formed by the erosion and deposition of the Yellowstone River in the Billings area. The Billings urban area is built mostly upon the 2^{nd} and 3^{rd} terraces which lie 20-90 feet above the modern floodplain. There does not appear to be any hydraulic connectivity between the terrace deposits and the Yellowstone River and its current floodplain (Olsen, 2005).

The alluvial deposits generally consist of a basal course-grained unit overlain by a fine-grained unit (Olsen, 2005). The coarse-grained unit consists of sand and gravel while the fine-grained unit is made up of silt and clay. Most wells in Billings tap into the saturated sand and gravel unit to obtain water. The sands and gravels can be as thick as 40 feet but are generally in the range of 20 feet. The fine-grained unit can be up to 100 feet thick (generally at the edges of the valley), however, based on driller logs for wells used during this project it is generally 10-20 feet thick with a maximum of 40 feet and a minimum of 5 feet. The upper fine-grained unit can be saturated in places but generally does not yield sufficient water for use.

Groundwater in the alluvial deposits under Billings flows to the east-southeast (Olsen, 2005). Recharge to the aquifer comes from precipitation, irrigation, irrigation canal leakage, and the watering of yards.

3.0 PREVIOUS WORK

This is the first comprehensive study of pesticide impacts to the water resources in the Billings urban area. However, there have been samples collected for nitrate analysis by the Montana Bureau of Mines and Geology (MBMG) as part of their statewide monitoring efforts. The MBMG has collected 12 groundwater samples from 10 wells in the Billings metro area between 1997 and 2007. Five of these wells were also sampled by the MDA during the present project.

MBMG nitrate concentrations ranged from non-detect to 20.1 mg/L. The median nitrate concentration was 5.3 mg/L. Only one sample, collected in 1997 on the southern edge of Billings, exceeded the drinking water standard of 10 mg/L. Subsequent samples from the same well in 2007 and two in 2010 had nitrate concentrations of 9.2, 7.2, and 6.5 mg/L, respectively.

4.0 MDA WATER AND SEDIMENT SAMPLING SUMMARY

4.1 Groundwater Sampling

Between May 31 and June 2, 2010, the MDA collected groundwater samples from 17 wells. On August 31–September 2, 2010, samples were collected from 15 wells. Two wells sampled in June were not sampled in September because of access issues. In sampled wells, the mean depth of well screens below the ground surface was 21 feet and mean total depth was 27 feet (Table 1). All wells were completed in the shallow alluvial aquifer. Sampling locations were chosen to optimize geographic distribution in the Billings metro area (Figure 1).

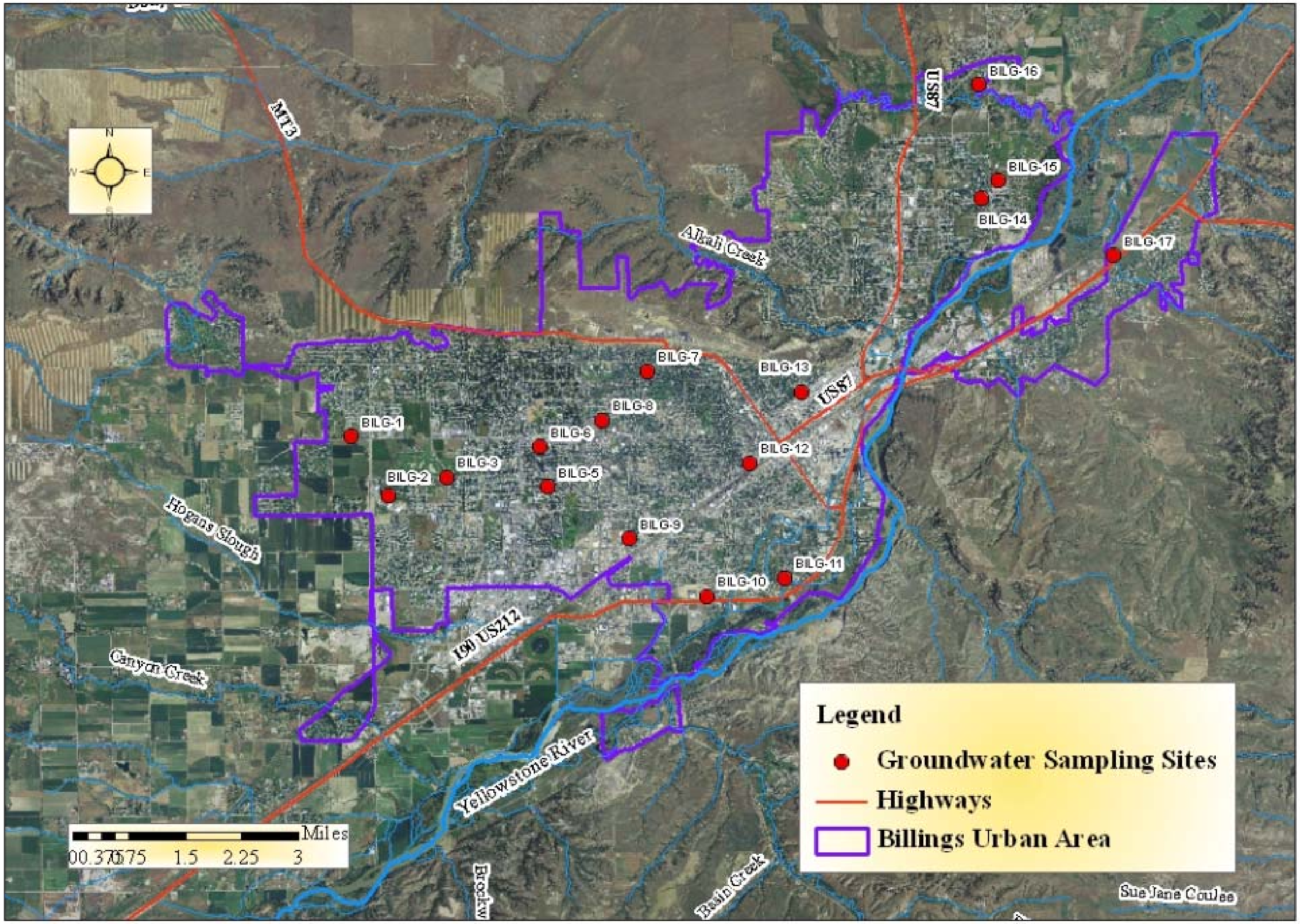
All wells were sampled after purging at least three well casing volumes and/or after field parameters (temperature, pH, specific conductivity, and dissolved oxygen) had stabilized. MDA utilized standard operating procedures (SOPs) for groundwater collection, storage, and transportation.

Table 1. Well Information for Groundwater Sampling Sites

Site ID	Water use	Total Depth (ft bgs)	Screened Interval (ft bgs)	Water Level (ft bgs)
BILG-1	D	58	Open bottom	13
BILG-2	D	40	34-39	8
BILG-3	I	27	Unknown	10
BILG-4	D	25	Unknown	13
BILG-5	I	25	20-25	12
BILG-6	I	26	21-26	12
BILG-7	I	46.5	Open bottom	25
BILG-8	I	21	16-21	12
BILG-9	I	33	26-31	12
BILG-10	I	26	21-26	13
BILG-11	I	23	13-23	8
BILG-12	I	28	Open bottom	Unknown
BILG-13	I	31	20-25	13
BILG-14	I	27	18-27	17
BILG-15	I	22	17-21	10
BILG-16	I	20	Open bottom	11
BILG-17	I	57	Open bottom	23

bgs = below ground surface; D = domestic; I = irrigation

Figure 1. Groundwater Sampling Locations



4.2 Surface Water Grab Sampling

The MDA collected surface water grab samples from 11 locations during the summer of 2010 (Figure 2). A range of surface water sites were selected to compliment groundwater sampling efforts. Irrigation canals that flow through Billings were sampled above city limits, within city limits, and below city limits. Creeks and drains that receive storm water from the City of Billings were also sampled. These creeks and drains empty into the Yellowstone River. Surface water sites included: the Billings Bench Water Association (BBWA) canal, the Big Ditch Company canal, Spring Creek, Canyon Creek, Hogans Slough, City-County Drain, and Alkali Creek (Table 2). Spring Creek is a natural drainage which receives irrigation canal overflows and storm water discharges and empties into the City-County Drain. Canyon Creek is a natural stream, however, it receives irrigation return flow, irrigation canal overflows, and storm sewer discharges. Both Hogans Slough and City-County Drain are artificial drains for groundwater discharges, irrigation canal overflows, and storm water discharges. Alkali Creek is a naturally occurring creek which receives storm water discharges.

Streams, drains, and canals were sampled using both vertical and horizontal integration techniques unless flow conditions did not allow for safe wading. If wading was unsafe, grab samples were obtained from flowing water by reaching out from the stream or canal bank or by wading into safe areas of the stream. Discharge measurements were collected when conditions allowed. Due to high flow conditions, discharge was not measured at Canyon Creek during any of the sampling events, and at Alkali Creek during the June 17 sampling. No discharge was measured at City-County Drain on June 1 because of equipment malfunction. Because of the depth of the BBWA canal no discharge measurements were made at any of the sites on the canal. MDA utilized standard operating procedures (SOPs) for surface water collection, storage, transportation, and discharge measurements.

Both surface water and groundwater samples were collected in 900-mL amber glass jars and 25-mL nalgene bottles, put on ice, and transported to the MDA Analytical Laboratory Bureau at Montana State University in Bozeman. The samples were analyzed using the “Montana Universal Method” (MT UM), an analytical method developed by the MDA Analytical Bureau for the detection of pesticides in water. The MT UM is a polar multi-residue method which analyzes for 93 pesticides and pesticide degradates. In addition to the MT UM, samples were analyzed for the herbicide glyphosate and its degradate AMPA. The MDA lab also performed all nitrate analyses. A list of analytes and their respective limits of quantification is included in Appendix A.

