

**Permanent Monitoring Well Network
Summary Report**

2003 – 2007



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Table of Contents

List of Tables.....	iii
List of Figures.....	iv
Chapter 1.....	1
1.1 Introduction.....	1
1.2 Objectives.....	2
Chapter 2.....	3
2.1 Methods.....	3
2.2 Data analysis.....	4
Chapter 3.....	7
3.1 Statewide.....	7
3.2 Watershed-level.....	9
3.3 County-level.....	14
Chapter 4.....	18
4.1 Discussion.....	18
4.2 Statewide.....	19
4.3 Watershed-level.....	19
4.4 County-level.....	26
Chapter 5.....	28
5.1 Conclusion.....	28
5.2 Recommendations.....	29
5.3 Future considerations.....	29
Literature Cited.....	30
Appendix A – Environmental Fate of Pesticides.....	32
Appendix B – PMW well location and length of record.....	38
Appendix C – Laboratory procedural changes (2003-2007).....	39
Appendix D – Results by watershed.....	41
Appendix E – Results by county.....	46

List of Tables

<u>Table</u>	<u>Page</u>
Chapter 3	
3.1.1. Table displaying analytes that were never detected in groundwater during the sampling period 2003-2007	7
3.2.1. List of detections and their frequencies for the State of Montana from 2003-2007.....	9
3.3.1. Analytes with significant detection frequencies displayed by watershed for the sampling period 2003-2007.....	13
3.4.1. Analytes with significant detection frequencies displayed by county for the sampling period 2003-2007.....	17

List of Figures

<u>Figure</u>	<u>Page</u>
Chapter 3	
3.1.1. Montana Department of Agriculture Permanent Monitoring Well Sites.....	8
3.1.2. Montana Department of Agriculture 4th Code Watershed Map.....	11
3.1.3. Montana Department of Agriculture County Map.....	15

Chapter 1

1.1 Introduction

The Agricultural Sciences Division of the Montana Department of Agriculture includes the Groundwater Protection Program. 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:

- (1) protect groundwater and the environment from impairment or degradation due to the use of agricultural chemicals
- (2) allow for the proper and correct use of agricultural chemicals
- (3) provide for the management of agricultural chemicals to prevent, minimize, and mitigate their presence in groundwater
- (4) 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

As part of its directive, the Groundwater Protection Program samples groundwater and surface water to determine the presence and concentrations of pesticides and nitrogen fertilizers. The department maintains a Permanent Monitoring Well (PMW) network that grew from 18 wells in 2003 to 44 wells in 2007. PMWs are primarily located throughout the major agricultural regions in the state. In addition, investigative and special projects are conducted in vulnerable areas, watersheds, and urban environments.

A summary of the PMW data collected from 2003 – 2007 was compiled in order to quantify the number and type of pesticides detected in the monitoring network. This information is intended for use by producers, government agencies and the general public.

1.2 Objectives

The objectives of this compilation is to provide a concise summary of the frequency of detections and types of analytes found in water samples collected from the PMW network from 2003 through 2007 and to highlight those analytes that were detected most frequently. This report will offer a baseline of observations and provide a resource for managers, producers, and other professionals with known findings of water quality in reference to pesticide detection in groundwater in Montana. The information will be presented at the 4th code watershed and by county in addition to a statewide summary.

The summary is presented as stand-alone data. Research quantifying the relative distribution and volume of pesticide use has not been done for the State of Montana. Data included in this report include only the observations made by the Montana Department of Agriculture in the analysis of samples collected from the PMW network from 2003 through 2007.

Chapter 2

2.1 Methods

Groundwater sampling in Montana for pesticides is primarily focused on wells in areas with known or suspected pesticide or nitrate detections and is concentrated in areas dominated by agriculture. Most of the detected compounds have relatively low soil adsorption values and long half-lives, contributing to their high leaching potential. For a thorough discussion on the fate and transport of pesticides in the environment refer to Appendix A.

Water samples from the PMW network were collected twice a year when possible. Well casing volumes were purged three times and water variables including pH, specific conductance, dissolved O₂, and temperature were stable before a sample was collected. Samples were stored in labeled amber glass bottles and kept at approximately 4°C prior to and in transport to the laboratory. A blank was also collected per sampling trip as part of the Quality Assurance protocol for sample collection. All field collection procedures are outlined in Standard Operating Procedures (SOPs) utilized by the Groundwater Program in the collection and documentation of groundwater samples. A complete list of all well locations and installation dates may be found in Appendix B.

Samples were analyzed at the Montana Department of Agriculture Analytical Laboratory. In 2006, in cooperation with the Technical Services Bureau of the Montana Department of Agriculture, a universal method was developed and validated by the Analytical Laboratory for the Groundwater Protection Program. Its use was instituted following the 2005 field season. The Universal Method was used to analyze 102 pesticides and degradates in 2006 and 96 in 2007. The new procedure greatly improved lab efficiency. A significant decrease in reporting limits with the adoption of the method was also realized. Due to advances in the understanding

of pesticide fate and transport and lowering of laboratory detection limits, lower recovery rates are accepted for many analytes improving the reporting capabilities of the laboratory.

The adoption of the Universal Method added new analytes and dropped analytes that had previously been investigated prior to 2006. In addition, changes to the Universal Method were made between the 2006 and 2007 field seasons to add new analytes of interest and drop analytes which had either been infrequently detected or not detected in sampling. As new products become available on the market and old pesticides fall out of use, the analyte list utilized by the Universal Method will continue to undergo modifications in the future^a.

2.2 Data analysis

For the summary analysis, frequency of detections summary statistics were utilized to present the data. Summary statistics include the number of samples collected from 2003-2007, the number of detections per analyte, and the maximum concentration observed per analyte. These are some of the most defensible statistics in regards to pesticide detections which have high temporal and spatial variability (Capel et al., 1996). It is a procedure most often used by the United States Geological Survey for pesticide studies as part of the National Water-Quality Assessment Program (NAWQA).

Criteria for data inclusion incorporated observations that fell below the limit of quantification (LOQ) but were greater than the limit of detection (LOD). Therefore, laboratory results frequently included Q^b observations where a pesticide was detected in a groundwater sample but was at a concentration which could not be dependably quantified. Q observations were included in data analysis as detections. Simply stated, the frequency of detection equals the

^a For a detailed outline of changes in laboratory procedures with the adoption of the Universal Method refer to Appendix C.

^b Q used where observation was more than 3.3X lower than the reporting limit.

total number of detections divided by the total number of samples. In addition, only pesticide analytes which had been tested for during the entire study period (2003-2007) were included in the analysis. Deethyl deisopropyl atrazine, an atrazine degradate, is the exception to this rule. This analyte was included because it was frequently detected in groundwater samples prior to its removal from investigated analytes following the 2005 field season.

It is important to note that over the course of the study period, reporting limits were increasingly lowered as laboratory procedures and equipment were refined and updated. This is particularly relevant following the adoption of the Universal Method in 2006. Therefore, it is possible that a pesticide analyte found to be a non-detect in 2003 may well have been detected using 2007 guidelines. For this reason, frequencies of detection summary statistics were utilized in the interest of reporting all established observations of pesticide detection. Quality assurance (QA) procedures were followed diligently by the laboratory and field staff throughout the study period and any observations that derived from samples that failed the QA criteria were discarded.

For this summary report, the frequency of detection of analytes was completed at the state level, by 4th-code watershed, and by county. The analysis becomes less robust with decreasing geographic area due to the decrease in data points. Several counties only contain a single well in the PMW network. Additionally, a few watersheds and several counties have no data to report as the PMW network does not include them. Only watersheds and counties containing data are included in this report. It was the interest of the authors to provide as succinct and comprehensive a summary as the data would allow.

Due to the limitations of the monitoring network and the limited number of samples collected yearly from the monitoring wells, results are limited to the cropping systems and environmental conditions (precipitation, temperature, soil texture, etc.) found in proximity of the

PMWs from which the samples were collected. The results reflect a snapshot of groundwater conditions, but are likely not comprehensive.

Chapter 3

3.1 Statewide

A total of 37 analytes were never detected in groundwater samples in the PMW network although samples were analyzed for them. These analytes are listed alphabetically in Table 3.1.1 and only apply to the sampling years 2003-2007.

Table 3.1.1. Table displaying analytes that were never detected in groundwater during the sampling period 2003-2007

Analyte	
2,4 DP	Halosulfuron methyl
2,4-DB	Imazalil
3-OH carbofuran	Imazapic
Acetochlor	Imine
Alachlor	Isoxazole
Aldicarb	Linuron
Carbofuran	Neburon
Chlorpyrifos	Propachlor
Cyanazine	Propachlor OA
Diazinon	Propanil
Dimethenamid	Propazine
Dinoseb	Prosulfuron
Disulfoton	Sulfometuron methyl
Disulfoton sulfone	Sulfosulfuron
Disulfoton sulfoxide	Terbacil
Ethion	Terbufos
Ethoprop	Thifensulfuron
Fenamiphos	Trione
Flufenacet OA	

A complete list of the analytes found in groundwater sampled from the State of Montana and the frequency of detection for each analyte is found below in Table 3.1.2. In total, 45 analytes were detected in varying frequencies. However, no analytes were found in concentrations greater than 50% of the human health standard. Figure 3.1.1 is a map of Montana with locations of all MDA PMWs.

