# 2014 Pesticide Surface Water Monitoring Report


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# Acknowledgements

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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 2014 to assess levels of pesticides and pesticide degradates in North Dakota rivers and streams. Thirty sites were sampled approximately seven times from April through October with additional targeted sampling occurring at six sites that showed a history of detections, resulting in a total of 194 river and stream samples collected. Each sample was analyzed for 96 different pesticides and pesticide degradates. The Department utilized the Montana State University Agriculture Experiment Station's Analytical Laboratory for sample analysis. The most commonly detected pesticide was atrazine which was detected in 98.97% of 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; pyrasulfotole; and bentazon.

Results indicate that while pesticides were found in North Dakota's rivers and streams, they were found at levels that pose 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 expanded its water quality focus to include 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 (Orr and Gray, 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 that the 2009 sampling start in June and end in November. There were a total of eleven detections of four different pesticides in 2009, 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 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 (Johnson and Gray, 2011).

In 2011, funding was directed to a wetland pesticide monitoring project. Fifty-four wetlands were sampled once during June through August. Atrazine and endosulfan were each detected once and pendimethalin and metolachlor were each detected twice in 2011. 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).

**2014 Project goals**
The goals of the 2014 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 five to seven times in 2014 at 30 sites from early April through late October. Targeted sampling was performed at six sites during the months of June, July, and August. Targeted sampling collected additional samples through these months with the goal of identifying pesticide spike duration. 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, flooding, and staffing. The 2014 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% 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 was approximately at its greatest depth in the cross section. The WBS was then lowered to a depth equal to approximately 60% 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 of 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% 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 96 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 was 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 was validated according to the requirements of the MT 2008 EPA Quality Assurance Project Plan (QAPP).

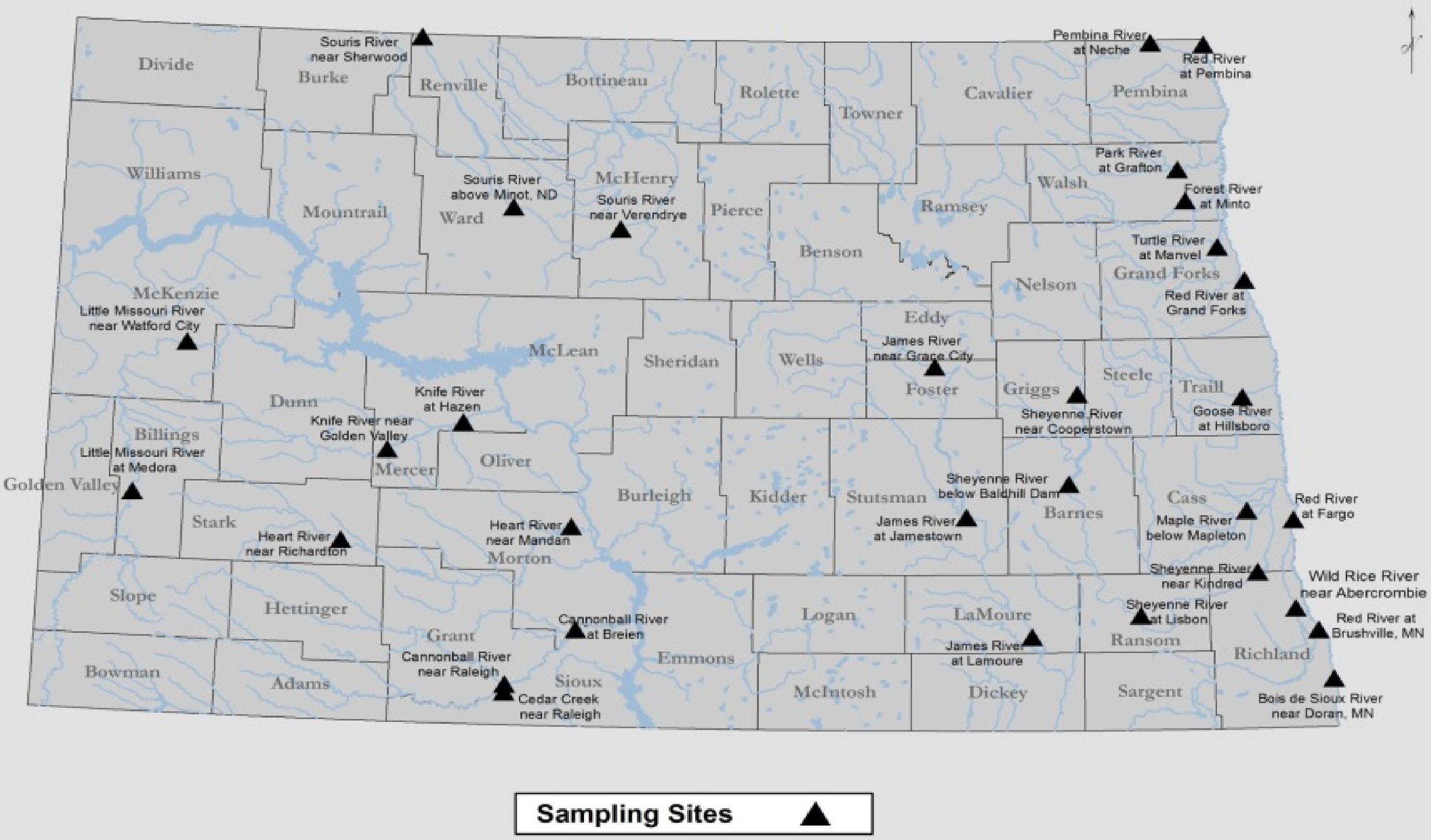
*Table 1.* **North Dakota pesticide surface water monitoring project sites in 2014.**

