Groundwater and Surface Water Monitoring for Pesticides and Nitrate in the Bitterroot Valley, Montana

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Cover photo: Bitterroot Mountains from the Lee Metcalf Wildlife Refuge.

1.0 Introduction

Pesticides refer to any organic or synthetic chemical used to kill unwanted pests. They include the full range of herbicides, insecticides, fungicides and rodenticides used in the environment. Pesticides have a wide spectrum of solubility, leaching potential and half-lives under different temperature and moisture regimes. The inherent characteristics of each respective chemical mark them as mobile or immobile in the environment and groundwater and surface waters may be susceptible to pesticide contamination in certain circumstances reflective of timing, method and rate of application. Concerns include the susceptibility of drinking water and ecological impacts from contamination.

During the summer of 2008, the Montana Department of Agriculture (MDA) conducted a monitoring project in the Bitterroot Valley of southwestern Montana between the towns of Darby and Lolo. 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, septage). The MDA collected 46 groundwater samples from 23 wells and 10 surface water samples from 5 sites and analyzed them for 95 pesticide compounds as well as nitrate/nitrite. Groundwater sampling included three MDA Permanent Monitoring Wells (PMWs) located in the project area.

Pesticides were detected in 25 of the 46 groundwater samples. There were a total of 53 detections of 14 different pesticide compounds and 3 pesticide degradates in the 25 samples with detections. All of the pesticide concentrations were low and none exceeded or approached human health drinking water standards, where such standards exist. Nitrate was detected in 24 of the 46 groundwater samples. Two samples from a single site had nitrate-N detections above the human health drinking standard of 10 mg L^{-1}.

Nine of the 10 surface water samples had one or more pesticide detections. Six pesticides and 2 pesticide degradates were detected in the surface water samples. The pesticide concentrations were low and did not exceed or approach the human health drinking water standard or EPA aquatic life benchmarks. Nitrate was not detected in any of the surface water samples.

2.0 Geology of the Bitterroot Valley

The Bitterroot Valley is an intermontane basin filled with Tertiary (65 to 1.5 million years before present) and Quaternary (1.5 million years to present) sediments. The valley is 52 miles long and averages 7 miles wide. The valley-floor area covers 380 mi^2 (Briar and Dutton, 2000). The valley is bordered on the west by the Bitterroot Mountains, on the east by the Sapphire Mountains, and on the southeast by the Anaconda Range.

Basin-fill sediments extend from near the confluence of the East and West Forks of the Bitterroot River to the Ravalli County line north of Florence (Briar and Dutton, 2000). The valley floor is characterized by the Bitterroot River floodplain and low river terraces

1 to 4 miles wide. Along the valley margin, these low terraces are flanked by high benches, which are more pronounced along the east side of the valley. The high benches are remnants of Tertiary alluvial fans that have been deeply incised by the Bitterroot River and its tributaries (LaFave, 2006). Bedrock comprised of granite and layered gneiss of the Idaho Batholith underlies the west side of the valley. The Sapphire Mountains on the east side and the northern Bitterroot Mountains are made up of metacarbonates, argillites, and quartzites of the Belt Supergroup (Smith, 2006).

Basin-fill deposits consist of unconsolidated to semi-consolidated Tertiary and Quaternary sediments and may be as much as 3,000 ft thick (Smith, 2006). Tertiary deposits dominate the solum along the valley margins on the east and west sides and is replaced by Quaternary deposits of coarse-grained alluvium near the valley-center. This alluvium was deposited by the ancestral Bitterroot River which deeply incised earlier Tertiary deposits creating the upland benches. Quaternary deposits include Pleistocene glacial outwash, alluvial and terrace deposits in the major drainages, and recent sand and gravel deposits in and near the Bitterroot River and its tributaries (LaFave, 2006).

All of the groundwater samples collected during this project were from wells obtaining water from Quaternary alluvium (n=19), undifferentiated Tertiary sedimentary rocks in the northern half of the valley (n=3), or Tertiary volcanic rocks in the southern part of the valley (n=1). No samples were collected from bedrock aquifers on the flanks of the valley.

The groundwater flow rate is slow in comparison with that of surface water and was estimated to be 400 feet per year through Tertiary sand, 700 feet per year through alluvium beneath the flood plain along the Bitterroot River, and 1,000 feet per year through the alluvium west of the river (McMurtrey et al., 1972). In general, the water table gradually declines through the winter and early spring, and then rises rapidly in May and June in response to recharge from precipitation and irrigation. Direction of groundwater flow is from the mountain fronts along the basin margins toward the center of the basin and diagonally down valley. Hydraulic gradients are steepest in the principal recharge areas near the mountain fronts and more gradual in discharge areas along the flood plain of the Bitterroot River. Due to stark differences in precipitation, there is almost a two fold difference between east (22.03 in/yr) and west (42.22 in/yr) sides of the valley in terms of the recharge rate of shallow aquifers (Briar and Dutton, 2000).

