2013 Pesticide Surface Water Monitoring Report

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ND Department of Health
ND Department of Parks and Recreation
ND Game and Fish Department
ND Geological Survey
ND State University Extension Service
ND State Water Commission
US Department of Agriculture-NRCS
US Fish and Wildlife Service
US Geological Survey

SUMMARY

The North Dakota Department of Agriculture, working in cooperation with the North Dakota Department of Health's Division of Water Quality and the U.S. Geological Survey, completed a surface water monitoring survey in 2013 to assess levels of pesticides and pesticide degradates in North Dakota rivers and streams. Thirty sites were sampled and tested for 99 different pesticides and pesticide degradates approximately seven times from April through October resulting in 200 total samples and 19,800 total analyses. The Department utilized the Montana State University Agriculture Experiment Station's Analytical Laboratory for sample analysis. This lab is able to provide lower detection levels than our previously utilized lab, and the number of detections increased because of this. Of all 19,800 analyses, there were a total of 2,105 (10.6%) detections, of which 30 (1.4%) were notable and 1,599 (8.1%) instances when an analyte was deemed present, but below the laboratory detection limit. The most commonly detected pesticide was atrazine which was detected in 188 samples and was found present, but below the detection limit, in all the remaining samples. The next most commonly detected pesticides were 2,4-D; prometon; and tebuconazole. Based on the levels detected, results indicate that pesticides in North Dakota's streams and rivers have minimal risk to human health or the environment. Because there were detections, the survey supports the need for regular, comprehensive monitoring of surface water for pesticides to monitor pesticide levels, continually assess risks of pesticides to human health and the environment, and identify long term trends.

INTRODUCTION

The North Dakota Department of Agriculture (hereafter "Department") is the lead pesticide regulatory agency in the state through the authority provided in Chapters 4-35, 4-35.1, and 19-18 of the North Dakota Century Code. Under a cooperative agreement with the U.S. Environmental Protection Agency (EPA), the Department is charged with regulating pesticides in the public's interest to ensure that they do not pose a risk of unreasonable adverse effects to human health or the environment. Before 2007, the Department's Pesticide Water Quality Program (hereafter "Program") was focused on those pesticides that posed a risk of contaminating groundwater. The Department has had a committee in place for over a decade to advise them on groundwater issues and establish a groundwater monitoring program. Agencies represented on the committee include the ND Department of Health (NDDH), US Department of Agriculture Natural Resource Conservation Service, ND State University Extension Service, US Geological Survey (USGS), ND Geological Survey and the ND State Water Commission.

The EPA has since shifted its water quality focus from groundwater to surface water. Therefore, the Program's focus has expanded to protect both groundwater and surface water from pesticide contamination. To reflect this expansion, the Groundwater Working Committee has been renamed the Water Quality Advisory Committee (WQAC) and now also includes representatives from the US Fish and Wildlife Service, ND Game and Fish Department, and the ND Parks and Recreation Department.

Identifying pesticide surface water issues is a priority for the Department and the WQAC. Before the first pilot monitoring project in 2006, no agency routinely monitored North Dakota's surface waters for pesticides. The pilot monitoring project coordinated between the Department and the NDDH was conducted in 2006. Eleven sites were sampled twice from late June through August and tested for 63 different pesticides. Results showed one detection of picloram at a concentration of 0.23 parts per billion (ppb), which is below any level of concern established by the EPA for human health or aquatic life.

The Department, working in cooperation with the NDDH's Division of Water Quality, resumed a surface water monitoring survey in 2008 for pesticides and pesticide degradates. Nine sample sites in three different North Dakota basins (Sheyenne, Souris, and Yellowstone Rivers) were sampled and tested for 184 different pesticides and pesticide degradates every three weeks from April through October. A total of nine pesticides and one pesticide degradate were detected. The most commonly detected pesticides in 2008 were the herbicides 2,4-D and diuron. For all but one pesticide, concentrations were below levels deemed harmful by the EPA. Diuron was found in the Souris River in 2008 at concentrations that could be harmful to aquatic life, specifically green algae (Gray and Orr, 2009).

The pesticide water quality monitoring program received an increase in funding in 2009 through an EPA Clean Water Act Section 319 grant. Because of this grant, a later start date, and a six week sampling schedule instead of a three week schedule, the program was able to dramatically expand the number of sites sampled and make the program truly state-wide to represent every major North Dakota river basin. The 2009 sampling program consisted of sampling and testing 29 sites every six weeks for 180 different pesticides and pesticide degradates. Because the detections during the 2008 monitoring project were not found until June, the WQAC recommended 2009 sampling start in June and end in November. There were a total of eleven detections of four different pesticides, including atrazine, bentazon, dimethenamid, and MCPA. The most commonly detected pesticides were the herbicides atrazine and bentazon which were detected four and three times, respectively. MCPA and dimethenamid were each detected twice. Concentrations of all pesticides were below levels deemed harmful by the EPA (Gray and Orr, 2010).

EPA Clean Water Act Section 319 funds continued into 2010. Sampling sites were chosen from the NDDH's Ambient River and Stream Water Quality Monitoring Program sites to make the sampling most efficient. Thirty three sites were sampled every six weeks from April to October of 2010 and tested for 180 different pesticides and pesticide degradates. There were a total of 43 detections of 9 different pesticides, including 2,4-D; atrazine; bentazon; bifenthrin; clopyralid; dicamba; diuron; MCPA; and metolachlor. The most commonly detected pesticide in 2010 was bentazon, which was detected 22 times. Metolachlor and 2,4-D were each detected four times. For all pesticides, concentrations were below levels deemed harmful by the EPA (Gray and Orr, 2011).

In 2011, funding was directed to a wetland pesticide monitoring project. This report is still being finalized. Due to staffing shortage, no monitoring was performed by the Department in 2012.

2013 Project goals

The goals of the 2013 monitoring study were to:

- Determine the occurrence and concentration of pesticides in North Dakota rivers and streams
- Identify trends in pesticide contamination to guide regulatory activities
- Determine whether any pesticides may be present at concentrations that could adversely affect human health, aquatic life, or wildlife dependent on aquatic life
- Continue to evaluate the temporal and spatial frequency of sampling needed to assess contamination to further refine future pesticide monitoring program design

The Department will also use the monitoring data as part of its cooperative agreement with the EPA. Under that agreement, the Department has committed to evaluate a pre-defined list of national and local pesticides of interest that may pose a risk to water quality. The Department is required to demonstrate that any risks are appropriately managed. Results may also be used by the Endangered Species Protection Program and evaluations for special pesticide registrations.

MATERIALS AND METHODS

Pesticide samples and associated field measurements were collected six to seven times in 2013 at 30 sites from early April through late October. Locations of the sampling sites, site IDs, GPS coordinates, and agency responsible for sample collection can be found in Table 1 and Figure 1. Sample collection dates can be found in Table 2. Samples were scheduled to be collected twice in April, and once in May, June, July, August, and October. Realistically, dates were variable and dependent on weather, flooding, staffing, and the federal government shutdown. The 2013 pesticide surface water sampling program featured good representation of North Dakota's rivers and streams and correlated well with the heaviest pesticide use period.

Dissolved oxygen, temperature, pH, and specific conductivity were measured at the time of sampling using standardized, calibrated data loggers. Results were recorded in the field on a sample log form (Appendix A). Samples for pesticide analysis were collected in the main current below the surface at a depth of approximately 60 percent of the total water depth. This depth was chosen for sample collection as it is assumed to be representative of the entire stream. Samples were collected using weighted bottle samplers (WBSs) or by wading the site. A WBS consists of a stainless steel or fiberglass tube that is approximately seven inches long and four inches inside diameter, which is connected to a rope. Each pesticide sample bottle was filled by placing the sample bottle in the WBS and lowering the WBS into the water from a bridge. The WBS was lowered into the stream at a point where the stream is approximately at its greatest depth in the cross section. The WBS was then lowered to a depth equal to approximately 60 percent of the total stream depth. For example, if the stream was five feet deep at its deepest point in the streams cross section, the sample would be collected at that point at a depth three feet off the bottom. When the bottle was completely filled (i.e., no bubbles observed) the WBS and bottle were retrieved. The bottle was capped, removed from the WBS, labeled, and placed in a cooler on ice until shipment. When necessary, wadeable grab samples were collected by wading into the stream. When the sample was collected by wading, the stream was entered slightly down current from the sampling point and then the sampler waded to the area with the greatest current. The sample bottle was then submerged to approximately 60 percent of the stream depth; the cap removed and the bottle was allowed to fill facing towards the current, allowing it to fill naturally.

Once the bottle was filled, the cap was replaced prior to removing the bottle from the stream. The samples were carefully packed with bubble wrap and/or rubber mesh and put into a cooler with ice and more packing materials shortly after collection. Coolers containing samples and ice were shipped to the laboratory using a next-day shipping service within seven days of collection.

Each pesticide sample consisted of one, 1-L amber glass jar with caps featuring a 1/8” PTFE-faced silicone seal. Sample bottles arrived precleaned according to EPA procedure 1 methods for extractable organic, semivolatile, and pesticide analysis.

Selected field samples were collected in replicate to provide estimates of sample variability. The replicates consisted of one separate sample collected directly after the original sample was collected. Field blank samples were also collected by each sampling entity twice during the season. Field blanks consisted of blank water received from the NDDH’s Laboratory Division. The blank water was received in 1-L amber glass bottles with Teflon lined lids. At the time of sampling, the blank water was poured into a sampling bottle, the lid was placed on the bottle, and the bottle was labeled and placed in a cooler with ice.

Samples were analyzed for 99 different pesticides and degradates (Appendix B) by Montana State University’s Agriculture Experiment Station Analytical Laboratory. Montana’s laboratory developed a customized method titled the MTUniversal method. This method was initially developed to analyze samples for their groundwater monitoring program, but it also fit this project. The method is modeled after the successful USDA PDP Water Survey Program which uses the analytical approach to universalize one method to capture as many compounds as possible at the lowest possible levels with a broader range of acceptable performance. The method is validated according to the requirements of the MT 2008 EPA QAPP.

