

2017 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 2017 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 with one site being sampled additional times as part of follow-up sampling resulting in a total of 180 river and stream samples collected. Each sample was analyzed for 102 different pesticides and pesticide degradates. The Department utilized the Montana State University Agriculture Experiment Station's Analytical Laboratory for sample analysis. Of all the river and stream analyses, there were a total of 1,649 (9%) detections, of which 48 (0.3%) were notable and 1,254 (6.8%) instances when an analyte was deemed present, but below the laboratory detection limit. The most commonly detected pesticide was atrazine which was detected in 78% of samples and was found present, but below the detection limit, in 21% of 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 4.1-33 and 4.1-34 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 Program has since expanded its water quality focus to include surface water. 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 (Orr and Gray, 2009).

The pesticide water quality monitoring program received an increase in funding in 2009 and because of this, 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 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).

The funding increase continued into 2010 and sampling sites were chosen from the NDDH's Ambient River and Stream Water Quality Monitoring Program sites to make 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. 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 NDDH'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 pesticide use 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 NDDH and USGS provided an opportunity to sample lakes throughout North Dakota for pesticides. This project consisted of collecting and analyzing samples from 27 lakes throughout the state, one time during mid to late summer. 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).

In 2015, river and stream monitoring continued and was similar in design to 2013 and 2014. 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. There were 29 notable detections of three pesticides including acetochlor, atrazine and terbufos sulfone. The most commonly detected pesticides were atrazine; 2,4-D, bentazon and metolachlor (Sauter, 2016).

In 2016, river and stream monitoring continued and was similar in design to 2015. Thirty sites were sampled approximately six times from April through October, and four additional sites were sampled either at random or as part of follow-up sampling, resulting in a total of 196 river and stream samples collected. Each sample was analyzed for 102 different pesticides and pesticide degradates. There were 51 notable detections of seven pesticides including 2,4-D, acetochlor, atrazine, chlorpyrifos, metolachlor, metsulfuron methyl and sulfometuron methyl. The most commonly detected pesticides were atrazine; 2,4-D, bentazon and prometon (Sauter, 2017).

2017 Project goals

The goals of the 2017 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
- Evaluate levels of certain neonicotinoid insecticides in North Dakota Rivers and streams

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 pesticide registrations.

MATERIALS AND METHODS

Pesticide samples and associated field measurements were collected approximately six times in 2017 at thirty sites from April through October. Locations of the sampling sites, site IDs, and GPS coordinates 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 2017 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). 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. 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 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 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.

Each sample was analyzed for 102 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. 2017 North Dakota pesticide surface water monitoring project sites.

Site ID	Site Name	Latitude	Longitude
380009	Sheyenne River near Cooperstown, ND	47.4328	-98.0276
380012	James River at Lamoure, ND	46.3555	-98.3045
380013	James River at Jamestown, ND	46.8897	-98.6817
380022	Little Missouri River at Medora, ND	46.9195	-103.528
380031	Wild Rice River near Abercrombie, ND	46.4680	-96.7837
380037	Turtle River at Manvel, ND	48.0786	-97.1845
380039	Forest River at Minto, ND	48.2858	-97.3681
380059	Little Missouri River nr Watford City, ND	47.5958	-103.263
380067	Cannonball River at Breien, ND	46.3761	-100.934
380077	Cedar Creek nr Raleigh, ND	46.0917	-101.334
380083	Red River at Brushville, MN	46.3695	-96.6568
380087	Knife River at Hazen, ND	47.2853	-101.622
380091	Souris River nr Sherwood	48.9900	-101.958
380095	Souris River nr Verendrye, ND	48.1597	-100.73
380105	Cannonball River nr Raleigh, ND	46.1269	-101.333
380151	Heart River nr Mandan, ND	46.8339	-100.975
380153	Sheyenne River below Baldhill Dam, ND	47.0339	-98.0837
380156	Goose River at Hillsboro, ND	47.4094	-97.0612
380157	Park River at Grafton, ND	48.4247	-97.412
380158	Pembina River at Neche, ND	48.9897	-97.557
380160	Heart River nr Richardton, ND	46.7456	-102.308
380161	Souris River above Minot, ND	48.2458	-101.371
384130	James River nr Grace City, ND	47.5581	-98.8629
384131	Knife River nr Golden Valley, ND	47.1545	-102.06
384155	Maple River below Mapleton, ND	46.9052	-97.0526
384156	Red River at Grand Forks, ND	47.9275	-97.0281
384157	Red River at Pembina, ND	48.9769	-97.2376
385001	Sheyenne River near Kindred, ND	46.6316	-97.0006

Table 1. 2017 North Dakota pesticide surface water monitoring project sites (continued).

385055	Bois de Sioux River near Doran, MN	46.1522	-96.5789
385168	Sheyenne River at Lisbon, ND	46.4469	-97.6793
385414	Red River at Fargo, ND	46.8611	-96.7837

Table 2. 2017 North Dakota pesticide river and stream monitoring sample collection dates.