Figure 3.1.1
 Montana Department of Agriculture
 Permanent Monitoring Well Sites

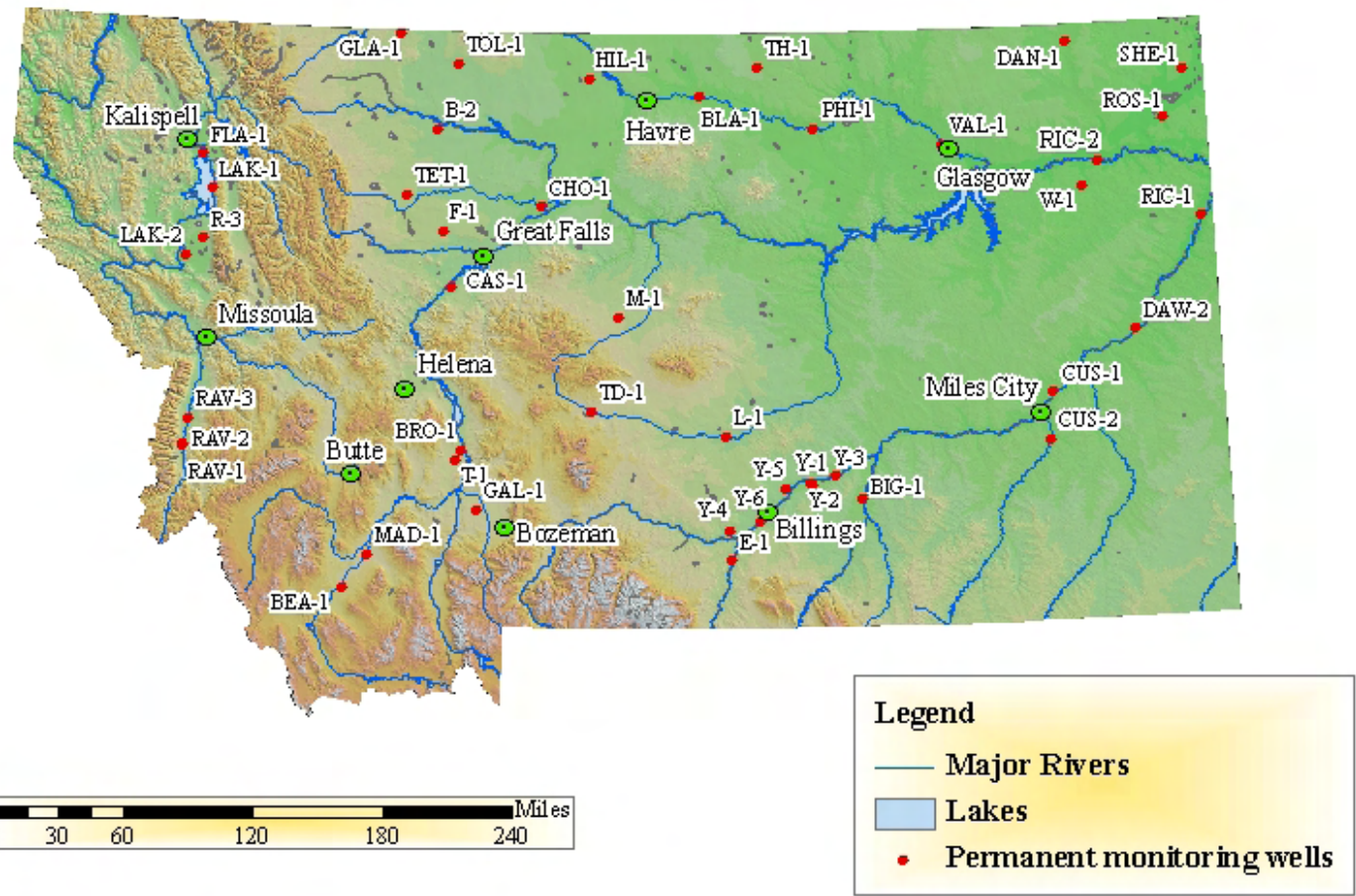


Table 3.1.2. List of detections and their frequencies for the State of Montana from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a	Human Health Standard (ppb)
2,4-D	223	17	7.6%	0.076	70
Acetochlor ESA	105	3	2.9%	0.016	140
Acetochlor OA	105	3	2.9%	0.005	140
Alachlor ESA	105	16	15.2%	0.37	2
Alachlor OA	105	12	11.4%	0.013	2
Aldicarb sulfone	162	2	1.2%	0.41	3
Aldicarb sulfoxide	162	1	0.6%	0.41	4
Atrazine	245	31	12.7%	0.23	3
Azoxystrobin	119	2	1.7%	LOQ	1000
Bentazon	223	2	0.9%	LOQ	200
Bromacil	217	1	0.5%	LOQ	90
Carbaryl	205	1	0.5%	LOQ	700
Chlorsulfuron	219	5	2.3%	0.021	1750
Clopyralid	227	14	6.2%	21	3500
Deethyl atrazine	182	38	20.9%	0.18	3
Deethyl deisopropyl atrazine ^b	76	29	38.2%	1.3	3
Deisopropyl atrazine	182	26	14.3%	0.19	3
Dicamba	223	2	0.9%	0.078	200
Dimethenamid OA	105	3	2.9%	LOQ	none
Diuron	105	2	1.9%	LOQ	10
Glutaric acid	159	2	1.3%	0.084	20
Hydroxy atrazine	181	14	7.7%	0.094	70
Hexazinone	217	5	2.3%	LOQ	400
Imazamethabenz methyl acid	138	20	14.5%	1.7	400
Imazamethabenz methyl ester	138	26	18.8%	2.8	400
Imazapyr	119	8	6.7%	0.19	21000
Imazethapyr	105	2	1.9%	LOQ	none
Imidacloprid	105	1	1.0%	LOQ	400
MCPD	223	1	0.4%	LOQ	7
Methomyl	205	1	0.5%	LOQ	200
Metolachlor	186	3	1.6%	0.033	100
Metolachlor ESA	105	30	28.6%	4	100
Metolachlor OA	105	12	11.4%	0.14	100
Metsulfuron methyl	217	1	0.5%	LOQ	1750
Nicosulfuron	186	5	2.7%	0.06	8750

^a Limit of Quantification^b not sampled after 2005

Table 3.1.2. (cont.) List of detections and their frequencies for the State of Montana from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a	Human Health Standard (ppb)
NOA 407854	105	7	6.7%	0.51	<i>none</i>
NOA 447204	105	5	4.8%	0.083	<i>none</i>
Picloram	224	6	2.7%	3.9	500
Prometon	218	15	6.9%	0.53	100
Propiconazole	105	1	1.0%	<i>LOQ</i>	<i>none</i>
Simazine	218	9	4.1%	0.016	4
Tebuthiuron	217	7	3.2%	0.0014	500
Tralkoxydim	159	25	15.7%	0.17	20
Tralkoxydim acid	145	11	7.6%	0.19	20
Triallate	217	1	0.5%	<i>LOQ</i>	5

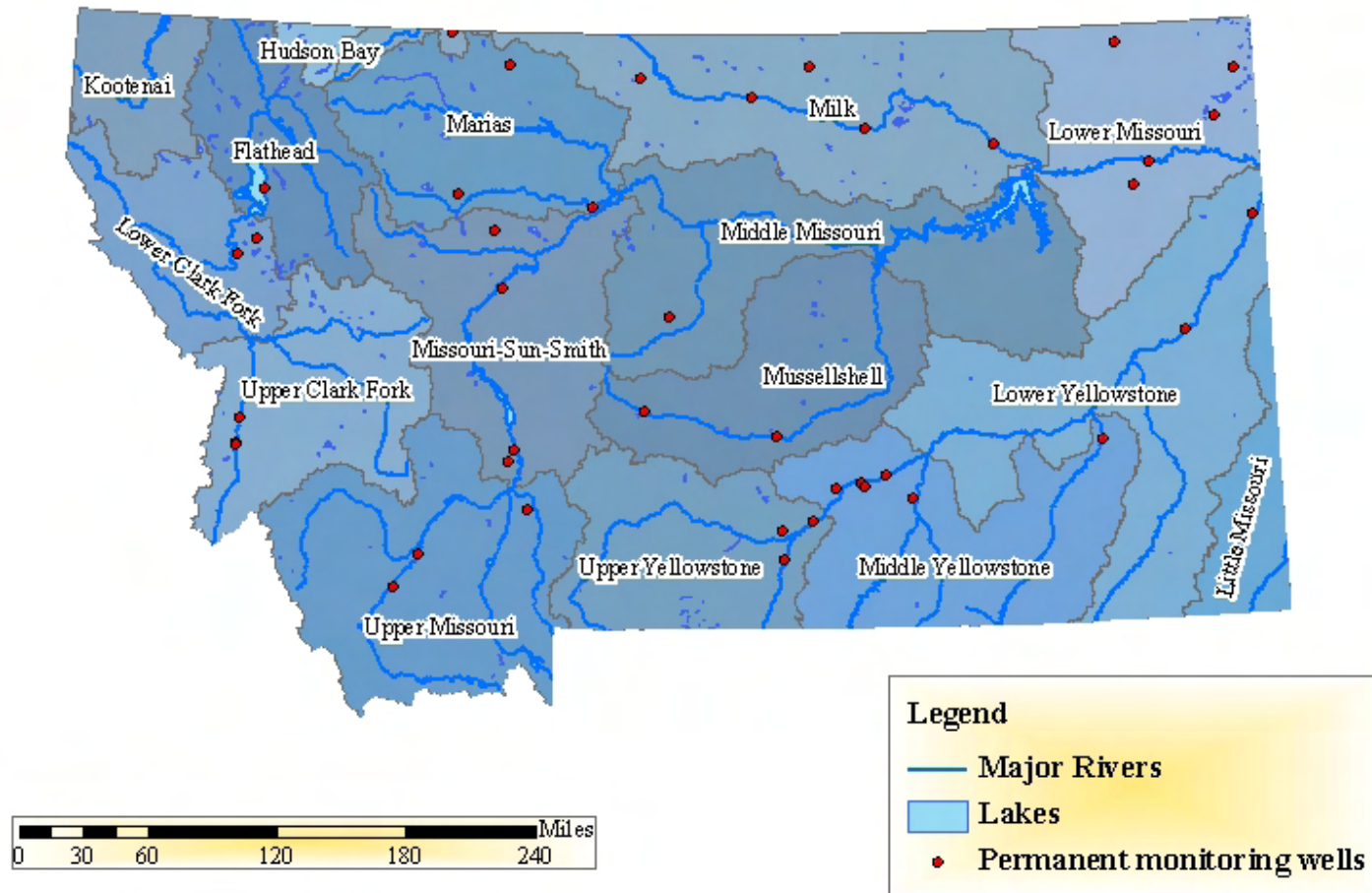
^a Limit of Quantification

3.2 Watershed-level

A watershed is an area characterized by all runoff being conveyed to the same outlet. Of the 16 4th code watersheds in Montana, only 13 are represented by the PMW network and of these 3 had no detections. Of the 11 watersheds that had detections, 2 reported only a single analyte detected from 2003-2007. Figure 3.2.1 is a map of 4th code watersheds in Montana.