Figure 2. Surface Water Sampling Locations

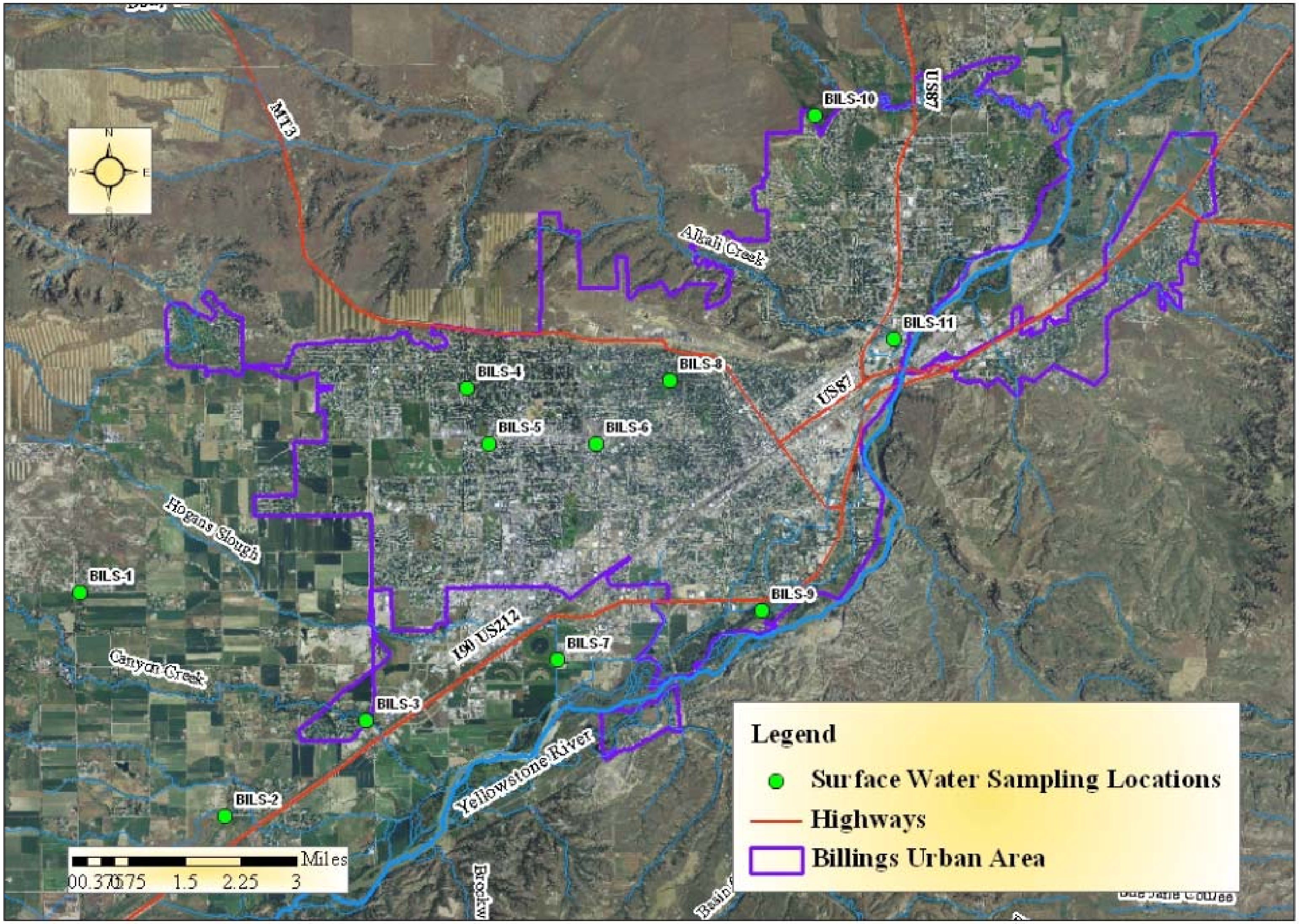


Table 2. Surface Water Site Information			
Site ID	**Location description**	**Date**	**Discharge (cfs)**
BILS-1	BDC Canal at King Ave and S 72nd St W	6/2/10	22.4
		9/2/10	24.4
BILS-2	BBWA Canal at S 56th St W and Danford Rd	6/2/10	NM
		9/1/10	NM
BILS-3	Canyon Creek at Neibauer Road	6/1/10	NM
		7/14/10	NM
		9/1/10	NM
		9/27/10	NM
BILS-4	BDC Canal at Rehberg Lane south of Poly Dr	6/2/10	4.8
		9/2/10	3.1
BILS-5	BBWA Canal at Parkview Dr and Lillis Ln	6/2/10	NM
		9/1/10	NM
BILS-6	Spring Creek at Lewis Ave and 15th St W	6/2/10	1.4
		9/2/10	1.5
BILS-7	Hogans Slough at Elysian Road	6/1/10	48.8
		7/14/10	NM
		9/1/10	49.8
		9/28/10	42.2
BILS-8	BBWA Canal at Poly Dr east of Highwood Dr	6/2/10	NM
		9/1/10	NM
BILS-9	City-County Drain at I-90 Frontage Road	6/1/10	NM
		7/13/10	21.7
		9/1/10	16.5
		9/27/10	12.9
BILS-10	BBWA Canal at Annandale Rd and Greenbriar Rd	6/2/10	NM
		9/1/10	NM
BILS-11	Alkali Creek east of Metra Park	6/1/10	1.6
		6/17/10	NM
		7/13/10	1.7
		9/1/10	4.4
		9/27/10	1.6

NM = not measured
BDC = Big Ditch Company
BBWA = Billings Bench Water Association

4.3 Surface Water Passive Sampling

In addition to surface water grab samples, Polar Organic Contaminant Integrative Samplers (POCIS) were deployed in four streams and drains in the Billings area. The streams and drains included Canyon Creek, Hogans Slough, City-County Drain, and Alkali Creek (sites BILS-3, BILS-7, BILS-9, and BILS-11 on Figure 2). POCIS are passive samplers left in streams for several weeks up to several months and are used to mimic aquatic respiration. If experiments have been performed to determine the sampling rate for individual chemicals the POCIS data can be used to calculate a time-weighted average water concentration. The use of POCIS has been detailed in Alvarez et al, 2004, and Alvarez et al, 2005.

Two POCIS per site were placed in stainless steel cages, tied to cement cinder blocks, and placed in the streams and drains from June 1 through July 14, 2010, and again from September 1 through September 27, 2010. The POCIS placed in Alkali Creek during June was washed away by heavy rains and flash floods on June 20 and was not recovered for analysis. The POCIS in City-County Drain during June was buried by a silty sand sediment when retrieved. The POCIS cage in Hogans Slough during June was filled with mud. Upon retrieval, POCIS were taken to the MDA analytical laboratory and analyzed using the 2008 MT UM, which has a slightly different analyte list then the 2010 MT UM. The 2008 MT UM was used because that is when sampling rate experiments were performed on the POCIS. Grab samples were collected from the streams when the POCIS were deployed and again when retrieved. These samples were analyzed using the 2010 MT UM.

POCIS device ready for deployment

4.4 Sediment Sampling

Sediment samples were collected for pyrethroid analyses in June, September, and November, 2010 (Table 3; Figure 3). Samples were collected at several locations along 2 irrigation canal networks (Big Ditch Company, Billings Bench Water Association) and along multiple, interconnected natural and man-made drainage networks in and around the City of Billings including Canyon Creek, Hogans Slough, City/County Drain and Alkali Creek. It is worth noting that there was a significant storm event on June 20, 2010, after the June sediment sampling. This storm event likely produced significant redistribution of sediments within the creeks and drains.

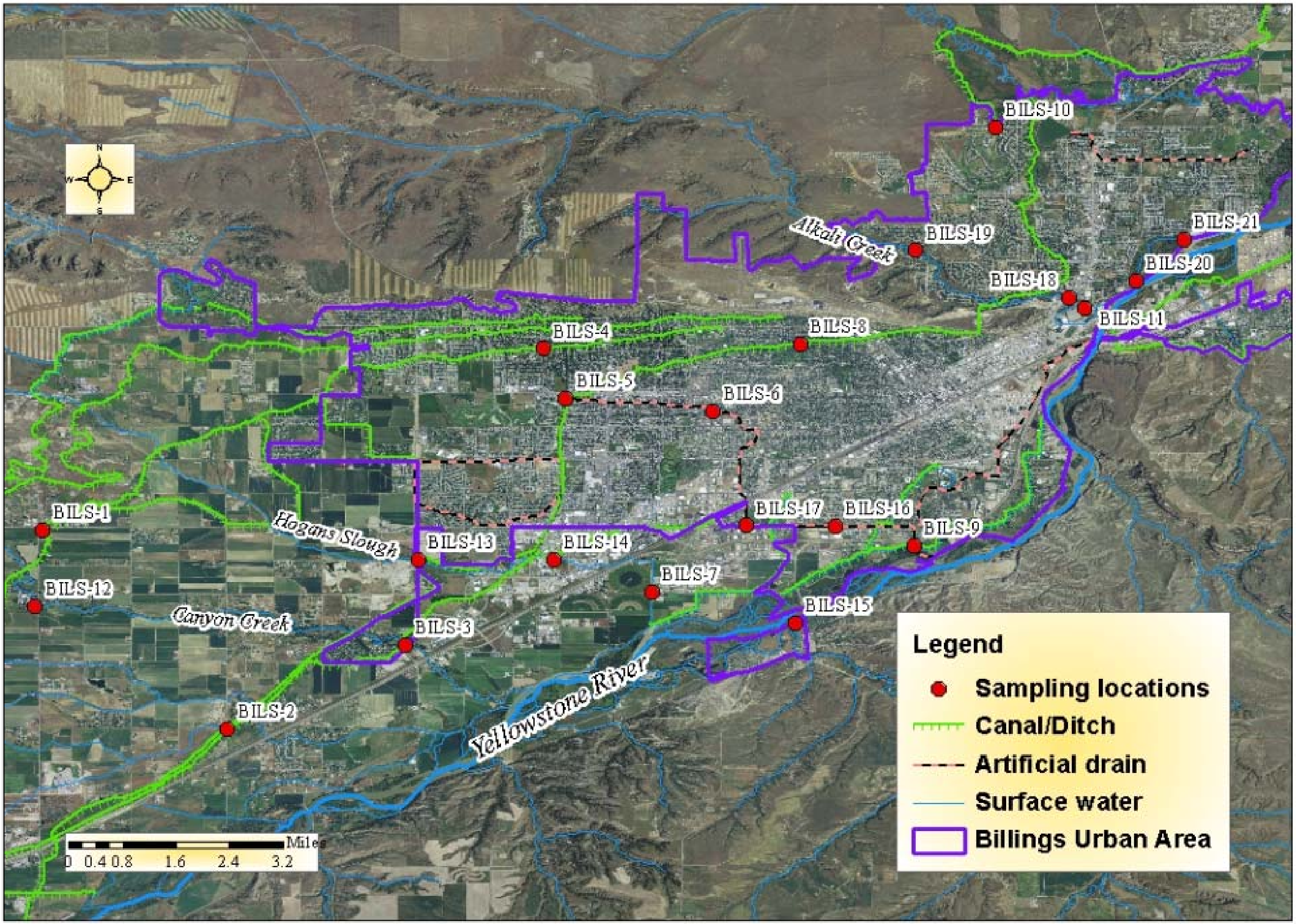
Table 3. Sediment Sample Site Information

Site ID[a]	Name	Location description	June 1st - 2nd	September 1st - 2nd	November 15th
BILS-1	High Ditch	King Ave W and S 72nd St W	X		
BILS-2	BBWA	S 56th St W and Danford Rd	X		X
BILS-3	Canyon Creek	Neibauer Rd	X		X
BILS-4	High Ditch	Rehberg Ln south of Poly Dr	X	X	
BILS-5	BBWA	Parkview Dr and Lillis Ln	X		
BILS-6	Spring Creek	Park at Lewis Ave and 15th St W	X		X
BILS-7	Hogan's Slough	Elysian Rd crossing	X	X	X
BILS-8	BBWA	Poly Dr east of Highwood Dr	X	X	
BILS-9	City/County Drain	S of I90 Frontage Rd	X		X
BILS-10	BBWA	Annandale Rd and Greenbriar Rd	X	X	
BILS-11	Alkali Creek	in city park east of Metra Park	X		X
BILS-12	Canyon Creek	72nd Street crossing			X
BILS-13	Hogan's Slough	40th Street crossing			X
BILS-14	Hogan's Slough	26th Street crossing			X
BILS-15	Blue Creek	N of Jellison Rd			X
BILS-16	City/County Drain	King Ave E and Orchard Lane			X
BILS-17	City/County Drain	King Ave E and Nimitz Dr			X
BILS-18	Alkali Creek	HWY 10W crossing			X
BILS-19	Alkali Creek	Senators Rd crossing			X
BILS-20	Hilltop Drain	S end of Two Moon Park			X
BILS-21	Two Moon Park	S of Yellowstone R. Rd			X

[a]Selected sampling locations for September and November were made in response to the results of June sediment samples

Pyrethroids are largely insoluble, non-persistent chemicals, and are relatively immobile in the environment. They have high adsorption coefficients and bind tightly to the organic fractions in soils and sediment and have low risk of leaching to groundwater. Bound to soil particles, pyrethroids are prone to off-site transportation and deposition in surface waters following a precipitation or irrigation event. Pyrethroids primarily sorb to organic matter and colloidal particles. Therefore, samples were preferentially collected from recently deposited fine sediments and organic matter. Two sampling environments were encountered during this project: slow stream flow with a soft bottom (type 1); slow stream flow with primarily coarse bottom material covered with filamentous algae and a thin layer of fine material (type 2). Different sample collection techniques were used for each environment. For type 1 environments, a trowel was used to remove the upper sediment layer (0.5 inches or less). For type 2 environments, latex gloved hands were used to collect sediment from algae and cobble surfaces. All subsamples were placed into a clean stainless steel bucket and homogenized before being transported in glass sample bottles. Pyrethroid analyses were performed by the Water Pollution Control Laboratory of the California Department of Fish and Game in Rancho Cordova, CA. Total organic carbon (TOC) analyses were completed by Energy Labs in Helena, MT.

Figure 3. Sediment Sampling Locations

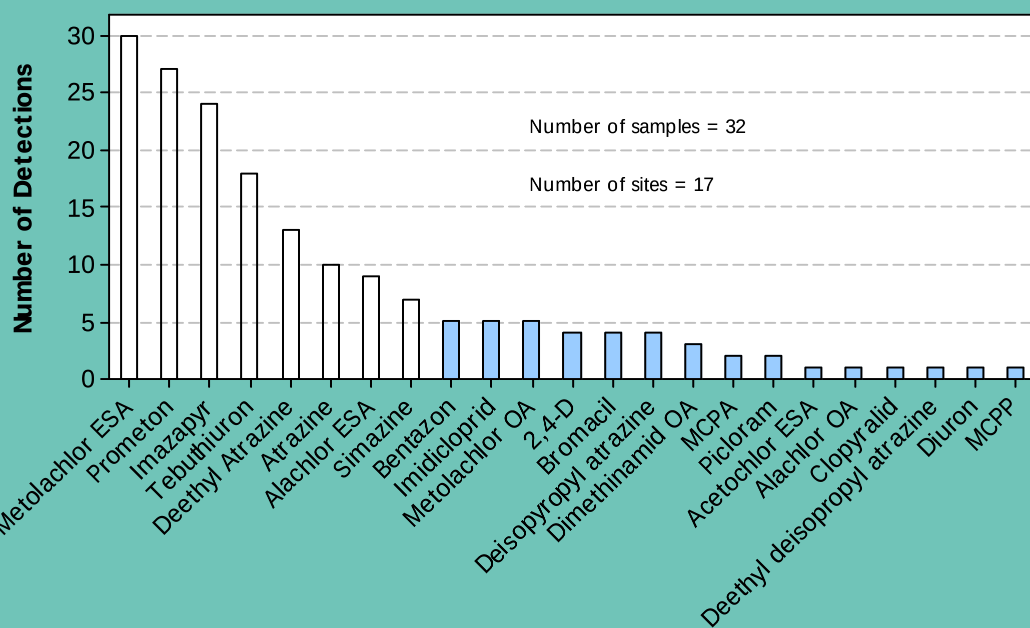


5.0 ANALYTICAL RESULTS

5.1 Groundwater Sampling Results - Pesticides

There were a total of 179 detections of 23 pesticides and pesticide degradates observed in 32 groundwater samples (Figure 4). Of the 179 detections, 82 were below the analytical method reporting limits and were not quantified. All of the groundwater samples contained at least one pesticide compound. On average, samples contained 5.6 pesticides per sample with a range of 1-10 pesticides per sample. Most significantly, no single pesticide detection exceeded or approached the human health standard (HHS) for drinking water (Table 4). Individual results for the samples are presented in Appendix B.