Site ID	Sample Date									
380009	4/25/2017	5/23/2017	6/19/2017	7/26/2017	8/22/2017	10/9/2017				
380012	4/26/2017	5/23/2017	6/20/2017	7/26/2017	8/23/2017	10/10/2017				
380013	4/26/2017	5/23/2017	6/20/2017	7/26/2017	8/23/2017	10/10/2017				
380022	4/19/2017	5/15/2017	6/14/2017	7/19/2017	8/14/2017	10/10/2017				
380031	4/24/2017	5/30/2017	6/27/2016	8/2/2017	8/29/2017	10/25/2017				
380037	4/21/2017	5/24/2017	6/28/2017	7/17/2017		10/12/2017				
380039	4/21/2017	5/24/2017	6/21/2017	7/18/2017		10/12/2017				
380059	4/19/2017	5/15/2017	6/14/2017	7/19/2017	8/14/2017	10/9/2017				
380067	4/18/2017	5/16/2017	6/13/2017	7/17/2017	8/15/2017	10/11/2017				
380077	4/18/2017	5/16/2017	6/13/2017	7/17/2017	8/15/2017	10/10/2017				
380083	4/25/2017	5/30/2017	6/28/2017	8/2/2017	8/30/2017	10/25/2017				
380087	4/19/2017	5/15/2017	6/14/2017	7/19/2017	8/14/2017	10/9/2017				
380091	4/18/2017	5/9/2017	6/13/2017	7/26/2017	8/29/2017	10/4/2017				
380095	4/17/2017	5/10/2017	6/15/2017	7/25/2017	8/28/2017	10/3/2017				
380105	4/18/2017	5/16/2017	6/13/2017	7/17/2017	8/15/2017	10/10/2017				
380151	4/20/2017	5/16/2017	6/13/2017	7/17/2017	8/14/2017	10/11/2017				
380153						10/9/2017				
380156	4/24/2017	6/2/2017	6/26/2017	7/5/2017	7/31/2017	10/10/2017				
380157	4/21/2017	5/24/2017	6/21/2017	7/18/2017		10/12/2017				
380158	4/19/2017	5/23/2017	6/20/2017	7/19/2017		10/10/2017				
380160	4/19/2017	5/15/2017	6/14/2017	7/19/2017	8/14/2017	10/10/2017				
380161	4/18/2017	5/9/2017	6/13/2017	7/26/2017	8/29/2017	10/3/2017				
384130	4/25/2017	5/23/2017	6/19/2017	7/26/2017	8/22/2017	10/9/2017				
384131	4/19/2017	5/15/2017	6/14/2017	7/19/2017	8/14/2017	10/9/2017				
384156	4/19/2017	5/17/2017	6/7/2017	7/12/2017	8/23/2017	10/13/2017				
384157	4/19/2017	5/23/2017	6/20/2017	7/19/2017		10/11/2017				
385001	4/24/2017	5/31/2017	6/26/2017	8/2/2017	8/29/2017	10/25/2017				
385055	4/24/2017	5/30/2017	6/28/2017	8/2/2017	8/28/2017	10/24/2017				
385169	4/26/2017	5/23/2017	6/20/2017	7/26/2017	8/23/2017	10/10/2017				
385414	4/24/2017	5/22/2017	6/26/2017	7/5/2017	7/31/2017	10/13/2017				
384155 2017	4/24	5/31	6/26	7/26	7/27	7/28	7/31	8/2	8/29	10/25

Figure 1. 2017 pesticide surface water sampling sites.



RESULTS AND DISCUSSION

River and stream sites

There were a total of 180 samples analyzed for 102 different pesticides. Of the 102 pesticides analyzed, 66 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 negatively impact aquatic ecosystems or human health.

Table 3. Common pesticides detected in North Dakota surface waters in 2017.

Common pesticides detected in ND Rivers and Streams in 2017						
Analyte	Quantifiable detections		Qs (Present but below reporting limit)		Total samples with quantifiable detections and Qs	
	Number	Percent of all samples	Number	Percent of all samples	Number	Percent of all samples
Atrazine	141	78	38	21	179	99
Deethyl atrazine	146	81	32	18	178	99
2,4-D	146	81	29	16	175	97
Hydroxy atrazine	128	71	38	21	166	92
Bentazon	121	67	12	7	133	74
Metolachlor ESA	102	57	20	11	122	68
Prometon	68	38	41	23	109	61
Acetochlor ESA	87	48	13	7	100	56
Acetochlor OA	97	54	1	1	98	54
Metolachlor OA	41	23	40	22	81	45
Tebuconazole	5	3	76	42	81	45
Imazethapyr	58	32	20	11	78	43
MCPA	33	18	45	25	78	43
Pyrasulfotole	8	4	70	39	78	43
IMAM	24	13	49	27	73	41
Metolachlor	53	29	17	9	70	39
Tebuthiuron	24	13	42	23	66	37
Propiconazole	13	7	51	28	64	36
Dimethenamid	41	23	22	12	63	35
Imazapyr	22	12	35	19	57	32
Dimethenamid OA	43	24	13	7	56	31
Saflufenacil	19	11	37	21	56	31
Sulfentrazone	24	13	30	17	54	30
Flucarbazone	14	8	34	19	48	27
FSA	3	2	39	22	42	23
Deisopropyl atrazine	9	5	31	17	40	22
Tetraconazole	18	10	22	12	40	22

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 48 detections of pesticides at or above these levels as detailed in Table 4.

