2015 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 project in 2015 to assess levels of pesticides and pesticide degradates in North Dakota rivers and streams. Thirty sites were sampled approximately six times from April through October resulting in a total of 178 river and stream samples collected. Each sample was analyzed for 101 different pesticides and pesticide degradates. The Department utilized the Montana State University Agriculture Experiment Station's Analytical Laboratory for sample analysis. Of all river and stream analyses, there were a total of 1,823 (10.14%) detections, of which 29 (.16%) were notable and 1,306 (7.26%) instances when an analyte was deemed present, but below the laboratory detection limit. The most commonly detected pesticide was atrazine which was detected in 83.71% of samples and was found present, but below the detection limit, in all but one of the remaining samples. Other commonly detected pesticides were 2,4-D; bentazon; and metolachlor.

Based on the levels detected, results indicate that pesticides in North Dakota's rivers and streams 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 (NDDoH), 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 NDDoH 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 NDDoH'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 (Orr and Gray, 2009).

The 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 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 was 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 (Johnson and Gray, 2010).

EPA Clean Water Act Section 319 funds continued into 2010. Sampling sites were chosen from the NDDoH'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 was 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 (Johnson and Gray, 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.

Monitoring of rivers and streams resumed in 2013. Sampling sites were chosen from the NDDoH's Ambient River and Stream Water Quality Monitoring Program to make sampling most efficient. Thirty sites were sampled approximately seven times from April to October and tested for 99 pesticides and pesticide degradates. There were 30 notable detections of 6 different pesticides including 2,4-D; acetochlor; atrazine; dimethenamid; diuron; and metolachlor. The most commonly detected pesticide was atrazine followed by 2,4-D (Sauter and Gray, 2014).

In 2014, river and stream monitoring continued and was similar in design to 2013. In 2014, targeted sampling was also performed in addition to monthly sampling. Targeted sampling consisted of higher frequency sampling during heaviest times at select sites that had a history of high detections. Because of targeted sampling there were more detections in 2014 than any previous year. There were 50 notable detections of 6 pesticides including acetochlor, atrazine, bromoxynil, chlorpyrifos, malathion, and metolachlor. The most commonly detected pesticide was Atrazine followed by 2,4-D (Sauter and Gray, 2015).

Also in 2014, the NDDoH and USGS provided an opportunity to sample lakes throughout North Dakota for pesticides. This project consisted of collecting and analyzing one sample during mid to late summer from 27 lakes throughout the state. These samples were analyzed by Montana State University Agriculture Experiment Station's Analytical Laboratory for 96 pesticides and pesticide degradates. There were two notable detections of chlorpyrifos and one notable detection of atrazine. Similar to river and stream results, atrazine and 2,4-D were the most commonly detected pesticides (Sauter and Gray, 2015).

2015 Project goals

The goals of the 2015 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 times in 2015 at 30 sites from April through 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 once in April, May, June, July, August, and October. Realistically, dates were variable and dependent on weather and staffing. The 2015 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). River and stream 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 naturally while facing towards the current. 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 within seven days of collection using a next-day shipping service.

Each pesticide sample consisted of one, 1-L amber glass jar with caps featuring a 1/8" PTFE-faced silicone seal. Sample bottles arrived pre-cleaned according to EPA procedure 1 methods for extractable organic, semi-volatile, 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 NDDoH'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.

Each sample was analyzed for 101 different pesticides and pesticide 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. 2015 North Dakota pesticide river and stream monitoring sample collection sites.