Figure 4. Pesticide Detections in Groundwater



Of the 23 pesticide compounds detected, 22 were herbicides and one was an insecticide (imidacloprid). The most common detection in groundwater was metolachlor ESA, a degradate of metolachlor, an herbicide used in corn, potato, and nursery crops. The next three most common detections, prometon, imazapyr, and tebuthiuron, are all herbicides used in non-crop areas. Atrazine and alachlor are herbicides used in corn crops, while simazine is an herbicide that can be used in corn crops, but can be used at higher application rates as a soil sterilant in non-crop areas. The remaining pesticides all had five or fewer detections.

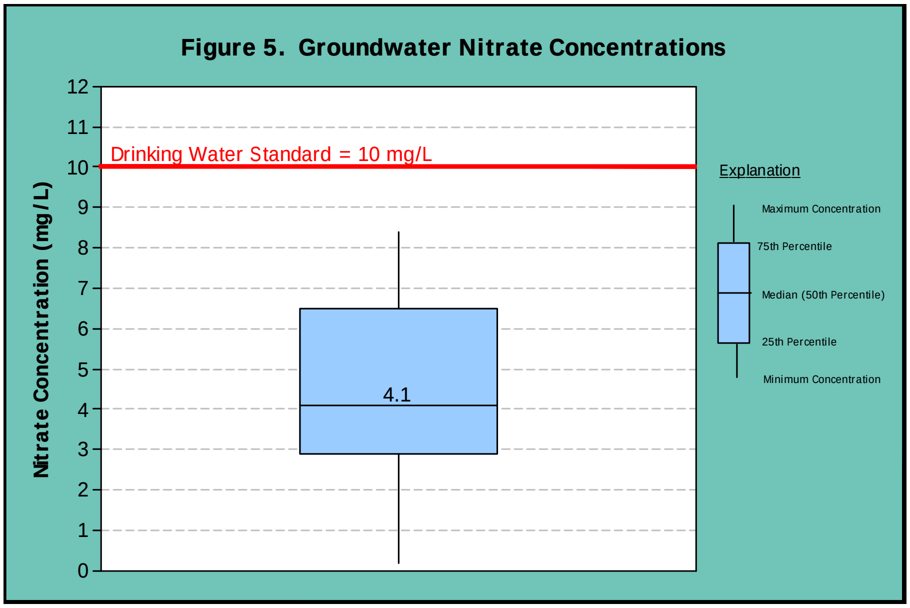
Pesticide Compound	Number of Samples	Number of Detections (percent of samples)	Summary of Detections			Human Health Standard for Drinking Water (µg/L)
			Minimum Concentration (µg/L)	Median Concentration (µg/L)	Maximum Concentration (µg/L)	
2,4-D	32	4 (13)	<0.0045	--	<0.0045	70
Acetachlor ESA	32	1 (3)	--	--	0.01	140
Alachlor ESA	32	9 (28)	<0.011	0.043	0.12	2*
Alachlor OA	32	1 (3)	--	--	<0.0034	2*
Atrazine	32	10 (31)	<0.0022	0.0025	0.0076	3*
Bentazon	32	5 (16)	<0.0011	--	<0.0011	200
Bromacil	32	4 (13)	0.0074	1.32	2.3	90
Clopyralid	32	1 (3)	--	--	<0.022	3,500
Deethyl deisopropyl atrazine	32	1 (3)	--	--	<0.5	3*
Deethyl atrazine	32	13 (41)	<0.0017	0.0036	0.024	3*
Deisopropal atrazine	32	4 (13)	--	--	<0.01	3*
Dimethenamid OA	32	3 (9)	<0.0038	0.004	0.0041	400
Diruon	32	1 (3)	--	--	<0.01	10
Imazapry	32	24 (75)	<0.011	0.029	4.7	21,000
Imidacloprid	32	5 (16)	0.0024	0.066	0.29	400
MCPA	32	2 (6)	<0.0023	0.003	0.0044	4
MCPP	32	1 (3)	--	--	0.0041	7
Metolachlor ESA	32	30 (94)	<0.0025	0.0025	0.18	100*
Metolachlor OA	32	4 (13)	<0.021	--	<0.021	100*
Picloram	32	2 (6)	<0.14	--	<0.14	500
Prometon	32	27 (84)	<0.0051	0.0195	0.34	100
Simazine	32	7 (22)	<0.0026	0.0026	0.0049	4
Tebuthiruon	32	18 (56)	<0.0011	0.0033	0.17	500

Table 3. Summary of Pesticide Detections in Groundwater

* Parent compound and metabolite concentrations are added together before being compared to the drinking water standard

5.2 Groundwater Sampling Results – Nitrate

Nitrate was detected in 31 of 32 groundwater samples collected. Concentrations ranged from non-detect (ND) to 8.4 mg/L, with a weighted mean concentration of 4.1 mg/L (Figure 5). None of the nitrate concentrations exceeded the HHS for drinking water of 10 mg/L.



5.3 Surface Water Grab Sample Results - Pesticides

There were a total of 229 detections of 29 different pesticides and pesticide degradates in 31 surface water samples (Figure 6). Of the 229 detections, 89 were below the analytical method reporting limit and were not quantified. All of the surface water samples contained at least two pesticide compounds. On average, samples contained 7.4 pesticides per sample with a range of 2-18 pesticides per sample. In general, pesticides were detected more frequently in the creeks and drains then in the irrigation canals (Figures 7 and 8). None of the pesticide concentrations exceeded or approached the HHS for drinking water (Table 5). In addition, there were no exceedances of EPA aquatic life benchmarks (Table 5). Individual results for the surface water samples are presented in Appendix B.

There was a single incident where a pesticide concentration approached an aquatic life benchmark. On June 1, 2010, diruon was found at a concentration of 1.3 µg/L in Alkali Creek (site ID = BILS-11), which is >50% of the acute aquatic life benchmark for non-vascular plants of 2.4 µg/L. A sample collected on June 17, 2010, to verify the diuron detection, contained a low concentration which did not approach the aquatic life benchmark. Two subsequent samples in Alkali Creek in July and early September also contained low concentrations of diruon. A sample collected in late September had no detection of diuron.

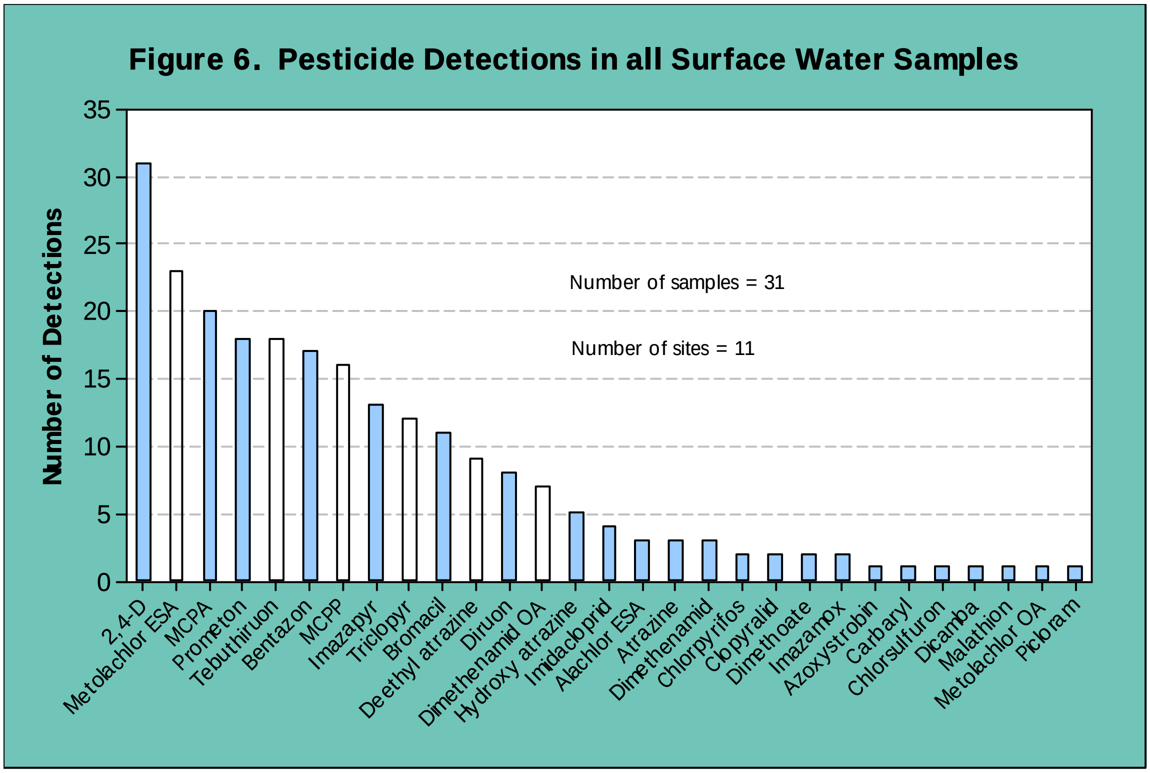


Figure 6. Pesticide Detections in all Surface Water Samples

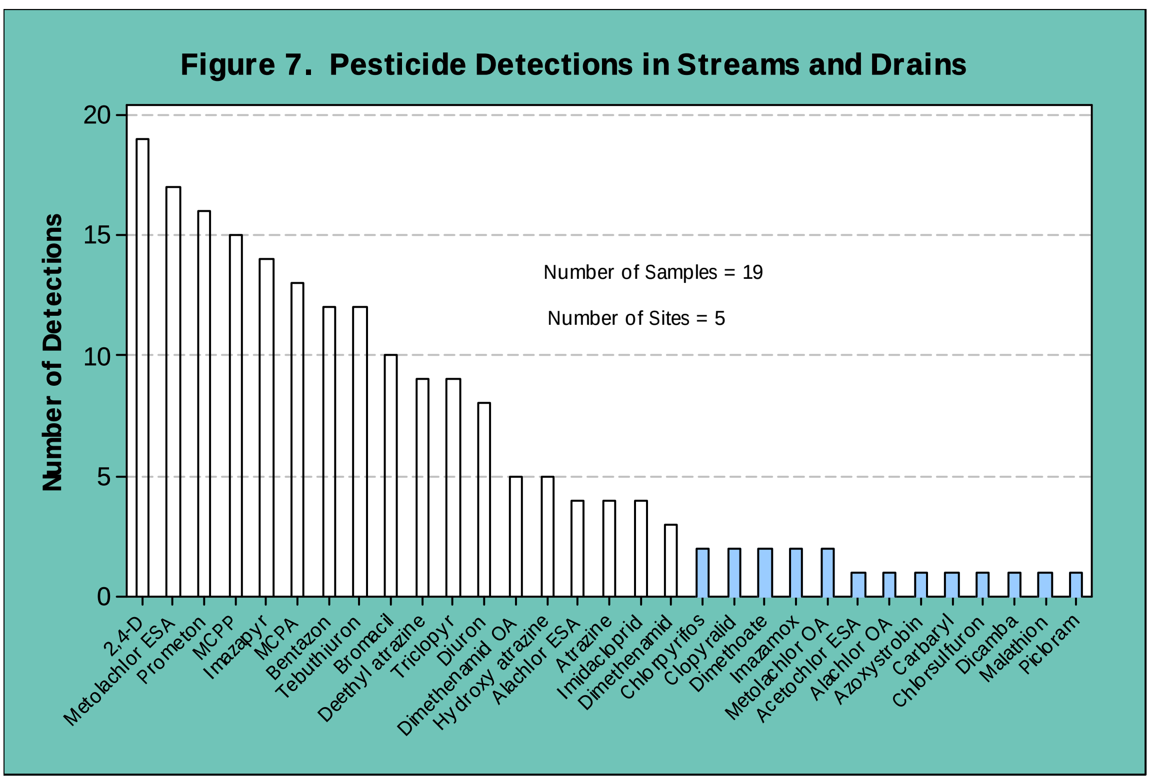
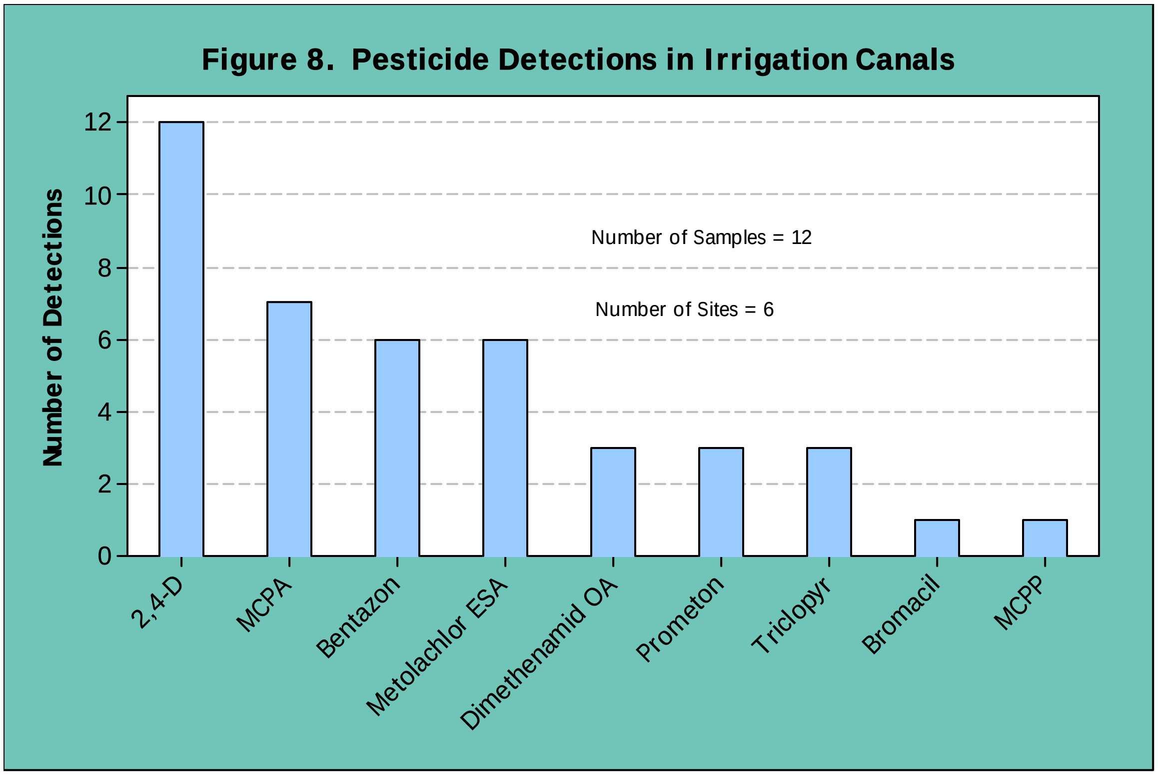