At the watershed-level, initial analyses of the detection frequency data were reduced further to provide a more concise summary. Detection frequencies were divided into three categories: (1) $\geq 30\%$ detection frequency; ≥ 10 observations, (2) $\geq 30\%$ detection frequency, < 10 observations, (3) $< 30\%$ detection frequency. Category 2 includes all analytes that had less than 10 observations, but had detection frequencies that would be $\geq 30\%$ even if the remaining number of samples to reach the minimum of 10 observations were non-detections (ND).

Figure 3.2.1
Montana Department of Agriculture
4th Code Watershed Map



In Table 3.3.1, significant detections of pesticide analytes are displayed by watershed. Only analytes that fell into category (1) or (2) as explained above are displayed. Analytes and their actual detection frequencies and maximum observed values for each individual watershed that reported detections may be found in Appendix D. Results are organized by watershed.

At the watershed-level, 17 pesticide analytes, all of them herbicides, were found to have 28 significant detection frequencies among 8 different watersheds for the sampling period 2003–2007 (Table 3.3.1.). The watersheds with the most detections were the Middle Yellowstone, Flathead, and Missouri-Sun-Smith watersheds.

Of the 17 different herbicide analytes with significant detection frequencies, 10 are the active ingredients or degradates of herbicides labeled for use in corn crops. These detections comprised 68% of the 28 observed high detection frequency analytes found at the watershed-level. The main concentrations of these corn-labeled herbicides were found along the Yellowstone River corridor in south-central and south-eastern Montana. In addition, high detection frequencies of atrazine and two degradate were found in the Flathead watershed which contains significant orchard acreages. Atrazine is labeled for use in orchards in addition to its dominant use in corn. It is also important to note that simazine and atrazine share a common degrade in deethyl atrazine. All three were found in significant frequencies in the Flathead watershed.

In examining herbicides labeled for small grains, 29% of the 28 observed high detection frequency analytes found were labeled for use in wheat, barley and oats. These comprised 6 of the analyte list of 17. The main concentrations of these herbicides were found in the Missouri-Sun-Smith watershed in west-central Montana. The remaining herbicide, prometon, is labeled for non-crop use. Prometon had a high detection frequency in the Flathead watershed.

Table 3.3.1. Analytes with significant detection frequencies displayed by watershed for the sampling period 2003-2007

Analyte	Flathead	Lower Yellowstone	Marias	Middle Missouri	Middle Yellowstone	Missouri- Sun- Smith	Upper Missouri	Upper Yellowstone
Alachlor ESA					<i>a</i>			
Alachlor OA		<i>b</i>			<i>a</i>			
Atrazine	<i>a</i>				<i>a</i>			
Chlorsulfuron				<i>b</i>				
Deethyl atrazine	<i>b</i>				<i>a</i>		<i>a</i>	
Deethyl deisopropyl atrazine ^c	<i>b</i>				<i>a</i>			<i>a</i>
Deisopropyl atrazine	<i>b</i>				<i>a</i>			
Hydroxy atrazine								
Imazamethabenz methyl acid						<i>a</i>		
Imazamethabenz methyl ester						<i>a</i>	<i>a</i>	
Metolachlor ESA					<i>a</i>			<i>a</i>
Metolachlor OA					<i>a</i>			
NOA 407854			<i>a</i>	<i>a</i>		<i>a</i>		
Prometon	<i>a</i>							
Simazine	<i>a</i>							
Tralkoxydim	<i>b</i>					<i>a</i>		
Tralkoxydim acid						<i>a</i>		

a - analytes with detection frequencies $\geq 30\%$; ≥ 10 observations

b - analytes with detection frequencies $\geq 30\%$; <10 observations

c - not sampled after 2005

3.3 County-level

There are 56 counties in the State of Montana. Of these, 31 counties contain at least one well within the PMW network. For the sampling period 2003-2007, 21 counties reported pesticide detections. Figure 3.3.1 is a map of Montana counties with well locations and 4th code watershed boundaries.

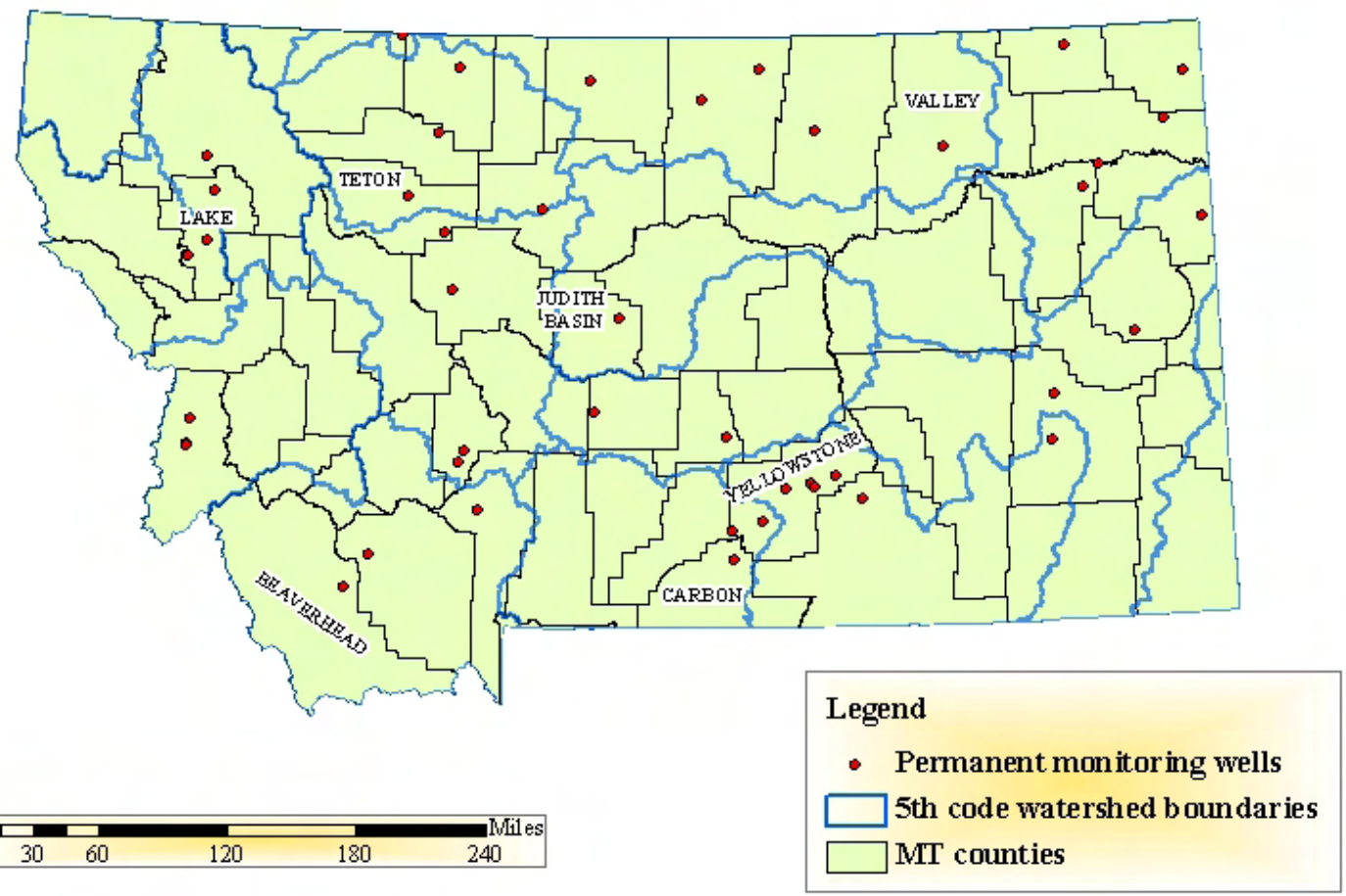
As with the watershed-level analysis, initial detection frequency analyses at the county-level were broken down further to provide a more concise summary. Detection frequencies were divided into three categories: (1) $\geq 30\%$ detection frequency; ≥ 10 observations, (2) $\geq 30\%$ detection frequency, < 10 observations, (3) $< 30\%$ detection frequency. Category 2 includes all analytes that had less than 10 observations, but had detection frequencies that would be $\geq 30\%$ even if the remaining number of samples to reach the minimum of 10 observations were non-detections (ND).

In Table 3.4.1, significant detections of pesticide analytes are displayed by county. Only analytes that fell into category (1) or (2) as explained above are displayed. Analytes and their actual detection frequencies and maximum observed values for each individual watershed that reported detections may be found in Appendix E.

At the county-level, 20 pesticide analytes, all of them herbicides were found to have 29 significant detection frequencies among 9 different counties for the sampling period 2003-2007 (Table 4.4.1.). The counties with the most detections were Yellowstone and Custer counties along the Yellowstone River and Teton County in west-central Montana.

As at the county-level, 55% of the 20 pesticide analytes with significant detection frequencies were the active ingredients or degradates of herbicides labeled for use in corn

Figure 3.3.1
Montana Department of Agriculture
County Map



and other row crops. The main concentrations of detections were found in Yellowstone County in south-central Montana. Herbicides labeled for use in wheat, barley and oats among other uses comprised 31% of the listed analytes with high detection frequencies with the main concentration of observations in Teton County.