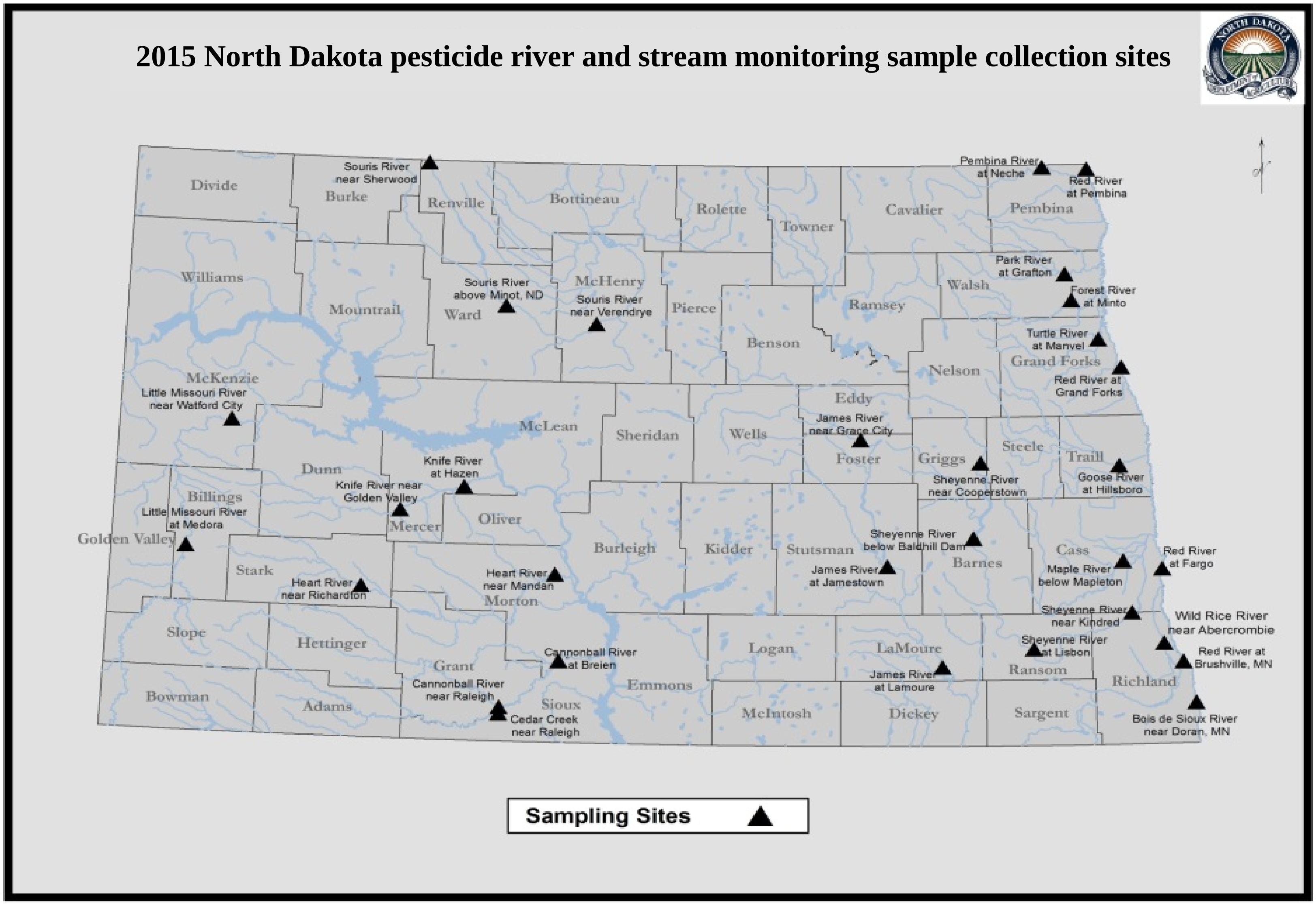
NDDoH Site ID	Site Name	Latitude	Longitude
380009	Sheyenne River near Cooperstown, ND	47.4328	-98.0276
385168	Sheyenne River at Lisbon, ND	46.4469	-97.6793
380022	Little Missouri River at Medora, ND	46.9195	-103.5282
380059	Little Missouri River nr Watford City, ND	47.5958	-103.263
384131	Knife River nr Golden Valley, ND	47.1545	-102.0599
380087	Knife River at Hazen, ND	47.2853	-101.6221
380160	Heart River nr Richardton, ND	46.7456	-102.3083
380151	Heart River nr Mandan, ND	46.8339	-100.9746
380105	Cannonball River nr Raleigh, ND	46.1269	-101.3332
380077	Cedar Creek nr Raleigh, ND	46.0917	-101.3337
380067	Cannonball River at Breien, ND	46.3761	-100.9344
384130	James River nr Grace City, ND	47.5581	-98.8629
380013	James River at Jamestown, ND	46.8897	-98.6817
380012	James River at Lamoure, ND	46.3555	-98.3045
385055	Bois de Sioux River near Doran, MN	46.1522	-96.5789
380083	Red River at Brushville, MN	46.3695	-96.6568
380031	Wild Rice River near Abercrombie, ND	46.468	-96.7837
385001	Sheyenne River near Kindred, ND	46.6316	-97.0006
384155	Maple River below Mapleton, ND	46.9052	-97.0526
380091	Souris River nr Sherwood	48.99	-101.9582
380161	Souris River above Minot, ND	48.2458	-101.3713
380095	Souris River nr Verendrye, ND	48.1597	-100.7296
385414	Red River at Fargo, ND	46.8611	-96.7837
380156	Goose River at Hillsboro, ND	47.4094	-97.0612
384156	Red River at Grand Forks, ND	47.9275	-97.0281
380037	Turtle River at Manvel, ND	48.0786	-97.1845
380039	Forest River at Minto, ND	48.2858	-97.3681
380157	Park River at Grafton, ND	48.4247	-97.412
380158	Pembina River at Neche, ND	48.9897	-97.557
384157	Red River at Pembina, ND	48.9769	-97.2376

Table 2. 2015 North Dakota pesticide river and stream monitoring sample collection dates.

Site ID	Sampling Dates					
380009	4/20/2015	5/11/2015	6/17/2015	7/13/2015	8/18/2015	10/13/2015
380012	4/21/2015	5/12/2015	6/18/2015	7/14/2015	8/18/2015	10/13/2015
380013	4/21/2015	5/12/2015	6/18/2015	7/14/2015	8/18/2015	10/13/2015
380022	4/15/2015	5/12/2015	6/9/2015	7/21/2015	8/25/2015	10/16/2015
380031	4/22/2015	5/20/2015			8/24/2015	10/5/2015
380037	4/20/2015	5/18/2015	6/3/2015	7/14/2015	8/3/2015	10/28/2015
380039	4/20/2015	5/18/2015	6/3/2015	7/14/2015	8/24/2015	10/29/2015
380059	4/15/2015	5/12/2015	6/9/2015	7/21/2015	8/25/2015	10/16/2015
380067	4/14/2015	5/13/2015	6/10/2015	7/22/2015	8/24/2015	10/19/2015
380077	4/13/2015	5/13/2015	6/10/2015	7/22/2015	8/24/2015	10/19/2015
380083	4/22/2015	5/19/2015	6/17/2015	7/22/2015	8/25/2015	10/7/2015
380087	4/13/2015	5/12/2015	6/8/2015	7/21/2015	8/25/2015	10/16/2015
380091	4/22/2015	5/28/2015	6/17/2015	7/22/2015	9/1/2015	10/7/2015
380095	4/21/2015	5/28/2015	6/16/2015	7/21/2015	9/2/2015	10/6/2015
380105	4/14/2015	5/13/2015	6/10/2015	7/22/2015	8/24/2015	10/19/2015
380151	4/14/2015	5/13/2015	6/9/2015	7/22/2015	8/24/2015	10/19/2015
380153						10/13/2015*
380156	4/22/2015	5/19/2015	6/10/2015	7/13/2015	8/19/2015	10/26/2015
380157	4/20/2015	5/18/2015	6/3/2015	7/14/2015	8/25/2015	10/29/2015
380158	4/21/2015	5/20/2015	6/15/2015	7/14/2015	8/11/2015	10/30/2015
380160	4/13/2015	5/12/2015	6/8/2015	7/21/2015	8/25/2015	10/16/2015
380161	4/23/2015	5/29/2015	6/16/2015	7/21/2015	9/3/2015	10/6/2015
384130	4/20/2015	5/11/2015	6/17/2015	7/13/2015	8/18/2015	10/13/2015
384131	4/13/2015	5/12/2015	6/8/2015	7/21/2015	8/25/2015	10/16/2015
384155	4/23/2015	5/20/2015	6/16/2015	7/21/2015	8/26/2015	10/5/2015
384156	4/28/2015	5/19/2015	6/3/2015	7/28/2015	8/25/2015	10/27/2015
384157	4/21/2015	5/20/2015	6/15/2015	7/14/2015	8/11/2015	10/30/2015
385001	4/23/2015	5/20/2015	6/16/2015	7/21/2015	8/24/2015	10/5/2015
385055	4/22/2015		6/17/2015	7/22/2015	8/25/2015	10/5/2015
385168	4/21/2015	5/11/2015	6/18/2015	7/13/2015	8/18/2015	10/13/2015
385414	4/22/2015	5/19/2015	6/8/2015	7/13/2015	8/18/2015	10/26/2015