Figure 7. Pesticide Detections in Streams and Drains



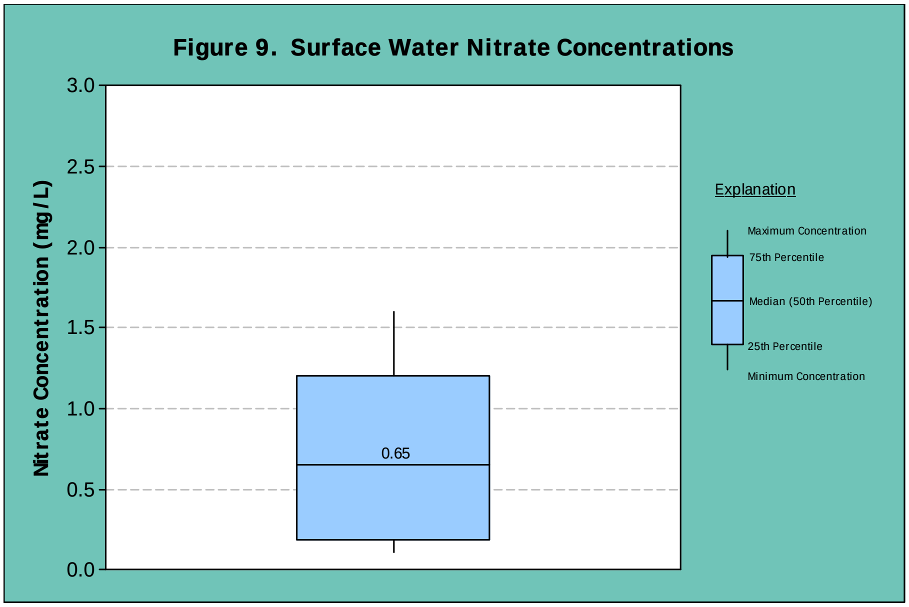
Of the 29 pesticide compounds detected, 23 were herbicides, five were insecticides (imidacloprid, chlorpyrifos, dimethoate, carbaryl, and malathion), and one was a fungicide (azoxystrobin). The herbicide 2,4-D was detected in every surface water sample collected. 2,4-D has many uses including in cereal crops, corn, pastures, rangeland, CRP lands, and in aquatic situations. It is also commonly used around homes in lawn and garden settings. 2,4-D also had the highest concentration in surface water with a detection of 11 µg/L in Alkali Creek on June 17, 2010. Metolachlor ESA is a degradate of metolachlor, an herbicide used in corn, potatoes, and nursery crops. MCPA is an herbicide similar to 2,4-D and is used in cereal crops, pastures, rangeland, and turf. Prometon, tebuthiuron, imazapyr, triclopyr, bromacil, and diuron, are all herbicides used in non-crop settings. All of these herbicides, with the exception of tebuthiuron, are used as soil sterilants, i.e., used in areas were long term weed and vegetation control is desired. Bentazon is an herbicide used in dry beans, peas, and corn. MCPP is used in turf and cereal crops. Deethyl atrazine and hydroxy atrazine are both degradates of atrazine, an herbicide used in corn crops. The remaining pesticides all had four or less detections.

Table 5. Summary of Pesticide Detections in Surface Water												
Pesticide Compound	Number of Samples	Number of Detections (percent of samples)	Summary of Detections			Human Health Drinking Water Standard (µg/L)	EPA Auatic Life Benchmarks					
			Minimum Concentration (µg/L)	Median Concentration (µg/L)	Maximum Concentration (µg/L)		Acute Fish (µg/L)	Chronic Fish (µg/L)	Acute Invertabrates (µg/L)	Chronic Invertabrates (µg/L)	Acute Non-Vascular Plants (µg/L)	Acute Vascular Plants (µg/L)
2,4-D	31	31 (100)	<0.0045	0.018	11	70	--	--	--	--	--	--
Alachlor ESA	31	3 (10)	<0.011	--	<0.011	140	52,000	--	52,000	--	--	--
Atrazine	31	3 (10)	<0.0022	--	<0.0022	3*	2,650	65	360	60	1	37
Azoxystrobin	31	1 (3)	--	--	0.0056	1,000	235	147	130	44	49	3,400
Bentazon	31	17 (55)	<0.0011	0.0012	0.19	200	>50,000	--	>50,000	--	4,500	5,350
Bromacil	31	11 (35)	<0.0074	0.017	0.069	90	18,000	3,000	60,500	8,200	6.8	45
Carbaryl	31	1 (3)	--	--	<0.04	700	110	6.8	0.85	0.5	660	1,500
Chlorpyrifos	31	2 (6)	<0.031	--	<0.031	20	0.9	0.57	0.05	0.04	140	--
Chlorsulfuron	31	1 (3)	--	--	0.0066	1,750	--	--	--	--	--	--
Clopyralid	31	2 (6)	<0.022	--	<0.022	3,500	984,000	--	56,500	--	--	--
Deethyl atrazine	31	9 (29)	<0.0017	--	<0.0017	3*	--	--	--	--	--	--
Dicamba	31	1 (3)	--	--	2.7	200	14,000	--	17,300	--	61	>3,250,000
Dimethenamid	31	3 (10)	0.069	0.076	0.092	400*	3,150	300	6,000	1,020	14	8.9
Dimethenamid OA	31	7 (23)	<0.0038	0.0038	0.013	400*	--	--	--	--	--	--
Dimethoate	31	2 (6)	<0.0011	--	0.0012	--	3,100	430	21.5	0.5	84	--
Diruon	31	8 (26)	<0.01	0.011	1.3	10	200	26	80	200	2.4	15
Hydroxy atrazine	31	5 (16)	<0.0064	--	<0.0064	70	--	--	--	--	--	--
Imazamox	31	2 (6)	<0.012	--	0.033	20,00	>59,500	--	>61,000	--	>40	11
Imazapry	31	13 (42)	<0.011	0.024	0.16	21,000	>50,000	43,100	50,000	97,100	11,500	18
Imidacloprid	31	4 (13)	0.0024	0.006	0.0083	400	>41,500	1,200	35	1.05	>10,000	--
Malathion	31	1 (3)	--	--	<0.028	100	16.4	8.6	0.3	0.035	2,400	--
MCPA	31	20 (65)	<0.0023	0.007	0.055	4	--	--	--	--	300	170
MCPP	31	16 (52)	<0.0022	0.006	0.1	7	--	--	>45500	50,800	--	--
Metolachlor ESA	31	23 (74)	<0.0025	0.004	0.032	100*	24,000	--	>54,000	--	>99,450	>95,100
Metolachlor OA	31	1 (3)	--	--	<0.021	100*	>46,550	--	7,700	--	57,100	>95,100
Picloram	31	1 (3)	--	--	<0.14	500	6,500	550	34,150	11,800	4,900	--
Prometon	31	18 (58)	<0.0051	0.008	0.17	100	6,000	9,500	12,850	3,500	98	624
Tebuthiruon	31	11 (36)	<0.0011	0.002	0.004	500	53,000	9,300	148,500	21,800	50	135
Triclopyr	31	12 (39)	<0.011	0.011	0.071	350	180	104,000	850	80,700	100	880

* Parent compound and degradate concentrations are added together before being compared with the drinking water standard

5.4 Surface Water Grab Sample Results – Nitrate

Nitrate was detected in 23 of 30 surface water samples. No nitrate analysis was performed on the diruon verification sample collected from Alkali Creek on June 17, 2010. Concentrations of nitrate in surface waters were all below 1.6 mg/L and none of the samples exceeded the HHS for drinking water of 10 mg/L (Figure 9).



5.5 Surface Water POCIS Results – Pesticides

An average of 22 pesticide compounds were detected in the POCIS (Table 6). The lowest number detected was 18 pesticides in Canyon Creek in September and the highest number detected was 26 in City-County Drain in June/July. All of the sites had slightly more detections in the June/July sampling then in the September sampling.

An average of 10 pesticide compounds per sample were detected in the grab samples collected when POCIS were deployed and retrieved, compared to an average of 22 in the POCIS (Table 6). This indicates that the presence of some pesticides were either episodic or the concentrations of the pesticides were too low to be detected in the grab samples. In addition, a couple of pesticides were detected in the grab samples but not in the POCIS (Table 6). This likely indicates that the POCIS were not able to sequester these chemicals or that the pesticides were in the water only briefly at the time of the grab sample and were not present long enough to be detected in the POCIS.

The amount of pesticides detected in the POCIS is not presented in this report because the data could be misinterpreted as a water concentration. The POCIS data only indicate how much pesticide was sequestered during the deployment period. This data can then be used to calculate a time-weighted average (TWA) water concentration using the following formula:

$$C_{TWA} = M_{ACC}/R_s t$$

Where: C_{TWA} = time weighted average concentration
M_{ACC} = mass accumulated on the POCIS in ng/POCIS
R_s = sampling rate in L/day determined through laboratory experiments
t = time of deployment in days

TWA concentrations are better data to use when determining potential chronic impacts to aquatic life. Grab samples only provide a snapshot of pesticide concentrations at the time of sampling. Since pesticide concentrations are likely transient, the use of grab sample concentrations for the determination of aquatic life impacts could over or under estimate the impacts occurring. Because the POCIS provide an average concentration over the time of deployment these data are more toxicologically relevant.

TWA water concentrations calculated using POCIS data are presented in Table 7. When sampling rate experiments were performed by the MDA Analytical Bureau, 54 of 95 pesticides did not show linear uptake over time, which is required to determine a sampling rate. In addition, many of the detections in the POCIS were below the analytical method reporting limit and not quantified. Therefore, a TWA water concentration could not be determined for many of the pesticides detected in the POCIS. If the calculated TWA water concentration was below 0.0001 µg/L, the pesticide was considered to be not detected. The 0.0001 µg/L cutoff is an arbitrary number used to censor ultra-low level detections which likely have no toxicological significance.