| USGS Site ID | **NDDoH Site ID** | **Site Name** | **Latitude** | **Longitude** |
|---|---|---|---|---|
| **5057000** | 380009 | Sheyenne River near Cooperstown, ND | 47.4328 | -98.0276 |
| **5058700** | 385168 | Sheyenne River at Lisbon, ND | 46.4469 | -97.6793 |
| **6336000** | 380022 | Little Missouri River at Medora, ND | 46.9195 | -103.5282 |
| **6337000** | 380059 | Little Missouri River nr Watford City, ND | 47.5958 | -103.263 |
| **6339500** | 384131 | Knife River nr Golden Valley, ND | 47.1545 | -102.0599 |
| **6340500** | 380087 | Knife River at Hazen, ND | 47.2853 | -101.6221 |
| **6345500** | 380160 | Heart River nr Richardton, ND | 46.7456 | -102.3083 |
| **6349000** | 380151 | Heart River nr Mandan, ND | 46.8339 | -100.9746 |
| **6351200** | 380105 | Cannonball River nr Raleigh, ND | 46.1269 | -101.3332 |
| **6353000** | 380077 | Cedar Creek nr Raleigh, ND | 46.0917 | -101.3337 |
| **6354000** | 380067 | Cannonball River at Breien, ND | 46.3761 | -100.9344 |
| **6468170** | 384130 | James River nr Grace City, ND | 47.5581 | -98.8629 |
| **6470000** | 380013 | James River at Jamestown, ND | 46.8897 | -98.6817 |
| **6470500** | 380012 | James River at Lamoure, ND | 46.3555 | -98.3045 |
| **5051300** | 385055 | Bois de Sioux River near Doran, MN | 46.1522 | -96.5789 |
| **5051510** | 380083 | Red River at Brushville, MN | 46.3695 | -96.6568 |
| **5053000** | 380031 | Wild Rice River near Abercrombie, ND | 46.468 | -96.7837 |
| **5059000** | 385001 | Sheyenne River near Kindred, ND | 46.6316 | -97.0006 |
| **5060100** | 384155 | Maple River below Mapleton, ND | 46.9052 | -97.0526 |
| **5114000** | 380091 | Souris River nr Sherwood | 48.99 | -101.9582 |
| **5117500** | 380161 | Souris River above Minot, ND | 48.2458 | -101.3713 |
| **5120000** | 380095 | Souris River nr Verendrye, ND | 48.1597 | -100.7296 |
| **5054000** | 385414 | Red River at Fargo, ND | 46.8611 | -96.7837 |
| **5066500** | 380156 | Goose River at Hillsboro, ND | 47.4094 | -97.0612 |
| **5082500** | 384156 | Red River at Grand Forks, ND | 47.9275 | -97.0281 |
| **5083000** | 380037 | Turtle River at Manvel, ND | 48.0786 | -97.1845 |
| **5085000** | 380039 | Forest River at Minto, ND | 48.2858 | -97.3681 |
| **5090000** | 380157 | Park River at Grafton, ND | 48.4247 | -97.412 |
| **5100000** | 380158 | Pembina River at Neche, ND | 48.9897 | -97.557 |
| **5102490** | 384157 | Red River at Pembina, ND | 48.9769 | -97.2376 |