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

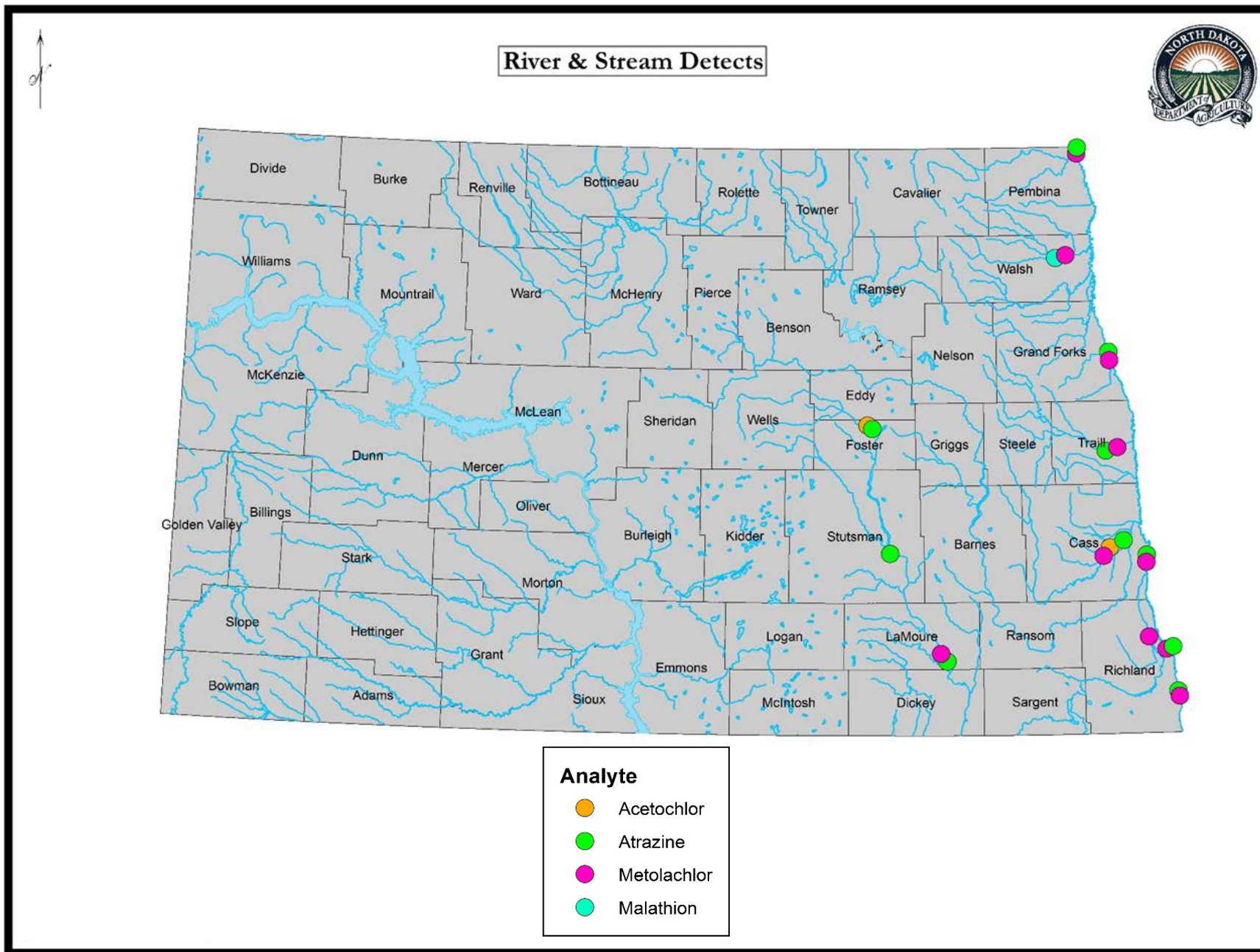
Detections that were 20% or more of lowest ALB or MCL			
Chemical	Number of detections	Range of detections (PPB)	Lowest ALB or MCL (PPB)
Atrazine	26	0.25-7.6	1
Acetochlor	2	0.35-0.92	1.43
Malathion	1	0.076	0.049
Metolachlor	19	0.21-2.8	1

There were 12 sites in which these chemicals were found at 20% or more of an ALB or MCL (Figure 2). All of the 12 sites are in the eastern third of North Dakota with the Red River basin containing most of the sites.

Within the Red River basin, the Bois de Sioux River sampled near Doran, MN had four detections; the pesticides detected were atrazine (three detections) and metolachlor. The Wild Rice River sampled near Abercrombie, ND had five detections; the pesticides detected were atrazine (two detections) and metolachlor (three detections). The Goose River sampled at Hillsboro, ND had five detections; the pesticides detected were atrazine (three detections) and metolachlor (two detections). The Red River at Brushville, MN had three detections; the pesticides detected were atrazine (two detections) and metolachlor. The Park River sampled at Grafton, ND had two detections, the pesticides detected were malathion and metolachlor. The Red River at Grand Forks, ND and the Red River at Pembina each had one atrazine detection and one metolachlor detection. The Red River sampled at Fargo, ND had two atrazine detections and two metolachlor detections. The Maple River below Mapleton, ND had fourteen pesticide detections; the pesticides detected were acetochlor, atrazine (seven detections) and metolachlor (six detections).