Table 1. 2013 North Dakota pesticide surface water monitoring project sites.

USGS site ID	NDDH site ID	Site name	Latitude	Longitude	Responsible agency
5051300	385055	Bois de Sioux River nr Doran, MN	46.1522	-96.5789	NDDH
5051510	380083	Red River at Brushville, MN	46.3695	-96.6568	NDDH
5053000	380031	Wild Rice River nr Abercrombie, ND	46.468	-96.7837	NDDH
5054000	385414	Red River at Fargo, ND	46.8611	-96.7837	USGS-GF
5057000	380009	Sheyenne River nr Cooperstown, ND	47.4328	-98.0276	NDDH
5058000*	380153*	Sheyenne River below Baldhill Dam, ND*	47.0339	-98.0837	NDDH
5058700	385168	Sheyenne River at Lisbon, ND	46.4469	-97.6793	NDDH
5059000	385001	Sheyenne River nr Kindred, ND	46.6316	-97.0006	NDDH
5060100	384155	Maple River below Mapleton, ND	46.9052	-97.0526	NDDH
5066500	380156	Goose River at Hillsboro, ND	47.4094	-97.0612	USGS-GF
5082500	384156	Red River at Grand Forks, ND	47.9275	-97.0281	USGS-GF
5083000	380037	Turtle River at Manvel, ND	48.0786	-97.1845	USGS-GF
5085000	380039	Forest River at Minto, ND	48.2858	-97.3681	USGS-GF
5090000	380157	Park River at Grafton, ND	48.4247	-97.412	USGS-GF
5100000	380158	Pembina River at Neche, ND	48.9897	-97.557	USGS-GF

5102490	384157	Red River at Pembina, ND	48.9769	-97.2376	USGS-GF
5114000	380091	Souris River nr Sherwood	48.99	-101.9582	USGS-Bis
5117500	380161	Souris River above Minot, ND	48.2458	-101.3713	USGS-Bis
5120000	380095	Souris River nr Verendrye, ND	48.1597	-100.7296	USGS-Bis
6336000	380022	Little Missouri River at Medora, ND	46.9195	-103.5282	NDDH
6337000	380059	Little Missouri River nr Watford City, ND	47.5958	-103.263	NDDH
6339500	384131	Knife River nr Golden Valley, ND	47.1545	-102.0599	NDDH
6340500	380087	Knife River at Hazen, ND	47.2853	-101.6221	NDDH
6345500	380160	Heart River nr Richardton, ND	46.7456	-102.3083	NDDH
6349000	380151	Heart River nr Mandan, ND	46.8339	-100.9746	NDDH
6351200	380105	Cannonball River nr Raleigh, ND	46.1269	-101.3332	NDDH
6353000	380077	Cedar Creek nr Raleigh, ND	46.0917	-101.3337	NDDH
6354000	380067	Cannonball River at Breien, ND	46.3761	-100.9344	NDDH
6468170	384130	James River nr Grace City, ND	47.5581	-98.8629	NDDH
6470000	380013	James River at Jamestown, ND	46.8897	-98.6817	NDDH
6470500	380012	James River at Lamoure, ND	46.3555	-98.3045	NDDH

* This site was not included in the original study design but was sampled in error one time. Data from this site is included in the report.

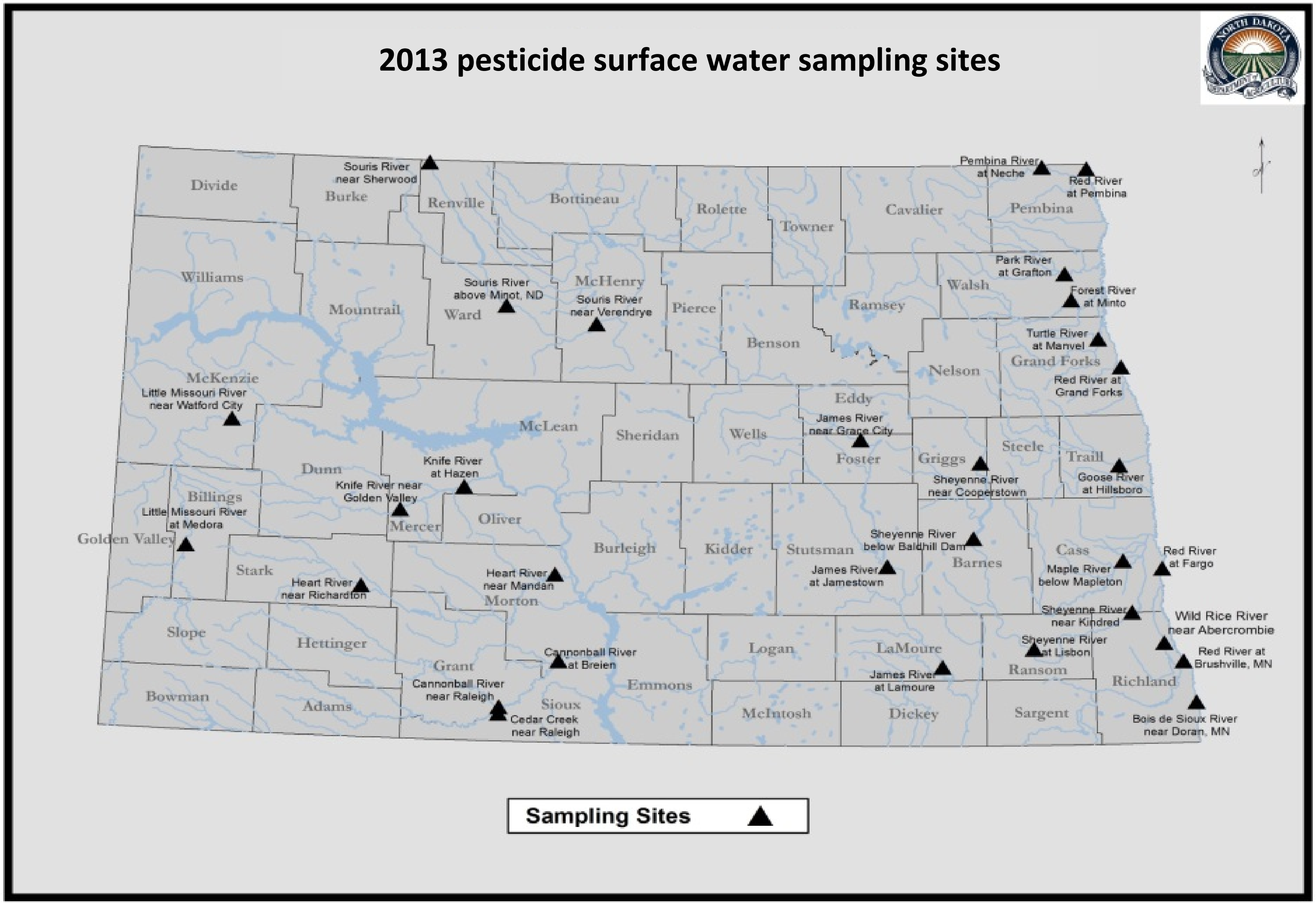
Table 2. 2013 North Dakota pesticide surface water monitoring sample collection dates.

Site ID	Sampling dates						
385055	4/30/2013	5/14/2013	5/29/2013	6/19/2013	7/15/2013	8/21/2013	10/14/2013
380083	4/30/2013	5/14/2013	5/29/2013	6/18/2013	7/15/2013	~~8/21/2013~~	10/14/2013
380031	4/30/2013	5/14/2013	5/29/2013	6/18/2013	7/15/2013	8/20/2013	10/14/2013
385414	4/30/2013	5/13/2013	6/11/2013	7/9/2013	8/12/2013	10/29/2013	
380009	5/1/2013	5/13/2013	5/29/2013	6/18/2013	7/16/2013	8/20/2013	10/15/2013
380153*							*10/15/2013**
385168	5/2/2013	5/14/2013	5/29/2013	6/18/2013	7/16/2013	8/20/2013	
385001	4/29/2013	5/15/2013	5/28/2013	6/18/2013	7/16/2013	8/20/2013	10/15/2013
384155	4/29/2013	5/13/2013	5/28/2013	6/17/2013	7/16/2013	8/19/2013	10/15/2013
380156	5/1/2013	5/13/2013	5/20/2013	6/10/2013	7/9/2013	7/29/2013	10/29/2013
384156	5/3/2013	4/28/2013	5/13/2013	6/12/2013	7/10/2013	8/20/2013	10/29/2013
380037	5/1/2013	5/29/2013	~~6/19/2013~~	7/8/2013	7/30/2013	10/28/2013	
380039	5/1/2013	5/29/2013	~~6/18/2013~~	7/8/2013	7/30/2013	10/28/2013	
380157	5/1/2013	5/8/2013	5/29/2013	6/18/2013	7/10/2013	7/30/2013	10/28/2013
380158	5/8/2013	5/21/2013	6/20/2013	7/10/2013	7/31/2013	10/30/2013	
384157	5/7/2013	5/22/2013	5/28/2013	6/19/2013	7/10/2013	7/31/2013	10/30/2013
380091	4/22/2013	5/9/2013	6/6/2013	6/12/2013	7/8/2013	8/26/2013	10/30/2013
380161	4/22/2013	5/7/2013	5/29/2013	6/13/2013	7/8/2013	8/29/2013	10/31/2013

380095	4/23/2013	5/7/2013	5/28/2013	6/11/2013	7/9/2013	8/27/2013	10/29/2013
380022	4/23/2013	5/7/2013	5/21/2013	6/11/2013	7/9/2013	8/13/2013	10/9/2013
380059	4/23/2013	5/7/2013	5/21/2013	6/11/2013	7/9/2013	8/13/2013	10/9/2013
384131	4/23/2013	5/7/2013	5/21/2013	6/11/2013	7/9/2013	8/13/2013	10/9/2013
380087	4/23/2013	5/7/2013	5/21/2013	~~6/11/2013~~	7/9/2013	8/13/2013	10/9/2013
380160	4/23/2013	5/7/2013	5/21/2013	~~6/11/2013~~	7/9/2013	8/13/2013	10/9/2013
380151	4/23/2013	5/8/202013	5/22/2013	6/10/2013	7/10/2013	8/14/2013	10/9/2013
380105	4/23/2013	5/8/2013	5/22/2013	6/10/2013	7/10/2013	8/14/2013	10/10/2013
380077	4/23/2013	5/8/2013	5/22/2013	6/10/2013	7/10/2013	8/14/2013	10/10/2013
380067	4/23/2013	5/8/2013	5/22/2013	6/10/2013	7/10/2013	8/14/2013	10/10/2013
384130	5/1/2013	5/13/2013	5/29/2013	6/18/2013	7/16/2013	8/20/2013	10/15/2013
380013	5/1/2013	5/13/2013	5/30/2013	6/19/2013	7/17/2013	8/20/2013	
380012	5/2/2013	5/14/2013	5/30/2013	6/19/2013	7/16/2013	8/20/2013	10/14/2013

* This site was not included in the original study design but was sampled in error one time. Data from this site is included in the report.
-Strikethrough indicates sample arrived at the lab broken.