Table 6. Pesticides Detected in POCIS

Canyon Creek (BILS-3) June	Canyon Creek (BILS-3) September	Hogans Slough (BILS-7) June	Hogans Slough (BILS-7) September	City-County Drain (BILS-9) June	City-County Drain (BILS-9) September	Alkali Creek (BILS-11) September
2,4-D	2,4-D	2,4-D	2,4-D	2,4-D	2,4-D	2,4-D
Alachlor ESA	Alachlor ESA	Alachlor ESA	Alachlor ESA	Alachlor ESA	Alachlor ESA	Alachlor ESA
Atrazine	Atrazine	Atrazine	Atrazine	Aldicarb sulfone	Atrazine	Atrazine
Bentazon	Bentazon	Azoxystrobin	Bentazon	Atrazine	Bentazon	Bentazon
Deethyl atrazine	Chlorsulfuron	Bentazon	Bromacil	Azoxystrobin	Bromacil	Bromacil
Dimethenamid	Deethyl atrazine	Bromacil	Deethyl atrazine	Bentazon	Chlorsulfuron	Carbaryl
Dimethoate	Dimethenamid	Carbaryl	Dimethenamid	Bromacil	Deethyl atrazine	Chlorsulfuron
Diuron	Diuron	Deethyl atrazine	Diuron	Carbaryl	Deisopropyl atrazine	Deethyl atrazine
Hexazinone	Hexazinone	Dimethenamid	Hydroxy atrazine	Chlorsulfuron	Dimethenamid	Diuron
Hydroxy atrazine	Hydroxy atrazine	Dimethenamid OA	Imidacloprid	Deethyl atrazine	Diuron	Hydroxy atrazine
Imazamethabenz	Imazamethabenz	Dimethoate	MCPA	Dimethenamid	Hexazinone	Imidacloprid
Malathion	MCPA	Diuron	MCPP	Dimethoate	Hydroxy atrazine	MCPA
MCPA	MCPP	Hydroxy atrazine	Metolachlor	Diuron	Imidacloprid	MCPP
Metolachlor	Metolachlor	Imidacloprid	Metolachlor ESA	Hydroxy atrazine	Malathion	Metolachlor ESA
Metolachlor ESA	Metolachlor ESA	Malathion	Metolachlor OA	Imidacloprid	MCPA	Prometon
Prometon	Prometon	MCPA	Prometon	Malathion	MCPP	Propiconazole
Simazine	Simazine	MCPP	Propiconazole	MCPA	Metolachlor ESA	Simazine
Tebuthiuron	Tebuthiuron	Metolachlor ESA	Simazine	MCPP	Metolachlor OA	Tebuconazole
Triclopyr		NOA 447204	Tebuconazole	Metalaxyl	Prometon	Tebuthiuron
		Prometon	Tebuthiuron	Metolachlor ESA	Propiconazole	Triclopyr
		Propiconazole	Triclopyr	Prometon	Simazine	
		Simazine		Propiconazole	Tebuconazole	
		Tebuconazole		Simazine	Tebuthiuron	
		Tebuthiuron		Tebuconazole	Triclopyr	
		Triclopyr		Tebuthiuron		
				Triclopyr		

Pesticides in red were detected in POCIS but not in grab samples

Pesticides Detected in Grab Samples but not in POCIS

Canyon Creek (BILS-3) June	Canyon Creek (BILS-3) September	Hogans Slough (BILS-7) June	Hogans Slough (BILS-7) September	City-County Drain (BILS-9) June	City-County Drain (BILS-9) September	Alkali Creek (BILS-11) September
Chlorpyrifos	Triclopyr	Chlopyralid	Dimethenamid OA	Imazapyr	Dimethenamid OA	Imazapyr
Dimethenamid OA		Imazamox	Imazapyr		Clopyralid	
					Imazapyr	

Table 7. Surface Water Grab Sample and TWA Concentrations from POCIS

Canyon Creek (BILS-3)

Analyte	6/1/10 Grab Sample (µg/L)	7/14/10 Grab Sample (µg/L)	June/July TWA Concentration from POCIS (µg/L)	9/1/10 Grab Sample (µg/L)	9/27/10 Grab Sample (µg/L)	Sept. TWA Concentration from POCIS (µg/L)
2,4-D	0.011	0.024	0.0048	0.011	<0.0045	0.008
Atrazine	ND	ND	0.0001	ND	ND	0.0003
Dimethenamid	ND	0.076	0.05	ND	ND	ND
Malathion	ND	ND	0.002	ND	ND	ND
Prometon	ND	ND	0.0014	ND	ND	ND

Hogans Slough (BILS-7)

Analyte	6/1/10 Grab Sample (µg/L)	7/14/10 Grab Sample (µg/L)	June/July TWA Concentration from POCIS (µg/L)	9/1/10 Grab Sample (µg/L)	9/27/10 Grab Sample (µg/L)	Sept. TWA Concentration from POCIS (µg/L)
2,4-D	0.018	0.24	0.215	0.12	0.019	0.092
Atrazine	ND	ND	ND	ND	ND	0.0003
Dimethenamid	ND	0.092	0.0004	ND	ND	0.0004
Diuron	ND	ND	0.066	<0.01	ND	0.0011
Imidacloprid	ND	ND	ND	ND	ND	0.0005
MCPA	0.012	0.0031	0.15	0.003	ND	0.059
MCPP	<0.0022	0.039	0.001	0.0031	<0.0022	0.0008
Prometon	<0.0051	<0.0051	0.0027	0.0078	<0.0051	0.0024
Tebuthiuron	ND	ND	ND	<0.0011	<0.0011	0.0002

City-County Drain (BILS-9)

Analyte	6/1/10 Grab Sample (µg/L)	7/14/10 Grab Sample (µg/L)	June/July TWA Concentration from POCIS (µg/L)	9/1/10 Grab Sample (µg/L)	9/27/10 Grab Sample (µg/L)	Sept. TWA Concentration from POCIS (µg/L)
2,4-D	0.038	0.33	0.082	0.56	0.025	0.784
Atrazine	ND	<0.0022	0.0005	ND	ND	0.0004
Bromacil	ND	0.0092	0.064	0.017	0.022	0.02
Dimethenamid	ND	0.069	0.004	ND	ND	0.0044
Diuron	<0.01	<0.01	0.074	0.036	ND	0.0098
Imidacloprid	ND	ND	0.004	ND	ND	0.0016
Malathion	ND	ND	0.011	<0.028	ND	0.0018
MCPA	0.0081	0.024	0.004	0.055	ND	0.0192
MCPP	0.0054	0.016	0.001	0.1	0.0056	0.0302
Prometon	0.019	0.0054	0.04	0.021	0.0088	0.0093
Propaconazole	ND	ND	0.0005	ND	ND	0.0008
Simazine	ND	ND	0.0004	ND	ND	ND
Tebuthiuron	0.0018	0.0016	0.0016	0.0018	0.0029	0.003
Triclopyr	<0.011	0.034	0.0082	<0.011	ND	0.0027

Alkali Creek (BILS-11)

Analyte	6/1/10 Grab Sample (µg/L)	6/17/10 Grab Sample (µg/L)	7/14/10 Grab Sample (µg/L)	9/1/10 Grab Sample (µg/L)	9/27/10 Grab Sample (µg/L)	Sept. TWA Concentration from POCIS (µg/L)
2,4-D	0.047	11	0.79	0.28	0.0047	0.077
Atrazine	ND	<0.0022	<0.0022	ND	<0.0022	0.0003
Bromacil	0.047	0.039	0.012	0.024	0.069	0.044
Chlorsulfuron	ND	0.0066	ND	ND	ND	0.0009
Diuron	1.3	0.063	<0.01	0.011	ND	0.0012
Imidacloprid	0.0032	0.041	ND	ND	0.0083	0.0029
MCPA	0.0053	0.014	0.054	0.013	ND	0.0062
MCPP	0.009	0.033	0.056	0.054	0.0045	0.0026
Prometon	0.012	0.012	0.012	0.018	0.015	0.0069
Tebuthiuron	<0.0011	0.004	0.0013	0.0014	0.0015	0.0012
Triclopyr	ND	<0.011	<0.011	<0.011	ND	0.003

TWA = Time weighted average

5.6 Sediment Sampling Results – Pyrethroid Insecticides

From the three sampling events in Billings in 2010, there were 80 detections of 8 different pyrethroids in 30 sediment samples. Samples had a mean of 2.67 pyrethroid detections per sample. Pyrethroids detected included: bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, fenpropathrin, permethrin (*cis*- and *trans*-), allethrin and prallethrin. Bifenthrin and the *cis*- and *trans*- isomers of permethrin comprised 75% of all detections.

Pyrethroid detections were OC-normalized using the results of the TOC analysis. As TOC increases, bioavailability decreases. To assess *H. azteca* toxicities for individual pyrethroid detections, concentrations were divided by the decimal value of TOC per respective sampling location per date. This calculation is expressed in the following formula.

$$\text{ng/g OC} = \frac{\text{ng/g dry weight}}{\text{ng TOC/g dry weight}}$$

OC-normalized pyrethroid concentrations were then divided by published *H. azteca* sediment toxicities for selected pyrethroids in order to calculate toxic units (TUs) per sediment sample (Maund et al, 2002; Amweg et al, 2005; Ding et al, 2009). This is expressed in the following formula.

$$\text{Toxic Unit (TU)} = \frac{\text{Actual concentration (organic carbon-normalized)}}{\text{Reported } \textit{H. azteca}\ LC_{50} \text{ concentration (organic carbon-normalized)}}$$

Toxic units were summed by location and sampling date to provide a total toxic unit recognizing the established additive effect of exposure to multiple pyrethroids. TUs had a range of 0.00 – 1.80 TUs with a mean of 0.32 TUs for all samples collected in 2010. Amweg et al. (2006) determined that a critical threshold existed at 0.4 TUs although more recent studies have used a threshold of 1 TU to ascertain significant mortality to aquatic invertebrates (Hintzen et al., 2009; Weston and Lydy, 2010). The mean TOC for canal/ditch sites and stream/drains was 0.96% and 1.27% respectively. Employing a simple *t*-test, the two populations were not significantly different at $\alpha = 0.05$ (95% CI). For all samples, the mean TOC was 1.19% with a range of 0.21% - 3.97%.

Where detected, bifenthrin accounted for ~72% of sample toxicity while permethrin accounted for ~33% of sample toxicity. Detections of bifenthrin and permethrin isomers were nearly identical but bifenthrin has significantly greater toxicity. Reporting limits, detection frequency and published LC_{50} data used in the Toxic Unit analysis may be found in Table 8. The most frequently detected pyrethroids include bifenthrin and *cis*- and *trans*- isomers of permethrin. Allethrin and prallethrin were also detected in sediment but no toxicity data exists for these compounds and they were not included in the TU analysis.

Table 8. Reporting limits (RL), detection frequency, mean, maximum and LC_{50}s

Pyrethroid insecticide	RL (µg/g)	Detection frequency (%)	Mean (µg/g)	Max (µg/g)	LC_{50}[a]
Bifenthrin	0.00002	63.3	0.09	0.38	0.52[b]
Cyfluthrin	0.0002	3.3	0.01	0.35	1.1[b]
Cyhalothrin, Lambda	0.0001	16.7	0.01	0.09	0.45[b]
Cypermethrin	0.0002	3.3	0.01	0.31	0.79[c]
Deltamethrin/Tralomethrin	0.0002	0.0	0.00	0.00	0.97[b]
Esfenvalerate	0.0002	0.0	0.00	0.00	1.5[b]
Fenpropathrin	0.0002	3.3	0.02	0.62	8.9[d]
Permethrin, Cis	0.0001	73.3	0.30	4.76	10.83[b]
Permethrin, Trans	0.0001	63.3	0.38	6.81	10.83[b]
Allethrin	0.0002	33.3	0.08	0.71	NA[e]
Prallethrin	0.0002	6.7	0.02	0.34	NA[e]
Resmethrin	0.0002	0.0	0.00	0.00	NA[e]
Tetramethrin	0.0002	0.0	0.00	0.00	NA[e]
Phenothrin	0.0002	0.0	0.00	0.00	NA[e]

[a]Median lethal concentration for *Hyallella azteca* 10-d test in sediment based on organic carbon normalization
[b] Amweg et al, 2005
[c] Maund et al, 2002
[d] Ding et al, 2009
[e] No value was available at the time of data analysis

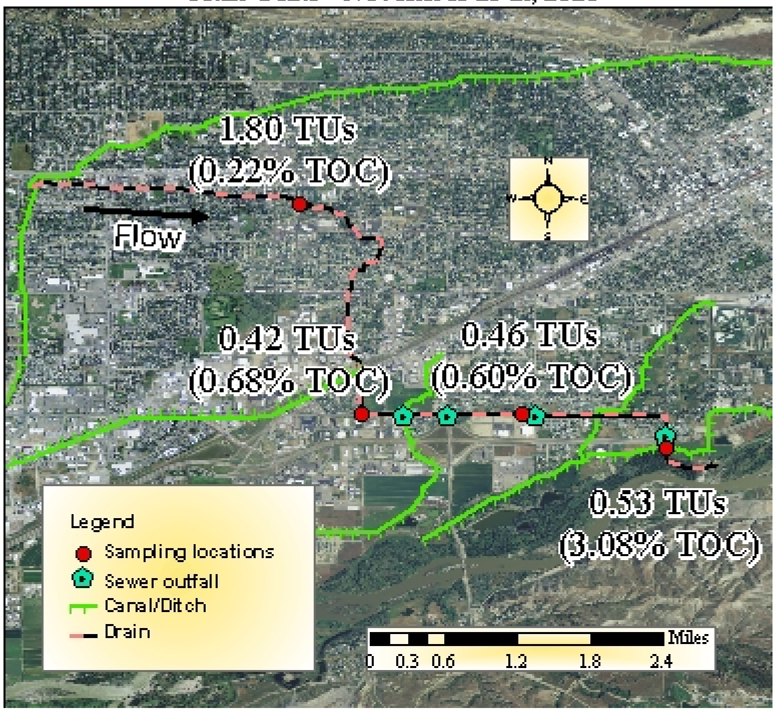
In surface water outfalls to the Yellowstone River, TU values greater than 0.4 were observed at several locations (Table 9). Sampling locations are part of the interconnected storm sewer system which receives regular and overflow discharges from storm water sewer systems and irrigation canals draining low and medium density developed areas within the City of Billings. These drainages include Hogans Slough, City/County Drain and Alkali Creek. At 2 sites, TUs were observed above 1 including Spring Creek Park (BILS-6) and in Big Ditch at Rehberg Lane (BILS-4).