3.0 Previous Work

Previous groundwater studies concerning water quality have been performed in the valley examining dissolved solids, nitrate-N, arsenic, and radon among other parameters (Uthman, 1988; Briar and Dutton, 2000; Norbeck and McDonanld, 2001; LaFave, 2006). Geologic assessments and potentiometric surveys have also been completed (McMurtrey et al., 1972; Lonn and Sears, 2001; LaFave, 2006). This is the first known comprehensive water-monitoring project for pesticides in the Bitterroot Valley. However, a few groundwater samples have been collected during other projects in the

past. In 1998, groundwater samples from 5 wells in the valley were collected by MDA and tested for 20 different pesticides and degradates. There were no detections in any of the samples. Laboratory detection limits were much higher in 1998 in contrast to the present capabilities of the Analytical Sciences Laboratory which can detect concentrations in the range of parts per trillion (ppt) (1 ppt = 1 $\mu g\ L^{-1}$).

The MDA maintains 3 monitoring wells in the Bitterroot Valley which are used to sample for pesticide residues in areas where active noxious weed control is taking place. Well RAV-1 is located about halfway between the towns of Hamilton and Darby and was drilled in a pasture (Figure 1). Well RAV-2 was drilled on the edge of a cattle pasture less than a mile south of RAV-1. Well RAV-3 is located northwest of Corvallis on a wildlife refuge. All the wells were installed in 2007. Samples taken from these PMWs during the 2008 field season are included in this report.

4.0 MDA Water Sampling

In June and September 2008, the MDA collected 46 groundwater samples from 23 wells (Figure 1). Twenty of the 23 wells were private domestic wells and 3 of the 23 wells were monitoring wells (Table 1). The purpose of the sampling was to investigate potential impacts of pesticide use and nitrogen sources on groundwater quality in the Bitterroot Valley.

Sampling locations were chosen in order to get a good geographic distribution so that the groundwater resource as a whole could be characterized. An attempt was made to sample the shallowest wells possible. Wells with unknown depths were reported by their owners to be relatively shallow but total depth was not verified.

All wells were sampled after purging at least three well casing volumes or until field parameters (temperature, pH, specific conductivity, and dissolved oxygen) had stabilized. If the water level or well depth was unknown, field parameters were taken every five minutes until they had stabilized.

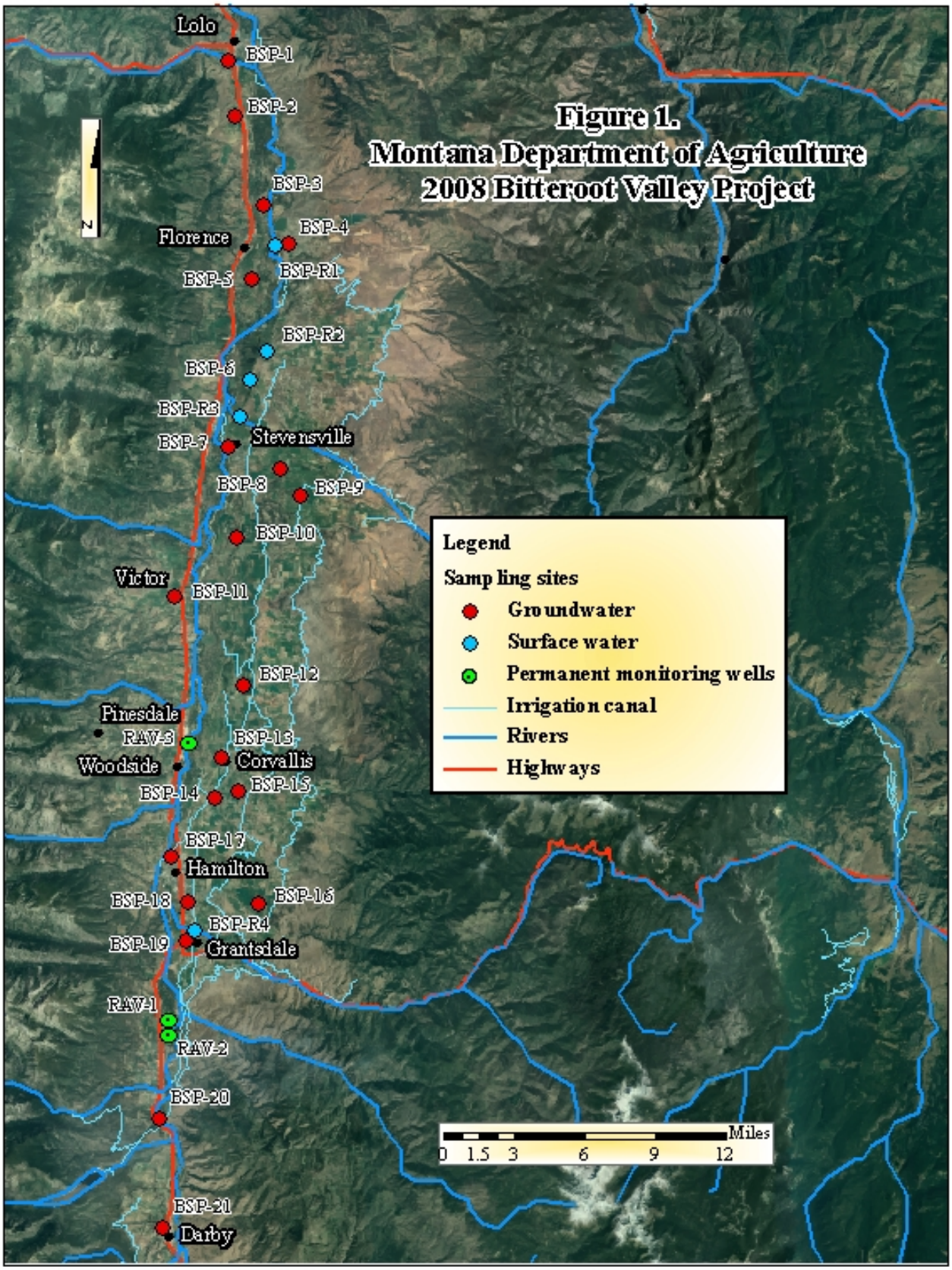
Figure 1.
Montana Department of Agriculture
2008 Bitterroot Valley Project
Lolo
BSP-1
BSP-2
BSP-3
BSP-4
Florence
BSP-5
BSP-R1
BSP-R2
BSP-6
BSP-R3
BSP-7
Stevensville
BSP-8
BSP-9
BSP-10
Victor
BSP-11
BSP-12
Pinesdale
RAV-3
BSP-13
Corvallis
Woodside
BSP-14
BSP-15
BSP-17
Hamilton
BSP-18
BSP-16
BSP-R4
BSP-19
Grantsdale
RAV-1
RAV-2
BSP-20
BSP-21
Darby
Legend
Sampling sites
Groundwater
Surface water
Permanent monitoring wells
Irrigation canal
Rivers
Highways
Miles
0 1.5 3 6 9 12