380153 was not part of the original scheduled sampling plan*

Figure 1. 2015 North Dakota pesticide river and stream monitoring sample collection sites.



RESULTS AND DISCUSSION

River and stream sites

There was a total of 178 samples analyzed for 101 different pesticides. Of the 101 pesticides analyzed, 64 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; 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 well below levels that may begin to impact aquatic ecosystems or human health.

Table 3. Common pesticides detected in North Dakota surface waters in 2015.

Common pesticides detected in ND rivers and streams in 2015						
	Quantifiable detects		Qs (Present but below reporting limit)		Total samples with quantifiable detects and Qs	
Analyte	**Number**	**Percent of all samples**	**Number**	**Percent of all samples**	**Number**	**Percent of all samples**
Deethyl atrazine	149.00	83.71	28.00	15.73	177.00	99.44
Atrazine	144.00	80.90	28.00	15.73	172.00	96.63
2,4-D	135.00	75.84	32.00	17.98	167.00	93.82
Hydroxy atrazine	121.00	67.98	44.00	24.72	165.00	92.70
Bentazon	128.00	71.91	4.00	2.25	132.00	74.16
Metolachlor ESA	99.00	55.62	22.00	12.36	121.00	67.98
Prometon	69.00	38.76	49.00	27.53	118.00	66.29
Acetochlor OA	93.00	52.25	17.00	9.55	110.00	61.80
Acetochlor ESA	71.00	39.89	31.00	17.42	102.00	57.30
Tebuconazole	22.00	12.36	79.00	44.38	101.00	56.74
MCPA	56.00	31.46	41.00	23.03	97.00	54.49
Propiconazole	32.00	17.98	63.00	35.39	95.00	53.37
IMAM	39.00	21.91	51.00	28.65	90.00	50.56
Pyrasulfotole	37.00	20.79	44.00	24.72	81.00	45.51
Imazethapyr	51.00	28.65	21.00	11.80	72.00	40.45
FSA	13.00	7.30	46.00	25.84	59.00	33.15
Flucarbazone	39.00	21.91	19.00	10.67	58.00	32.58
Metolachlor OA	19.00	10.67	39.00	21.91	58.00	32.58
Dimethenamid	35.00	19.66	21.00	11.80	56.00	31.46
Dimethenamid OA	29.00	16.29	27.00	15.17	56.00	31.46
Diuron	20.00	11.24	36.00	20.22	56.00	31.46
Bromacil	24.00	13.48	31.00	17.42	55.00	30.90
Metalaxyl	23.00	12.92	30.00	16.85	53.00	29.78
Metolachlor	33.00	18.54	18.00	10.11	51.00	28.65
Sulfentrazone	27.00	15.17	24.00	13.48	51.00	28.65

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 29 detections of 3 pesticides at 20% or more of the lowest ALB value. Two pesticides were herbicides and included six acetochlor detections and twenty atrazine detections. The other pesticide, terbufos sulfone, is an insecticide and was detected three times as detailed in Table 4.

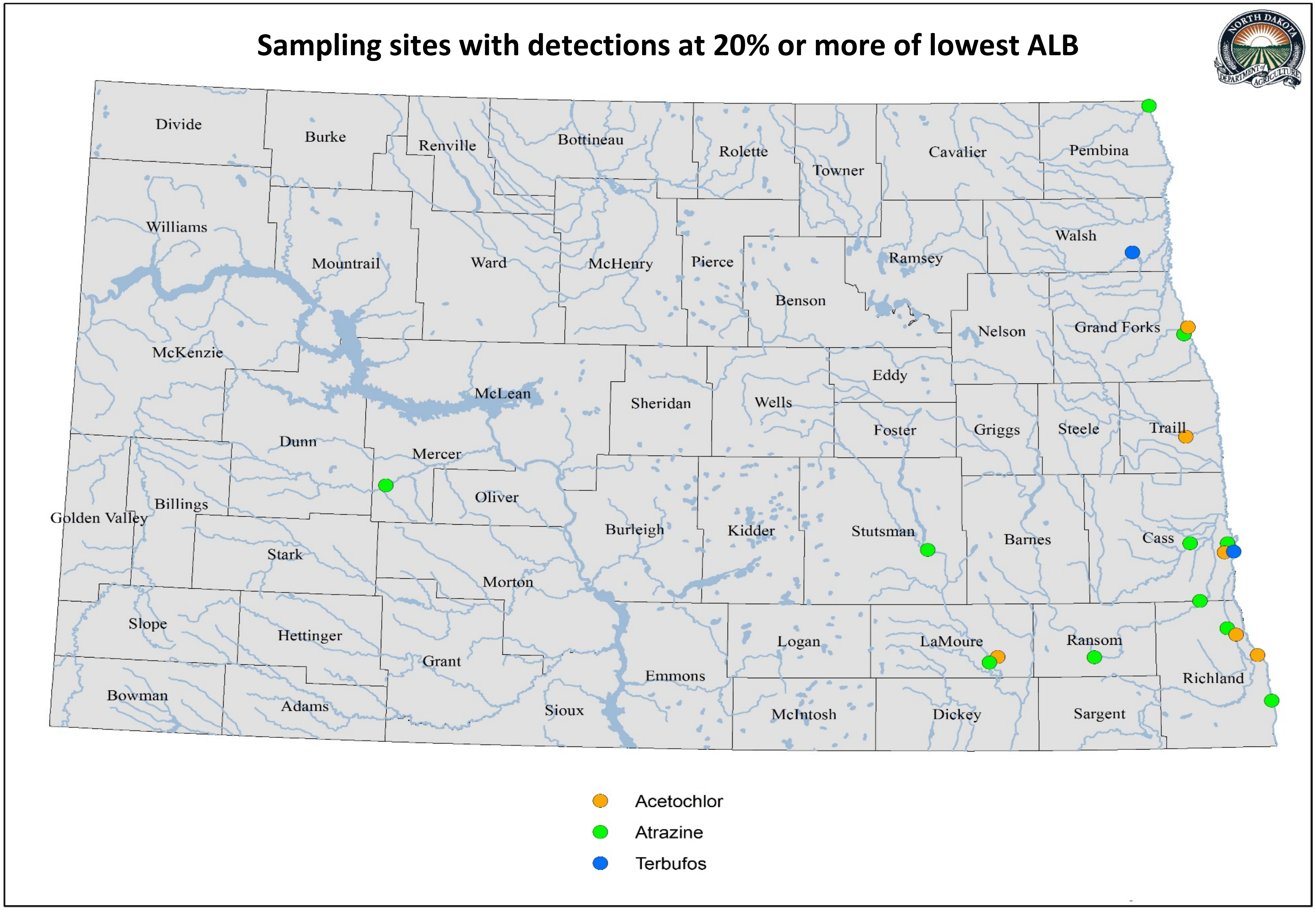
Table 4. Detections that were 20% or more of lowest ALB.