| *Table 2.* **North Dakota river and stream sample collection dates in 2014.** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Site ID** | Sampling Dates | | | | | | | | |
| **380009** | 4/30/2014 | 5/21/2014 | 6/18/2014 | 7/22/2014 | 8/19/2014 | 10/28/2014 | | | |
| **385168** | 4/30/2014 | 5/21/2014 | 6/18/2014 | 7/22/2014 | 8/19/2014 | 10/29/2014 | | | |
| **380022** | 4/22/2014 | 5/13/2014 | 6/10/2014 | 7/7/2014 | 8/12/2014 | 10/13/2014 | | | |
| **380059** | 4/22/2014 | 5/13/2014 | 6/10/2014 | 7/7/2014 | 8/12/2014 | 10/13/2014 | | | |
| **384131** | 4/22/2014 | 5/13/2014 | 6/10/2014 | 7/7/2014 | 8/12/2014 | 10/13/2014 | | | |
| **380087** | 4/22/2014 | 5/13/2014 | 6/10/2014 | 7/7/2014 | 8/12/2014 | 10/13/2014 | | | |
| **380160** | 4/22/2014 | 5/13/2014 | 6/10/2014 | 7/7/2014 | 8/12/2014 | 10/13/2014 | | | |
| **380151** | 4/22/2014 | 5/13/2014 | 6/11/2014 | 7/8/2014 | 8/11/2014 | 10/13/2014 | | | |
| **380105** | 4/23/2014 | 5/14/2014 | 6/11/2014 | 7/8/2014 | 8/11/2014 | 10/14/2014 | | | |
| **380077** | 4/23/2014 | 5/14/2014 | 6/11/2014 | 7/8/2014 | 8/11/2014 | 10/14/2014 | | | |
| **380067** | 4/23/2014 | 5/14/2014 | 6/11/2014 | 7/8/2014 | 8/11/2014 | 10/14/2014 | | | |
| **384130** | 4/30/2014 | ~~5/21/2014~~ | 6/18/2014 | 7/22/2014 | 8/19/2014 | 10/28/2014 | | | |
| **380013** | 4/30/2014 | 5/21/2014 | 6/18/2014 | 7/22/2014 | 8/19/2014 | 10/29/2014 | | | |
| **380012** | 4/30/2014 | 5/21/2014 | 6/18/2014 | 7/22/2014 | 8/19/2014 | 10/29/2014 | | | |
| **385055** | 4/28/2014 | 5/20/2014 | 6/17/2014 | 7/10/2014 | 7/22/2014 | 7/29/2014 | 8/27/2014 | 9/4/2014 | 10/21/2014 |
| **380083** | 4/28/2014 | 5/20/2014 | 6/17/2014 | 7/22/2014 | 9/4/2014 | 8/26/2014 | 10/21/2014 | | |
| **380031** | 4/29/2014 | 5/20/2014 | 6/17/2014 | 7/10/2014 | 7/22/2014 | 7/29/2014 | 8/26/2014 | 9/4/2014 | 10/22/2014 |
| **385001** | 4/29/2014 | 5/21/2014 | 6/18/2014 | 7/23/2014 | 8/26/2014 | 10/22/2014 | | | |
| **384155** | 4/30/2014 | 5/21/2014 | 6/16/2014 | 7/10/2014 | 7/21/2014 | 7/29/2014 | 8/25/2014 | 9/4/2014 | 10/20/2014 |
| **380091** | 4/28/2014 | 5/29/2014 | 6/18/2014 | 7/21/2014 | 8/19/2014 | 10/8/2014 | | | |
| **380161** | 4/28/2014 | 5/30/2014 | 6/17/2014 | 7/21/2014 | 8/20/2014 | 10/8/2014 | | | |
| **380095** | 4/28/2014 | 5/29/2014 | 6/17/2014 | 7/9/2014 | 7/22/2014 | 7/28/2014 | 8/20/2014 | 9/4/2014 | 10/7/2014 |
| **385414** | 4/24/2014 | 5/20/2014 | 7/9/2014 | 7/14/2014 | 7/29/2014 | 8/6/2014 | 9/3/2014 | 10/14/2014 | |
| **380156** | 4/24/2014 | 5/20/2014 | 7/7/2014 | 7/9/2014 | 7/28/2014 | 8/6/2014 | 9/3/2014 | 10/14/2014 | |
| **384156** | 4/29/2014 | 5/14/2014 | 6/10/2014 | 7/10/2014 | 8/18/2014 | 10/29/2014 | | | |
| **380037** | 4/23/2014 | 5/13/2014 | 7/8/2014 | 7/9/2014 | 8/13/2014 | 10/20/2014 | | | |
| **380039** | 4/23/2014 | 5/13/2014 | 7/8/2014 | 7/9/2014 | 8/13/2014 | 10/20/2014 | | | |
| **380157** | 4/23/2014 | 5/13/2014 | 7/8/2014 | 7/9/2014 | 8/13/2014 | 10/20/2014 | | | |
| **380158** | 5/1/2014 | 5/21/2014 | 7/9/2014 | 8/12/2014 | 10/22/2014 | | | | |
| **384157** | 4/22/2014 | 5/14/2014 | 7/15/2014 | 8/12/2014 | 10/22/2014 | | | | |