Table 9. Toxic Unit Analysis for Sediment Samples				
Site ID	**Toxic Units (TUs)[abc]**			**Name**
	6/1-6/2	**9/1-9/2**	**11/15**	
BILS-1	0.11	NS	NS	High Ditch
BILS-2	0.00	NS	NS	BBWA
BILS-3	0.00	NS	0.00	Canyon Creek
BILS-4	0.11	1.26	NS	High Ditch
BILS-5	ND	NS	NS	BBWA
BILS-6	0.10	NS	1.80	Spring Creek
BILS-7	0.39	0.49	0.13	Hogan's Slough
BILS-8	0.01	0.01	NS	BBWA
BILS-9	0.78	NS	0.53	City/County Drain
BILS-10	0.07	0.04	NS	BBWA
BILS-11	0.65	NS	0.14	Alkali Creek
BILS-12	NS	NS	ND	Canyon Creek
BILS-13	NS	NS	ND	Hogan's Slough
BILS-14	NS	NS	0.18	Hogan's Slough
BILS-15	NS	NS	0.00	Blue Creek
BILS-16	NS	NS	0.46	City/County Drain
BILS-17	NS	NS	0.42	City/County Drain
BILS-18	NS	NS	0.18	Alkali Creek
BILS-19	NS	NS	0.55	Alkali Creek
BILS-20	NS	NS	0.29	Hilltop Drain
BILS-21	NS	NS	0.00	Two Moon Park - North

[a] *0.00* = pyrethroids detected at concentration(s) < 0.01TUs
[b] ND = no pyrethroids detected in sample
[c] NS = not sampled

In the 11/15/2010 sampling, sediment collection was expanded along several drainages that had TUs of concern as observed in the June 2010 sampling. Drainages with expanded sampling included Hogans Slough, City/County Drain and Alkali Creek in addition to previously unsampled outfalls to the Yellowstone River. Sediment TUs ranged from non-detect to 0.18 TUs (n=3) along Hogans Slough in west-central Billings. Samples were collected at 40th St. crossing, 26th St. crossing and at Elysian Road. TOC ranged from 0.43% - 0.79%. Significant differences in TUs among the sites was not observed. Previous samples at the Elysian Road crossing yielded TU values of 0.39 (6/1/2010) and 0.49 (9/1/2010) before falling to 0.13 on 11/15/2010.

Figure 10. City/County Drain Reach
Toxic Units - November 15th, 2010



Along the City/County Drain reach in central Billings, sediment was collected at 4 locations in November, 2010 (Figure 10). The City/County drain receives flow from the Bannister Drain (not shown), overflow from the BBWA ditch and sewer outfalls before discharging in the Yellowstone River. The 1.80 TUs at Spring Creek Park was the highest observed in all samples. Subsequent samples along the flow direction display a decrease in TUs more strongly correlated with increasing TOC than decreasing total pyrethroid concentrations. The 1.80 TUs was a significant increase from 0.10 TUs observed at the same location (BILS-6) in the June sampling. At the lower end (BILS-9), TUs decreased from 0.78 TUs in June to 0.53 TUs in November.

Figure 11. Alkali Creek
Toxic Units - November 15th, 2010

Along Alkali Creek, sediment was collected at 3 points in the November 2010 sampling (Figure 11). TUs were <0.2 at the lower sampling locations and 0.55 TUs at the Senators Blvd crossing. TOC was highest at the BILS-11 (0.14 TUs) even though total pyrethroid concentration was 5 times higher than at BILS-19 (0.55 TUs). The lower sampling point (BILS-11) had a TU of 0.65 (2.84% TOC) at the June sampling. In both Alkali Creek and the City/County Drain, concentrations decreased between the June and November.

6.0 DISCUSSION

6.1 Water Detections

The pesticides with the most detections in groundwater and surface water in Billings fall into three general categories: (1) herbicides used in corn crops; (2) herbicides used in non-crop areas; and (3) herbicides used in turf applications. Herbicides commonly used on turf (2,4-D, MCPA, MCPP, and dicamba) were mostly detected in surface water with very few detections in groundwater. Studies in turfgrasses indicate that leaching of pesticide compounds and nitrate are mitigated by high uptake by the turf, uptake by thatch and other soil organic matter, a high microbial population that promotes chemical degradation, and a high retention of water because of an extensive root system (Racke and Leslie, 1993, and Beard and Kenna, 2006). However, pesticides and nitrate can be carried away from turfgrass application sites by soil runoff from heavy precipitation events or irrigation. This runoff washes directly into surface waters or ends up in storm sewers which empty into surface waters.

On the other hand, pesticides such as 2,4-D and MCPA, which were detected in 100% and 65% of surface water samples during this project, are very commonly detected in surface waters all over Montana (82% and 51% of samples, respectively) and their presence may not be due to turf applications but may represent their uses in various crop and non-crop settings. MCPP has been detected in 16% of surface water samples across the state but was detected in 50% of surface water samples collected in Billings indicating a potential link with turf applications.

The herbicides used in corn crops and detected during this project include metolachlor, atrazine, alachlor, and bentazon. Metolachlor ESA, a degradate of metolachlor, was the most widespread pesticide detected during this project. It was detected in 94% of groundwater samples and 74% of surface water samples. Deethyl atrazine, a degradate of atrazine, was detected in 41% of groundwater samples and 29% of surface water samples. Atrazine was detected in 31% of groundwater samples but only 10% of surface water samples. Alachlor ESA, a degradate of alachlor, was detected in 28% of groundwater samples and 10% of surface water samples. Bentazon was detected in 16% of groundwater samples and 55% of surface water samples. The detection of corn crop herbicides is not unusual in the Yellowstone River Valley, as corn crops are fairly common. However, their widespread presence in all areas of the Billings urban area was unexpected. Some of these detections may be caused by atmospheric deposition of the pesticides from nearby applications as many of the detections are at very low concentrations.

The non-crop herbicides commonly detected include prometon, imazapyr, tebuthiuron, triclopyr, bromacil, and diuron. Most of these chemicals, with the exception of tebuthiuron and triclopyr, are used as soil sterilants, i.e., used in areas where long term control of weeds and vegetation is desired. While soil sterilants are commonly associated with urban use, these pesticides are used in rural areas as well. Soil sterilants are used along road, railway, and other rights-of-way, industrial areas, around buildings and homes, driveways, patios, fences, storage areas, etc. These types of application areas exist all over the state but are concentrated in urban areas, so the use of soil sterilants is concentrated in urban areas. This is backed up by the high detection frequency of soil sterilants in Billings. For instance, since 2006, prometon has been detected in 28% of groundwater samples and 38% of surface water samples across the state. A majority of these samples were collected in rural areas. For the Billings project prometon was detected in 84% of groundwater samples and 58% of surface water samples. Imazapyr, which is detected in 13% of groundwater samples and 9% of surface water samples across the state, was detected in 75% of groundwater samples and 42% of surface water samples in Billings.

One herbicide that was not detected during this project was glyphosate, which is a commonly used urban pesticide. There are two reasons for the lack of detections. One, glyphosate is a hydrophobic chemical, meaning it does not readily dissolve in water; therefore it is not likely to be detected in water except at low concentrations. Second, the detection limit for glyphosate was very high at 10 ppb, compared to the other pesticide compounds that have detection limits 2-5 orders of magnitude lower. The glyphosate degradate AMPA, which does readily dissolve in water, was also not detected during this project, perhaps because of the high detection limit.

The BBWA irrigation canal was sampled at four different locations to determine if the urban environment is having an impact on the water quality of the canal. The BBWA canal receives storm water discharges and can also receive overland runoff during precipitation events or irrigation occurring in lawns and gardens. In theory, if pesticide impacts are occurring to the canal then the number of pesticides detected should increase and potentially the concentration should increase, as the water moves down the canal through the urban areas of Billings. The concentration of a pesticide would only increase down the canal if there were multiple sources of the same pesticide. If there were only one source, i.e., a storm sewer outfall, then the concentration would remain relatively constant down the canal.

The canal was sampled once above Billings (site ID BILS-2), twice within Billings (site IDs BILS-5 and BILS-8), and once below Billings (site ID BILS-10). For the June sampling there was no clear cut increase in the number of pesticides detected with three pesticides, three pesticides, four pesticides, and four pesticides detected, respectfully down the canal. During the September sampling the number of pesticides detected did increase down the canal with four detections, five detections, six detections, and eight detections, respectfully. There was no indication of increasing concentrations of pesticides down the canal during either the June or September sampling events.

While nitrate was detected in a majority of water samples none of the concentrations exceeded the HHS for drinking water of 10 mg/L. Nitrate concentrations were higher in groundwater then in surface water. In all, 72% of groundwater samples were above 3 mg/L, which is generally considered the concentration were anthropogenic impacts are occurring. There are likely numerous sources of nitrate in the Billings area including, but not limited to, septic effluent, fertilizer used in gardens and lawns, fertilizer used in agricultural fields which still exist in the urban area, and possibly natural sources. No attempt was made to determine the source of nitrate detections during this project.

6.1 Sediment Detections

There were 8 different pyrethroids detected in the sediment analyses for the three sampling events in 2010. Bifenthrin and permethrin isomers comprised 75% of all detections and accounted for 72% and 33% of total toxicity where detected respectively. The half-life of bifenthrin is 12-16 months and the half-life of permethrin is 3-4.7 months for *cis*- permethrin and 2-10 months for *trans*-permethrin (Laskowski, 2002; Gan et al., 2005). The more recently synthesized pyrethroids such as bifenthrin have far greater aquatic toxicity than first generation pyrethroids such as allethrin. Permethrin has numerous residential and commercial uses. Bifenthrin is used for structural pest control and lawn and garden applications. It is likely that retail sales and structural pest control and residential maintenance and control by professional applicators are the source of detected pesticides in the project area.

Amweg et al., 2005 observed greater than 40% mortality of the macro-invertebrate *Hyalella azteca* when TUs exceeded 0.4. In 2010, 9 samples from 8 sites in Billings exceeded 0.4 TUs. However, Hintzen et al (2009) observed that sites with <1 TU were generally non-toxic based on the authors' mortality experiments with collected sediment from urban watersheds in central Texas. This is in agreement with other sediment pyrethroid studies from California (Weston et al, 2005; Amweg et al, 2006). Hitzen et al (2009) also observed that sediments with low TOC displayed lower than predicted mortality rates and theorized that OC normalization may not be estimating bioavailability sufficiently and overestimating toxicity in sediments with low TOC. In the MDA study, only samples collected from BILS-4 and BILS-6 exceeded 1 TU. The TOC for BILS-4 was 1.21% (1.26 TUs; 9/2/10) and for BILS-6 the TOC was 0.22% (1.80 TUs; 11/15/10) and for. The BILS-6 sediment sample may have overestimated toxicity based on Hintzen et al (2009). Big Ditch (BILS-4) is an irrigation canal which diverts water from the Yellowstone River upstream of Park City and flows through the agricultural area west of Billings before continuing through the residential/suburban areas of north-central Billings along Poly Drive. The ditch ultimately discharges to the storm water system near Shady Lane. Several overflow structures do exist before the terminus including one at Rehberg Lane which flows into City/County Drain. Spring Creek (BILS-6) is also part of the City/County Drain network.

The pesticide synergist piperonyl butoxide (PBO) was not detected in sediments in this study. PBO does not have pesticidal properties but when added to pyrethoid formulations PBO considerably increases chemical potency. The detection of PBO would have provided a potential marker for pyrethroid use and deposition. In sediment, PBO half-life is up to 24 days (Arnold, 1998). This is significantly less than the half-lives for pyrethroids detected in Billings and may explain the lack of PBO detections.

Differences in sediment toxicities may be due to undetermined factors affecting bioavailability or toxic elements that remained undetected in the samples. Pyrethroid distributions have been found to be dependent upon adsorption coefficients (K_d) which increase with increasing organic carbon and clay contents of sediments (Gan et al., 2005). Preferential accumulation and deposition occurs where stream sediments contain a large fraction of these fractions. As total concentration increases with increasing organic carbon and clay, bioavailability may simultaneously decrease. Selective transport via erosion and subsequent enrichment of fine particles is the main mechanism for transportation of pyrethroids off-site (Gan et al., 2005). However, net export of pyrethroid contaminated sediments to receiving water bodies may be limited to extreme precipitation events capable of flushing sediments downstream.

The question of total sediment transport and discharge to the Yellowstone River of sediment-bound pyrethroids was not addressed by this study but should be recognized as a potentially significant transport mechanism of contaminant delivery to the Yellowstone River. This is perhaps highlighted in comparing pyrethroid results from June and November. In several outfalls to the Yellowstone River, pyrethroid concentrations decreased in sediment samples collected in the fall compared with the June 1-2 results. There was a significant rain event on June 20th, 2010 where a storm total of 2.24 in of precipitation was recorded at Billings International Airport. Precipitation intensity overwhelmed the storm water sewers in several parts of the city. The volume of sediment transported to the river is unknown, but a decrease in pyrethroid concentrations in Alkali Creek, Hogans Slough and City/County Drain for samples collected before and after June 20th, 2010 indicate that pyrethroids were carried in sediment to the Yellowstone River in the period between sample collections.