Detections that were 20% or more of lowest aquatic life benchmark (ALB)			
Chemical	**Number of detections**	**Range of detections (PPB)**	**ALB (PPB)**
Acetochlor	6	0.32-0.77	1.43
Atrazine	20	0.22-1.3	1
Terbufos sulfone	3	0.03-0.038	0.03

There were 14 sites in which these chemicals were found at 20% or more of an ALB (Figure 2). The majority of the 14 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 Red River at Fargo, ND had five detections; the pesticides detected included acetochlor (one detection), atrazine (three detections), and terbufos sulfone (one detection). The Forest River at Minto, ND had two terbufos sulfone detections. The Red River at Grand Forks, ND had two detections; the pesticides detected were acetochlor and atrazine. The Maple River below Mapleton, ND had two atrazine detections. The Wild Rice River near Abercrombie, ND had two pesticide detections; the pesticides detected were acetochlor and atrazine. The Red River at Brushville, MN and the Goose River at Hillsboro, ND each had one acetochlor detection. The Sheyenne River at Lisbon, ND; the Bois de Sioux near Doran, MN; the Sheyenne River near Kindred, ND; and the Red River at Pembina, ND each had one atrazine detection.

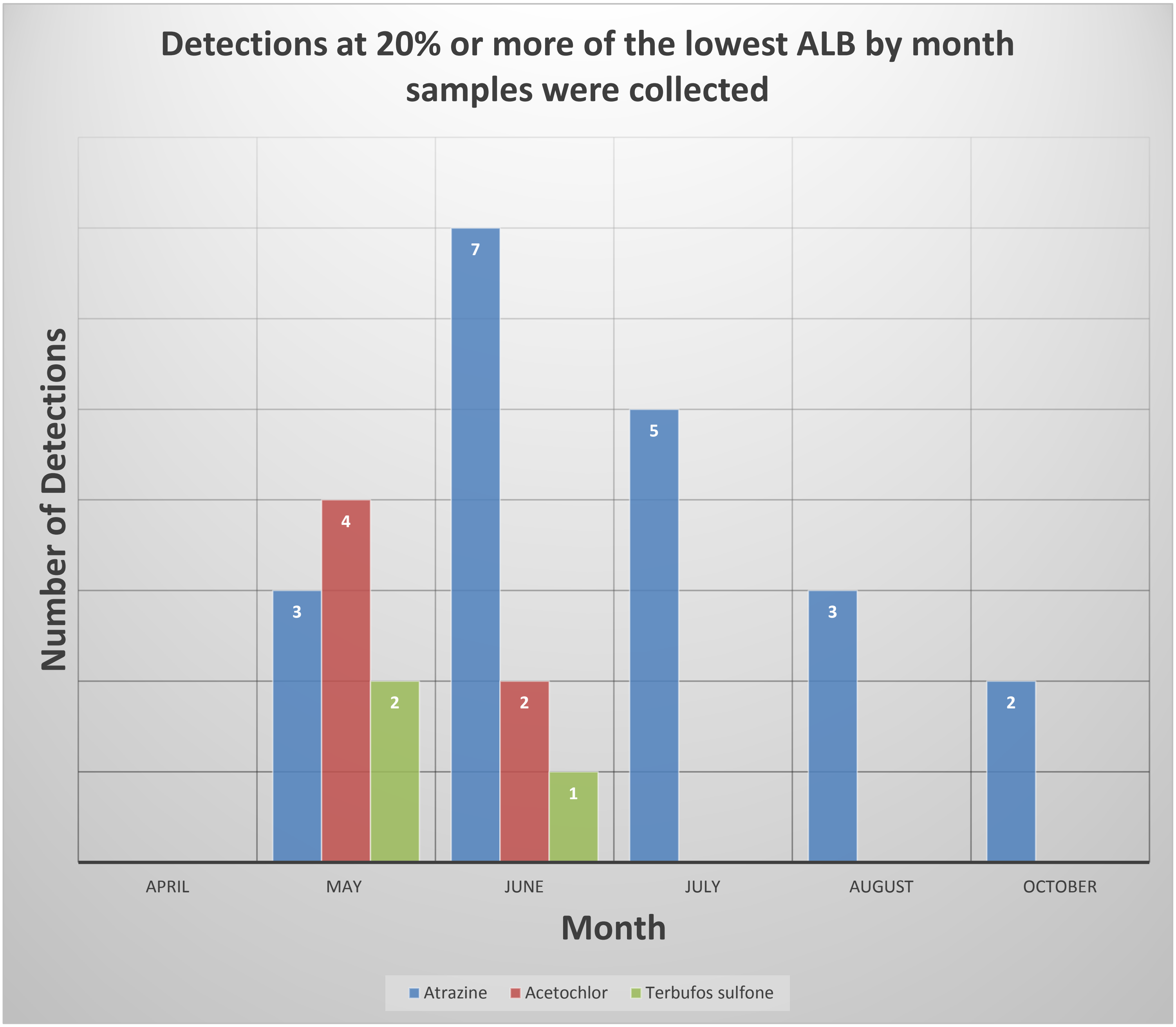
Outside of the Red River basin, the James River at Lamoure, ND had five detections; the pesticides detected were acetochlor (one detection) and atrazine (four detections). The James River at Jamestown, ND had four atrazine detections. The Knife River near Golden Valley, ND had one atrazine detection.