-Strikethrough indicates sample arrived at the lab broken.

*Figure 1.* **2014 pesticide surface water sampling sites.**



## RESULTS AND DISCUSSION

There were a total of 196 samples analyzed for 96 different pesticides and degradates. Seventy-three 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; pyrasulfotole; bentazon; tebuconazole; prometon; and metolachlor were present in over 70% of the samples collected, although 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 rivers and streams in 2014.**

| | 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 |
| **Atrazine** | 192 | 98.97 | 2 | 1.03 | 194 | 100.00 |
| **Deethyl atrazine (atrazine breakdown product)** | 181 | 93.30 | 13 | 6.70 | 194 | 100.00 |
| **2,4-D** | 161 | 82.99 | 31 | 15.98 | 192 | 98.97 |
| **Hydroxy atrazine (atrazine breakdown product)** | 136 | 70.10 | 46 | 23.71 | 182 | 93.81 |
| **Pyrasulfotole** | 88 | 45.36 | 67 | 34.54 | 155 | 79.90 |
| **Bentazon** | 144 | 74.23 | 7 | 3.61 | 151 | 77.84 |
| **Tebuconazole** | 69 | 35.57 | 76 | 39.18 | 145 | 74.74 |
| **Prometon** | 82 | 42.27 | 61 | 31.44 | 143 | 73.71 |
| **Metolachlor ESA (metolachlor breakdown product)** | 122 | 62.89 | 19 | 9.79 | 141 | 72.68 |
| **Propiconazole** | 60 | 30.93 | 67 | 34.54 | 127 | 65.46 |
| **Flucarbazone sulfonamide (flucarbazone breakdown product)** | 68 | 35.05 | 58 | 29.90 | 126 | 64.95 |
| **Deisopropyl atrazine (atrazine breakdown product)** | 56 | 28.87 | 69 | 35.57 | 125 | 64.43 |
| **Acetochlor ESA (acetochlor breakdown product)** | 103 | 53.09 | 21 | 10.82 | 124 | 63.92 |
| **Acetochlor OA (acetochlor breakdown product)** | 111 | 57.22 | 12 | 6.19 | 123 | 63.40 |
| **MCPA** | 68 | 35.05 | 55 | 28.35 | 123 | 63.40 |
| **Imazethapyr** | 75 | 38.66 | 38 | 19.59 | 113 | 58.25 |
| **Flucarbazone** | 79 | 40.72 | 27 | 13.92 | 106 | 54.64 |
| **Imazamethabenz methyl acid metabolite** | 41 | 21.13 | 64 | 32.99 | 105 | 54.12 |
| **Dimethenamid** | 67 | 34.54 | 25 | 12.89 | 92 | 47.42 |

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. Seven pesticides detected at 20% or more of the lowest ALB value (Table 4). Atrazine was detected 27 times at or above 20% of the ALB, followed by acetochlor detected 10 times, metolachlor detected 9 times, chlorpyrifos detected twice, and malathion and bromoxynil each detected once.