Figure 1. 2013 pesticide surface water sampling sites.



RESULTS AND DISCUSSION

There were a total of 200 samples analyzed for 99 different pesticides. Of the 99 pesticides analyzed, 68 different pesticides were present in at least one of the samples. Several pesticides were present in a high percentage of the samples as indicated in Table 3. Atrazine; 2,4-D; prometon; tebuconazole; and bentazon were present in over 70% of the samples collected. Although these pesticides were present in 70% or more of samples collected, a high percentage of the detections were at levels well below a level that may impact aquatic ecosystems or human health.

Table 3. Common pesticides detected in North Dakota surface waters in 2013.

Common pesticides detected in ND surface water in 2013						
	Quantifiable detections		**Qs (present but below reporting limit)**		**Total samples with quantifiable detections and Qs**	
Analyte	**Number**	**Percent of all samples**	**Number of Qs**	**Percent of all samples**	**Number**	**Percent of all samples**
Atrazine	189	94.50	11	5.50	200	100.00
Deethyl atrazine (atrazine breakdown product)	176	88.00	21	10.50	197	98.50
2,4-D	142	71.00	44	22.00	186	93.00
Hydroxy atrazine (atrazine breakdown product)	117	58.50	55	27.50	172	86.00
Prometon	94	47.00	51	25.50	145	72.50
Tebuconazole	68	34.00	76	38.00	144	72.00
Bentazon	141	70.50	0	0.00	141	70.50
Deisopropyl atrazine (atrazine breakdown product)	44	22.00	82	41.00	126	63.00
Metolachlor ESA (metolachlor breakdown product)	104	52.00	19	9.50	123	61.50
Acetochlor OA (acetochlor breakdown product)	105	52.50	13	6.50	118	59.00
MCPA	46	23.00	68	34.00	114	57.00
Acetochlor ESA (acetochlor breakdown product)	96	48.00	15	7.50	111	55.50
Imazethapyr	79	39.50	31	15.50	110	55.00
IMAM (imazamethabenz methyl acid metabolite)	61	30.50	43	21.50	104	52.00
Dimethenamid	66	33.00	31	15.50	97	48.50
Metolachlor	67	33.50	29	14.50	96	48.00
Dimethenamid OA (dimethenamid breakdown product)	42	21.00	39	19.50	81	40.50
Metalaxyl	14	7.00	61	30.50	75	37.50
Azoxystrobin	37	18.50	37	18.50	74	37.00

Data were compared to EPA established aquatic life benchmark (ALB) values and human health maximum contaminant level (MCL) values. Detections at 20% or more of the lowest of either of these values were further reviewed. There were 30 detections of 6 pesticides detected at 20% or more of the lowest value. All six pesticides were herbicides and included two 2,4-D detections, two acetochlor detections, eighteen atrazine detections, one dimethenamid detection, one diuron detection, and six metolachlor detections as detailed in Table 4.

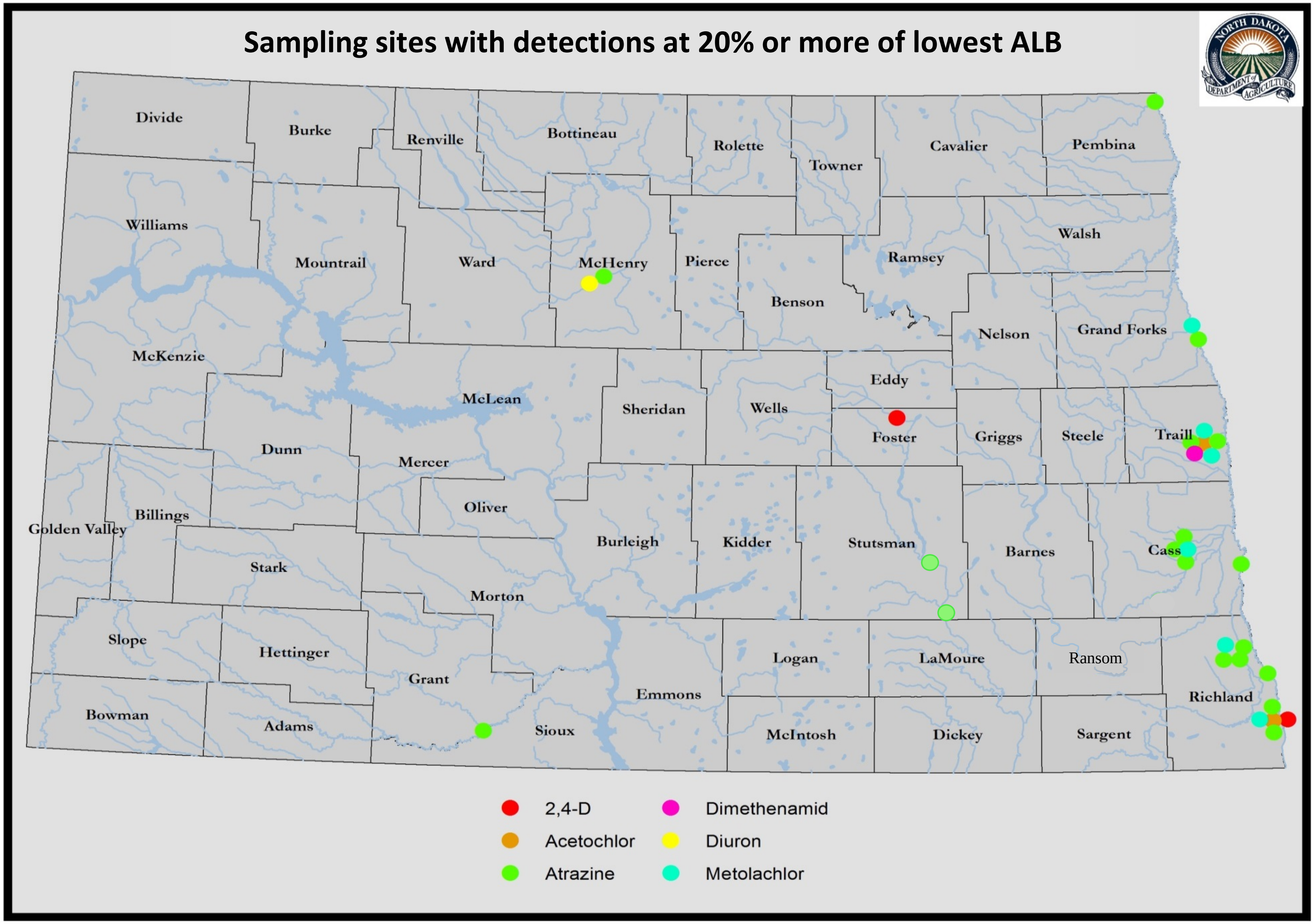
Table 4. Detections that were 20% or more of lowest ALB.

Detections that were 20% or more of lowest aquatic life benchmark (ALB)			
Analyte	Detections	Range of Detections (ppb)	ALB (ppb)
2,4-D	2	4.2-46.0	13.10
Acetochlor	2	0.46-0.76	1.43
Atrazine	18	0.2-1.8	1.00
Dimethenamid	1	3.1	8.90
Diuron	1	0.88	2.40
Metolachlor	6	0.23-0.54	1.00

There were 13 sites in which these chemicals were found at 20% or more of an ALB (Figure 2). The majority of the 13 sites are in the eastern third of North Dakota with the Red River basin containing the largest concentration of detections at 20% or more of the lowest ALB. Within the Red River basin, the Goose River sampled at Hillsboro, ND had six detections; the pesticides detected were acetochlor, atrazine (two detections), dimethenamid, and metolachlor (two detections). The Bois de Sioux River sampled near Doran, MN had five detections; the pesticides detected were 2,4-D, acetochlor, atrazine (two detections), and metolachlor. The Wild Rice River sampled near Abercrombie, ND had four detections; the pesticides detected were atrazine (three detections) and metolachlor. The Maple River below Mapleton ND had four detections; the pesticides detected were atrazine (three detections) and metolachlor. The Red River at Grand Forks, ND had two detections; the pesticides detected were atrazine and metolachlor. The following sites had one atrazine detection each: the James Rivers sampled at Jamestown, ND; the James River at Lamoure, ND; the Red River sampled at Brushville, MN; the Red River sampled at Pembina, ND; and the Red River sampled at Fargo, ND.