Findings included two non-crop herbicides. Prometon had a significant detection frequency in Beaverhead and Lake Counties, and imazapyr was found in Yellowstone County.

Table 3.4.1. Analytes with significant detection frequencies displayed by county for the sampling period 2003-2007

Analyte	Beaverhead	Carbon	Custer	Dawson	Judith Basin	Lake	Teton	Valley	Yellowstone
2,4-D									<i>b</i>
Alachlor ESA			<i>b</i>	<i>b</i>					
Alachlor OA			<i>b</i>	<i>b</i>					
Atrazine						<i>a</i>			<i>a</i>
Chlorsulfuron					<i>b</i>				
Clopyralid							<i>a</i>		
Deethyl atrazine	<i>b</i>					<i>a</i>			<i>b</i>
Deethyl deisopropyl atrazine ^c									<i>b</i>
Deisopropyl atrazine									<i>b</i>
Dimethenamid OA			<i>b</i>						
Hydroxy atrazine									<i>b</i>
Imazamethabenz methyl acid	<i>b</i>						<i>a</i>		
Imazamethabenz methyl ester	<i>b</i>						<i>a</i>		
Imazapyr									<i>b</i>
Metolachlor ESA			<i>b</i>	<i>b</i>					
NOA 407854							<i>b</i>		
NOA 447204							<i>b</i>		
Picloram								<i>b</i>	
Prometon	<i>b</i>					<i>a</i>			
Tralkoxydim acid							<i>a</i>		

a - analytes with detection frequencies $\geq 30\%$; ≥ 10 observations

b - analytes with detection frequencies $\geq 30\%$; <10 observations

c - not sampled after 2005

Chapter 4

4.1 Discussion

In examining the results of the statewide, watershed, and county analyses, there were several observations that stood out. These observations include a list of analytes that were commonly observed in groundwater at the state level and others that were significant by watershed and county. In order to provide a succinct summary, discussion of high detection analytes were limited to those analytes which exhibited significant detection frequencies at these levels of analysis. The most significant finding of this summary report is that not a single analyte detection exceeded established human health standards for drinking water from 2003 through 2007. In fact, only two detections approached 50% of the standard^c. The detections were degradates of the herbicides atrazine and alachlor.

Deethyl deisosopropyl atrazine had a maximum detection of 1.3 ppb that was 1.15X below ½ of the standard (Table 3.2.1). The detection was from a sample taken in Yellowstone County along the Yellowstone River east of Worden, MT on April 2, 2004. An alachlor degradate, alachlor ESA, had a maximum detection of 0.37 ppb that was 2.7X below ½ of the drinking water standard (Table 3.2.1). The detection was from a sample taken in Dawson County along the Yellowstone River south of Glendive, MT on August 15, 2006

^c Fifty percent of the standard is the benchmark of the Montana Department of Agriculture at which remediation is required.

4.2 Statewide

In the analysis of pesticide detections at the state-level, there were three analytes that had a frequency of detection greater than 20% (1 in 5 samples). These were degradates of atrazine and metolachlor. Atrazine is an herbicide commonly used for corn production in Montana though, historically, it was a general use herbicide that was labeled for multiple uses and has been found to be very persistent in the environment. Atrazine was relabeled by the EPA in 1990 as a restricted-use herbicide with limited uses in corn, sorghum, and wheat (fallow, stubble) along with some non-crop applications. The main region of corn production in Montana is along the Yellowstone River corridor in south-central and southeastern Montana. However, atrazine may be used in wheat (fallow, stubble) applications. This labeled use likely accounts for atrazine detections in areas where corn is not a significant crop. Deethyl atrazine and deethyl deisopropyl atrazine had detection frequencies of 20.9% and 38.2% respectively (Table 4.2.1). It is important to note that, concerning water quality standards, the chlorinated degradates of atrazine are additive^d. This includes the atrazine degradates deethyl atrazine, deethyl deisopropyl atrazine, and deisopropyl atrazine.

A metolachlor degrade, metolachlor ESA, had a detection frequency of 28.6% (Table 3.1.2). Metolachlor is an herbicide used for corn, grain, potatoes, safflower, ornamentals and other crops as a pre-emergence herbicide used to control certain broad-leaf and annual grassy weeds.

4.3 Watershed-level

Of the 11 watersheds that reported detections, 8 had analytes with detection frequencies

^d Discussion of additive concentrations was not included as this applies to singular samples and not to maximum concentrations as in this summary document.

≥ 30% (~2 in 7 samples) that met the reporting criteria. Significant watersheds will be discussed by the major river systems.

Flathead Lake

Flathead Watershed

On the west side of the continental divide in northwestern Montana, the Flathead watershed includes the cities of Kalispell and Whitefish, all of Flathead Lake, and flows of the Stillwater and Flathead Rivers.

The watershed was found to have five analytes with high detection frequencies. These included the herbicides atrazine, prometon, and simazine (Table 3.3.1). Atrazine is a restricted-use; selective herbicide that is applied pre- and post-emergence in the control of broad-leaved weeds and grasses. Deethyl atrazine is a degradate of atrazine and was one of the five significant analytes. Atrazine is used most often in corn production although it is also used in orchard operations with wheat applications as well. Atrazine belongs to the chemical group *triazine*. Simazine also belongs to the chemical group *triazine* and is a selective herbicide that is used to control a range of germinating annual grasses and broad-leaved weeds. It is labeled for use in corn, fruit and nut crops, Christmas tree plantings, nursery operations, and turf production with some forestry applications. Both atrazine and simazine are moderately persistent in the soil and present a high leaching risk. It is important to note that the two analytes share a common degradate. Deisopropyl atrazine is a degradate of atrazine and simazine and had a high detection frequency in the watershed (Table 3.3.1).

Prometon was also found to have a high detection frequency (80%) in the watershed. Prometon belongs to the chemical group *methoxytriazine* and is a very persistent (average field half life ~500 days), non-selective herbicide that is used for total vegetation control on industrial

sites, on non-crop areas on farms, and in and under asphalt. It has a high risk of leaching to groundwater. The Flathead watershed was the only Montana watershed where prometon had a $\geq 30\%$ detection frequency.

The watershed includes portions of Lake and Flathead counties. According to the 2002 U.S. Farm Census, these counties contain 77% of the total orchard acreage in Montana with a disproportionate amount in Lake County (71% - 1232 acres). While both counties contained small amounts of corn acreage in 2002, 45.8% of the harvested acreage in Flathead County was in small grain production as opposed to 18.3% in Lake County. The majority of harvested acreage in 2002 in Lake County was in forage.

Missouri River

Upper Missouri

The Upper Missouri watershed is located in southwestern Montana and includes the cities of Dillon and Bozeman. It is the headwaters of the Missouri River containing the full lengths of the Big Hole, Beaverhead, Gallatin, Jefferson, and Madison Rivers and their drainages.

In the watershed, 2 analytes met the criteria of $\geq 30\%$ detection frequency with a minimum of 10 observations. Deethyl atrazine displayed a 38.5% detection frequency although no detections were greater than the limit of quantification. Deethyl atrazine is a highly leachable degradate of the herbicide atrazine.

The other high detection frequency analyte was imazamethabenz methyl ester. This pesticide is a moderately persistent (25-36 days), selective herbicide used post-emergence to control grasses and some dicotyledonous weeds in barley and wheat. For the Upper Missouri watershed, imazamethabenz methyl ester did not have a detection greater than the limit of quantification.

The watershed is comprised of all or parts of Gallatin, Madison, and Beaverhead Counties. The U.S. Farm Census reported that in 2002, Gallatin County contained 1.5% of the state total of corn acreage though 50% of the harvested acreage in the county was put in small grains. Madison and Beaverhead Counties had 12.5% and 7.6% of their harvested acreages in small grains with no corn production reported in either county. In both counties, more than $\frac{3}{4}$ of the harvested acreage was dedicated to forage during the 2002 growing season.

Missouri-Sun-Smith

The Missouri-Sun-Smith watershed is located in west-central Montana and includes the cities of Helena and Great Falls. The western boundary of the watershed runs along the eastern edge of the continental divide. The watershed includes portions of the Missouri, Sun, and Smith Rivers and their drainages.

A total of 4 pesticide analytes displayed detection frequencies $\geq 30\%$ with a minimum of 10 observations. In the chemical group *imidazolinone*, imazamethabenz methyl ester and its acid metabolite had detection frequencies $> 50\%$. The analyte and the acid metabolite pose a high leaching risk.

The other analytes with high detection frequencies included a metabolite of pinoxaden, NOA 407854, and the herbicide tralkoxydim and a degradate, tralkoxydim acid, belonging to the chemical groups of *phenylpyrazoline* and *cyclohexadione oxime* respectively. These three analytes are similar as they have low persistence (< 4 days) and are highly leachable with low soil sorption. They are selective herbicides used for post-emergence weed control in cereal crops and are labeled for use in wheat, barley and durum. Pinoxaden and its degradates, NOA 407854 and NOA 447204 concentrations are additive. This applies to tralkoxydim and tralkoxydim acid concentrations as well.

It is important to note that all of the analytes with significant detection frequencies in the watershed are labeled for use in small grains production. In 2002, there was no appreciable corn production in the counties of Cascade, Lewis and Clark, and Teton and these counties had, respectively, 66.4%, 24.5%, and 76.9% of their total harvested acreages in small grains (2002 Farm Census).

Marias

The Marias watershed is located just to the north of the Missouri-Sun-Smith watershed in west-central Montana. It includes nearly the full lengths of the Marias and Teton Rivers both of which join the Missouri River near Fort Benton, Montana.