Table 1. Sampled Well Information

Site ID*	Well Use	Total Depth (ft bgs)	Screened Interval (ft bgs)	Water Level (ft bgs)
BSP-1	D	43	35-40	15
BSP-2	D	39	34-39	8
BSP-3	D	39	34-39	7
BSP-4	D	39	34-39	17
BSP-5	D	35	30-35	8
BSP-7	I	40	25-40	14
BSP-8	D	40	N/A	15
BSP-9	U	48	N/A	28
BSP-10	D	40	N/A	10
BSP-11	D	37	UN	UN
BSP-12	U	40	40	7
BSP-13	U	40	UN	9
BSP-14	D	38	N/A	17
BSP-15	D	40	40	20
BSP-16	S	28	UN	10
BSP-17	D	UN	UN	UN
BSP-18	I	49	UN	UN
BSP-19	D	30	UN	10
BSP-20	D	39	34-39	6
BSP-21	I	UN	UN	UN
RAV-1	M	12	7-12	4
RAV-2	M	19	9-19	11
RAV-3	M	6.35	UN	2

bgs = below ground surface; D = domestic; I = irrigation; M = monitoring; S = stockwater; U= unused; UN = unknown
* BSP-6 is a groundwater drain (see Table 2)

In addition to groundwater sampling, the MDA collected 10 surface water samples from 5 locations in June and September 2008. The streams sampled included a groundwater drain/ditch system about 3 miles north of Stevensville (site ID BSP-6), the Bitterroot River at the Eastside Highway Bridge (site ID BSP-R1), Threemile Creek at Rathbun Lane (site ID BSP-R2), North Burnt Fork Creek at Wild Fowl Lane (site ID BSP-R3) and

Skalkaho Creek at Grantsdale Road (site ID BSP-R4). Sampling locations are shown on Figure 1.
Streams were sampled using both vertical and horizontal integration techniques. Stream flow data for the Bitterroot River was obtained from the Montana Department of Environmental Quality (MT DEQ) gauging stations. Flow data for all other surface water sampling sites were obtained through discharge measurements when conditions allowed (Table 2). Due to high flow conditions, discharge was not measured for three of the sampling sites in June, 2008.

Table 2. Surface Water Information

Surface Water Name (Site ID)	Discharge June 17, 2008 (cfs)	Discharge September 16, 2008 (cfs)
BSP-6	2.5	3.0
Bitterroot River @ Eastside Highway Bridge (BSP-R1)	8720.0	972.0
Threemile Creek @ Rathbun Lane (BSP-R2)	*Not measured*	21.7
Northburnt Fork Creek @ Wild Fowl Lane (BSP-R3)	*Not measured*	33.4
Skalkaho Creek @ Grantsdale Road (BSP-R4)	*Not measured*	45.7

cfs = cubic feet per second

Both surface water and groundwater samples were collected in 900-mL amber glass jars, put on ice, and transported to the MDA Analytical Laboratory at Montana State University in Bozeman. The samples were analyzed using the Universal Method, an analytical method developed by the MDA Analytical Bureau for the detection of pesticides in water. The Universal Method analyzes for 95 pesticide compounds and for nitrate/nitrite. A list of analytes and the limits of quantification for the Universal Method is included in Appendix A.