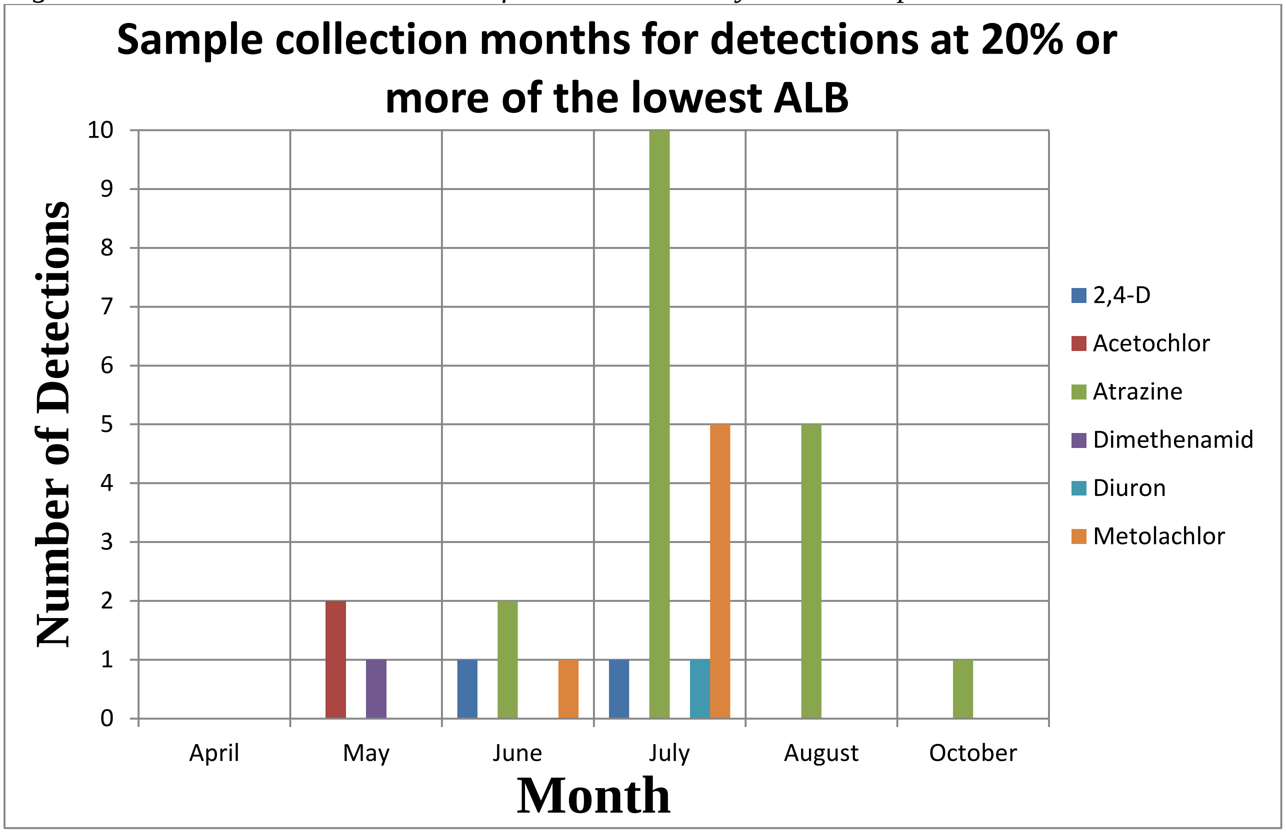
Outside of the Red River basin, the Souris River sampled near Verendrye, ND had two detections; the pesticides detected were atrazine and diuron. The Cannonball River sampled near Raleigh, ND had one atrazine detection and the James River sampled near Grace City, ND had one 2,4-D detection.

Figure 2. Sampling sites where pesticides were detected at 20% or more of lowest ALB.



There were 30 pesticide detections at concentrations of 20% or more of the lowest ALB (Figure 3). There were no detections of pesticides at 20% or more of the lowest ALB in April. The only pesticides detected at or above 20% of the lowest ALB in May were acetochlor and dimethenamid, and May was the only month these two pesticides were detected above this level. June featured one detection of 2,4-D, two detections of atrazine, and one detection of metolachlor at 20% or more of an ALB. July had the most pesticide detections at 20% or more of an ALB with one 2,4-D detection, ten atrazine detections, one diuron detection, and five metolachlor detections. June and July were the only months that 2,4-D and metolachlor were detected at 20% or more of the lowest ALB. The only pesticide found in August and October at 20% or more of the lowest ALB was atrazine.

Figure 3. Detections at 20% or more of the lowest ALB by month sample was collected.



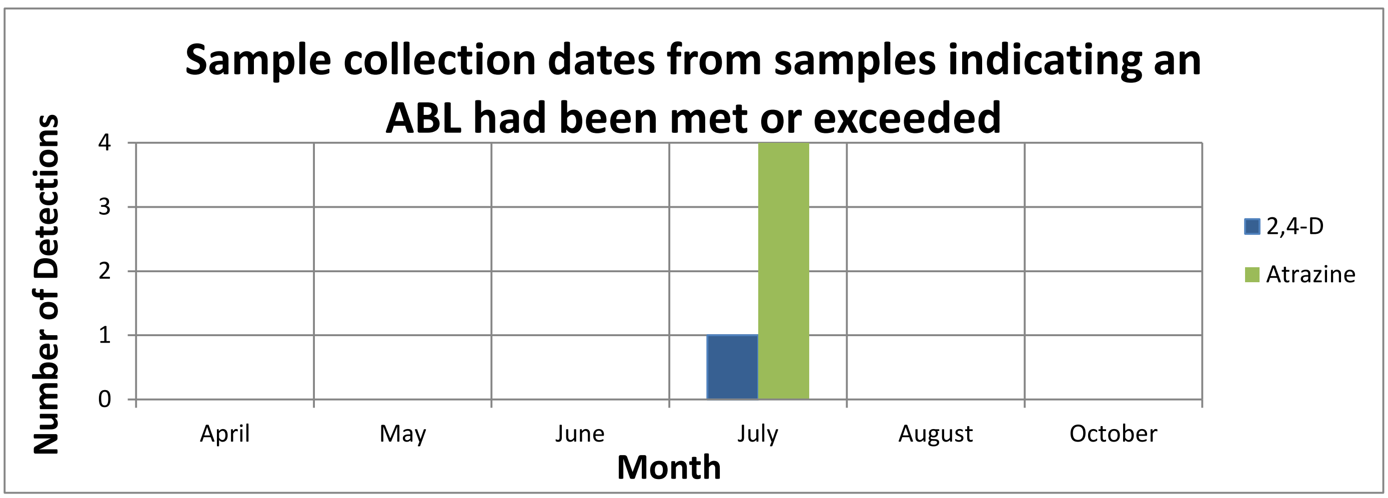
No pesticides were detected at concentrations exceeding an MCL, although there were five detections at or above an ALB (Table 4). Looking at values at or above 20% of an ALB is a very conservative means to filter data and does not automatically indicate significant risk to aquatic ecosystems. In looking for levels that may pose risk, results were further reviewed to identify instances in which an ALB or MCL had been exceeded. No detections indicated an MCL had been exceeded, but five detections indicated an ALB may have been exceeded. ALBs are commonly based on continuous exposure to a pesticide over several days. The pesticide sampling program does not provide continuous monitoring but consists of several snapshots in time. Because of this, it is impossible to say for certain that ALBs are truly exceeded.

Table 4. Detections indicating an aquatic life benchmark (ALB) was met or exceeded.

Detections that indicated an aquatic life benchmark (ALB) was met or exceeded				
Site Name	Site ID	Analyte	Detected level (ppb)	ALB (ppb)
Maple River below Mapleton, ND	384155	Atrazine	1.6	1.0
Red River at Fargo, ND	385414	Atrazine	1.3	1.0
Red River at Pembina, ND	384157	Atrazine	1.0	1.0
Wild Rice River near Abercrombie, ND	380031	Atrazine	1.8	1.0
James River near Grace City, ND	384130	2,4-D	46.0	13.1

All five samples indicating an ALB had been met or exceeded were collected in July (Figure 4). The fact that these pesticides were detected in July is not surprising considering 2013 featured a wet spring with late planting dates. Both atrazine and 2,4-D are herbicides commonly applied shortly before or shortly after planting and would typically require some amount of time to be moved off site.

Figure 4. Sample collection dates from samples indicating lowest ALB had been met or exceeded.



Data were reviewed to determine if the pesticide level was increasing before the spike (detection that indicated an ALB had been met or exceeded) and how quickly the level dissipated after the spike (Table 5). All but one of the spikes had very low levels before and after the spike, indicating that the concentration was not found for an extended period of time. Atrazine was found at the Wild Rice River near Abercrombie, ND at 1.8 ppb on July 15th and at 0.76 ppb on August 20th. This indicates that atrazine may have been present at a level approaching the ALB for several days. Given that current EPA guidance gives a value of 10 ppb over 60 days of continuous exposure to atrazine to have aquatic community effects, the duration and level of the spike is well below a level that will harm aquatic communities.

Table 5. Results at sites where a sample indicated an ALB was met or exceeded of the specific pesticide and each sampling event.

Results at sites where a sample indicated an ALB was met or exceeded of the specific pesticide and each sampling event							
Maple River below. Mapleton ND							
Date (2013)	4/29	5/13	5/28	6/17	7/16	8/19	10/15
Atrazine Detections (ppb)	0.11	0.16	0.075	0.21	**1.6**	0.22	0.090
Red River at Fargo ND							
Date (2013)	4/30	5/13	6/11	7/9	8/12	10/29	
Atrazine Detections (ppb)	0.022	0.030	0.073	**1.3**	0.17	0.047	
Red River at Pembina ND							
Date (2013)	5/7	5/22	5/28	6/19	7/10	7/31	10/30
Atrazine Detections (ppb)	0.022	0.015	0.080	0.071	**1.0**	0.17	0.039
Wild Rice near Abercrombie ND							
Date (2013)	4/30	5/14	5/29	6/18	7/15	8/20	10/14
Atrazine Detections (ppb)	0.025	0.070	0.15	0.11	**1.8**	0.76	0.21
James River nr. Grace City							
Date (2013)	5/1	5/13	5/29	6/18	7/16	8/20	10/15
2,4-D Detections (ppb)	0.036	0.039	0.013	0.0091	**46.0**	0.0063	0.0065

Further ALB discussion
The EPA has established ALBs for several chemicals, relying on studies required under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), as well as a wide range of environmental, laboratory, field studies, and modeling available in published scientific literature. ALBs, which are based on the most sensitive toxicity endpoint for a given taxa, are estimates of the concentrations below which pesticides are not expected to harm aquatic life. ALBs are typically based on continuous exposure over a window of time, such as 96 hours or more depending on the chemical. EPA-established ALBs are guidance for states to use and are not regulatory thresholds. NDDA sampling consists of one grab sample, so essentially it is one point in time and is difficult to correlate with a true ALB. In most cases, the Department was able to compare the concentration detected in surface water to the EPA-established ALB as a reference. Any value that exceeded an ALB constitutes an indication of exceedance and does not constitute a true exceedance as samples are not collected the same as in the established ALB.