Only one analyte in the watershed was observed to meet the reporting criteria. A degradate of pinoxaden, NOA 407854, had a detection frequency of 30%. Pinoxaden is labeled for use in wheat, barley, and durum. The watershed forms part of the Golden Triangle region in Montana; a region known for its small grains agriculture.

Middle Missouri

The Middle Missouri watershed is a large sub basin which spans nearly 200 miles in north-central Montana. The only PMW, 25 miles west of Lewistown, reported one significant analyte meeting the reporting criteria. Chlorsulfuron had a detection frequency of 42.9%.

Chlorsulfuron is in the chemical group *sulfonylurea*. It has a persistence of ~ 40 days, has low soil sorption rates and is highly leachable. It is a selective, systemic herbicide that is used in small grains with some non-cropland uses. Chlorsulfuron is used to control most broad leaved weeds and some annual grasses. According to the 2002 Farm Census, small grains in Judith Basin, the county in which the PMW is located, accounted for ~ 50% of the harvested acreage in the county in 2002.

Yellowstone River

Upper Yellowstone

The Upper Yellowstone watershed is in south-central Montana and includes the town of Livingston. It contains the headwater flows of the Yellowstone River as it flows north out of Wyoming, although the sampling wells are concentrated in the eastern half of the watershed near Billings, MT.

Two analytes had high detection frequencies. They were deethyl deisopropyl atrazine, an atrazine degradate, and metolachlor ESA, a metolachlor degradate (Table 3.3.11). Atrazine belongs to the chemical group *triazine* and metolachlor belongs to the chemical group *chloroacetamide*.

Metolachlor is a selective herbicide which inhibits seed germination. It is used pre-emergence to control broad leaved weeds and annual grasses in corn and small grains in Montana. It has low to moderate persistence with low soil sorption and presents a significant leaching risk.

Middle Yellowstone

The Middle Yellowstone watershed is located in southeastern Montana and encompasses a long stretch of the Yellowstone River. There are 6 wells in the watershed with four of them in close proximity to the Yellowstone River, one near the Bighorn River and the last well on the Tongue River. The watershed includes the city of Billings, MT.

This watershed reported 9 analytes with high detection frequencies ($\geq 30\%$). This is the most of any watershed in Montana for the time period 2003-2007. The analytes are all degradates of the herbicides alachlor, atrazine, and metolachlor.

Degradates of atrazine, including deethyl atrazine, deethyl deisopropyl atrazine, deisopropyl atrazine^e and hydroxy atrazine had high detection frequencies in the watershed. The high detection frequency of atrazine degradates in the Middle Yellowstone watershed is likely a consequence of the corn production along the Yellowstone River. The Middle Yellowstone contains most of Yellowstone County which was responsible for 23.3% of all corn acreage in the State of Montana in 2002. The control of broad-leaved weeds and grasses by atrazine in corn production is the most common use of the herbicide.

The remaining analytes that displayed high detection frequencies include two degradates of alachlor and two degradates of metolachlor both belonging to the chemical group *chloracetamide*. Alachlor EAS, alachlor OA, metolachlor ESA and metolachlor OA all had high detection frequencies ($\geq 30\%$, $n=10$) with metolachlor ESA having been found in 100% of the samples collected from 2003-2007.

Where alachlor has systemic action and is absorbed by germinating shoots, metolachlor inhibits seed germination. Alachlor is a selective herbicide used for pre-emergence control of annual grasses and broadleaf weeds in corn, soybeans, and dry beans. It has moderately high persistence (56-84 days) and moderate soil sorption rates.

The analytes which displayed high detection frequencies are all labeled for corn, but do include other crops as well such as wheat (fallow) and wheat (stubble) applications. This is an interesting finding as, in 2002, only 8.7% of the harvested acreage in the county was in corn production though 54.2% was in small grains. However, the majority of the corn acreage is located in the valley bottom near the river while small grains are grown in and out of the valley. The PMWs are located in the valley. The disproportionate contributions of corn herbicides to groundwater may be attributable to a few factors. In 2002, 99% of all corn acreage in

^e Deisopropyl atrazine is also a degradate of simazine.

Yellowstone County was irrigated as opposed to 17.5% of small grain acreage. Corn water requirements ensure that corn fields are located in proximity to a ready water source, and irrigation adds a solvent capable of carrying herbicide residues off-site.

Lower Yellowstone

The Lower Yellowstone River, in southeastern Montana, includes Miles City and contains the flow of the Yellowstone River to the western border of North Dakota. It also includes the Powder River from where it enters Montana at the Wyoming line to where it joins the Yellowstone River northeast of Miles City.

Three analytes met the reporting criteria for significance. Alachlor ESA and alachlor OA, degradates of alachlor, had significant detection frequencies. Alachlor is a herbicide used predominantly in corn. The other significant analyte was metolachlor ESA, a metolachlor degradate, which is labeled for use in corn and small grains in Montana.

4.4 County-level

A complete discussion of detection frequencies at the county-level has not been done for this report. For reasons of duplicity, repetition of findings at the watershed-level would simply occur along county lines with the former being more representative of regional trends in agricultural production and pesticide use.

However, there were 6 pesticide analytes that had significant detection frequencies at the county-level that were not reported at the watershed-level. This is due to the smaller number of data points available at the county-level which in some cases included only a single well.

In Teton County in north-central Montana, clopyralid and a pinoxaden metabolite, NOA 447204, had high detection frequencies ($\geq 30\%$, minimum 10 samples) (Table 3.4.1.).

Clopyralid is a pyridine compound and is a moderately persistent herbicide that has a high risk of

leaching to groundwater. It is a selective systemic herbicide that is used as a post-emergent control of many broad-leaved weeds and is used in noxious weed management. In Teton County, its dominant use is in small grains production.

Along the Yellowstone River, high detection frequencies were observed for 2,4-D and imazapyr in Yellowstone County and a dimethenamid degradate, diemthenamid OA, in Custer County. The pesticide 2,4-D is an all-purpose herbicide in the chemical family *alkylchlorophenoxy* that has low persistence (~10 days) but is a high leaching risk. It can also be a degradation product of other herbicides. Imazapyr is a herbicide labeled for use in non-cropland with some limited corn applications. In the chemical group *imidazolinone*, it has a persistence of 25-142 days and presents a significant leaching risk. Dimethenamid, in the chemical family *chloroacetamide* is a soil-applied herbicide that has low persistence, but poses a high leaching risk. It is labeled for use in corn, dry beans and other row crops.

In Valley County, in northeastern Montana, picloram was found to have a high detection frequency in the lone PMW located there. Valley County falls in the Milk River watershed. Picloram is a pyridine compound that has moderate persistence and is highly leachable. It is a selective herbicide used in small grains, non-crop applications and utility areas.

Finally, in Beaverhead County in southwestern Montana, the soil sterilant prometon had a high detection frequency in the only PMW in the county located northeast of Dillon adjacent to the Beaverhead River. Prometon was also observed in the Flathead watershed in northwestern Montana in the watershed analysis.

Chapter 5

5.1 Conclusion

The most significant finding of the 2003-2007 summary of detections in the MDA PMW network was that there was not a single instance where the concentrations of a detected pesticide analyte was $\geq 50\%$ of the human health standard (Table 4.2.1).

In general, analytes with significant detection frequencies reflected the growing practices in the watersheds/counties in which they were observed. Detections of corn labeled herbicides were highest along the Yellowstone River corridor. These analytes include atrazine and its degradates and the degradates of alachlor and metolachlor. Conversely, herbicides used in small grains dominated significant observations along the Missouri River. These analytes include imazamethabenz methyl ester, tralkoxydim and their degradates along with pinoxaden degradates. Areas utilizing intensive agriculture practices such as irrigation and continuous cropping exhibited the largest number of detections such as the corn growing region along the Yellowstone River, particularly in the area around Billings, Montana.

All observed significant detection frequencies were for herbicides which are the most common types of pesticide used in the State of Montana. Of these, *triazine*^f and *acetanilide*^g herbicides were the most commonly detected. The two groups comprised 71.4% of the significant detections at the watershed level and 62% at the county level. This is not surprising as the two groups have been estimated to comprise more than 50% of the total herbicide use in the United States (Barbash and Resek, 1996).

^f Triazine herbicides include: atrazine, prometon and simazine

^g Acetanilide herbicides include: alachlor, dimethenamid and metolachlor

5.2 Recommendations

It is the recommendation of this summary report that sampling and expansion of the PMW network should continue to address water quality issues. A study of soil characteristics in and around wellheads in the PMW network would also prove advantageous to the program.

The program of surface water sampling should also be expanded. During periods of low flow, groundwater recharges surface waters via baseflow (i.e. a 'gaining' stream) and during periods of high runoff surface waters can recharge groundwater (i.e. a 'losing' stream). These processes elicit a mechanism by which contaminants may enter either system depending upon flow conditions.

5.3 Concerns for the future

As commodity prices rise, growing practices and pesticide applications will likely change. Possible results of these changes include: increases in continuous cropping practices, increases in irrigated land, and re-entry of Crop Reserve Program lands into production. Crops with greater water requirements and herbicide use such as corn may steadily increase in acreage. As the value of small grains and corn increases, the opportunity cost of fertilizer, pesticides and irrigation installation and operation expenses will decrease. This will slowly but inexorably change the agricultural industry in Montana and will likely impact groundwater resources. The continuous sampling of water resources across the state is necessary to monitor water quality.

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Appendix A

A.1 Environmental Fate of Pesticides

Once applied to the environment, pesticides are susceptible to a range of transfer and degradation pathways. Relative loss pathways are influenced by climatic, environmental, hydrologic, and pesticide properties. The physical and chemical properties of pesticides such as persistence and partition coefficient (K_{oc}) interact with climatic and environmental factors such as precipitation rates, soil texture and organic carbon content to dictate the loss mechanism. Patterns and trends that influence loss pathways of pesticides will be examined.