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



The 29 pesticide detections at concentrations of 20% or more of the lowest ALB were spread throughout the growing season with the most detections occurring in June in 2015 (Figure 3). In May, atrazine was detected three times, acetochlor was detected four times, and terbufos sulfone was detected twice. In June, atrazine was detected seven times, acetochlor was detected twice and terbufos sulfone was detected once. In July, there were five atrazine detections. In August atrazine was detected three times and in October atrazine was detected twice at levels 20% or more of the lowest ALB.

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



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 pesticides were detected at concentrations exceeding an MCL, although there were six detections at or above an ALB (Table 5). 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 5. Detections indicating an aquatic life benchmark (ALB) was met or exceeded.

Detections indicating an aquatic life benchmark (ALB) was met or exceeded				
Site Name	Date	Chemical	Detected level (ppb)	ALB (ppb)
James River at Jamestown, ND	8/18/2015	Atrazine	1	1
Maple River below Mapleton, ND	6/16/2015	Atrazine	1.2	1
Wild Rice River near Abercrombie, ND	5/20/2015	Atrazine	1.3	1
Red River at Fargo, ND	5/19/2015	Terbufos sulfone	0.038	0.03
Forest River at Minto, ND	5/18/2015	Terbufos sulfone	0.03	0.03
Forest River at Minto, ND	6/3/2015	Terbufos sulfone	0.03	0.03

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 study. 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 estimated pesticide use throughout the state. The information is derived from a comprehensive survey of North Dakota farm operators on 2012 practices published by North Dakota State University Extension (Zollinger et al. 2013) and county estimate data collected by USDA’s National Agricultural Statistics Service (NASS). 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 2013.

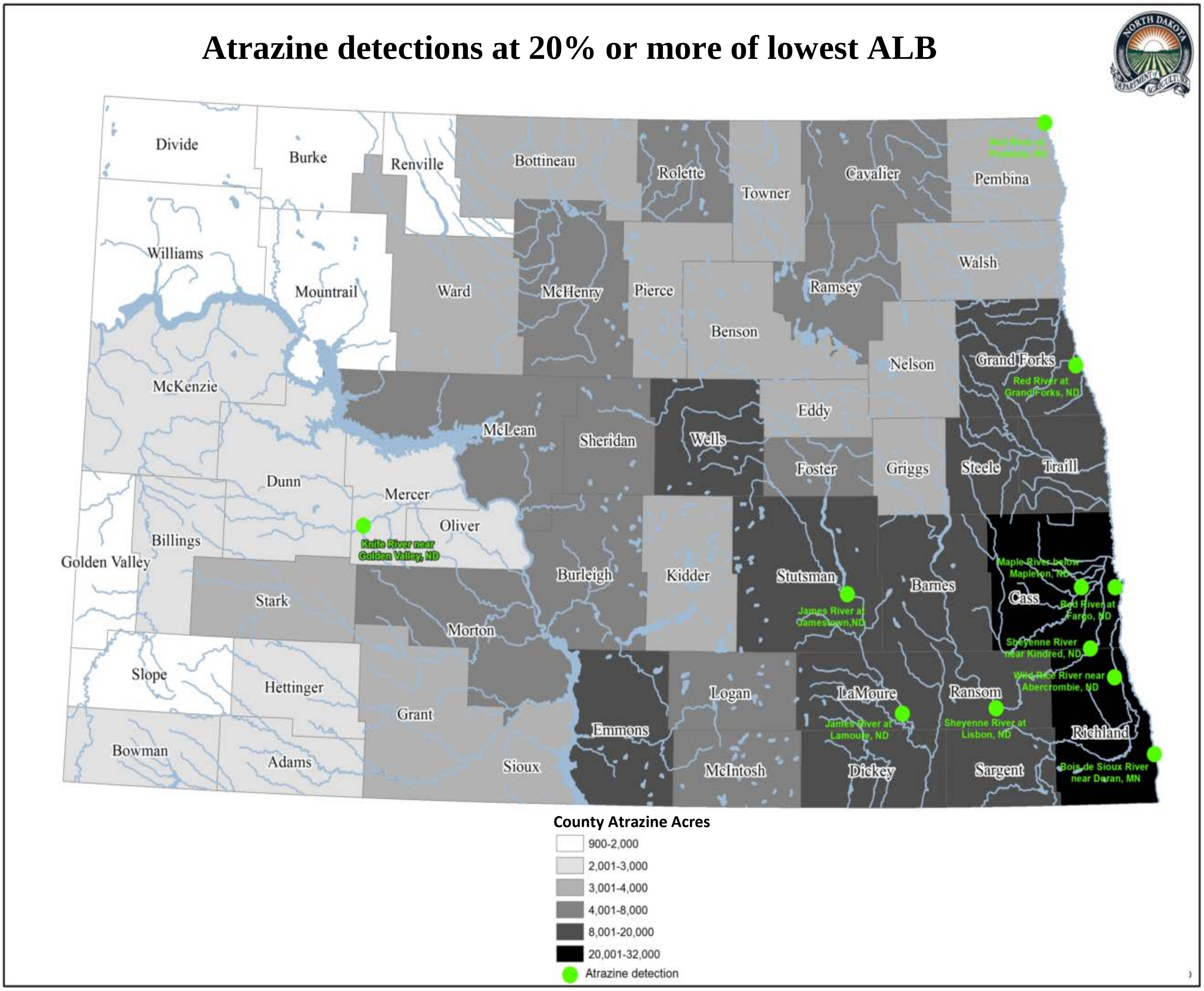
Atrazine

Atrazine, a broadleaf herbicide used primarily on corn, was applied to approximately 146,300 acres as a stand-alone product and to an additional 309,800 acres in mixtures in 2012. (Zollinger et al. 2013). Atrazine was detected in 84% (149) of samples and present in 15% (28) of samples.