7.0 SUMMARY

A monitoring project was undertaken by the MDA to determine impacts to both groundwater and surface water from the use of pesticides and fertilizer in urban areas of Billings, Montana. A total of 32 groundwater and 31 surface water samples were collected during the summer of 2010 and analyzed for 95 pesticide compounds and the nutrient nitrate. In addition, 31 sediment samples were collected from streams, drains, and irrigation canals and analyzed for pyrethroid insecticides.

Pesticides were detected in all water samples collected. However, none of the pesticide concentrations exceeded human health drinking water standards developed by the Montana Department of Environmental Quality or aquatic life benchmarks developed by the EPA for surface waters. Groundwater detections were dominated by non-crop herbicides such as prometon, imazapyr, and tebuthiuron, although the most common detection in groundwater was metolachlor ESA, a degradate of a product used in corn, potatoes, and nursery crops. Surface water detections were dominated by herbicides which can be used in turfgrass such as 2,4-D, MCPA, and MCPP. However, these herbicides have numerous other uses in both crop and non-crop settings and their presence in water around Billings cannot be solely attributed to turfgrass uses. Other common detections in surface water included the corn herbicides metolachlor ESA and bentazon, and non-crop herbicides such as prometon and tebuthiuron.

Groundwater nitrate concentrations were generally slightly elevated indicating impacts from nitrogen sources (fertilizer, manure, sewage), but none of the concentrations exceeded drinking water standards. Surface water nitrate concentrations were all below 1.6 mg/L.

Sediment analyses for pyrethroid insecticides yielded a wide range of toxicity and pyrethroids in the sediments of irrigation canals and natural and artificial drainages in and around the City of Billings. The generally low total organic carbon (TOC) of sediments in the project area increases the bioavailability of pyrethroids to aquatic macro-invertebrates. Greater than 72% of the total toxicity was from bifenthrin. This is in agreement with other pyrethroid studies by Hintzen et al (2009), Amweg et al (2006) and Weston et al (2005) where bifenthrin is the most commonly detected pyrethroid contributing the greatest fraction of toxicity in urban watersheds. Research has also established that toxicity from pyrethroids is more severe and widespread in urban areas compared with agricultural lands (Weston et al, 2004; Ng et al, 2008; Weston and Lydy, 2010). In Billings, pyrethroids are being transported through the drainage network of interconnected irrigation canals and the storm water sewer system with multiple discharge points in the Yellowstone River. The relatively impervious nature of urban watersheds promotes overland runoff and high velocity flows in comparison with undisturbed catchments and facilitates sediment deposition and contaminant transport to the Yellowstone River.

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APPENDIX A

ANALYTE LIST AND LIMITS OF QUANTIFICATION (LOQ)

2010 MDA Montana Universal Method Analyte List and Limits of Quantification (LOQ)						
ANALYTE NAME	**LOQ**	**UNITS**		**ANALYTE NAME**	**LOQ**	**UNITS**
2,4-D	0.0045	ug/L (ppb)		Imazamethabenz methyl acid metabolite	0.0052	ug/L (ppb)
3-OH Carbofuran	0.01	ug/L (ppb)		Imazamethabenz methyl ester	0.001	ug/L (ppb)
Acetochlor	0.14	ug/L (ppb)		Imazamox	0.012	ug/L (ppb)
Acetochlor ESA	0.01	ug/L (ppb)		Imazapic	0.011	ug/L (ppb)
Acetochlor OA	0.0042	ug/L (ppb)		Imazapyr	0.011	ug/L (ppb)
Alachlor	0.11	ug/L (ppb)		Imazethapyr	0.01	ug/L (ppb)
Alachlor ESA	0.011	ug/L (ppb)		Imidacloprid	0.0018	ug/L (ppb)
Alachlor OA	0.0034	ug/L (ppb)		Isoxaflutole	0.13	ug/L (ppb)
Aldicarb	0.065	ug/L (ppb)		Linuron	0.011	ug/L (ppb)
Aldicarb sulfone	0.022	ug/L (ppb)		Malathion	0.028	ug/L (ppb)
Aldicarb sulfoxide	0.056	ug/L (ppb)		MCPA	0.0023	ug/L (ppb)
Aminopyralid	0.053	ug/L (ppb)		MCPP	0.0022	ug/L (ppb)
AMPA	10	ug/L (ppb)		Metalaxyl	0.012	ug/L (ppb)
Atrazine	0.0022	ug/L (ppb)		Methomyl	0.0016	ug/L (ppb)
Azinphos methyl	0.037	ug/L (ppb)		Metolachlor	0.012	ug/L (ppb)
Azinphos methyl oxon	0.031	ug/L (ppb)		Metolachlor ESA	0.0025	ug/L (ppb)
Azoxystrobin	0.0025	ug/L (ppb)		Metolachlor OA	0.021	ug/L (ppb)
Bentazon	0.0011	ug/L (ppb)		Metsulfuron methyl	0.026	ug/L (ppb)
Bromacil	0.0074	ug/L (ppb)		Nicosulfuron	0.011	ug/L (ppb)
Bromoxynil	0.006	ug/L (ppb)		NOA 407854	0.0052	ug/L (ppb)
Carbaryl	0.04	ug/L (ppb)		NOA 447204	0.01	ug/L (ppb)
Carbofuran	0.0052	ug/L (ppb)		Norflurazon	0.02	ug/L (ppb)
Chlorpyrifos	0.031	ug/L (ppb)		Norflurazon desmethyl	0.02	ug/L (ppb)
Chlorsulfuron	0.0056	ug/L (ppb)		Picloram	0.14	ug/L (ppb)
Clodinafop-propargyl acid	0.013	ug/L (ppb)		Prometon	0.0051	ug/L (ppb)
Clopyralid	0.022	ug/L (ppb)		Propachlor	0.0028	ug/L (ppb)
DEDIA	0.5	ug/L (ppb)		Propachlor OA	0.0094	ug/L (ppb)
Deethyl atrazine	0.0017	ug/L (ppb)		Propiconazole	0.01	ug/L (ppb)
Deisopropyl atrazine	0.01	ug/L (ppb)		Prosulfuron	0.005	ug/L (ppb)
Dicamba	0.22	ug/L (ppb)		Pyrasulfatole	0.023	ug/L (ppb)
Difenoconazole	0.02	ug/L (ppb)		Pyroxsulam	0.027	ug/L (ppb)
Dimethenamid	0.01	ug/L (ppb)		Simazine	0.0026	ug/L (ppb)
Dimethenamid OA	0.0038	ug/L (ppb)		Sulfometuron methyl	0.01	ug/L (ppb)
Dimethoate	0.0011	ug/L (ppb)		Sulfosulfuron	0.0054	ug/L (ppb)
Diuron	0.01	ug/L (ppb)		Tebuconazole	0.01	ug/L (ppb)
Ethofumesate	0.025	ug/L (ppb)		Tebuthiuron	0.0011	ug/L (ppb)
Ethoprop	0.012	ug/L (ppb)		Tembotrione	0.22	ug/L (ppb)
Fenbuconazole	0.0053	ug/L (ppb)		Tetraconazole	0.0062	ug/L (ppb)
Flucarbazone	0.0012	ug/L (ppb)		Thiamethoxam	0.02	ug/L (ppb)
Flucarbazone sulfonamide	0.00097	ug/L (ppb)		Thifensulfuron	0.026	ug/L (ppb)
Flumetsulam	0.063	ug/L (ppb)		Tralkoxydim	0.0051	ug/L (ppb)
Fluroxypyr	0.035	ug/L (ppb)		Tralkoxydim acid	0.005	ug/L (ppb)
Glutaric Acid	0.0074	ug/L (ppb)		Triadimefon	0.0057	ug/L (ppb)
Glyphosate	10	ug/L (ppb)		Triallate	0.3	ug/L (ppb)
Halosulfuron methyl	0.01	ug/L (ppb)		Triasulfuron	0.026	ug/L (ppb)
Hexazinone	0.0059	ug/L (ppb)		Triclopyr	0.011	ug/L (ppb)
Hydroxy atrazine	0.0064	ug/L (ppb)		Triticonazole	0.032	ug/L (ppb)
Imazalil	0.01	ug/L (ppb)				

APPENDIX B

INDIVIDUAL SAMPLE RESULTS

Groundwater Laboratory Results, Billings, 2010

Site ID	Date	2,4-D (µg/L)	Acetachlor ESA (µg/L)	Alachlor ESA (µg/L)	Alachlor OA (µg/L)	Atrazine (µg/L)	Bentazon (µg/L)	Bromacil (µg/L)	Clopyralid (µg/L)	Deethyl deisopropal atrazine (µg/L)	Deethyl Atrazine (µg/L)	Deisopropyl atrazine (µg/L)	Diuron (µg/L)
BILG-1	5/31/2010	ND	ND	**0.041**	ND	ND	**<0.0011**	ND	ND	ND	ND	ND	ND
	8/31/2010	ND	ND	**0.044**	ND	ND	**<0.0011**	ND	ND	ND	ND	ND	ND
BILG-2	6/2/2010	ND	**<0.01**	**0.12**	**<0.0034**	ND	**<0.0011**	ND	ND	ND	ND	ND	ND
BILG-3	5/31/2010	ND	ND	**0.076**	ND	ND	**<0.0011**	ND	ND	ND	ND	ND	ND
	8/31/2010	ND	ND	**0.071**	ND	ND	**<0.0011**	ND	ND	ND	ND	ND	ND
BILG-4	6/1/2010	ND	ND	**<0.011**	ND	**<0.0022**	ND	ND	ND	ND	**0.0051**	**<0.01**	ND
	8/31/2010	ND	ND	**<0.011**	ND	**<0.0022**	ND	ND	ND	**<0.5**	**0.0045**	**<0.01**	ND
BILG -5	6/2/2010	ND	ND	ND	ND	**<0.0022**	ND	ND	ND	ND	**0.0025**	ND	ND
	9/1/2010	ND	ND	ND	ND	**0.0028**	ND	ND	ND	ND	**0.0045**	ND	ND
BILG -6	6/2/2010	ND	ND	**<0.011**	ND	ND	ND	**0.64**	ND	ND	**<0.0017**	ND	**<0.01**
BILG -7	5/31/2010	**<0.0045**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/31/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILG -8	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILG -9	6/2/2010	ND	ND	ND	ND	**0.0071**	ND	**2.0**	ND	ND	**0.0036**	**<0.01**	ND
	9/1/2010	ND	ND	ND	ND	**0.0076**	ND	**2.3**	ND	ND	**0.0047**	**<0.01**	ND
BILG -10	6/2/2010	**<0.0045**	ND	ND	ND	**0.0045**	ND	ND	ND	ND	**0.02**	ND	ND
	9/1/2010	**<0.0045**	ND	ND	ND	**0.0052**	ND	ND	ND	ND	**0.024**	ND	ND
BILG -11	6/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILG -12	6/1/2010	ND	ND	ND	ND	ND	ND	ND	**<0.022**	ND	ND	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND	**0.0074**	ND	ND	ND	ND	ND
BILG -13	6/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILG -14	6/2/2010	ND	ND	ND	ND	**<0.0022**	ND	ND	ND	ND	**<0.0017**	ND	ND
	9/1/2010	ND	ND	ND	ND	**<0.0022**	ND	ND	ND	ND	**<0.0017**	ND	ND
BILG -15	5/31/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	**<0.0017**	ND	ND
	8/31/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	**<0.0017**	ND	ND
BILG -16	5/31/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/31/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILG -17	5/31/2010	**<0.0045**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/31/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Human Health Standard for Drinking Water		**70**	**140**	**2**	**2**	**3**	**200**	**90**	**3,500**	**3**	**3**	**3**	**10**