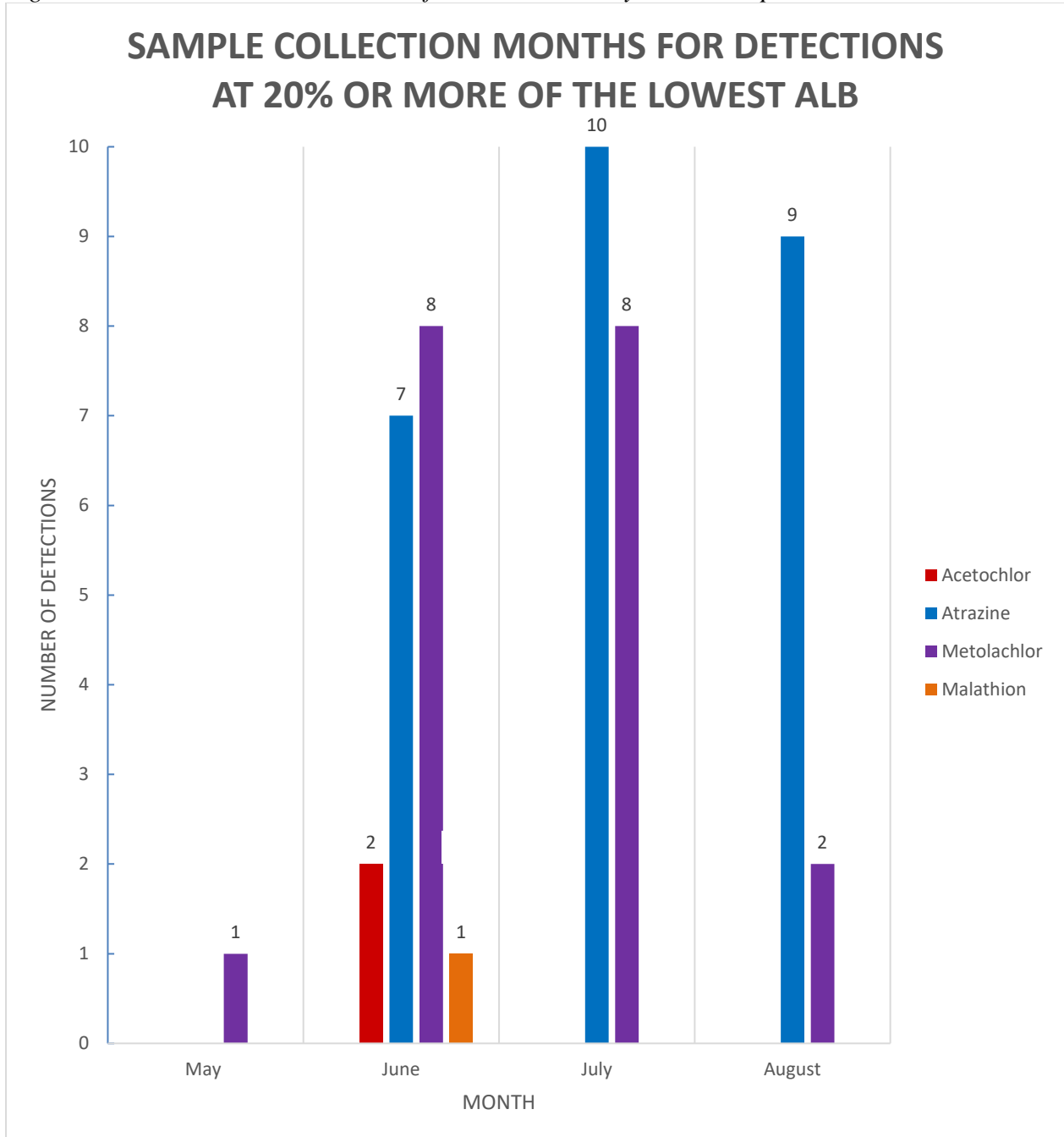
Outside of the Red River basin, the James River sampled near Grace City, ND had four detections; the pesticides detected were acetochlor and atrazine (three detections). The James River at Jamestown, ND had one atrazine detection. The James River at Lamoure, ND had one atrazine detection and one metolachlor detection.

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



The 48 pesticide detections at concentrations of 20% or more of the lowest ALB were spread throughout the growing season with most detections occurring in June and July (Figure 3). There were no pesticide detections above 20% of an ALB or MCL in April. There was one pesticide detection above 20% of an ALB in May, the pesticide detected was metolachlor. In June, acetochlor, atrazine, metolachlor and malathion were detected multiple times at levels 20% or more of the lowest ALB. July and August had multiple detections of atrazine and metolachlor. No pesticide samples were collected in September. There were no pesticide detections above 20% of an ALB or MCL in October.

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 or human health. In looking for levels that may pose risk, results were further reviewed to identify instances in which an ALB or MCL had been exceeded (Tables 4 & 5). The most conservative ALBs and MCLs which are displayed below, are based on long-term exposure to a pesticide and are discussed in detail below.

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 could 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.