5.0 Analytical Results

Twenty-five of the 46 samples from 14 of the 23 wells contained at least one pesticide (Table 3). Twelve of the samples contained two or more pesticides. In total, there were 53 detections of 14 pesticides and 3 pesticide degradates in the 25 samples with detections. All of the detections were herbicides and insecticides; no fungicides were detected. The most commonly detected pesticide was prometon which accounted for 18 of the 53 detections. The prometon detections came from 9 groundwater wells. The second most commonly detected pesticide was atrazine and one of its degradates, or breakdown products, deethyl atrazine, which was detected 9 times at 5 sampling sites. Other pesticides detected include tebuthiuron (5 detections from 3 sites), simazine (4

detections from 3 sites), 2,4-D (2 detections from 2 sites), ethofumesate (2 detections from 2 sites), hexazinone (2 detections from 1 site), MCPA (2 detections from 2 sites), and metolachlor (2 detections from 2 sites). Several pesticides had only a single detection. These include: aldicarb sulfone, aminopyralid, carbofuran, chlorsulfuron, imazamethabenz methyl ester, imazapyr, and metolachlor. Complete laboratory results are included in Appendix B.

All of the pesticide concentrations were low and none of the concentrations exceeded or approached the human health drinking water standards, where such standards exists. Of the 53 detections, 35 were below the analytical method limit of quantification and were therefore not quantified (*Q* values in Table 3).

There were sixteen total pesticide detections in surface water samples. Pesticides were detected in 9 of 10 samples collected. Detections included 6 pesticides and 2 pesticide degradates. Five of the 10 surface water samples from 3 of the 4 sampling sites contained 2,4-D (Table 4). Diuron was detected in 4 samples from 2 different sites and ethofumesate was found in 2 samples from 2 different sites. Pesticides that had only a single detection include: aldicarb and a degradate of aldicarb, aldicarb sulfone, hexazinone, imazapyr, and metolachlor ESA. Metolachlor ESA is a degradate of the herbicide metolachlor. All of the pesticide concentrations were low and none exceeded or approached the drinking water standard or the aquatic life benchmarks. Complete laboratory results are included in Appendix B.

Nitrate was detected in 24 of the 46 groundwater samples and at 13 of the 23 sampling sites. Where detected, nitrate concentrations ranged from 1.0 – 17.0 mg/L (Table 5). Two samples from a single site (BSP-9) exceeded the human health standard for drinking water of 10 mg/L. Nitrate was not detected in any of the surface water samples. Nitrite was not detected in any of the water samples.

Nitrate-N has several potential sources including fertilizers, animal waste (including septage effluent), and natural sources. The source of the nitrates detected during this project was not determined.

Table 3. Summary of Pesticide Detections in Groundwater

Site ID	Date	Analyte (and Common Trade Names) (µg/L)																
		2,4-D (numerous)	Aldicarb sulfone	Aminopyralid (Milestone)	Atrazine (Atrazine, Aatrex)	Carbofuran (Furadan)	Chlorsulfuron (Cimarron, Telar)	Deethyl atrazine	Ethofumesate (Norton, Progress)	Hexazinone (Velpar)	Imazamethabenz methyl ester (Assert)	Imazapyr (Arsenal, Chopper)	MCPA (Encore)	Metolachlor (Cinch, Parrallel)	Metolachlor ESA	Prometon (Pramitol)	Simazine (Simazat, Simazine)	Tebuthiuron (Spike)
BSP-1	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-2	6/16/08	ND	ND	ND	ND	ND	ND	Q	ND	ND	ND	ND	ND	ND	ND	Q	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Q	ND	ND
BSP-3	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-4	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-5	6/16/08	ND	**0.012**	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	**Q**	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-7	6/16/08	ND	ND	ND	**Q**	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	**0.0082**	ND	**0.0027**
	9/15/08	ND	ND	**0.1**	**0.011**	ND	ND	**Q**	ND	**Q**	**Q**	ND	ND	ND	ND	**0.011**	**Q**	**0.0055**
BSP-8	6/16/08	ND	ND	ND	ND	ND	ND	ND	**0.051**	ND	ND	ND	ND	ND	ND	**Q**	ND	ND
	9/15/08	ND	ND	ND	ND	**0.01**	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND
BSP-9	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-10	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-11	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.039**	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.042**	ND	ND
Drinking Water Standard		**70**	**3**	**--**	**3**	**40**	**1750**	**--**	**--**	**400**	**400**	**21,000**	**4**	**100**	**--**	**100**	**4**	**500**

µg/L = micrograms per liter (1 µg/L = 1 part per billion)

ND = not detected

Q = analayte detected below analytical method limit of quantification (see Appendix A for limits of quantification)