Groundwater Laboratory Results, Billings, 2010												
Site ID	Date	Imazapyr (µg/L)	Imidacloprid (µg/L)	MCPA (µg/L)	MCPP (µg/L)	Metolachlor ESA (µg/L)	Metolachlor OA (µg/L)	Nitrate as Nitrogen (mg/L)	Picloram (µg/L)	Prometon (µg/L)	Simazine (µg/L)	Tebuthiuron (µg/L)
BILG-1	5/31/2010	<0.011	ND	ND	ND	0.0099	ND	3.4	ND	ND	ND	ND
	8/31/2010	<0.011	ND	ND	ND	0.014	ND	3.8	ND	ND	ND	ND
BILG-2	6/2/2010	0.045	ND	ND	ND	0.044	0.027	4.1	ND	0.0085	ND	ND
BILG-3	5/31/2010	0.034	ND	ND	ND	0.018	<0.021	4.2	ND	0.044	ND	ND
	8/31/2010	0.035	ND	ND	ND	0.021	0.021	4.1	ND	0.035	ND	ND
BILG-4	6/1/2010	<0.011	0.22	ND	ND	0.14	ND	7.4	ND	0.016	ND	0.011
	8/31/2010	<0.011	0.29	ND	ND	0.15	ND	7.0	ND	0.016	ND	0.0092
BILG -5	6/2/2010	0.38	ND	<0.0023	ND	<0.0025	ND	8.4	ND	0.05	0.0049	0.0087
	9/1/2010	0.42	ND	ND	ND	<0.0025	ND	7.9	ND	0.046	0.0043	0.0098
BILG -6	6/2/2010	0.073	0.0033	ND	ND	0.013	ND	4.3	ND	0.035	<0.0026	0.0073
BILG -7	5/31/2010	ND	ND	ND	ND	ND	ND	5.4	ND	<0.0051	ND	ND
	8/31/2010	ND	ND	ND	ND	ND	ND	5.2	ND	<0.0051	ND	ND
BILG -8	6/2/2010	ND	ND	ND	ND	<0.0025	ND	2.9	ND	0.032	<0.0026	ND
	9/1/2010	<0.011	0.066	ND	ND	<0.0025	ND	2.9	ND	0.028	<0.0026	<0.0011
BILG -9	6/2/2010	4.7	ND	ND	ND	<0.0025	ND	8.1	ND	0.31	<0.0026	0.17
	9/1/2010	4.7	ND	ND	ND	<0.0025	ND	8.1	ND	0.34	<0.0026	0.15
BILG -10	6/2/2010	0.022	ND	0.0044	0.0044	0.16	<0.021	7.2	ND	0.011	ND	0.0033
	9/1/2010	0.026	ND	ND	ND	0.18	<0.021	6.5	ND	0.012	ND	0.0036
BILG -11	6/1/2010	0.029	ND	ND	ND	0.015	ND	1.9	ND	0.017	ND	0.003
	9/2/2010	0.013	ND	ND	ND	0.01	ND	0.58	<0.14	0.014	ND	0.0032
BILG -12	6/1/2010	0.033	ND	ND	ND	<0.0025	ND	1.6	ND	0.022	ND	<0.0011
	9/2/2010	0.03	ND	ND	ND	<0.0025	ND	0.59	ND	0.021	ND	<0.0011
BILG -13	6/1/2010	<0.011	ND	ND	ND	<0.0025	ND	ND	ND	<0.0051	ND	ND
	9/2/2010	<0.011	ND	ND	ND	<0.0025	ND	0.19	ND	<0.0051	ND	ND
BILG -14	6/2/2010	<0.011	0.0024	ND	ND	<0.0025	ND	3.2	ND	0.023	ND	<0.0011
	9/1/2010	<0.011	ND	ND	ND	<0.0025	ND	2.9	<0.14	0.018	ND	<0.0011
BILG -15	5/31/2010	0.036	ND	ND	ND	<0.0025	ND	4.1	ND	0.051	ND	0.0029
	8/31/2010	0.07	ND	ND	ND	<0.0025	ND	3.9	ND	0.05	ND	0.0033
BILG -16	5/31/2010	ND	ND	ND	ND	<0.0025	ND	5.6	ND	<0.0051	ND	ND
	8/31/2010	ND	ND	ND	ND	<0.0025	ND	4.2	ND	<0.0051	ND	ND
BILG -17	5/31/2010	ND	ND	ND	ND	<0.0025	ND	3.1	ND	ND	ND	ND
	8/31/2010	ND	ND	ND	ND	<0.0025	ND	3.4	ND	ND	ND	ND
Human Health Standard for Drinking Water		21,000	400	4	7	100	100	10	500	100	4	500

Surface Water Laboratory Results, Billings, 2010

Site ID	Date	2,4-D (µg/L)	Alachlor ESA (µg/L)	Atrazine (µg/L)	Azoxystrobin (µg/L)	Bentazon (µg/L)	Bromacil (µg/L)	Carbaryl (µg/L)	Chlorpyrifos (µg/L)	Chlorsulfuron (µg/L)	Clopyralid (µg/L)	Deethyl atrazine (µg/L)	Dicamba (µg/L)
BILS-1	6/2/2010	0.0045	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/2/2010	<0.0045	ND	ND	ND	<0.0011	ND	ND	ND	ND	ND	ND	ND
BILS-2	6/2/2010	<0.0045	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/1/2010	0.011	ND	ND	ND	<0.0011	ND	ND	ND	ND	ND	ND	ND
BILS-3	6/1/2010	0.011	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	7/14/2010	0.024	ND	ND	ND	0.0018	ND	ND	<0.031	ND	ND	ND	ND
	9/1/2010	0.011	ND	ND	ND	<0.0011	ND	ND	ND	ND	ND	<0.0017	ND
	9/27/2010	<0.0045	ND	ND	ND	<0.0011	ND	ND	ND	ND	ND	<0.0017	ND
BILS-4	6/2/2010	0.017	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/2/2010	0.014	ND	ND	ND	0.0015	0.016	ND	ND	ND	ND	ND	ND
BILS -5	6/2/2010	<0.0045	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/1/2010	0.016	ND	ND	ND	<0.0011	ND	ND	ND	ND	ND	ND	ND
BILS -6	6/2/2010	0.024	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/2/2010	0.017	ND	ND	ND	<0.0011	0.011	ND	ND	ND	ND	<0.0017	ND
BILS -7	6/1/2010	0.018	<0.011	ND	ND	<0.0011	ND	ND	ND	ND	ND	ND	ND
	7/14/2010	0.24	ND	ND	ND	0.19	ND	ND	ND	ND	<0.022	ND	ND
	9/1/2010	0.12	<0.011	ND	ND	0.0023	<0.0074	ND	ND	ND	ND	<0.0017	ND
	9/28/2010	0.019	<0.011	ND	ND	0.0017	ND	ND	ND	ND	ND	<0.0017	ND
BILS -8	6/2/2010	<0.0045	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/1/2010	0.02	ND	ND	ND	0.0012	ND	ND	ND	ND	ND	ND	ND
BILS -9	6/1/2010	0.038	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	7/13/2010	0.33	ND	<0.0022	0.0056	0.041	0.0092	ND	ND	ND	<0.022	ND	ND
	9/1/2010	0.56	ND	ND	ND	0.0027	0.017	ND	ND	ND	ND	<0.0017	ND
	9/27/2010	0.025	ND	ND	ND	<0.0011	0.022	ND	ND	ND	ND	<0.0017	ND
BILS -10	6/2/2010	<0.0045	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/1/2010	0.029	ND	ND	ND	0.0015	ND	ND	ND	ND	ND	ND	ND
BILS -11	6/1/2010	0.047	ND	ND	ND	ND	0.047	ND	ND	ND	ND	ND	ND
	6/17/2010	11	ND	<0.0022	ND	ND	0.039	<0.04	ND	0.0066	ND	ND	2.7
	7/13/2010	0.79	ND	<0.0022	ND	ND	0.012	ND	<0.031	ND	ND	ND	ND
	9/1/2010	0.28	ND	ND	ND	ND	0.024	ND	ND	ND	ND	<0.0017	ND
	9/27/2010	0.0047	ND	<0.022	ND	ND	0.069	ND	ND	ND	ND	<0.0017	ND
Human Health Standard for Drinking Water		70	2	3	1,000	200	90	700	20	1,750	3,500	3	200

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Site ID	Date	Dimethenamid (µg/L)	Dimethenamid OA (µg/L)	Dimethoate (µg/L)	Diuron (µg/L)	Hydroxy atrazine (µg/L)	Imazamox (µg/L)	Imazapyr (µg/L)	Imidacloprid (µg/L)	Malathion (µg/L)	MCPA (µg/L)	MCPP (µg/L)	Metolachlor ESA (µg/L)
BILS-1	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.003	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILS-2	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0059	ND	ND
	9/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0031
BILS-3	6/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.005	ND	<0.0025
	7/14/2010	0.076	<0.0038	ND	ND	<0.0064	ND	ND	ND	ND	<0.0023	ND	0.0041
	9/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0035
	9/27/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0032
BILS-4	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0055	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BILS -5	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0032	ND	ND
	9/1/2010	ND	<0.0038	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0034
BILS -6	6/2/2010	ND	ND	ND	ND	ND	ND	<0.011	0.0022	ND	0.011	0.0063	<0.0025
	9/2/2010	ND	ND	ND	ND	ND	ND	<0.011	ND	ND	ND	0.0026	0.003
BILS -7	6/1/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.012	<0.0022	0.012
	7/14/2010	0.092	0.013	ND	ND	<0.0064	0.033	ND	ND	ND	0.0031	0.039	0.01
	9/1/2010	ND	<0.0038	ND	<0.01	ND	ND	<0.011	ND	ND	0.003	0.0031	0.032
	9/28/2010	ND	ND	ND	ND	ND	ND	<0.011	ND	ND	ND	<0.0022	0.023
BILS -8	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0073	ND	<0.0025
	9/1/2010	ND	<0.0038	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.004
BILS -9	6/1/2010	ND	ND	ND	<0.01	ND	ND	0.029	ND	ND	0.0081	0.0054	<0.0025
	7/13/2010	0.069	<0.0038	ND	<0.01	<0.0064	<0.012	0.038	ND	ND	0.024	0.016	0.0048
	9/1/2010	ND	ND	0.0012	0.036	ND	ND	0.024	ND	<0.028	0.055	0.1	0.0051
	9/27/2010	ND	ND	ND	ND	ND	ND	0.031	ND	ND	ND	0.0056	0.0068
BILS -10	6/2/2010	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0039	ND	<0.0025
	9/1/2010	ND	<0.0038	ND	ND	ND	ND	ND	ND	ND	0.0072	<0.0022	0.004
BILS -11	6/1/2010	ND	ND	ND	1.3	ND	ND	0.16	0.0032	ND	0.053	0.009	ND
	6/17/2010	ND	ND	ND	0.063	ND	ND	0.014	0.041	ND	0.014	0.033	ND
	7/13/2010	ND	ND	ND	<0.01	<0.0064	ND	0.045	ND	ND	0.054	0.056	ND
	9/1/2010	ND	ND	<0.0011	0.011	ND	ND	0.018	ND	ND	0.013	0.054	<0.0025
	9/27/2010	ND	ND	ND	ND	<0.0064	ND	0.032	0.0083	ND	ND	0.0045	<0.0025
Human Health Standard for Drinking Water		400	400	--	10	70	20,000	21,000	400	100	4	7	100

Surface Water Laboratory Results, Billings, 2010							
Site ID	**Date**	**Metolachlor OA (µg/L)**	**Nitrate as Nitrogen (mg/L)**	**Picloram (µg/L)**	**Prometon (µg/L)**	**Tebuthiuron (µg/L)**	**Triclopyr (µg/L)**
BILS-1	6/2/2010	ND	**0.11**	ND	ND	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND
BILS-2	6/2/2010	ND	**0.12**	ND	ND	ND	ND
	9/1/2010	ND	ND	ND	ND	ND	**0.042**
BILS-3	6/1/2010	ND	**0.18**	ND	ND	ND	ND
	7/14/2010	ND	**0.51**	ND	ND	ND	ND
	9/1/2010	ND	**0.23**	ND	ND	ND	**<0.011**
	9/27/2010	ND	**0.2**	ND	ND	ND	ND
BILS-4	6/2/2010	ND	ND	ND	ND	ND	ND
	9/2/2010	ND	ND	ND	ND	ND	ND
BILS -5	6/2/2010	ND	**0.12**	ND	ND	ND	ND
	9/1/2010	ND	ND	ND	**<0.0051**	ND	ND
BILS -6	6/2/2010	ND	**1.2**	ND	**0.17**	ND	**<0.011**
	9/2/2010	ND	**1.6**	ND	**<0.0051**	ND	ND
BILS -7	6/1/2010	ND	**0.59**	ND	**<0.0051**	ND	ND
	7/14/2010	ND	**0.66**	ND	**<0.0051**	ND	ND
	9/1/2010	**<0.021**	**1.2**	ND	**0.0078**	**<0.0011**	**<0.011**
	9/28/2010	ND	**0.74**	ND	**<0.0051**	**<0.0011**	ND
BILS -8	6/2/2010	ND	**0.12**	ND	ND	ND	ND
	9/1/2010	ND	ND	ND	**<0.0051**	ND	**0.02**
BILS -9	6/1/2010	ND	**1.3**	ND	**0.019**	**0.0018**	**<0.011**
	7/13/2010	ND	**1.3**	ND	**0.0054**	**0.0016**	**0.034**
	9/1/2010	ND	**1.2**	ND	**0.021**	**0.0018**	**<0.011**
	9/27/2010	ND	**1.5**	ND	**0.0088**	**0.0029**	ND
BILS -10	6/2/2010	ND	**0.12**	ND		ND	ND
	9/1/2010	ND	ND	ND	**<0.0051**	ND	**0.071**
BILS -11	6/1/2010	ND	**0.65**	ND	**0.012**	**<0.0011**	ND
	6/17/2010	ND	--	**<0.14**	**0.012**	**0.004**	**<0.011**
	7/13/2010	ND	**0.71**	ND	**0.012**	**0.0013**	**<0.011**
	9/1/2010	ND	**0.56**	ND	**0.018**	**0.0014**	**<0.011**
	9/27/2010	ND	**0.91**	ND	**0.015**	**0.0015**	ND
Human Health Standard for Drinking Water		**100**	**10**	**500**	**100**	**500**	**350**