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

Site Name	Sample Date	Analyte	Level (ppb)	ALB (ppb)
Bois de Sioux River near Doran, MN	6/28/2017	Atrazine	2.0	1.0
Bois de Sioux River near Doran, MN	6/28/2017	Metolachlor	2.2	1.0
Goose River at Hillsboro, ND	6/26/2017	Atrazine	1.1	1.0
Goose River at Hillsboro, ND	7/5/2017	Atrazine	1.3	1.0
James River near Grace City, ND	6/19/2017	Atrazine	1.6	1.0
Maple River below Mapleton, ND	6/26/2017	Atrazine	7.6	1.0
Maple River below Mapleton, ND	7/26/2017	Atrazine	1.5	1.0
Maple River below Mapleton, ND	7/27/2017	Atrazine	1.4	1.0
Maple River below Mapleton, ND	7/28/2017	Atrazine	1.2	1.0
Maple River below Mapleton, ND	7/31/2017	Atrazine	1.0	1.0
Maple River below Mapleton, ND	8/2/2017	Atrazine	1.2	1.0
Maple River below Mapleton, ND	6/26/2017	Metolachlor	2.8	1.0
Park River at Grafton, ND	6/20/2017	Malathion	0.076	0.049
Wild Rice River near Abercrombie, ND	6/26/2017	Atrazine	1.1	1.0

MCL discussion

The EPA sets a Maximum Contaminant Level (MCL) for many contaminants including some pesticides. The MCL is the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. The MCL is a legal limit set by EPA and is based on a lifelong

exposure to a contaminant. For known cancer-causing contaminants the MCL is set at zero, because any chemical exposure could present a cancer risk.

Table 5. Detections indicating a Maximum Contaminant Level (MCL) was met or exceeded.

Site Name	Date	Chemical	Detected level (ppb)	MCL (ppb)
Maple River below Mapleton, ND	6/26/2017	Atrazine	7.6	3

Targeted Sampling

In 2017 there was one detection that exceeded an MCL which resulted in targeted sampling being performed. Targeted sampling consisted of additional sample collection at the site with the exceedance (Table 6).

Table 6. Atrazine MCL exceedance and targeted sampling results.

Season Sampling Results for Atrazine at the Maple River below Mapleton, ND										
Sampling Date	4/21	5/31	6/26	7/26	7/27	7/28	7/31	8/2	8/29	10/25
Atrazine Level (ppb)	0.011	0.017	7.6	1.5	1.4	1.2	1.0	1.2	0.29	0.093

Highlighted cell indicates MCL exceedance.

The EPA set the MCL value for atrazine at 3 ppb. A sample collected from the Maple River below Mapleton collected on June 26, 2017 indicated an atrazine level of 7.6 ppb or 2.53 times higher than the MCL. As a result of this detection, targeted sampling was performed and revealed that although there was a spike above an MCL, it was short in duration and decreased to a level well below the MCL in one month. Risk from atrazine will be discussed further below.

Risk from ALB and MCL Exceedance

Atrazine

Atrazine, a broadleaf herbicide used primarily on corn, was present in 21% (38) of samples and quantifiably detected in 78% (141) of samples. Of those detections, 26 of them were at 20% or more of an MCL or ALB. Atrazine detections indicated an MCL was met or exceeded once with a value of 7.6 ppb. Atrazine detections indicated an ALB was met or exceeded eleven times with values ranging from 1.0-7.6 ppb.

The EPA established MCL is 3 ppb which is the regulatory level set by EPA. This level is based on risk assessment data, peer-reviewed research, and discussion with other agencies. There are high levels of safety factors built into the MCL which consider safe levels of contaminants in drinking water exposure over a lifetime. Sampling showed that levels at or above an MCL were short in duration and do not pose risk from chronic exposure; which is what the MCL value is developed on. It is important to note these detections and compare to future data.

The Refined Ecological Risk Assessment for Atrazine (EPA 2016) discusses risk from atrazine to the environment. This document lists the most sensitive aquatic endpoint for atrazine at less than 1.0 ppb. This value is based on a study performed in 1976 that demonstrated a 67%

reduction in chlorophyll production in green algae over a seven-day exposure period (Torres and O'flaherty 1976). The EPA risk assessment states average atrazine concentrations in water at or above 5.0 ppb for several weeks are predicted to lead to reproductive effects in fish, while a 60-day average of 3.4 ppb has a high probability of impacting aquatic plant community primary productivity, structure, and function. The highest concentration detected was 7.6 ppb. The sample collected before this detection indicated atrazine was at 0.017 ppb and the sample collected one month after at this site indicated an atrazine level of 1.5 ppb. Without continuous monitoring it is impossible to determine when the level rose above 3.4 ppb and when the level decreased below 3.4 ppb, but the level was not above 3.4 ppb for 60 days. Assuming a worst-case scenario, it is possible that algae populations were impacted at and near this site, however no aquatic impacts were noted by samplers or were reported to the NDDA by any other entities. Although there was ALB exceedance it is important to note that out of 180 samples, atrazine was only found above an ALB eleven times. This shows that there is a small risk to aquatic ecosystems and risk is limited to a select number of sites and is short in duration. These sites will continue to be monitored closely and if funding allows, additional targeted sampling will be performed.