Table 3. (cont.) Summary of Pesticide Detections in Groundwater

Site ID	Date	Analyte (and Common Trade Names) (µg/L)																
		2,4-D (numerous)	Aldicarb sulfone	Aminopyralid (Milestone)	Atrazine (Atrazine, Aatrex)	Carbofuran (Furadan)	Chlorsulfuron (Cimarron, Telar)	Deethyl atrazine	Ethofumesate (Norton, Progress)	Hexazinone (Velpar)	Imazamethabenz methyl ester (Assert)	Imazapyr (Arsenal, Chopper)	MCPA (Encore)	Metolachlor (Cinch, Parrallel)	Metolachlor ESA	Prometon (Pramitol)	Simazine (Simazat, Simazine)	Tebuthiuron (Spike)
BSP-12	**6/16/08**	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-13	**6/16/08**	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	ND	**Q**	**Q**	**0.0067**	**Q**
	9/15/08	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	ND	ND	**Q**	**0.0032**	**Q**
BSP-14	**6/16/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND
	9/15/08	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND
BSP-15	**6/16/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.0053**	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	**0.0051**	ND	ND
BSP-16	**6/16/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-17	**6/17/08**	**Q**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.016**	**Q**	**Q**
	9/16/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.021**	ND	ND
BSP-18	**6/17/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND
BSP-19	**6/17/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-20	**6/17/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BSP-21	**6/17/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Drinking Water Standard		**70**	**3**	**--**		**40**	**1750**	**--**	**--**	**400**	**400**	**21,000**	**4**	**100**	**--**	**100**	**4**	**500**

µg/L = micrograms per liter (1 µg/L = 1 part per billion)

ND = not detected

Q = analayte detected below analytical method limit of quantification (see Appendix A for limits of quantification)

Table 3. (cont.) Summary of Pesticide Detections in Groundwater

Site ID	Date	Analyte (and Common Trade Names) (µg/L)																
		2,4-D (numerous)	Aldicarb sulfone	Aminopyralid (Milestone)	Atrazine (Atrazine, Aatrex)	Carbofuran (Furadan)	Chlorsulfuron (Cimarron, Telar)	Deethyl atrazine	Ethofumesate (Norton, Progress)	Hexazinone (Velpar)	Imazamethabenz methyl ester (Assert)	Imazapyr (Arsenal, Chopper)	MCPA (Encore)	Metolachlor (Cinch, Parrallel)	Metolachlor ESA	Prometon (Pramitol)	Simazine (Simazat, Simazine)	Tebuthiuron (Spike)
RAV-1	**5/28/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/25/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND
RAV-2	**5/28/08**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/25/08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
RAV-3	**5/28/08**	**Q**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/25/08	ND	ND	ND	ND	ND	**Q**	ND	ND	ND	ND	ND	**0.0027**	ND	ND	ND	ND	ND
Drinking Water Standard		**70**	**3**	**--**	**3**	**40**	**1750**	**--**	**--**		**400**	**21,000**	**4**	**100**	**--**	**100**	**4**	**500**

µg/L = micrograms per liter (1 µg/L = 1 part per billion)

ND = not detected

Q = analayte detected below analytical method limit of quantification (see Appendix A for limits of quantification)

400

Table 4. Summary of Pesticide Detections in Surface Water

Site ID	Date	Analyte (and Common Trade Names) (µg/L)							
		2,4-D (numerous)	Aldicarb (Temik)	Aldicarb sulfone	Diuron (Karmex, Velpar)	Ethofumesate (Norton, Progress)	Hexazinone (Velpar)	Imazapyr (Arsenal, Chopper)	Metolachlor ESA
BSP-6	6/16/08	ND	ND	ND	ND	ND	ND	ND	ND
	9/15/08	ND	ND	ND	ND	ND	ND	Q	ND
BSP-R1	6/16/08	0.0046	ND	ND	Q	0.0032	ND	ND	ND
	9/15/08		ND	ND	Q	ND	Q	ND	Q
BSP-R2	6/17/08	0.0045	ND	ND	ND	ND	ND	ND	ND
	9/16/08	Q	ND	ND	ND	ND	ND	ND	ND
BSP-R3	6/17/08	0.0074	Q	Q	ND	Q	ND	ND	ND
	9/15/08	Q	ND	ND	ND	ND	ND	ND	ND
BSP-R4	6/17/08	ND	ND	ND	Q	ND	ND	ND	ND
	9/15/08	ND	ND	ND	Q	ND	ND	ND	ND
Drinking Water Standard		70	3	3	3	--	400	21,000	--

µg/L = micrograms per liter (1 µg/L = 1 part per billion)

ND = not detected

Q = analyte detected below analytical method limit of quantitation (see Appendix A for limits of quantitation)

US EPA established aquatic life benchmarks for detected surface water pesticides (µg/L)

Pesticide compound	Acute fish	Chronic fish	Acute invertebrates	Chronic invertebrates	Acute nonvascular plants	Acute vascular plants	Chronic aquatic community
Aldicarb	26	0.46	10	1	500,008	—	—
Aldicarb sulfone	21,000	—	140	—	—	—	—
2,4-D	50,500	14,200	12,500	16,400	3,880	299.2	—
Diuron	355	26	80	1609	2.4	—	—

US EPA aquatic life benchmarks for ethofumesate, hexazinone, imazapyr and metolachlor ESA do not exist.