A.2 Loss Pathways

There are 5 main pathways of pesticide transfer: volatilization, biological uptake, runoff, leaching, and adsorption. Volatilization is the conversion of a solid or liquid into a gaseous state. High temperatures with low relative humidity and air movement will propagate volatilization. Once volatilized, pesticides can be carried long distances before being deposited attached to dust particles in rain or snow. The atmosphere is the most geographically widespread source of pesticides to groundwaters (Barbash and Resek, 1996).

Biological uptake refers to the absorption or ingestion by plants and animals of applied pesticides. This includes both target and non-target organisms.

Runoff is the movement of water over a sloping surface. Runoff occurs when the infiltration capacity of a soil is exceeded and water flows along the surface. Runoff water can carry pesticides in water itself or bound to eroding particles. Pesticide runoff is usually greatest when a heavy or sustained rain or the use of flood irrigation follows soon after pesticide application.

Leaching is the movement of pesticides through the soil. As water moves downward through the soil matrix it may carry pesticides in solution. Adsorption refers to the chemical attraction whereby pesticides are attached to soil particles. A pesticide held strongly to soil particles by adsorption is less likely to leach and decreases the concentration of pesticides in solution and thus decreases availability for downward movement in water. Also, adsorption increases the length of time pesticides are subject to decomposition by microorganisms in the more active surface soil.

A.3 Soil Properties

Soil texture and organic matter content greatly influence the relative rates of runoff, leaching and adsorption. Soil texture refers to the relative proportion of sand, silt, and clay in a soil. As soil texture changes from large particles (sand) to medium-sized particles (loam) to fine particles (clay), infiltration rates decrease, soil adsorption rates increase, and runoff-potential increases. Greater soil organic matter content also increases pesticide adsorption rates.

Soil permeability and organic carbon content control the degree to which pesticides pass through the rhizosphere^h to groundwater. Relative leaching susceptibility is greater with lower organic matter content, low field capacityⁱ and high permeability. The likelihood of runoff events is greater in soils with high field capacity and low permeability. Organic carbon content (f_{oc}) tends to increase with increasing clay content. Observations from multiple studies have recorded high frequencies of pesticide detections beneath coarse-grained (and usually low f_{oc}) soils than beneath finer grained (and usually high f_{oc}) soils (Barbash and Resek, 1996). The inversely related parameters permeability and f_{oc} are the soil properties that exert the strongest

^h An environment regarded as that region of the soil modified as a result of the uptake and deposition of substances by a growing root; the root surface together with that region of the surrounding soil.

ⁱ The percentage of water remaining in a soil two or three days after its having been saturated and after free drainage has practically ceased.

influence on pesticide movement in the subsurface. Also important, microbial populations typically increase with increases in f_{oc} and are responsible for biotransformation of pesticides in the subsurface.

Increases in soil pH have been found to increase the rate of pesticide mobility in soil, though a compensatory effect may exist whereby greater base hydrolysis with an increase in pH may offset some of the enhanced pesticide mobility (Gustafson, 1993). Increases in soil temperature and soil moisture contents have also been found to increase the rate of pesticide dissipation particularly for those pesticides that lack mobility to migrate downward in the soil profile. Conversely, pesticides are more likely to persist long enough to reach groundwater if applied at colder times of the year due to the decrease in the rates of chemical reactions with decreases in temperature.

It has proven difficult to correlate soil texture and pesticide occurrence in groundwater in many studies, likely because soil texture in the immediate vicinity of the well is not necessarily uniform throughout the recharge area. Pesticide studies examining this relationship in California (Teso et al., 1988), Wisconsin (Harkin et al., 1986) and Pennsylvania (Pionke et al., 1988) have provided little quantitative evidence to support such a relationship. This is likely due to two factors that change within a given recharge area: (1) the heterogeneous nature of soils; (2) changing agricultural practices and farming intensity.

Pesticide detections in groundwater are more likely to be observed beneath coarse-textured soils that are highly permeable with low organic carbon content as opposed to fine-textured soils with lower permeability and high organic carbon contents. These effects are more visible in areas with either substantial contrasts in these soil properties or with little variation in

farm management practices such as cropping systems and pesticide application rates and timing (Barbash and Resek, 1996).

A.4 Pesticide Properties

Soil-half lives have been found to increase with decreasing temperature at the time of application for many pesticides (Frank et al., 1991). Although it is generally accepted that pesticide detection frequencies are correlated with long dissipation half-lives and low soil affinity values (K_{oc}), these values are often unreliable predictors of pesticide detection and should not be interpreted as strictly diagnostic tools (Barbash and Resek, 1996).

Water solubility is often referred to as an influential characteristic in regards to the fate of pesticides in the environment. However, concentrations of pesticides in soil water rarely approach the water solubility of the pesticide (Logan et al, 1994). Water solubility offers little insight regarding the tendency of a pesticide to associate with a solid particle in soil where adsorption to soil particles can remove a pesticide from solution and make it unavailable to be leached to groundwater. For this reason, partition coefficients (K_{oc}) or the propensity of a pesticide to sorb to soil particles provides a more valuable indication of leaching susceptibility than water solubility.

A.5 Hydrology

The PMW network is designed to sample shallow groundwater in order to best identify anthropogenic inputs to groundwater. Therefore agricultural areas with known pesticide applications are the foci of sampling. Shallow groundwater may discharge to surface waters within days or weeks following recharge. This process is expedited when the system is altered by tile drains or drainage ditches. Thus, shallow groundwaters may represent a significant source of contaminants to surface waters. Two parameters control the amount of time for

contaminants to pass through the unsaturated zone to drinking water supplies: depth of the water table and depth of the well screen below the water table. Increases in either distance allow for more time for concentrations to decrease through dispersion, sorption to soil particles, transformation or volatilization (Barbash and Resek, 1996).

Dissolved solutes move through the subsurface by two principal processes, advection and hydrodynamic dispersion. Advection of a solute is “the process by which solutes are transported by the bulk motion of the flowing groundwater” (Freeze and Cherry, 1979). Hydrodynamic dispersion is the combined processes of mechanical dispersion and molecular diffusion that result in the broadening of a contaminant pulse over time (Barbash and Resek, 1996). The preferential transport of the hydrodynamic dispersion of pesticides may be substantially more common than is generally acknowledged.

Advection and hydrodynamic dispersion are significantly influenced by precipitation rates and irrigation practices. Groundwater pesticide studies in the Midwest found that pesticides were detected more frequently in areas with more precipitation the year prior to sampling (Klaseus et al., 1988). A study in Iowa in the late 1980s found that falling detection frequencies were mirrored by a long-term drought in the study area (Kross et al., 1990).

Irrigation systems are an important source of water to the unsaturated zone. Irrigation rates are more pronounced on pesticide transport to groundwater in more permeable soils. The Midcontinent Pesticide Study (MCPS) found that wells containing detectable levels of pesticides were nearly twice as high if located within 3.2 km (35%) of irrigated areas in contrast to wells located beyond 3.2 km (19%) (Burkart and Kolpin, 1993). With more intensive irrigation, pesticides in groundwater may increase. Pesticide contamination of groundwater has been found to be more prevalent under flood irrigation as opposed to sprinkler irrigation. Pesticide losses to

groundwater in irrigation systems have been found to decrease when irrigation is delayed following application. This relationship does not hold true with more soil persistent herbicides (Troiano and Garretson; unpublished data cited by Mae et al., 1991).

The hydrogeologic environments most susceptible to pesticide contamination are shallow, unconfined and unconsolidated aquifers and mature karst areas. It has been suggested by Barbash and Resek, 1996 that the detection of pesticides in groundwater becomes *less likely* with:

- 1) decreasing hydraulic conductivity of the aquifer materials surrounding the well screen
- 2) increasing thickness of low-permeability materials at or close to the land surface
- 3) increasing depth of the top of the sampled aquifer
- 4) increasing depth of the water table
- 5) increasing depth of the well screen below the water table

The effects of surface water recharge to groundwater can provide a significant contribution of pesticide contamination. It is generally accepted that pesticide concentrations are greater in surface waters than in groundwater in regions dominated by agriculture (Hallberg, 1987; Blum et al., 1993; and Kahlkoff and Schaap, 1995). The entry of surface water into the subsurface is most likely during spring runoff events when pesticide concentrations in surface waters and runoff are at their greatest. Substantial increases in pesticide concentrations have been observed in groundwaters drawn from alluvial aquifers in agricultural areas (Barbash and Resek, 1996). This is of particular importance for groundwater wells located within 30 m of a stream^j (Burkart and Kolpin, 1993). During periods of low stream flow, groundwater recharges surface water baseflows. This groundwater derived baseflow is responsible for maintaining chronic, low pesticide concentrations of more persistent pesticides (Hallberg, 1987).

^j None of the wells in the PMW network meet this criteria.