Estimates of pesticide use and detections
Detections were compared to pesticide use throughout the state. The information is derived from a comprehensive survey of North Dakota farm operators on 2008 practices conducted by USDA's National Agricultural Statistics Service (NASS) in the spring of 2009. Data were summarized by obtaining percent total acres of each crop treated with specific chemicals and multiplying this percentage by acres of specific crops grown per county in 2008.

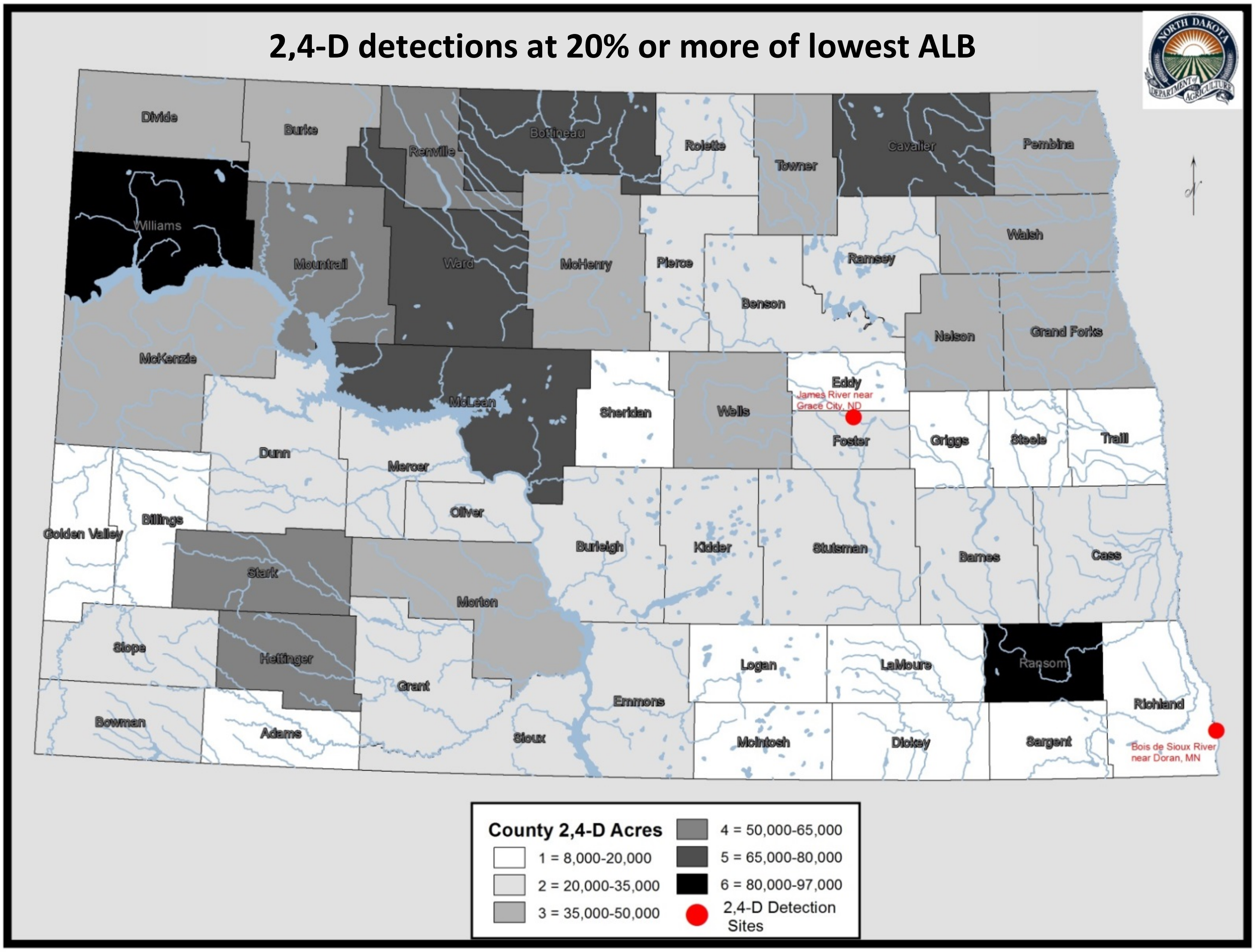
Diuron
Diuron is a broad-spectrum residual herbicide registered for pre-emergence and post-emergence control of both broadleaf and annual grassy weeds. In North Dakota, it is not commonly used in agricultural settings. Diuron is believed to be used more commonly in rights of ways and as a soil sterilant, but this usage is not tracked and no county estimates were possible. Diuron was detected at 20% or more of an ALB once in 2013. The lowest EPA established ALB is 2.4 ppb for acute aquatic non-vascular plants and is representative of the toxicity value times the level of concern (LOC, value is 1). The toxicity value is based on an EC50 (estimated concentration that kills 50% of a population over a short-term (less than 10 days)) and typically green algae or diatoms are the surrogate species. The highest concentration detected was 0.88 ppb which is 2.7 times less than the ALB. This indicates minimal risk to aquatic ecosystems. There is no EPA established drinking water standard for diuron.

2,4-D
2,4-D was present in 93% of the samples collected in 2013, twice at concentrations 20% or more of an ALB. 2,4-D is a systemic herbicide used to control broadleaf weeds in wheat, barley, oats corn, sunflowers, alfalfa, hay, CRP, pastures, rights of way and in residential settings. In agriculture, 2,4-D is used on approximately 1,861,500 acres in ND as a stand-alone product and 349,100 acres as a mixture (Zollinger et al. 2009). The amount used in urban areas and rights of way is not known. Given this information, it is very difficult to estimate total use per county.

There were two 2,4-D detections at 20% of the lowest EPA ALB, one on the James River near Grace City, ND and one on the Bois de Sioux River near Doran, MN (Figure 5). Neither detection was in a county with high 2,4-D use.

The lowest EPA established ALB for 2,4-D is 13.10 ppb for acute vascular plants and is representative of the toxicity value times the level of concern (LOC, value is 1). The toxicity value is based on an EC50 (estimated concentration that kills 50% of a population over a short-term (less than 10 days)), and duckweed is typically the surrogate species. The highest concentration detected was 46 ppb, exceeding the ALB value by 3.5 times. As stated earlier, the sample is a snapshot in time, and for an ALB to be truly exceeded, 2,4-D would need to be monitored continuously for up to 10 days and exceed 13.10 ppb continuously during that time. Samples from the site before and after the 46 ppb detection were well below the 13.10 ppb ALB. The drinking water MCL for 2,4-D is 70 ppb. The highest concentration detected is approximately 1.5 times lower than the MCL, suggesting that the detected concentration does not pose a significant risk to human health.

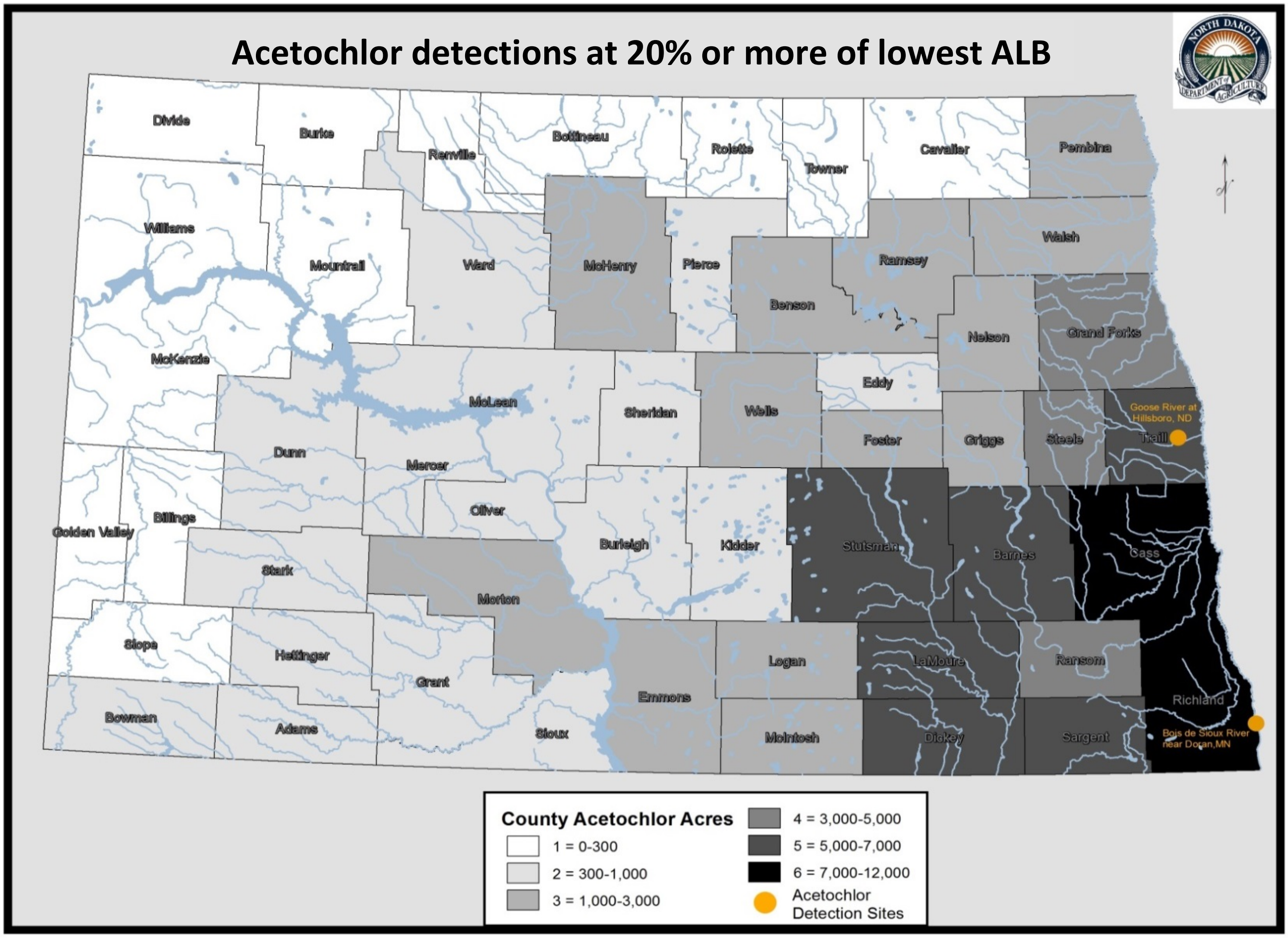
Figure 5. Sampling locations where 2,4-D was detected at 20% or more of lowest EPA ALB.