Table 5. Summary of Nitrate/Nitrite Results					
Site ID	**Date**	**Nitrate (mg/L)**	**Drinking Water Standard (mg/L)**	**Nitrite (mg/L)**	**Drinking Water Standard (mg/L)**
BSP-1	**6/16/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-2	**6/16/08**	2.7	10	ND	1
	9/15/08	2.4	10	ND	1
BSP-3	**6/16/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-4	**6/16/08**	1.3	10	ND	1
	9/15/08	1.2	10	ND	1
BSP-5	**6/16/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-7	**6/16/08**	1.9	10	ND	1
	9/15/08	2.3	10	ND	1
BSP-8	**6/16/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-9	**6/16/08**	16	10	ND	1
	9/15/08	17	10	ND	1
BSP-10	**6/16/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-11	**6/16/08**	1.1	10	ND	1
	9/15/08	1.9	10	ND	1
BSP-12	**6/16/08**	2.8	10	ND	1
	9/15/08	2.7	10	ND	1
BSP-13	**6/16/08**	1.5	10	ND	1
	9/15/08	1.6	10	ND	1
BSP-14	**6/16/08**	2.1	10	ND	1
	9/15/08	2.2	10	ND	1
BSP-15	**6/16/08**	5.8	10	ND	1
	9/15/08	4.5	10	ND	1
BSP-16	**6/16/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-17	**6/17/08**	1.1	10	ND	1
	9/16/08	1.4	10	ND	1
BSP-18	**6/17/08**	1	10	ND	1
	9/15/08	1.3	10	ND	1
BSP-19	**6/17/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-20	**6/17/08**	ND	10	ND	1
	9/15/08	ND	10	ND	1
BSP-21	**6/17/08**	1.1	10	ND	1
	9/15/08	ND	10	ND	1

mg/L = milligrams per liter (1 mg/L = 1 part per million)
ND = not detected above analytical method detection limit of 1mg/L

Table 5. (cont.) Summary of Nitrate/Nitrite Results					
Site ID	**Date**	**Nitrate (mg/L)**	**Drinking Water Standard (mg/L)**	**Nitrite (mg/L)**	**Drinking Water Standard (mg/L)**
RAV-1	**5/28/08**	ND	10	ND	1
	8/25/08	ND	10	ND	1
RAV-2	**5/28/08**	ND	10	ND	1
	8/25/08	ND	10	ND	1
RAV-3	**5/28/08**	ND	10	ND	1
	8/25/08	3	10	ND	1
mg/L = milligrams per liter (1 mg/L = 1 part per million) ND = not detected above analytical method detection limit of 1mg/L					

6.0 Uses of Pesticides Detected in Water Samples

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) established the authority of the Environmental Protection Agency (EPA) over the distribution, sales, and uses of all pesticides. Under FIFRA, all pesticides (herbicides, insecticides, fungicides, and rodenticides) must be labeled for specific uses. The use of any pesticide outside of those specified on the label is against federal and state law. For example, bensulfuron is an herbicide labeled for use in rice crops. The use of bensulfuron on any other crops or on non-crop areas is prohibited under FIFRA. However, not all pesticides are labeled for a single use and most pesticides, including all of the pesticides detected during this project, are labeled for multiple uses. The following bullets summarize some of the uses of the pesticides detected in the water samples from the Bitterroot Valley:

- 2,4-D is a very common general use herbicide that has both agricultural crop uses (wheat, barley, corn and many other crops) and non-agricultural uses (i.e. residential weed control, noxious weed control, etc.).
- Aminopyralid is an herbicide for use in rangeland, permanent grass pastures, non-cropland areas (rights-of-way, roadsides and non-irrigation ditch banks), natural areas (wildlife management areas, natural recreation areas, campgrounds, trailheads, and trails), and grazed areas in and around these sites, as well as wheat.
- Aldicarb is an insecticide used in corn, potatoes, sugar beets, seed alfalfa, grain sorghum and dry beans.
- Atrazine was a common general use herbicide until 1993 when its use was largely restricted to corn and sorghum crops because of concerns over groundwater impacts. Atrazine and its degradates (i.e., deethyl atrazine) have proven to be very persistent in the environment. Atrazine is commonly found in groundwater across the U.S. even in areas where it is no longer used.
- Carbofuran is an insecticide and nematicide registered for use in alfalfa, corn, potatoes, sunflowers, vegetables and forest trees.

- Chlorsulfuron is an herbicide that may be used in wheat, barley, durum, oats and has non-cropland uses in addition to small grain production.
- Diuron is an algaecide and herbicide that is used in alfalfa, wheat, orchards, and vineyards. Non-cropland uses include weed control on hard surfaces such as roads, railway tracks, and paths and irrigation and drainage ditches.
- Ethofumesate is an herbicide used in ornamental turf, sugar beets, and outdoor nurseries. Non-cropland uses include rights-of-way.
- Hexazinone is an herbicide registered for use on alfalfa, rangeland, fallowed land, ditch banks and orchards with some forestry applications.
- Imazamethabenz is an herbicide registered for use in wheat, barley, and sunflower crops.
- Imazapyr is a non-cropland herbicide used in areas such as fence rows, farm building sites, pipeline and highway rights-of-way, utility and pumping installations, roadsides, storage areas, and non-irrigation ditch banks.
- Metolachlor is used for weed control in corn, soybeans, potatoes, sugar beets, sunflowers and woody ornamentals.
- MCPA is an herbicide which can be used in wheat, barley, oats, rye, flax, and pea crops as well as in pasture, rangeland, established turf, and grasses grown for seed production.
- Prometon is a non-selective herbicide used on non-cropland, including industrial sites, around farm buildings, railroad rights-of-way, underneath asphalt, or other places where long-term vegetation control is desired.
- Simazine is an herbicide used in corn, alfalfa, and in fruit orchards. Non-cropland uses include ornamental trees and shrubs, rights-of-way, and industrial sites.
- Tebuthiuron is an herbicide used in pastures, rangeland, and non-crop areas such as industrial sites.