Of those detections, 20 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 4). Atrazine detections indicated an ALB was met or exceeded three times with values of 1 ppb, 1.2 ppb, and 1.3 ppb.

EPA risk assessment and peer-reviewed articles have shown the most sensitive endpoint for atrazine is 0.001 ppb. A study demonstrated a biomass reduction in *Elodea canadensis* (waterweed) at a continuous concentration of 0.001 ppb of atrazine for 14 days. Although 0.001 ppb is the most sensitive endpoint, it is not a realistic value to use as an ALB for comparing sampling data. The level does not indicate risk to aquatic communities, it is simply the most sensitive endpoint for the most sensitive plant species tested. Furthermore, lab detection limits are greater than 0.001 making it impossible to determine the true number of samples that may exceed this value. A realistic ALB value that is both above the laboratory's detection limit and sufficiently conservative to ensure minimal risk to aquatic organisms is 1 ppb. This value is based on reduction in chlorophyll production for green algae. The highest concentration detected was 1.3 ppb, exceeding the ALB value by 1.3 times. As stated earlier, the sample is a snapshot in time, and for an ALB to be truly exceeded, atrazine would need to be monitored continuously for up to 7 days and exceed 1 ppb continuously. The drinking water MCL for atrazine is 3 ppb. The highest concentration detected is approximately 2.3 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.

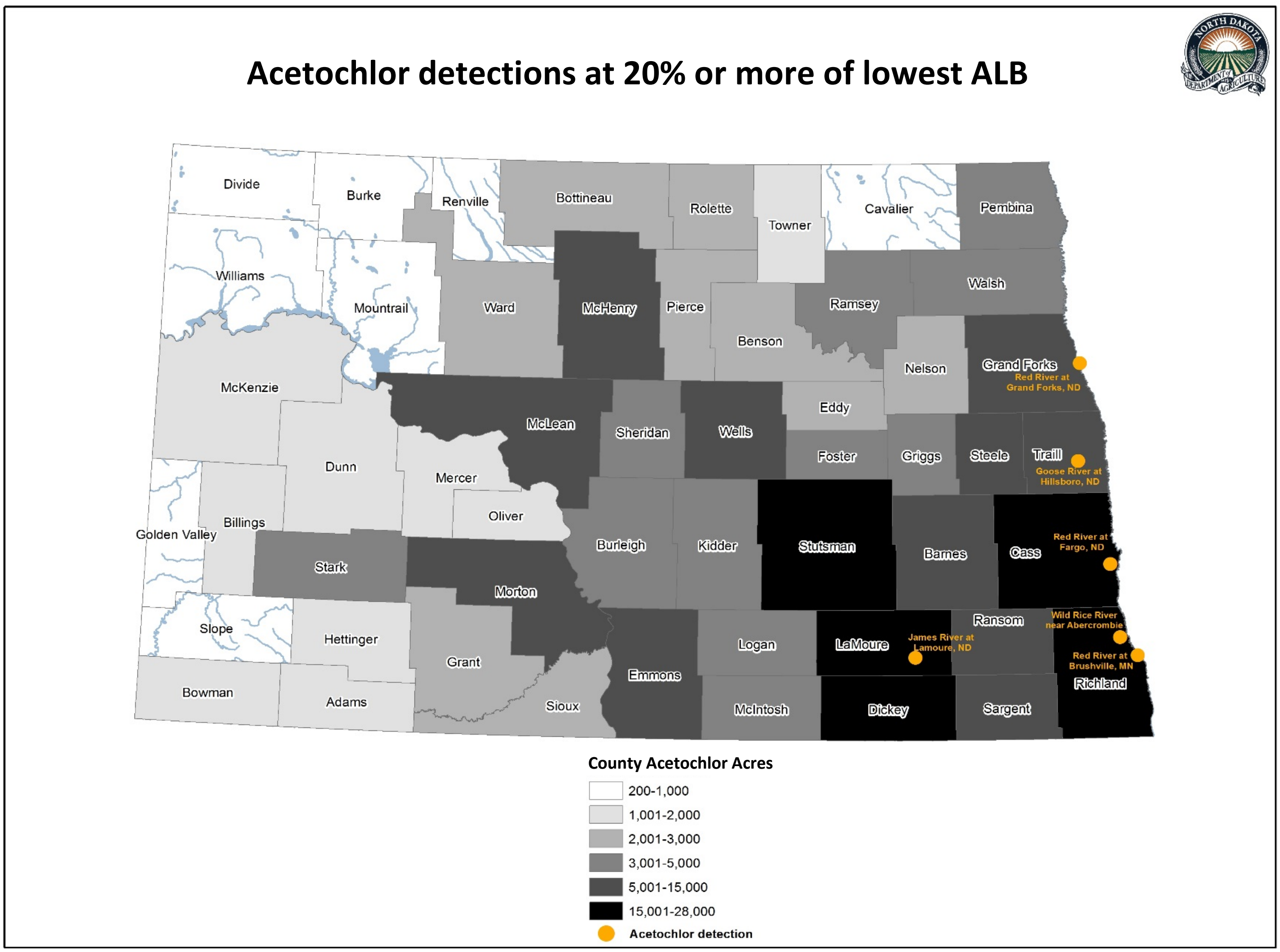
Figure 4. Sampling locations where atrazine was detected at 20% or more of lowest EPA ALB.