Metolachlor

Metolachlor is used primarily on corn in North Dakota for grass and broadleaf weed control. Metolachlor and metolachlor degradates were detected or present in as high as 68% of samples. Metolachlor was detected at or above an ALB twice in 2017. The lowest EPA established ALB is 1 ppb for chronic risk to invertebrates and is based on the lowest no observed adverse effects concentration (NOAEC) from a life-cycle test with water flea (*Daphnia magna*). The lowest observed adverse effects concentration (LOAEC) for water flea is 10 ppb. The highest concentration detected was 2.8 ppb which is over the NOAEC but well below the LOAEC. This indicates minimal risk to aquatic ecosystems. There is no EPA MCL for metolachlor.

Malathion

Malathion is labeled to control insect pests on various crops grown in North Dakota. Based on the 2012 NDSU Pesticide Use Survey, malathion is not widely used when compared to other insecticide active ingredients. Malathion was present in just one sample in 2018 at a level of 0.076 ppb. The lowest EPA established ALB is 0.060 ppb for chronic risk to invertebrates and is based on the lowest no observed adverse effects concentration (NOAEC) from a life-cycle test with water flea (*Daphnia magna*). The lowest observed adverse effects concentration (LOAEC) for water flea is 0.098 ppb. The facts that there was only one detection and it was below the LOAEC indicates minimal risk to aquatic invertebrate species and aquatic ecosystems.

Neonicotinoid discussion

As neonicotinoid insecticides continue to gain attention and discussions about prevalence in the environment become more common, it is important to discuss them as part of river and stream sampling. In 2008 and 2009 imidacloprid was analyzed for, in 2010 clothianidin was added and since 2013, the neonicotinoid insecticides clothianidin, imidacloprid, and thiamethoxam have been analyzed for in ND river and stream sampling. Compared to herbicides such as atrazine and 2,4-D the neonicotinoids are not frequently detected. When detections do occur, they are at very low levels. In 2018, clothianidin was detected two times and present below the reporting limit in

17 samples; the highest detection was 0.020 ppb. Imidacloprid was detected in 16 samples and present below the reporting limit in 13 samples; the highest detection was 0.0064 ppb. Thiamethoxam was detected three times and present below the reporting limit 14 times with the highest detection being 0.037 ppb. The detections are well below ALBs for any of the three chemicals with the most sensitive ALB being 1.05 ppb for imidacloprid. River and stream sampling does not indicate neonicotinoid insecticides are prevalent at levels that pose risk to aquatic ecosystems in ND.

Conclusion

Results of the 2017 monitoring study indicate that pesticides were found at similar levels in 2017 as they were in 2016. This is somewhat surprising given the contrast in rainfall totals and timing between 2016 and 2017. Looking at trends over the last few years shows certain pesticides are consistently being found in North Dakota rivers and streams. In 2017 there were fourteen detections that indicated MCL and/or ALB had been exceeded, but this is still a very small percentage of samples. Overall, detections ranged widely in level and frequency based on the pesticide, with a very large percentage being below 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, acetochlor, 2,4-D, metolachlor, prometon, tebuconazole, and bentazon need to continue to be monitored. Sampling shows these pesticides are present in a high percentage of samples and occasionally approach levels that may begin to impact aquatic ecosystems. It is imperative to monitor, and if necessary, implement risk mitigation before significant impacts to human health or the environment happen. 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.

Comparing river and stream data from 2008-2017 showed a few potential trends. Atrazine continues to be found in a high percentage of samples which is not surprising given the large-scale use and its chemical properties. Atrazine is also the most common pesticide found at higher levels, especially in the eastern third of the state. This is also not surprising since atrazine is predominantly used on corn which was planted on a large number of acres in the Red River Valley. 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 years of data reveals the highest number of detections comes from samples collected in June through August which is to be expected, as most of the pesticides detected are pre-emergence herbicides which are typically applied around planting and can 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. As laboratory testing capabilities improve, more data will be available leading to a better understanding of pesticide movement and aquatic ecosystem health in North Dakota. 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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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: <input type="checkbox"/>	Temperature: <input type="checkbox"/>
Yes: <input type="checkbox"/>	
Initials: <input type="text"/>	