Acetochlor

Acetochlor is a herbicide used primarily on corn and is applied to approximately 68,300 acres as a stand-alone product and to an additional 75,200 acres in mixtures in North Dakota each year. (Zollinger et al. 2009). Acetochlor was detected at 20% or more of an ALB twice in 2013, both times in counties with relatively high levels of estimated acetochlor use (Figure 6). Acetochlor breakdown products were detected or present in 50%-60% of samples. The lowest EPA established ALB for acetochlor is 1.43 ppb for acute aquatic non-vascular plants and is representative of the toxicity value times the level of concern (LOC, value is 1). The toxicity value is based on an EC50 (estimated concentration that kills 50% of a population over a short-term (less than 10 days)) and typically green algae or diatoms are the surrogate species. The highest concentration detected was 0.76 ppb, which is 1.9 times less than the ALB. This indicates minimal environmental risk. There is no EPA established drinking water standard for Acetochlor.

Figure 6. Sampling locations where acetochlor was detected at 20% or more of lowest EPA ALB.

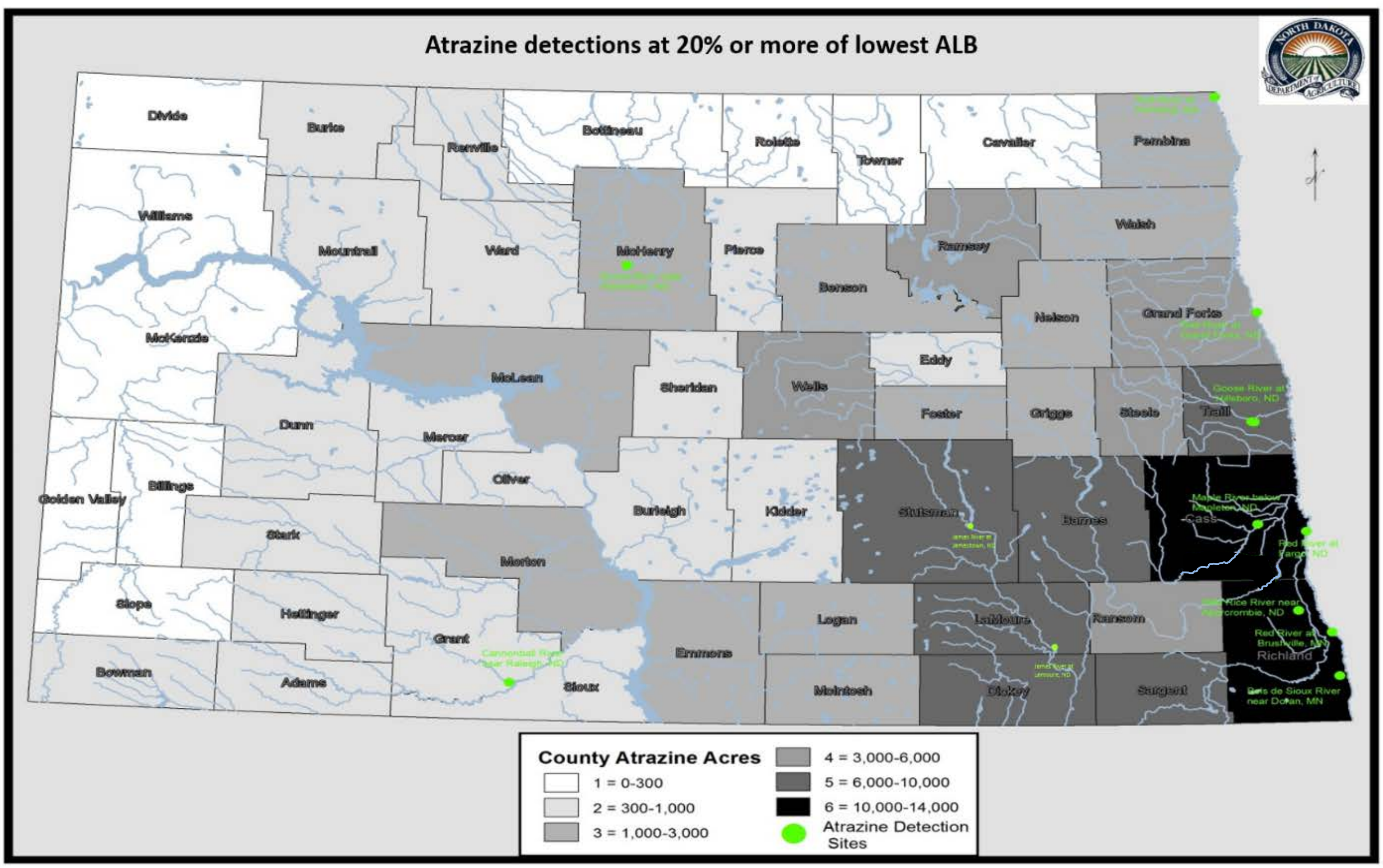


Atrazine

Atrazine, a broadleaf herbicide used primarily on corn, is applied to approximately 59,500 acres as a stand-alone product and to an additional 113,800 acres in mixtures in North Dakota each year (Zollinger et al. 2009). Atrazine was detected in 94.5% (189) and present in the remaining 5.5% (11) of samples. Of those detections, 18 of them were at 20% or more of an ALB. Most atrazine detections at 20% or more of the lowest ALB were in counties with high atrazine estimated use (Figure 7). Atrazine detections indicated an ALB was met or exceeded 4 times with values of 1.8 ppb, 1.6 ppb, 1 ppb, and 1.3 ppb.

The lowest EPA established ALB is 1 ppb for acute aquatic non-vascular plants and is representative of the toxicity value times the level of concern (LOC, value is 1). The toxicity value is based on an EC50 (estimated concentration that kills 50% of a population over a short-term (less than 10 days)), and green algae or diatoms are typically the surrogate species. The highest concentration detected was 1.8 ppb, exceeding the ALB value by 1.8 times. As stated earlier, the sample is a snapshot in time, and for a ALB to be truly exceeded, atrazine would need to be monitored continuously for up to 10 days and exceed 1 ppb continuously. The drinking water MCL for atrazine is 3 ppb. The highest concentration detected is approximately 1.7 times lower than the MCL. Given the ALB is a very conservative value and detections were well under levels that begin to affect aquatic communities, detections do not indicate a significant risk to human health or the environment.

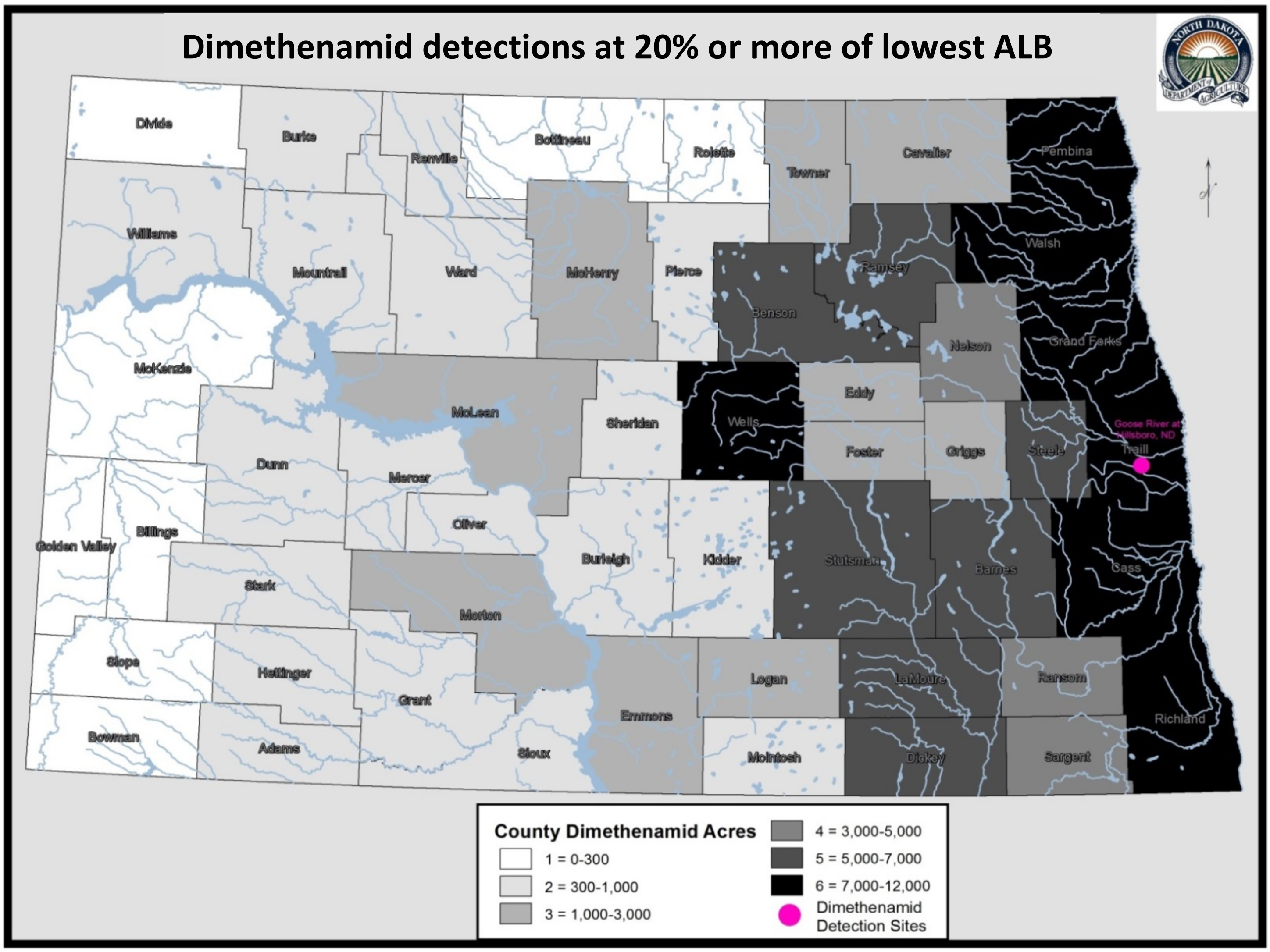
Figure 7. Sampling locations where atrazine was detected at 20% or more of lowest EPA ALB.