Acetochlor

Acetochlor is an herbicide used on corn and soybeans and is applied to approximately 35,600 acres as a stand-alone product and to an additional 304,800 acres in mixtures in North Dakota in 2012. (Zollinger et al. 2013). Acetochlor was detected at 20% or more of an ALB six times at six sites in 2015. All of the sites are in counties with high levels of estimated acetochlor use (Figure 5). Acetochlor breakdown products were detected or present in about 62% 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 affects 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 0.77 ppb, which is 1.9 times lower than the ALB. This indicates minimal environmental risk. There is no EPA established drinking water standard for Acetochlor.

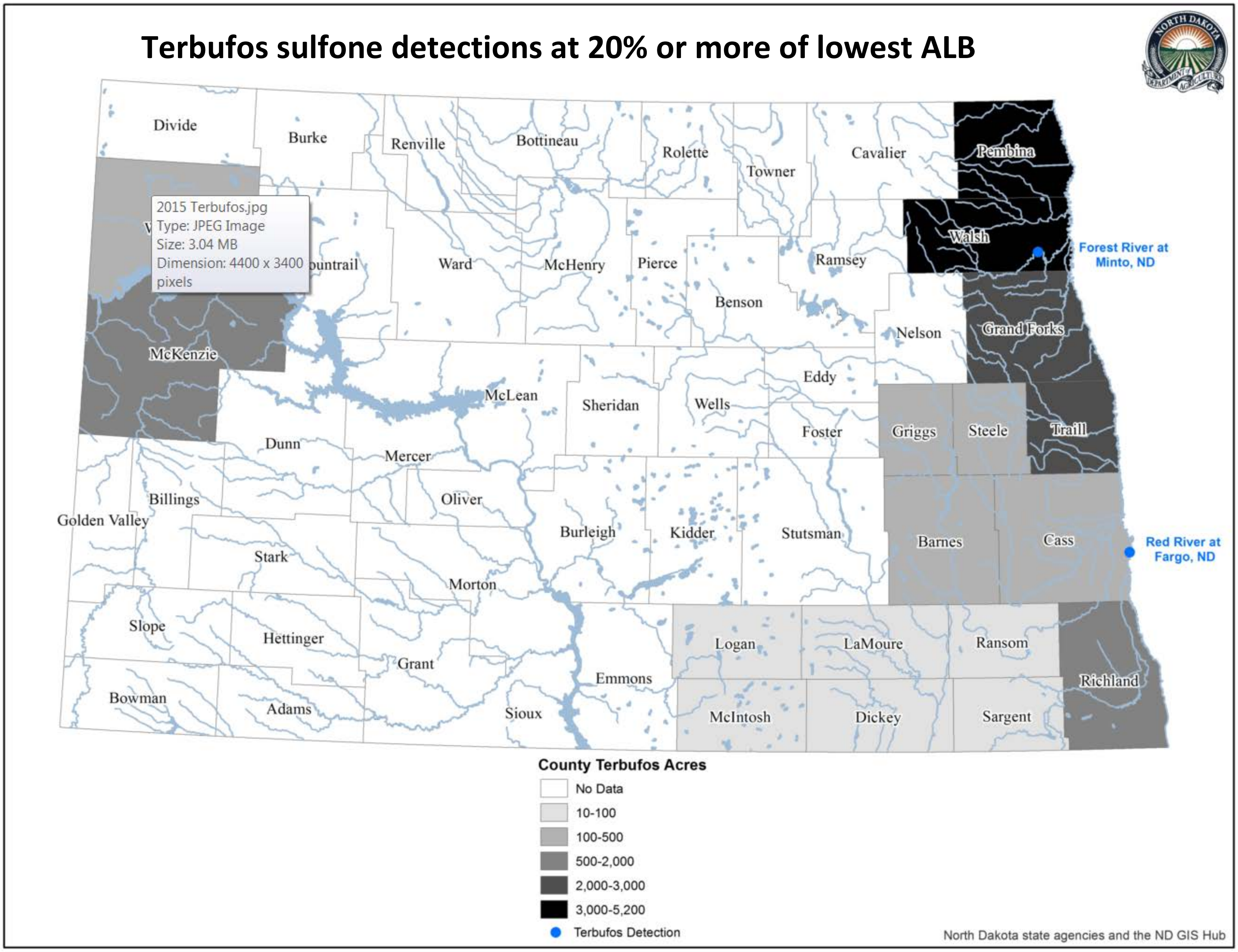
Figure 5. Sampling locations where acetochlor was detected at 20% or more of lowest EPA ALB.



Terbufos

Terbufos is primarily used on sugar beets in North Dakota for control of springtails, sugar beet root maggot larvae, and wireworms. Terbufos was applied to approximately 20,300 acres in North Dakota in 2012 (Zollinger et al. 2013). Montana State University does not analyze for terbufos but they do analyze for terbufos sulfone, a breakdown product of terbufos. Terbufos sulfone was detected or present in 8 samples in 2015. Terbufos sulfone is expected to have the same toxicity characteristics as the parent compound. The most sensitive endpoint for terbufos is 0.030 ppb which is the no observed adverse effect concentration (NOAEC) for freshwater invertebrates. The highest concentration detected in 2015 was 0.03 ppb indicating minimal risk to aquatic ecosystems. There is no EPA established drinking water standard for terbufos.

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



Conclusion

Results of the 2015 monitoring study indicate that North Dakota rivers and streams do not have pesticide levels that pose 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 in surface water. 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 utmost 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, 2013, 2014, and 2015 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 almost all of the samples in 2013, 2014, and 2015. 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 six 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 2015 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.

REFERENCES

Orr, J.N., Gray, J.A. 2009. Surface Water Pesticide Monitoring and Assessment Project, 2008. North Dakota Department of Agriculture, http://www.nd.gov/ndda/program/pesticide-water-quality-program

Orr, J.N., Gray, J.A. 2009. Quality Assurance Plan for the Pesticide Water Quality Monitoring Program. North Dakota Department of Agriculture, unpublished.