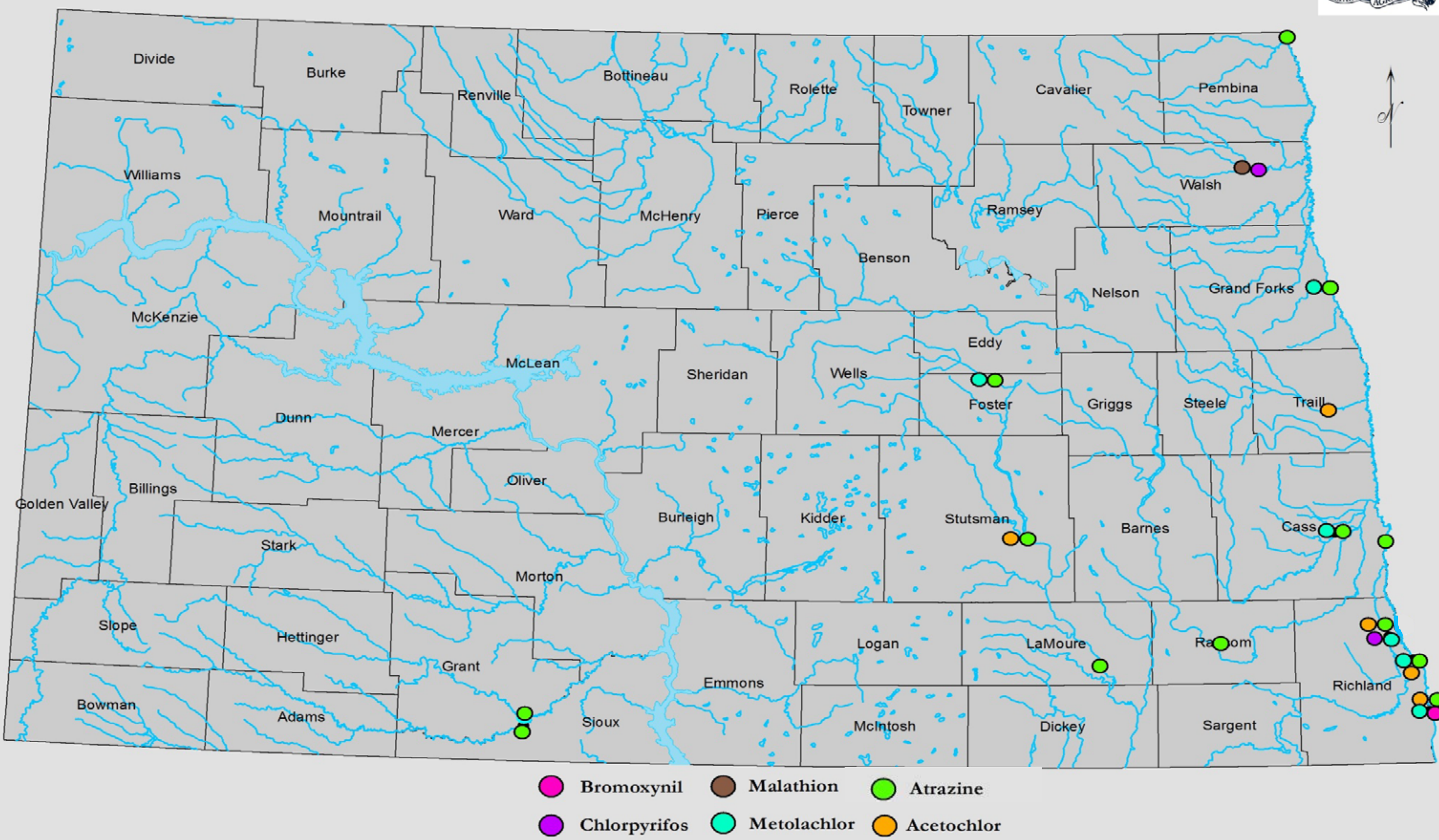
***Table 4.* Detections that were 20% or more of lowest ALB.**

| Chemical | Number of detections | Range of detections (PPB) | ALB (PPB) |
|---|---|---|---|
| Acetochlor | 10 | 0.3-4.3 | 1.43 |
| Atrazine | 27 | 0.21-1.7 | 1 |
| Bromoxynil | 1 | 0.53 | 2.5 |
| Chlorpyrifos | 2 | 0.036-0.092 | 0.04 |
| Malathion | 1 | 0.023 | 0.035 |
| Metolachlor | 9 | 0.25-0.93 | 1 |