Appendix B – PMW well location and length of record

Table B.1. Table of PMW network additions in new wells constructed from 2003-2007

MDA Site ID	Watershed	County	PMW Construction ^a				
			2003 ^b	2004	2005	2006	2007
B-2	Marias	Pondera	X				
BEA-1	Upper Missouri	Beaverhead		X			
BIG-1	Middle Yellowstone	Big Horn					X
BLA-1	Milk	Blaine		X			X
BRO-1	Upper Missouri	Broadwater		X			
CAS-1	Missouri-Sun-Smith	Cascade					X
CHO-1	Marias	Chouteau		X			
CUS-1	Lower Yellowstone	Custer					X
CUS-2	Middle Yellowstone	Custer					X
DAN-1	Lower Missouri	Daniels		X			
DAW-2	Lower Yellowstone	Dawson			X		
E-1	Upper Yellowstone	Carbon	X				
F-1	Missouri-Sun-Smith	Teton	X				
FLA-1	Flathead	Flathead					X
GAL-1	Upper Missouri	Gallatin					X
GLA-1	Milk	Glacier		X			
HIL-1	Milk	Hill		X			
L-1	Musselshell	Golden Valley	X				
LAK-1	Flathead	Lake		X			
LAK-2	Lower Clark Fork	Lake			X		
M-1	Middle Missouri	Judith Basin	X				
MAD-1	Upper Missouri	Beaverhead					X
PHI-1	Milk	Phillips					X
R-3	Lower Clark Fork	Lake	X				
RAV-1	Upper Clark Fork	Ravalli					X
RAV-2	Upper Clark Fork	Ravalli					X
RAV-3	Upper Clark Fork	Ravalli					X
RIC-1	Lower Yellowstone	Richland		X			
RIC-2	Lower Missouri	Richland					X
ROS-1	Lower Missouri	Roosevelt					X
SHE-1	Lower Missouri	Sheridan					X
T-1	Missouri-Sun-Smith	Broadwater	X				
TD-1	Musselshell	Wheatland	X				
TET-1	Missouri-Sun-Smith	Teton		X			
TH-1	Milk	Blaine	X				
TOL-1	Marias	Toole	X				
VAL-1	Milk	Valley		X			
W-1	Lower Missouri	McCone	X				
Y-1	Middle Yellowstone	Yellowstone	X				
Y-2	Middle Yellowstone	Yellowstone	X				
Y-3	Middle Yellowstone	Yellowstone	X				
Y-4	Upper Yellowstone	Yellowstone	X				
Y-5	Middle Yellowstone	Yellowstone	X				
Y-6	Middle Yellowstone	Yellowstone	X				

^a No new wells were added to the PMW network in 2006

^b Includes wells installed prior to 2003

Appendix C – Laboratory procedural changes (2003 - 2007)

Table C.1. Table displaying changes in MSU laboratory analyte investigations between the 2005 and 2006 field seasons with adoption of the Universal Method

Analytes dropped	Analytes added
5-OH Dicamba	Acetochlor ESA
Butachlor	Acetochlor OA
Butylate	Alachlor ESA
Carboxin	Alachlor OA
Chlorfenvinphos	Azinphos methyl oxon
Chlorpyrifos	Azoxystrobin
Cycloate	Bromuconazole-46
Deethyl deisopropyl atrazine	Bromuconazole-47
Deethyl hydroxy atrazine	Cyproconazole
Deisopropyl hydroxy atrazine	Difenoconazole
Dichlorvos	Dimethenamid
EPTC	Dimethenamid OA
Ethametsulfuron methyl	Dimethoate
Fenthion	Diuron
Methidathion	Epoxyconazole
Metribuzin	Fenbuconazole
Mevinphos	Flufenacet OA
Parathion ethyl	Flumetsulam
Parathion methyl	Imazamox
Pentachlorophenol	Imazapic
Primisulfuron methyl	Imazethapyr
Prometryn	Imidacloprid
Pronamide	Linuron
Thifensulfuron methyl	Metolachlor ESA
Triflusulfuron methyl	Metolachlor OA
	Myclobutanil
	Neburon
	NOA 407854
	NOA 447204
	Propachlor OA
	Propanil
	Propiconazole
	Sulfosulfuron
	Tebuconazole
	Tetraconazole
	Thifensulfuron
	Triadimefon
	Triadimenol
	Triticonazole

Table C.2. Table displaying changes in analyte investigations using the Universal Method between the 2006 and 2007 field seasons

Analytes dropped	Analytes added
Bromuconazole-46	Aminopyralid
Bromuconazole-46	Chlorpyrifos
Cyanazine	Clopyralid
Imine	Dimethamid
Isoxazole	Ethofumesate
Myclobutanil	
Neburon	
Oxazole	
Propanil	
Propazine	
Trione	

Table C.3. List of 2007 analytes that were investigated in groundwater samples

Analytes investigated		
2,4-D	Dimethenamid	Metolachlor
2,4-DB	Dimethenamid OA	Metolachlor ESA
2,4-DP	Dimethoate	Metolachlor OA
3-OH Carbofuran	Disulfoton	Metsulfuron methyl
Acetochlor	Disulfoton sulfone	Nicosulfuron
Acetochlor ESA	Disulfoton sulfoxide	NOA 407854
Acetochlor OA	Diuron	NOA 447204
Alachlor	Epoxyconazole	Picloram
Alachlor ESA	Ethion	Prometon
Alachlor OA	Ethofumesate	Propachlor
Aldicarb	Ethoprop	Propachlor OA
Aldicarb sulfone	Fenamiphos	Propiconazole
Aldicarb sulfoxide	Fenbuconazole	Prosulfuron
Aminopyralid	Flufenacet OA	Simazine
Atrazine	Flumetsulam	Sulfometuron methyl
Azinphos methyl	Glutaric Acid	Sulfosulfuron
Azinphos methyl oxon	Halosulfuron methyl	Tebuconazole
Azoxystrobin	Hexazinone	Tebuthiuron
Bentazon	Hydroxy atrazine	Terbacil
Bromacil	Imazalil	Terbufos
Carbaryl	Imazamethabenz methyl acid	Tetraconazole
Carbofuran	Imazamethabenz methyl ester	Thifensulfuron
Chlorpyrifos	Imazamox	Tralkoxydim
Chlorsulfuron	Imazapic	Tralkoxydim acid
Clodinafop acid	Imazapyr	Triadimefon
Clopyralid	Imazethapyr	Triadimenol
Cyproconazole	Imidacloprid	Triallate
Deethyl atrazine	Linuron	Triasulfuron
Deisopropyl atrazine	Malathion	Tricopyr
Diazinon	MCPA	Triticonazole
Dicamba	MCPP	
Difenoconazole	Metalaxyl	
Dimethamid	Methomyl	

Appendix D – Results by watershed

Flathead

Table D.1. Frequency of detection and maximum observation of analytes detected in the Flathead watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	9	2	22.2%	-
Atrazine	10	5	50.0%	-
Deethyl atrazine	8	5	62.5%	0.0068
Deisopropyl atrazine	8	3	37.5%	0.0058
Prometon	10	8	80.0%	0.53
Simazine	10	5	50.0%	0.0075

^a denotes only Q values (Q = detection below the limit of quantification)

Lower Clark Fork

Table D.2. Frequency of detection and maximum observation of analytes detected in the Lower Clark Fork watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb)
Metolachlor ESA	4	1	25.0%	0.0031

Lower Missouri

Table D.3. Frequency of detection and maximum observation of analytes detected in the Lower Missouri watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	21	4	19.0%	0.076
MCPA	21	3	14.3%	-
Picloram	21	3	14.3%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Lower Yellowstone

Table D.4. Frequency of detection and maximum observation of analytes detected in the Lower Yellowstone watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Alachlor ESA	9	6	66.7%	0.37
Alachlor OA	9	6	66.7%	0.013
Bentazon	15	1	6.7%	-
Clopyralid	15	1	6.7%	-
Dimethenamid OA	9	2	22.2%	-
Imazethapyr	9	1	11.1%	-
Metolachlor ESA	9	7	77.8%	0.07
Metolachlor OA	9	1	11.1%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Marias

Table D.5. Frequency of detection and maximum observation of analytes detected in the Marias watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb)
2,4-D	22	2	9.1%	0.0055
Hexazinone	22	4	18.2%	-
Imazamethabenz methyl acid	18	4	22.2%	0.031
Imazamethabenz methyl ester	18	5	27.8%	0.36
Metsulfuron methyl	22	1	4.5%	-
NOA 407854	10	3	30.0%	0.011
NOA 447204	10	1	10.0%	-
Tralkoxydim	22	2	9.1%	0.0051

Middle Missouri

Table D.6. Frequency of detection and maximum observation of analytes detected in the Middle Missouri watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Chlorsulfuron	7	3	42.9%	0.021
Imazamethabenz methyl acid	1	1	100.0%	-
Imazamethabenz methyl ester	1	1	100.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Middle Yellowstone

Table D.7. Frequency of detection and maximum observation of analytes detected in the Middle Yellowstone watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	37	3	8.1%	0.066
Acetochlor ESA	15	3	20.0%	0.016
Acetochlor OA	15	3	20.0%	0.005
Alachlor ESA	15	8	53.3%	0.3
Alachlor OA	15	6	40.0%	0.013
Aldicarb sulfone	29	2	6.9%	0.41
Aldicarb sulfoxide	29	1	3.4%	0.41
Atrazine	46	20	43.5%	0.23
Carbaryl	36	1	2.8%	0.045
Clopyralid	40	6	15.0%	21
Deethyl atrazine	39	21	53.8%	0.18
Deethyl deisopropyl atrazine ^b	24	16	66.7%	1.3
Deisopropyl atrazine	39	19	48.7%	0.19
Dimethenamid OA	15	1	6.7%	-
Hydroxy atrazine	39	16	41.0%	0.094
Imazapyr	21	5	23.8%	0.19
Imazethapyr	15	1	6.7%	-
MCPA	37	1	2.7%	-
Metolachlor	29	3	10.3%	0.033
Metolachlor ESA	15	15	100.0%	4
Metolachlor OA	15	11	73.3%	0.14
Nicosulfuron	37	5	13.5%	0.06
NOA 407854	15	1	6.7%	0.21
NOA 447204	15	1	6.7%	0.083
Picloram	38	2	5.3%	3.9
Simazine	36	3	8.3%	0.016
Tebuthiuron	36	4	11.1%	-
Tralkoxydim	15	2	13.3%	0.662
Tralkoxydim acid	15	3	20.0%	-
Triallate	36	1	2.8%	-

^a denotes only Q values (Q = detection below the limit of quantification)

^b not sampled after 2005

Milk

Table D.8. Frequency of detection and maximum observation of analytes detected in the Milk watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	30	4	13.3%	0.042
Chlorsulfuron	30	1	3.3%	-
Dicamba	30	2	6.7%	0.078
Imazamethabenz methyl acid	24	1	4.2%	-
MCPA	30	2	6.7%	-
Picloram	30	3	10.0%	-
Propiconazole	17	1	5.9%	-
Simazine	30	1	3.3%	-
Tralkoxydim	24	1	4.2%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Missouri-Sun-Smith**