7.0 Summary

During the summer of 2008, the Montana Department of Agriculture conducted a project to determine pesticide and nitrate impacts to the water resources of the Bitterroot Valley. Forty-six groundwater samples from 23 wells and 10 surface water samples from 5 sites were collected in June and September and analyzed for 95 pesticide compounds as well as nitrate and nitrite. Although pesticides were detected in a little more than half of the samples (54%), the concentrations were very low and the overall impact appears to be minimal. Nitrate was also detected in a little more than half the samples (52%), but concentrations were low in most samples.

There were 53 detections of 14 different pesticides and 3 pesticide degradates in 25 of the 46 groundwater samples from 14 of the 23 sampling sites. The most commonly detected pesticide in groundwater was prometon. Atrazine and one of its degradates, deethyl atrazine was also a common detection. Prometon is a non-crop herbicide used in areas where long term control of weeds is desired. Atrazine detections are likely due to historical uses before 1993 when it was a common general use herbicide. Beginning in 1993 the use of atrazine was restricted mostly to corn crops. All of the pesticide concentrations in groundwater were low and none exceeded or approached human health

drinking water standards, where such standards exist. Nitrate was detected in 24 of the 46 groundwater samples from 13 of the 23 sites. Three samples exceeded 50% of the human health drinking water standard of 10 mg/L. The source(s) of nitrate in groundwater were not determined during this project.

There were 16 detections of 6 pesticides and 2 pesticide degradates in the surface water samples collected. There was at least one detection at each sampling site. Five of the 10 surface water samples from 3 of the 4 sampling sites contained 2,4-D. Diuron was detected 4 times at 2 sites and ethofumesate was found twice at two sites. All other pesticides had only a single detection. Of all detections, only 3 of the 4 2,4-D detections and 1 of 2 ethofumesate detections exceeded the LOQ and were reported as real numbers. All of the concentrations in surface water samples were low and none exceeded or approached the human health drinking water standards or the EPA aquatic life benchmarks. Nitrate was not detected in any of the surface water samples.

8.0 References

Briar, D.W., and Dutton, D.M., 2000, Hydrogeology and aquifer sensitivity of the Bitterroot Valley, Ravalli County, Montana: U.S. Geological Survey Water-Resources Investigations Report 99-4219, 114 p.

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., and Wolock, D.M. 2006. The Quality of Our Nation's Waters – Pesticides in the Nation's Streams and Ground Water, 1992-2001: U.S. Geological Survey Circular 1291, 172 p.

LaFave, J.I. 2006. Ground-water quality in shallow basin-fill, deep basin-fill and bedrock aquifers, Bitterroot Valley, Missoula and Ravalli counties, southwest Montana (open-file version): Montana Bureau of Mines and Geology Ground-Water Assessment Atlas 4B-09, 1 sheet, 1:500,000.

Kiely, T., Donaldson, D., and Grube, A. 2004. Pesticide Industry Sales and Usage, 2000 and 2001 Market Estimates: U.S. Environmental Protection Agency.

Lonn, J.D., and Sears, J.W. 2001. Geology of the Bitterroot Valley: Montana Bureau of Mines and Geology Open-File Report 441C. Scale 1:48,000.

McMurtrey, R.G., Konizeski, R.L., Johnson, M.V., and Bartells, J.H., 1972, Geology and water resources of the Bitterroot Valley, southwestern Montana with a section on Chemical quality of water by H.A. Swenson: U.S. Geological Survey Water-Supply Paper 1889, 80 p.

Norbeck, P.M., and McDonald, C. 2001. Ground-water evaluation, Florence, Montana. Montana Bureau of Mines and Geology Open-File Report 455. 20 pp.

Smith, L.N. 2006. Altitude of the bedrock surface in the Bitterroot Valley: Southern Lolo-Bitterroot Area, Missoula and Ravali Counties, Montana. Montana Bureau of Mines Ground-Water AssessmentAtlas 4, Part B, Map 5. Scale 1:125,000.

Uthman, W. 1988. Hydrogeology of the Hamilton North and Corvallis quadrangles, Bitterroot Valley, southwestern Montana. University of Montana, M.S. thesis. 323 p.