There were 15 sites in which these chemicals were found at 20% or more of an ALB (Figure 2). The majority of the 15 sites were 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 Bois de Sioux River sampled near Doran, MN had 11 detections; the pesticides detected were acetochlor (three detections), atrazine (four detections), bromoxynil, and metolachlor (three detections). The Wild Rice River sampled near Abercrombie, ND had eight detections; the pesticides detected were acetochlor (two detections), atrazine (four detections), chlorpyrifos, and metolachlor. The Maple River below Mapleton ND had seven detections; the pesticides detected were atrazine (five detections) and metolachlor (two detections). The Red River sampled at Brushville, MN had five detections; the pesticides detected were acetochlor (three detections), atrazine, and metolachlor. The Red River sampled at Fargo, ND had two atrazine detections. The Red River at Grand Forks, ND had two detections; the pesticides detected were metolachlor and atrazine. The Park River at Grafton, ND had two detections; the pesticides detected were chlorpyrifos and malathion. The Goose River sampled at Hillsboro, ND had one acetochlor detection. The Red River at Pembina, ND and the Sheyenne River at Lisbon, ND each had one atrazine detection.

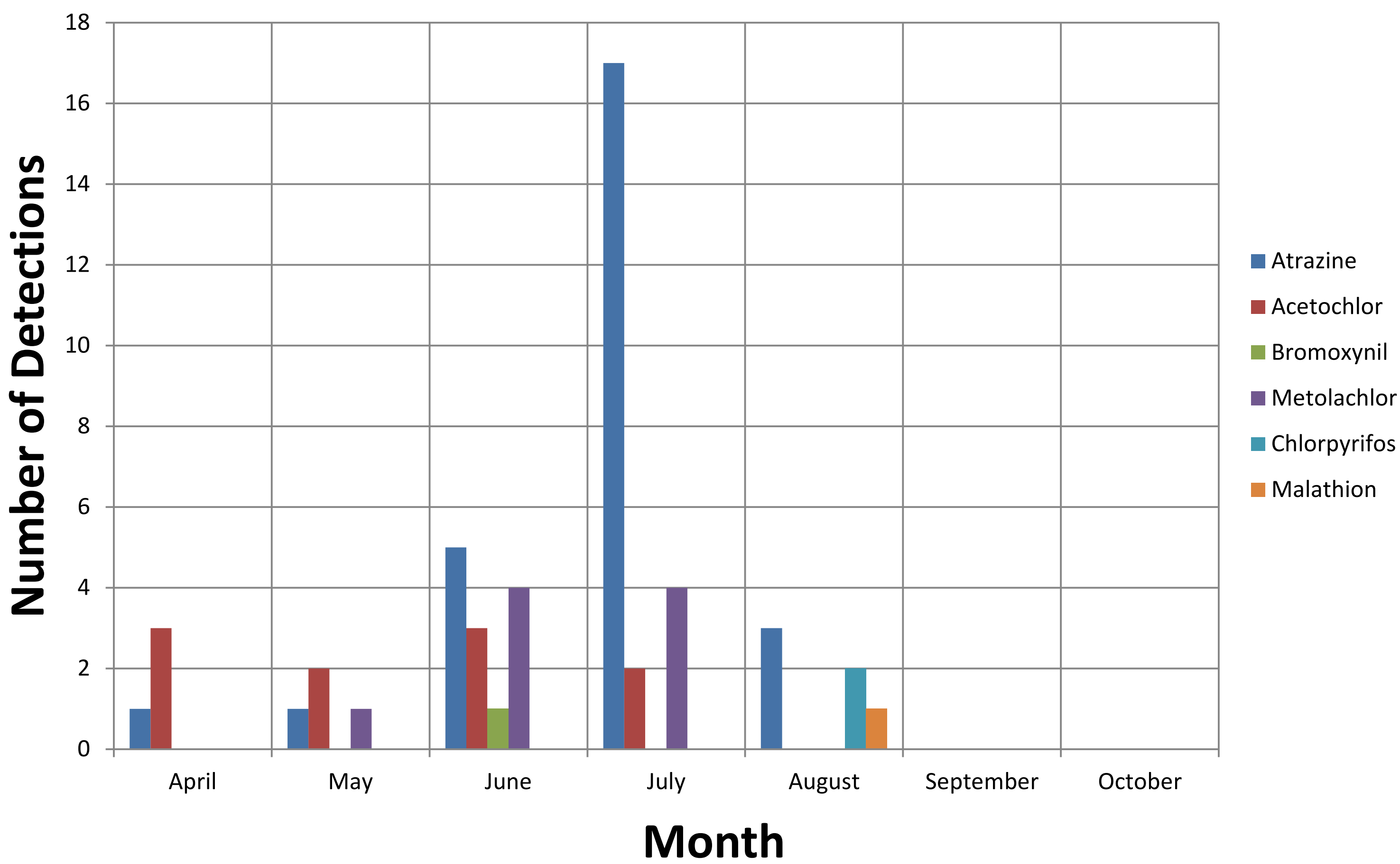
Outside of the Red River basin, the James River at Jamestown, ND had three detections; the pesticides detected were acetochlor and atrazine (two detections). The James River sampled near Grace City, ND had three detections; the pesticides detected were atrazine (two detections) and metolachlor. The James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