Dimethenamid

Dimethenamid is typically used as a pre-emergent herbicide to control grasses, sedges, and some broadleafs on corn and dry beans. It is applied to approximately 145,400 acres as a stand-alone product in North Dakota each year (Zollinger et al. 2009). Dimethenamid was present in 48.5% of samples, one of which was at 20% or more of an ALB. This detection was in a county of high estimated use (Figure 8). The lowest EPA established ALB is 8.9 ppb for acute vascular plants and is representative of the toxicity value times the level of concern (LOC, value is 1). The toxicity value is based on an EC50 (estimated concentration that kills 50% of a population over a short-term (less than 10 days)) and typically duckweed is the surrogate species. The highest concentration detected was 3.1 ppb which is 2.9 times less than the ALB. This indicates minimal risk to aquatic ecosystems. There is no EPA established drinking water standard for dimethenamid.

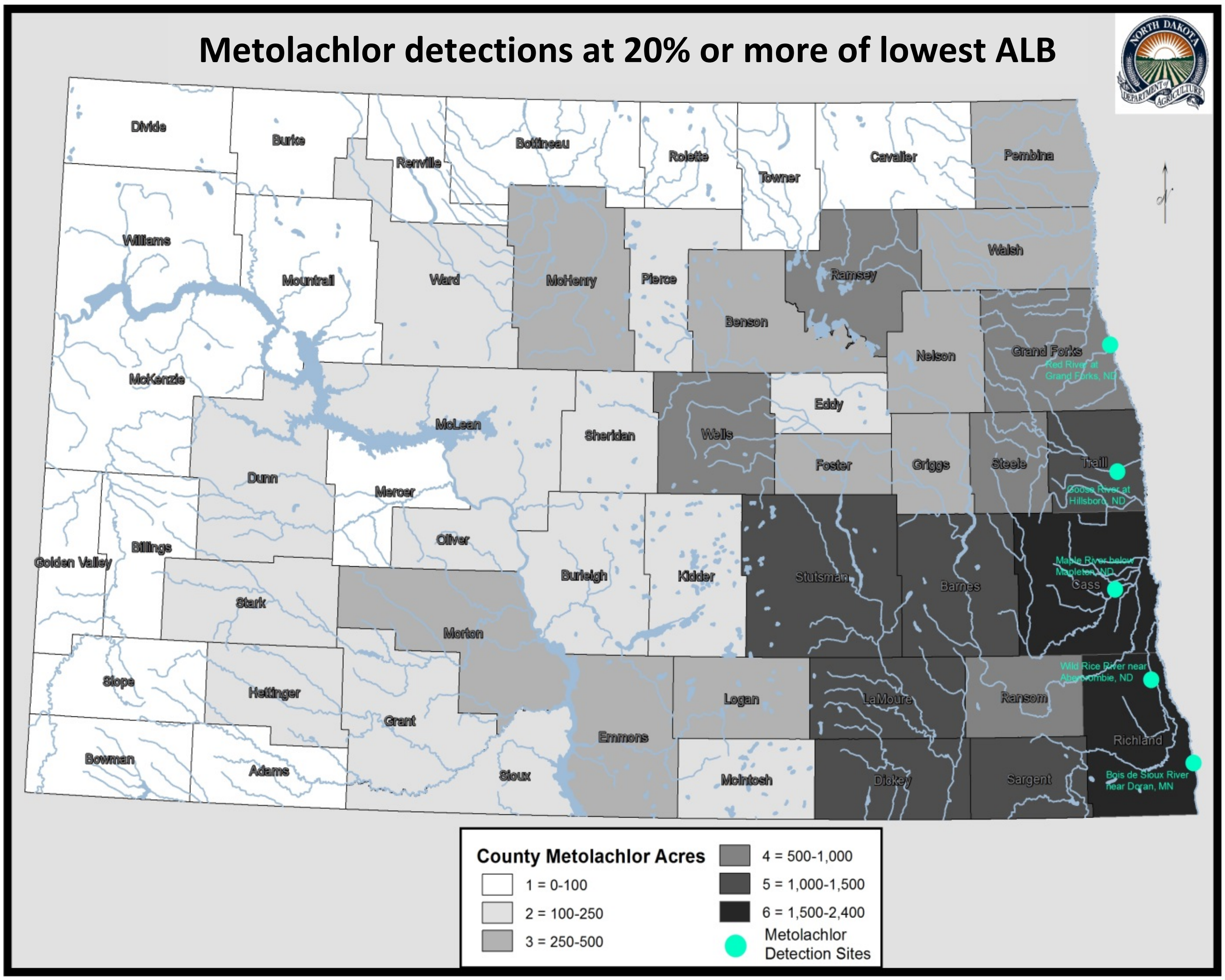
Figure 8. Sampling locations where dimethenamid was detected at 20% or more of lowest EPA ALB.



Metolachlor

Metolachlor is used primarily on corn in North Dakota for grass and broadleaf weed control. Metolachlor's primary use is in a mix with atrazine and mesotrione on an estimated 21,800 acres in North Dakota in 2008 (Zollinger et al. 2009). Metolachlor and metolachlor degradates were detected or present in as high as 61% of samples. Metolachlor was detected at 20% or more of an ALB six times in 2013, all in counties with high estimates of metolachlor use (Figure 9). The lowest EPA established ALB is 1 ppb for chronic risk to invertebrates and is representative of the toxicity value times the level of concern (LOC, value is 1). The toxicity value is based on the lowest no observed adverse effects concentration (NOAEC) from a life-cycle test with invertebrates (usually with midge, scud, or daphnids). The highest concentration detected was 0.54 ppb, which is 1.9 times less than the ALB. This indicates minimal risk to aquatic ecosystems. There is no EPA established drinking water standard for metolachlor.

Figure 9. Sampling locations where metolachlor was detected at 20% or more of lowest EPA ALB.



Conclusion

Results of the 2013 monitoring study indicate that pesticides are not being found in North Dakota rivers and streams at levels posing a risk of unreasonable adverse effects on human health or the environment. Results further illustrate that current approaches are effective in mitigating the risk of pesticide contamination of surface water. Sampling frequency and laboratory analysis changed in 2013, and as a result there were several more detections than in previous years. Detections ranged widely in level and frequency based on the pesticide, with a very large percentage being near the laboratory's reporting limits.

The need for continued sampling is of upmost importance not only to continue to ensure rivers and streams in ND are safe, but also to identify trends and build on the existing data set. Levels of atrazine, 2,4-D, prometon, tebuconazole, and bentazon need to continue to be monitored. Although these pesticides do not pose a risk at this time, sampling shows they are present in a high percentage of samples, some approaching levels that may impact aquatic ecosystems. It is imperative to monitor, and if necessary, implement risk mitigation before problems are found. Mitigation measures could include increased use inspections focused on specific pesticides, increased user education and compliance assistance, and site-specific or chemical-specific use restrictions.

The Department has addressed problematic pesticide detections before. For example, diuron was found in the Souris River in 2008 at a concentration posing a risk to aquatic ecosystems. The Department conducted investigations and outreach to the area following the 2008 detections. There were no detections of diuron in the Souris River in 2009 and 2010. Despite the inherent uncertainty of the cause of the diuron decrease, this is an excellent example of how a monitoring system can be useful in finding and mitigating a previously unnoticed problem.

Comparing river and stream data from 2008, 2009, 2010, and 2013 showed a few potential trends. In the eastern third of the state, atrazine was detected once in 2008, three times each in 2009 and 2010, and was present in all of the samples in 2013. This is not surprising since atrazine is predominantly used on corn and a large portion of acres planted in the Red River valley are planted in corn. In addition, use of atrazine and other herbicides has likely increased due to the expansion in acres infested with glyphosate-resistant weeds. Another trend across all four years of data reveals the highest number of detections comes from samples collected in June through August. This is also not surprising as the majority of pesticides detected are pre-emergence herbicides which are typically applied around planting and take several weeks to move into surface water.

This project is the only state-wide comprehensive surface water monitoring project for pesticides in North Dakota. Just as sampling in 2013 revealed more information as laboratory testing capabilities improved, technology will continue to advance in the future. Resources permitting, the Department will continue to work with its state and federal partners to monitor surface water for pesticides to ensure that pesticides are not negatively impacting water resources. These data are also effective in demonstrating the effectiveness of current approaches and to argue against unnecessary use restrictions. If impairments of rivers are found, these can be addressed through education and if necessary, regulation. This mix of compliance assistance and regulatory oversight has been shown to be highly effective, especially when supported by sound data.