Table D.9. Frequency of detection and maximum observation of analytes detected in the Missouri-Sun-Smith watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Clopyralid	30	7	23.3%	2.3
Deethyl atrazine	12	3	25.0%	0.025
Glutaric acid	36	2	5.6%	0.084
Imazamethabenz methyl acid	23	14	60.9%	1.7
Imazamethabenz methyl ester	23	14	60.9%	2.8
Imidacloprid	11	1	9.1%	-
NOA 407854	11	3	27.3%	0.51
NOA 447204	11	3	27.3%	0.07
Picloram	29	1	3.4%	-
Prometon	24	1	4.2%	-
Tralkoxydim	36	20	55.6%	0.17
Tralkoxydim acid	26	8	30.8%	0.19

^a denotes only Q values (Q = detection below the limit of quantification)**Musselshell**

Table D.10. Frequency of detection and maximum observation of analytes detected in the Musselshell watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Hexazinone	10	1	10.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Upper Missouri

Table D.11. Frequency of detection and maximum observation of analytes detected in the Upper Missouri watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	17	1	5.9%	0.0053
Chlorsulfuron	16	1	6.3%	-
Deethyl atrazine	13	5	38.5%	-
Diuron	11	2	18.2%	-
Imazamethabenz methyl ester	13	4	30.8%	-
MCCPP	17	1	5.9%	-
Methomyl	17	1	5.9%	-
Picloram	17	1	5.9%	-
Prometon	17	4	23.5%	0.011

^a denotes only Q values (Q = detection below the limit of quantification)

Upper Yellowstone

Table D.12. Frequency of detection and maximum observation of analytes detected in the Upper Yellowstone watershed from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	23	1	4.3%	-
Alachlor ESA	7	2	28.6%	-
Atrazine	30	4	13.3%	0.0067
Bromacil	23	1	4.3%	-
Deethyl atrazine	24	5	20.8%	0.0082
Deethyl deisopropyl atrazine ^b	17	13	76.5%	0.97
Deisopropyl atrazine	24	4	16.7%	0.035
Imazamethabenz methyl ester	7	2	28.6%	-
Imazapyr	11	3	27.3%	0.024
Metolachlor ESA	7	7	100.0%	0.1
Prometon	23	2	8.7%	0.0052
Tebuthiuron	23	3	13.0%	0.0014

^a denotes only Q values (Q = detection below the limit of quantification)

^b not sampled after 2005

Appendix E – Results by county

Beaverhead

Table E.1. Frequency of detection and maximum observation of analytes detected in Beaverhead County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Deethyl atrazine	5	4	80.0%	-
Imazamethabenz methyl ester	5	3	60.0%	-
Prometon	7	4	57.1%	0.011

^a denotes only Q values (Q = detection below the limit of quantification)

Big Horn

Table E.2. Frequency of detection and maximum observation of analytes detected in Big Horn County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Alachlor ESA	2	2	100.0%	0.037
Alachlor OA	2	2	100.0%	-
Alachlor OA	2	2	1.0%	-
Deisopropyl atrazine	2	2	100.0%	0.013
Metolachlor ESA	2	2	100.0%	0.074
Metolachlor OA	2	2	100.0%	0.047
Simazine	2	2	100.0%	0.016

^a denotes only Q values (Q = detection below the limit of quantification)

Blaine

Table E.3. Frequency of detection and maximum observation of analytes detected in Blaine County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb)
2,4-D	8	2	25.0%	0.42
Chlorsulfuron	8	1	12.5%	-
Imazamethabenz methyl acid	4	1	25.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Broadwater

Table E.4. Frequency of detection and maximum observation of analytes detected in Broadwater County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Chlorsulfuron	12	1	8.3%	-
Deethyl atrazine	1	1	100.0%	-
Imazamethabenz methyl acid	6	2	33.3%	0.074
Imazamethabenz methyl ester	6	2	33.3%	0.0038
Picloram	12	1	8.3%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Carbon

Table E.5. Frequency of detection and maximum observation of analytes detected in Carbon County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Deethyl deisopropyl atrazine ^b	7	7	100.0%	0.67
Metolachlor ESA	2	2	100.0%	0.1
Tebuthiuron	8	2	25.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)^b not sampled after 2005**Custer**

Table E.6. Frequency of detection and maximum observation of analytes detected in Custer County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Alachlor ESA	3	3	100.0%	0.3
Alachlor OA	3	3	100.0%	0.013
Bentazon	3	1	33.3%	-
Dimethenamid OA	3	3	100.0%	-
Imazethapyr	3	2	66.7%	-
Metolachlor ESA	3	3	100.0%	0.07
Metolachlor OA	3	1	33.3%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Dawson**

Table E.7. Frequency of detection and maximum observation of analytes detected in Dawson County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Alachlor ESA	4	4	100.0%	0.37
Alachlor OA	4	4	100.0%	0.008
Metolachlor ESA	4	4	100.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Flathead**

Table E.8. Frequency of detection and maximum observation of analytes detected in Flathead County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	2	2	100.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Gallatin**

Table E.9. Frequency of detection and maximum observation of analytes detected in Gallatin County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Diuron	2	2	100.0%	-
Imazamethabenz methyl ester	2	1	50.0%	-
Methomyl	2	1	50.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Hill**

Hill

Table E.10. Frequency of detection and maximum observation of analytes detected in Hill County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Tralkoxydim	7	1	14.3%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Judith Basin**

Table E.11. Frequency of detection and maximum observation of analytes detected in Judith Basin County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Chlorsulfuron	7	3	42.9%	0.021
Imazamethabenz methyl acid	1	1	100.0%	-
Imazamethabenz methyl ester	1	1	100.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Lake**

Table E.12. Frequency of detection and maximum observation of analytes detected in Lake County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Atrazine	19	5	26.3%	-
Deethyl atrazine	11	5	45.5%	0.0068
Deisopropyl atrazine	11	3	27.3%	0.0058
Metolachlor ESA	8	1	12.5%	0.0031
Prometon	19	8	42.1%	0.53
Simazine	19	5	26.3%	0.0075

^a denotes only Q values (Q = detection below the limit of quantification)**Madison**

Table E.13. Frequency of detection and maximum observation of analytes detected in Madison County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	2	1	50.0%	-
MCP	2	1	50.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Philips**

Table E.14. Frequency of detection and maximum observation of analytes detected in Philips County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	2	1	50.0%	0.0066
Dicamba	2	2	100.0%	0.078
MCPA	2	2	100.0%	-
Propiconazole	2	1	50.0%	-
Simazine	2	1	50.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)

Richland

Table E.15. Frequency of detection and maximum observation of analytes detected in Richland County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	8	1	12.5%	-
Clopyralid	8	1	12.5%	-
MCPA	8	1	12.5%	-
Metolachlor ESA	5	1	20.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Roosevelt**

Table E.16. Frequency of detection and maximum observation of analytes detected in Roosevelt County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	2	1	50.0%	0.076
MCPA	2	1	50.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Sheridan**

Table E.17. Frequency of detection and maximum observation of analytes detected in Sheridan County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	2	2	100.0%	-
MCPA	2	1	50.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Teton**

Table E.18. Frequency of detection and maximum observation of analytes detected in Teton County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Azoxystrobin	8	2	25.0%	-
Bentazon	22	1	4.5%	-
Clopyralid	23	7	30.4%	2.3
Glutaric Acid	31	2	6.5%	0.084
Hexazinone	17	4	23.5%	-
Imazamethabenz methyl acid	22	16	72.7%	1.7
Imazamethabenz methyl ester	22	17	77.3%	2.8
Imidacloprid	8	1	12.5%	-
Metsulfuron methyl	17	1	5.9%	-
NOA 407854	8	6	75.0%	0.51
NOA 447204	8	4	50.0%	0.07
Prometon	17	1	5.9%	-
Tralkoxydim	31	22	71.0%	0.17
Tralkoxydim acid	23	8	34.8%	0.19

^a denotes only Q values (Q = detection below the limit of quantification)

Toole

Table E.19. Frequency of detection and maximum observation of analytes detected in Toole County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	2	2	100.0%	0.055

Valley

Table E.20. Frequency of detection and maximum observation of analytes detected in Valley County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Picloram	6	3	50.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Wheatland**

Table E.21. Frequency of detection and maximum observation of analytes detected in Wheatland County 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
Hexazinone	5	1	20.0%	-

^a denotes only Q values (Q = detection below the limit of quantification)**Yellowstone**

Table E.22. Frequency of detection and maximum observation of analytes detected in Yellowstone County from 2003-2007

Analyte	Total samples	Total detections	Frequency of detection	Maximum observation (ppb) ^a
2,4-D	9	3	33.0%	0.0066
Acetochlor ESA	3	3	100.0%	0.016
Acetochlor OA	3	3	100.0%	0.005
Alachlor ESA	3	3	100.0%	0.068
Alachlor OA	3	3	100.0%	0.0095
Atrazine	10	10	100.0%	0.23
Carbaryl	8	1	12.5%	0.045
Clopyralid	9	2	22.2%	0.12
Deethyl atrazine	9	9	100.0%	0.16
Deethyl deisopropyl atrazine ^b	6	4	66.7%	0.12
Deisopropyl atrazine	9	5	55.6%	0.068
Hydroxy atrazine	9	4	44.4%	0.024
Imazapyr	5	5	100.0%	0.19
MCPA	9	1	11.1%	-
Metolachlor ESA	3	3	100.0%	0.1
Metolachlor OA	3	3	100.0%	0.024
Simazine	8	1	12.5%	-
Tebuthiuron	8	1	12.5%	-

^a denotes only Q values (Q = detection below the limit of quantification)^b not sampled after 2005