Appendix A

Universal Method Analyte List and Limits of Quantification (LOQ)

2008 MDA Universal Method Analytes and the Limits of Quantification (LOQ)

Analyte Name	LOQ	Units	Analyte Name	LOQ	Units
2,4-D	0.0045	ug/L (ppb)	Hexazinone	0.0059	ug/L (ppb)
2,4-DB	0.091	ug/L (ppb)	Hydroxy atrazine	0.0064	ug/L (ppb)
2,4-DP	0.011	ug/L (ppb)	Imazalil	0.01	ug/L (ppb)
3-OH Carbofuran	0.01	ug/L (ppb)	Imazamethabenz methyl acid met.	0.0052	ug/L (ppb)
Acetochlor	0.14	ug/L (ppb)	Imazamethabenz methyl ester	0.001	ug/L (ppb)
Acetochlor ESA	0.01	ug/L (ppb)	Imazamox	0.012	ug/L (ppb)
Acetochlor OA	0.0042	ug/L (ppb)	Imazapic	0.011	ug/L (ppb)
Alachlor	0.11	ug/L (ppb)	Imazapyr	0.011	ug/L (ppb)
Alachlor ESA	0.011	ug/L (ppb)	Imazethapyr	0.01	ug/L (ppb)
Alachlor OA	0.0034	ug/L (ppb)	Imidacloprid	0.0018	ug/L (ppb)
Aldicarb	0.0028	ug/L (ppb)	Linuron	0.011	ug/L (ppb)
Aldicarb sulfone	0.0011	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)
Atrazine	0.0022	ug/L (ppb)	Metalaxyl	0.012	ug/L (ppb)
Azinphos methyl	0.037	ug/L (ppb)	Methomyl	0.0016	ug/L (ppb)
Azinphos methyl oxon	0.031	ug/L (ppb)	Metolachlor	0.012	ug/L (ppb)
Azoxystrobin	0.0011	ug/L (ppb)	Metolachlor ESA	0.0025	ug/L (ppb)
Bentazon	0.0011	ug/L (ppb)	Metolachlor OA	0.021	ug/L (ppb)
Bromacil	0.0074	ug/L (ppb)	Metsulfuron methyl	0.026	ug/L (ppb)
Carbaryl	0.04	ug/L (ppb)	Nicosulfuron	0.011	ug/L (ppb)
Carbofuran	0.0052	ug/L (ppb)	Nitrate as Nitrogen	1.0	mg/L (ppb)
Chlorpyrifos	0.031	ug/L (ppb)	Nitrite as Nitrogen	0.1	ug/L (ppb)
Chlorsulfuron	0.0056	ug/L (ppb)	NOA 407854	0.0052	ug/L (ppb)
Clodinafop-propargyl-acid metabolite	0.013	ug/L (ppb)	NOA 447204	0.01	mg/L (ppm)
Clopyralid	0.022	ug/L (ppb)	Picloram	0.14	mg/L (ppm)
Cyproconazole	0.0051	ug/L (ppb)	Prometon	0.0051	ug/L (ppb)
Deethyl atrazine	0.0017	ug/L (ppb)	Propachlor	0.0028	ug/L (ppb)
Deisopropyl atrazine	0.01	ug/L (ppb)	Propachlor OA	0.0094	ug/L (ppb)
Diazinon	0.01	ug/L (ppb)	Propiconazole	0.01	ug/L (ppb)
Dicamba	0.051	ug/L (ppb)	Prosulfuron	0.005	ug/L (ppb)
Difenoconazole	0.02	ug/L (ppb)	Simazine	0.0026	ug/L (ppb)
Dimethenamid	0.01	ug/L (ppb)	Sulfometuron methyl	0.01	ug/L (ppb)
Dimethenamid OA	0.0038	ug/L (ppb)	Sulfosulfuron	0.0054	ug/L (ppb)
Dimethoate	0.0011	ug/L (ppb)	Tebuconazole	0.01	ug/L (ppb)
Disulfoton	0.13	ug/L (ppb)	Tebuthiuron	0.0011	ug/L (ppb)
Disulfoton sulfone	0.014	ug/L (ppb)	Terbacil	0.0051	ug/L (ppb)
Disulfoton sulfoxide	0.064	ug/L (ppb)	Terbufos	0.17	ug/L (ppb)
Diuron	0.01	ug/L (ppb)	Tetraconazole	0.0062	ug/L (ppb)
Epoxyconazole	0.028	ug/L (ppb)	Thifensulfuron	0.026	ug/L (ppb)
Ethion	0.39	ug/L (ppb)	Tralkoxydim	0.0051	ug/L (ppb)
Ethofumesate	0.025	ug/L (ppb)	Tralkoxydim acid	0.005	ug/L (ppb)
Ethoprop	0.012	ug/L (ppb)	Triadimefon	0.0057	ug/L (ppb)
Fenamiphos	0.0011	ug/L (ppb)	Triadimenol	0.026	ug/L (ppb)
Fenbuconazole	0.0053	ug/L (ppb)	Triallate	0.039	ug/L (ppb)
Flufenacet OA	0.0053	ug/L (ppb)	Triasulfuron	0.026	ug/L (ppb)
Flumetsulam	0.063	ug/L (ppb)	Triclopyr	0.011	ug/L (ppb)
Glutaric Acid	0.0074	ug/L (ppb)	Triticonazole	0.032	ug/L (ppb)
Halosulfuron methyl	0.01	ug/L (ppb)			

Appendix B

Analytical Results