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Preservation: Yes ☐	Temperature:
Initials:	

Sample Identification Record
North Dakota Department of Health Telephone: 701.328.6140
Division of Laboratory Services–Chemistry Fax: 701.328.6280

Sample Collection/Billing Information						
Account #	**Project Code:**		**Project Description:** Ambient Water Quality Monitoring			
Collected By:						
Analyte Groups:		**Collection Method:** Grab			**Matrix:** Water	
For Laboratory Use Only Lab ID:	Site ID:		Site Description:		**DO**	**pH**
	Date Collected:	Time Collected:	Depth (m): Surface	Comments:	**Temp.**	**SC**
	Site ID:		Site Description:		**DO**	**pH**
	Date Collected:	Time Collected:	Depth (m): Surface	Comments:	**Temp.**	**SC**
	Site ID:		Site Description:		**DO**	**pH**
	Date Collected:	Time Collected:	Depth (m): Surface	Comments:	**Temp.**	**SC**
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	Site ID:		Site Description:		**DO**	**pH**
	Date Collected:	Time Collected:	Depth (m): Surface	Comments:	**Temp.**	**SC**

Appendix B. List of analytes and reporting limits.

List of analytes 2013			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit ppb**
2,4-D	2,4-D, Curtail	H	0.00450
3-OH Carbofuran	Furadan	D	0.01000
Acetochlor	Surpass, Harness	H	0.14000
Acetochlor ESA	degradate	D	0.01000
Acetochlor OA	degradate	D	0.00420
Alachlor	Intrro, Lariat, Lasso	H	0.11000
Alachlor ESA	degradate	D	0.01100
Alachlor OA	degradate	D	0.00340
Aldicarb	Temik	I	0.06500
Aldicarb sulfone	degradate	D	0.02200
Aldicarb sulfoxide	degradate	D	0.05600
AMBA (mesotrione metabolite)	degradate	D	0.02100
Aminocyclopyrachlor	Method, Perspective	H	0.02500
Aminopyralid	Cleanwave	H	0.01500
Atrazine	Aatrex	H	0.00220
Azoxystrobin	Quadris	F	0.00260
Bentazon	Basagran	H	0.00110
Bromacil	Hyvar, Bromax	H	0.00410
Bromoxynil	Huskie, Buctril	H	0.00600
Carbaryl	Sevin, Savit	I	0.00400
Chlorpyrifos	Lorsban, Dursban	I	0.03100
Chlorsulfuron	Finesse, Glean	H	0.00560
Clodinafop acid	Discover NG	H	0.01300
Clopyralid	Stinger, Curtail	H	0.02200
Clothiandin	Poncho	I	0.01600
Deethyl atrazine	degradate	D	0.00170
Deethyl Deisopropyl Atrazine (DEDIA)	degradate	D	0.10000
Deisopropyl atrazine	degradate	D	0.01000
Dicamba	Banvel	H	0.22000
Difenoconazole	CruiserMaxx, InspireF		0.01100
Dimethenamid	Outlook	H	0.00300
Dimethenamid OA	degradate	D	0.00380
Dimethoate	Cygon, Roxion	I	0.00110
Disulfoton sulfone	degradate	D	0.00660

List of analytes 2013			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit ppb**
Diuron	Direx, Karmex	H	0.00530
Fenbuconazole	Indar	F	0.00530
Fipronil	Regent	I	0.00120
Flucarbazone	Everst, Prepare	H	0.00120
Flucarbazone sulfonamide (FSA)	degradate	D	0.00097
Flumetsulam	Python	H	0.02900
Fluroxypyr	Starane	H	0.01600
Glutaric Acid	degradate	D	0.00740
Hydroxy atrazine	degradate	D	0.00400
Halosulfuron methyl	Permit	H	0.00600
Hexazinone	Velpar	H	0.00150
Imazamethabenz methyl acid metabolite (IMAM)	degradate	D	0.00250
Imazamethabenz methyl ester (IME)	degradate	D	0.00100
Imazamox	Raptor, Beyond	H	0.00570
Imazapic	Plateau	H	0.00300
Imazapyr	Imazapyr, Lineage	H	0.00350
Imazethapyr	Authority Assist, Pursuit	H	0.00400
Imidacloprid	Touchstone PF	I	0.00180
Isoxaflutole	Corvus, Balance Flexx	H	0.13000
Linuron	Linex, Lorox	H	0.00540
Malathion	Malathion, Cythion	I	0.02800
Malathion oxon	degradate	D	0.00120
MCPA	MCP	H	0.00230
MCPP	Encore, Trimec	H	0.00220
Metalaxyl	Hi-Yield, Ridomil	F	0.00350
Methomyl	Lannate	I	0.00160
Methoxyfenozide	Intrepid	I	0.00230
Metolachlor	Dual Magnum	H	0.01200
Metolachlor ESA	degradate	D	0.00250
Metolachlor OA	degradate	D	0.02100
Metsulfuron methyl	Ally, Cimarron	H	0.01000
Nicosulfuron	Accent, Steadfast	H	0.01100
NOA 407854 (Pinoxaden metabolite)	degradate	D	0.00520
NOA 447204 (Pinoxaden metablolite)	degradate	D	0.01000
Norflurazon	Solicam	H	0.02000

List of analytes 2013			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit ppb**
Norflurazon desmethyl	degradate	D	0.02000
Oxamyl	Vydate	I	0.01000
Parathion methyl oxon	degradate	D	0.01200
Phorate sulfone	degradate	D	0.00610
Phorate sulfoxide	degradate	D	0.00150
Picloram	Tordon	H	0.14000
Prometon	Pramitol	H	0.00100
Propiconazole	Banner, Tilt, Radar	F	0.01000
Prosulfuron	Peak, Spirit	H	0.00500
Pyrasulfatole	Huskie, Wolverine	H	0.00930
Pyroxsulam	GR1, Powerflex	H	0.01300
Saflufenacil	Sharpen	H	0.01000
Simazine	Princep	H	0.00260
Sulfentrazone	Spartan	H	0.03500
Sulfometuron methyl	Lineage, Oust	H	0.00250
Sulfosulfuron	Maverick, Outrider	H	0.00540
Tebuconazole	Folicur	F	0.00700
Tebuthiuron	Spike	H	0.00110
Tembotrione	Capreno, Laudis	H	0.01800
Terbacil	Sinbar	H	0.00240
Terbufos sulfone	degradate	D	0.00530
Tetraconazole	Domarck, Eminent	F	0.00390
Thiamethoxam	CruiserMaxx, Meridian	I	0.02000
Thifensulfuron	Supremacy Harmony	H	0.01100
Tralkoxydim	Achieve	H	0.00510
Tralkoxydim acid	degradate	D	0.00500
Triallate	Far-Go	H	0.30000
Triasulfuron	Dally, Rave	H	0.00550
Tricolpyr	Garlon	H	0.01100
Triticonazole	Pillar, Trinity	F	0.01600

*Common trade names do not represent all trade names containing an active ingredient. Trade names chosen are for example purposes only and this list is not endorsing or making any recommendations.

H=Herbicide; I=Insecticide; F=Fungicide; D=Degradate (breakdown product)

Appendix C. List of detections that were 20% or more of an aquatic life benchmark.

Detections that were 20% or more of an aquatic life benchmark					
Site Name	Site ID	Sample Date	Analyte	Level (ppb)	ALB (ppb)
Goose River at Hillsboro, ND	380156	5/20/2013	Acetochlor	0.46	1.43
Goose River at Hillsboro, ND	380156	7/9/2013	Atrazine	0.42	1
Goose River at Hillsboro, ND	380156	7/29/2013	Atrazine	0.22	1
Goose River at Hillsboro, ND	380156	5/20/2013	Dimethenamid	3.1	8.9
Goose River at Hillsboro, ND	380156	6/10/2013	Metolachlor	0.26	1
Goose River at Hillsboro, ND	380156	7/9/2013	Metolachlor	0.54	1
Bois de Sioux River nr Doran, MN	385055	6/19/2013	2,4-D	4.2	13.1
Bois de Sioux River nr Doran, MN	385055	5/29/2013	Acetochlor	0.76	1.43
Bois de Sioux River nr Doran, MN	385055	7/15/2013	Atrazine	0.35	1
Bois de Sioux River nr Doran, MN	385055	8/21/2013	Atrazine	0.42	1
Bois de Sioux River nr Doran, MN	385055	7/15/2013	Metolachlor	0.23	1
Wild Rice River nr Abercrombie, ND	380031	7/15/2013	Atrazine	1.8	1
Wild Rice River nr Abercrombie, ND	380031	8/20/2013	Atrazine	0.76	1
Wild Rice River nr Abercrombie, ND	380031	10/14/2013	Atrazine	0.21	1
Wild Rice River nr Abercrombie, ND	380031	7/15/2013	Metolachlor	0.53	1
Maple River below Mapleton, ND	384155	6/17/2013	Atrazine	0.21	1
Maple River below Mapleton, ND	384155	7/16/2013	Atrazine	1.6	1
Maple River below Mapleton, ND	384155	8/19/2013	Atrazine	0.22	1
Maple River below Mapleton, ND	384155	7/16/2013	Metolachlor	0.42	1
Souris River nr Verendrye, ND	380095	7/9/2013	Atrazine	0.45	1
Souris River nr Verendrye, ND	380095	7/9/2013	Diuron	0.88	2.4
Red River at Grand Forks, ND	384156	7/10/2013	Atrazine	0.92	1
Red River at Grand Forks, ND	384156	7/10/2013	Metolachlor	0.27	1
James River at Lamoure, ND	380012	8/20/2013	Atrazine	0.21	1
James River at Jamestown, ND	380013	8/20/2013	Atrazine	0.25	1
Red River at Brushville, MN	380083	7/15/2013	Atrazine	0.21	1
Cannonball River nr Raleigh, ND	380105	6/10/2013	Atrazine	0.2	1
James River nr Grace City, ND	384130	7/16/2013	2,4-D	46	13.1
Red River at Pembina, ND	384157	7/10/2013	Atrazine	1	1
Red River at Fargo, ND	385414	7/9/2013	Atrazine	1.3	1