Sample Collection/Billing Information							
Account #		Project Code		Project Description			
				Ambient Water Quality Monitoring			
Collected By							
Analyte Groups			Collection Method		Matrix		
			Grab		Water		
For Laboratory Use Only		Site ID	Site Description			DO	pH
Lab ID							
	Date Collected	Time Collected	Depth (m)	Surface	Comments	Temp	SC
	Date Collected	Time Collected	Depth (m)	Surface	Comments	Temp	SC
	Date Collected	Time Collected	Depth (m)	Surface	Comments	Temp	SC
	Date Collected	Time Collected	Depth (m)	Surface	Comments	Temp	SC
	Date Collected	Time Collected	Depth (m)	Surface	Comments	Temp	SC
	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 2017			
Analyte	Common Trade Names*	Type	Reporting Limit (ppb)
2,4-D	2,4-D, Curtail	H	0.009
Acetochlor	Surpass, Harness	H	0.14
Acetochlor ESA	degrade	D	0.02
Acetochlor OA	degrade	D	0.0084
Alachlor	Intrro, Lariat, Lasso	H	0.11
Alachlor ESA	degrade	D	0.044
Alachlor OA	degrade	D	0.0068
AMBA (mesotrione metabolite)	degrade	D	0.021
Aminocyclopyrachlor	Method, Perspective	H	0.025
Aminopyralid	Cleanwave	H	0.03
Atrazine	Aatrex	H	0.0022
Azoxystrobin	Quadris	F	0.0052
Bentazon	Basagran	H	0.0022
Bromacil	Hyvar, Bromax	H	0.0041
Bromoxynil	Huskie, Buctril	H	0.012
Carbaryl	Sevin, Savit	I	0.014
Chlorpyrifos	Lorsban, Dursban	I	0.06
Chlorsulfuron	Finesse, Glean	H	0.0056
Clodinafop acid	Discover NG	H	0.013
Clopyralid	Stinger, Curtail	H	0.088
Clothiandin	Poncho	I	0.016
Deethyl atrazine	degrade	D	0.0017
Deethyl Deisopropyl Atrazine (DEDIA)	degrade	D	0.1
Deisopropyl atrazine	degrade	D	0.04
Dicamba	Banvel	H	0.88
Difenoconazole	CruiserMaxx, InspireF	H	0.011
Dimethenamid	Outlook	H	0.006
Dimethenamid OA	degrade	D	0.0072
Dimethoate	Cygon, Roxion	I	0.0022
Disulfoton sulfone	degrade	D	0.0066
Diuron	Direx, Karmex	H	0.0053
Fluoroethyldiaminotriazine (FDAT)	degrade	D	0.0051
Fipronil	Regent	I	0.0024
Fipronil desulfinyl	degrade	D	0.14
Fipronil sulfide	degrade	D	0.08
Fipronil sulfone	degrade	D	0.04
Flucarbazone	Everst, Prepare	H	0.0024
Flucarbazone sulfonamide (FSA)	degrade	D	0.0039
Flumetsulam	Python	H	0.029

Appendix B. List of analytes and reporting limits (continued).

List of analytes and reporting limits in 2017			
Analyte	Common Trade Names*	Type	Reporting Limit (ppb)
Flupyradifurone	Sivanto	I	0.045
Fluroxypyr	Starane	H	0.035
Glutaric Acid	degrade	D	0.03
Hydroxy atrazine	degrade	D	0.004
Halosulfuron methyl	Permit	H	0.01
Hexazinone	Velpar	H	0.0015
Imazamethabenz methyl acid metabolite (IMAM)	degrade	D	0.0025
Imazamethabenz methyl ester (IME)	degrade	D	0.001
Imazamox	Raptor, Beyond	H	0.0057
Imazapic	Plateau	H	0.003
Imazapyr	Imazapyr, Lineage	H	0.0035
Imazethapyr	Authority Assist, Pursuit	H	0.004
Imidacloprid	Touchstone PF	I	0.0018
Indaziflam	Alion, Specticle	H	0.002
Isoxaben	Gallery, Snapshot	H	0.003
Isoxaflutole	Corvus, Balance Flexx	H	0.13
Malathion	Malathion, Cythion	I	0.028
Malathion oxon	degrade	D	0.0024
MCPA	MCP	H	0.0046
MCPP	Encore, Trimec	H	0.0044
Metalaxyl	Hi-Yield, Ridomil	F	0.0035
Methomyl	Lannate	I	0.012
Methoxyfenozide	Intrepid	I	0.01
Metolachlor	Dual Magnum	H	0.024
Metolachlor ESA	degrade	D	0.005
Metolachlor OA	degrade	D	0.042
Metsulfuron methyl	Ally, Cimarron	H	0.01
Nicosulfuron	Accent, Steadfast	H	0.011
NOA 407854 (Pinoxaden metabolite)	degrade	D	0.0052
NOA 447204 (Pinoxaden metabolite)	degrade	D	0.02
Norflurazon	Solicam	H	0.02
Norflurazon desmethyl	degrade	D	0.02
Oxamyl	Vydate	I	0.01
Parathion methyl oxon	degrade	D	0.012
Phorate sulfone	degrade	D	0.024
Phorate sulfoxide	degrade	D	0.003
Picloram	Tordon	H	0.28
Picoxystrobin	Approach	F	0.0075
Prometon	Pramitol	H	0.001

Appendix B. List of analytes and reporting limits (continued).

List of analytes and reporting limits in 2017			
Analyte	Common Trade Names*	Type	Reporting Limit (ppb)
Propiconazole	Banner, Tilt, Radar	F	0.01
Prosulfuron	Peak, Spirit	H	0.005
Pyrasulfatole	Huskie, Wolverine	H	0.02
Pyroxsulam	GR1, Powerflex	H	0.013
Saflufenacil	Sharpen	H	0.01
Simazine	Princep	H	0.0026
Sulfentrazone	Spartan	H	0.035
Sulfometuron methyl	Lineage, Oust	H	0.0025
Sulfosulfuron	Maverick, Outrider	H	0.0054
Tebuconazole	Folicur	F	0.014
Tebuthiuron	Spike	H	0.0011
Tembotrione	Capreno, Laudis	H	0.073
Terbacil	Sinbar	H	0.0048
Terbufos sulfone	degrade	D	0.011
Tetraconazole	Domarck, Eminent	F	0.0039
Thiamethoxam	CruiserMaxx, Meridian	I	0.02
Thiencarbazone methyl	Corvus, Huskie Complete	H	0.04
Thifensulfuron	Supremacy Harmony	H	0.022
Tralkoxydim	Achieve	H	0.0051
Tralkoxydim acid	degrade	D	0.005
Triallate	Far-Go	H	0.3
Triasulfuron	Dally, Rave	H	0.0055
Tricolpyr	Garlon	H	0.022
Trifloxystrobin	Compass, Stratego	F	0.02