Johnson, J.N., Gray, J.A. 2010. Surface Water Pesticide Monitoring and Assessment Project, 2009. North Dakota Department of Agriculture, http://www.nd.gov/ndda/program/pesticide-water-quality-program

Johnson, J.N., Gray, J.A. 2011. Surface Water Pesticide Monitoring and Assessment Project, 2010. North Dakota Department of Agriculture, http://www.nd.gov/ndda/program/pesticide-water-quality-program

Sauter J. D., Gray, J.A. 2014. Surface Water Pesticide Monitoring and Assessment Project, 2013. North Dakota Department of Agriculture, http://www.nd.gov/ndda/program/pesticide-water-quality-program

Sauter J. D., Gray, J.A. 2015. Surface Water Pesticide Monitoring and Assessment Project, 2014. North Dakota Department of Agriculture, http://www.nd.gov/ndda/program/pesticide-water-quality-program

Liu, H, Ye, W, Zhan, X, Liu, W. (2006). A Comparative Study of rac- and S-metolachlor Toxicity to Daphnia magna. Ecotox. Environ. Safety. 63: 451-455.

NDDoH. 2009. Quality Assurance Project Plan for the Ambient River and Stream Water Quality Monitoring Program. North Dakota Department of Health, Division of Water Quality, Bismarck, North Dakota.

Torres, A.M.R. and L.M. O'Flaherty. 1976. Influence of pesticides on *Chlorella*, *Chlorococcum*, *Stigeoclonium* (Chlorophyceae), *Tribonema*, *Vaucheria* (Xanthophyceae) and *Oscillatoria* (Cyanophyceae). Phycologia 15(1):25-36.

U.S. EPA Office of Pesticides and Toxic Substances. 1988. Fact Sheet No. 177 Bifenthrin. U.S. EPA. Washington D.C.

Zollinger, R.K., M.P. McMullen, J. Knodel, J.A. Gray, D. Jantzi, G. Kimmet, K. Hagameister, and C. Schmitt. 2009. Pesticide use and pest management practices in North Dakota, 2008. North Dakota State University Ext. Publication W-1446.

Federoff, N.E. and E. Gelmann. 2013. EFED Registration Review Problem Formulation for Bromoxynil and Bromoxynil Esters. U.S. EPA. DP Barcode:406427.

Appendix A. Sample identification record.

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

Preservation: Yes □	Temperature:
Initials:	

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**
	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**
	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 and reporting limits in 2015			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit (ppb)**
2,4-D	2,4-D, Curtail	H	0.00450
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
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
Diuron	Direx, Karmex	H	0.00530
Fluoroethyldiaminotriazine (FDAT)	degradate	D	0.00530
Fipronil	Regent	I	0.00120
Fipronil desulfinyl	degradate	D	0.14
Fipronil sulfide	degradate	D	0.080

List of analytes 2015			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit (ppb)**
Fipronil sulfone	degradate	D	0.040
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
Indaziflam	Alion, Specticle	H	0.00200
Isoxaben	Gallery, Snapshot	H	0.00210
Isoxaflutole	Corvus, Balance Flexx	H	0.13000
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	0.0052
NOA 447204 (Pinoxaden metablolite)	degradate	D	0.02000
Norflurazon	Solicam	H	0.02000

List of analytes 2015			
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
Picoxystrobin	Approach	F	0.00510
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
Thiencarbazone methyl	Corvus, Huskie Complete	H	0.040
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
Trifloxystrobin	Compass, Stratego	F	0.020

*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)
Bois de Sioux River near Doran, MN	385055	8/25/2015	Atrazine	0.43	1.00
Forest River at Minto, ND	380039	5/18/2015	Terbufos sulfone	0.03	0.03
Forest River at Minto, ND	380039	6/3/2015	Terbufos sulfone	0.03	0.03
Goose River at Hillsboro, ND	380156	5/19/2015	Acetochlor	0.38	1.43
James River at Jamestown, ND	380013	6/18/2015	Atrazine	0.78	1.00
James River at Jamestown, ND	380013	7/14/2015	Atrazine	0.63	1.00
James River at Jamestown, ND	380013	8/18/2015	Atrazine	1.00	1.00
James River at Jamestown, ND	380013	10/13/2015	Atrazine	0.26	1.00
James River at Lamoure, ND	380012	6/18/2015	Acetochlor	0.32	1.43
James River at Lamoure, ND	380012	6/18/2015	Atrazine	0.72	1.00
James River at Lamoure, ND	380012	7/14/2015	Atrazine	0.53	1.00
James River at Lamoure, ND	380012	8/18/2015	Atrazine	0.40	1.00
James River at Lamoure, ND	380012	10/13/2015	Atrazine	0.33	1.00
Knife River nr Golden Valley, ND	384131	7/21/2015	Atrazine	0.22	1.00
Maple River below Mapleton, ND	384155	5/20/2015	Atrazine	0.37	1.00
Maple River below Mapleton, ND	384155	6/16/2015	Atrazine	1.20	1.00
Red River at Brushville, MN	380083	5/19/2015	Acetochlor	0.46	1.43
Red River at Fargo, ND	385414	5/19/2015	Acetochlor	0.42	1.43
Red River at Fargo, ND	385414	5/19/2015	Atrazine	0.26	1.00
Red River at Fargo, ND	385414	6/8/2015	Atrazine	0.68	1.00
Red River at Fargo, ND	385414	7/13/2015	Atrazine	0.23	1.00
Red River at Fargo, ND	385414	5/19/2015	Terbufos sulfone	0.038	0.03
Red River at Grand Forks, ND	384156	6/3/2015	Acetochlor	0.54	1.43
Red River at Grand Forks, ND	384156	6/3/2015	Atrazine	0.50	1.00
Red River at Pembina, ND	384157	7/14/2015	Atrazine	0.22	1.00
Sheyenne River near Kindred, ND	385001	6/16/2015	Atrazine	0.83	1.00
Sheyenne River at Lisbon, ND	385168	6/18/2015	Atrazine	0.28	1.00
Wild Rice River near Abercrombie, ND	380031	5/20/2015	Acetochlor	0.77	1.43
Wild Rice River near Abercrombie, ND	380031	5/20/2015	Atrazine	1.30	1.00