*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=Degrade (breakdown product)

Appendix C. List of 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	6/28/2017	Atrazine	2.0	1.0
Bois de Sioux River near Doran, MN	385055	6/28/2017	Metolachlor	2.2	1.0
Bois de Sioux River near Doran, MN	385055	8/2/2017	Atrazine	0.6	1.0
Bois de Sioux River near Doran, MN	385055	8/28/2017	Atrazine	0.57	1.0
Goose River at Hillsboro, ND	380156	6/26/2017	Atrazine	1.1	1.0
Goose River at Hillsboro, ND	380156	6/26/2017	Metolachlor	0.53	1.0
Goose River at Hillsboro, ND	380156	7/5/2017	Atrazine	1.3	1.0
Goose River at Hillsboro, ND	380156	7/5/2017	Metolachlor	0.27	1.0
Goose River at Hillsboro, ND	380156	7/31/2017	Atrazine	0.28	1.0
James River at Jamestown, ND	380013	8/23/2017	Atrazine	0.35	1.0
James River at Lamoure, ND	380012	6/20/2017	Metolachlor	0.71	1.0
James River at Lamoure, ND	380012	8/23/2017	Atrazine	0.33	1.0
James River nr Grace City, ND	384130	6/19/2017	Acetochlor	0.92	1.43
James River nr Grace City, ND	384130	6/19/2017	Atrazine	1.6	1.0
James River nr Grace City, ND	384130	7/26/2017	Atrazine	0.8	1.0
James River nr Grace City, ND	384130	8/22/2017	Atrazine	0.25	1.0
Maple River below Mapleton, ND	384155	6/26/2017	Acetochlor	0.35	1.43
Maple River below Mapleton, ND	384155	6/26/2017	Atrazine	7.6	1.0
Maple River below Mapleton, ND	384155	6/26/2017	Metolachlor	2.8	1.0
Maple River below Mapleton, ND	384155	7/26/2017	Atrazine	1.5	1.0
Maple River below Mapleton, ND	384155	7/26/2017	Metolachlor	0.38	1.0
Maple River below Mapleton, ND	384155	7/27/2017	Atrazine	1.4	1.0
Maple River below Mapleton, ND	384155	7/27/2017	Metolachlor	0.37	1.0
Maple River below Mapleton, ND	384155	7/28/2017	Atrazine	1.2	1.0
Maple River below Mapleton, ND	384155	7/28/2017	Metolachlor	0.27	1.0
Maple River below Mapleton, ND	384155	7/31/2017	Atrazine	1.0	1.0
Maple River below Mapleton, ND	384155	7/31/2017	Metolachlor	0.21	1.0
Maple River below Mapleton, ND	384155	8/2/2017	Atrazine	1.2	1.0
Maple River below Mapleton, ND	384155	8/2/2017	Metolachlor	0.26	1.0
Maple River below Mapleton, ND	384155	8/29/2017	Atrazine	0.29	1.0
Park River at Grafton, ND	380157	6/20/2017	Malathion	0.076	0.049
Park River at Grafton, ND	380157	6/20/2017	Metolachlor	0.49	1.0
Red River at Brushville, MN	380083	6/28/2017	Atrazine	0.75	1.0
Red River at Brushville, MN	380083	6/28/2017	Metolachlor	0.65	1.0
Red River at Brushville, MN	380083	8/30/2017	Atrazine	0.27	1.0
Red River at Fargo, ND	385414	6/26/2017	Atrazine	0.77	1.0
Red River at Fargo, ND	385414	6/26/2017	Metolachlor	0.64	1.0
Red River at Fargo, ND	385414	7/5/2017	Atrazine	0.49	1.0
Red River at Fargo, ND	385414	7/5/2017	Metolachlor	0.59	1.0
Red River at Grand Forks, ND	384156	7/12/2017	Atrazine	0.4	1.0
Red River at Grand Forks, ND	384156	7/12/2017	Metolachlor	0.51	1.0

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

Site Name	Site ID	Sample Date	Analyte	Level (ppb)	ALB (ppb)
Red River at Pembina, ND	384157	7/19/2017	Atrazine	0.48	1.0
Red River at Pembina, ND	384157	7/19/2017	Metolachlor	0.25	1.0
Wild Rice River near Abercrombie, ND	380031	5/30/2017	Metolachlor	0.21	1.0
Wild Rice River near Abercrombie, ND	380031	6/26/2017	Atrazine	1.1	1.0
Wild Rice River near Abercrombie, ND	380031	6/26/2017	Metolachlor	0.43	1.0
Wild Rice River near Abercrombie, ND	380031	8/2/2017	Atrazine	0.29	1.0
Wild Rice River near Abercrombie, ND	380031	8/2/2017	Metolachlor	0.69	1.0