***Figure 2.*** **Sampling sites in 2014 where pesticides were detected at 20% or more of lowest ALB.**



The 50 pesticide detections at concentrations of 20% or more of the lowest ALB were spread throughout the growing season with the most detections occurring in July in 2014 (Figure 3). In April, atrazine was detected once and acetochlor was detected twice at levels 20% or more of the lowest ALB. Atrazine and metolachlor were detected once and acetochlor twice at or above 20% of the lowest ALB in May. June featured one bromoxynil detection, one sulfentrazone detection, three acetochlor detections, four metolachlor detections, and five atrazine detections. July had the most pesticide detections at 20% or more of an ALB with two acetochlor detections, four metolachlor detections, and seventeen atrazine detections. In August, malathion was detected once, chlorpyrifos was detected twice, and atrazine was detected three times at levels 20% or more of the lowest ALB. No pesticide detections in September and October were at or above 20% of the lowest ALB. It is important to point out that targeted sampling occurred in June, July, and August in which sites with a history of detections were sampled additional times throughout these months. These additional sampling events account for some of the increased detections during June and July.

***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 actually been exceeded. No pesticides were detected at concentrations exceeding an MCL, although there were eight detections at or above an ALB (Table 5).

***Table 5.* Detections indicating an aquatic life benchmark (ALB) was met or exceeded.**

| Site Name | Date | Chemical | Detected level (ppb) | ALB (ppb) |
|---|---|---|---|---|
| Bois de Sioux River near Doran, MN | 5/20/2014 | Acetochlor | 3.3 | 1.43 |
| Red River at Brushville, MN | 6/17/2014 | Acetochlor | 1.7 | 1.43 |
| Wild Rice River near Abercrombie, ND | 6/17/2014 | Acetochlor | 4.3 | 1.43 |
| Wild Rice River near Abercrombie, ND | 6/17/2014 | Atrazine | 1.7 | 1 |
| Maple River below Mapleton, ND | 7/10/2014 | Atrazine | 1.1 | 1 |
| James River at Jamestown, ND | 7/22/2014 | Atrazine | 1.3 | 1 |
| Park River at Grafton, ND | 8/13/2014 | Chlorpyrifos | 0.092 | 0.04 |

Aquatic life benchmarks are a function of both pesticide level and time (i.e. if acetochlor is present at a continuous level of 1.43 ppb for 5 days, 50% of the freshwater green algae populations may be affected) and are commonly based on continuous pesticide exposure over several days. Since the surface water sampling program does not provide continuous monitoring, but consists of several grab samples over time, it is impossible to determine whether the ALBs were truly exceeded and aquatic ecosystems were at significant risk.

Targeted sampling was performed in 2014 to determine pesticide levels at more frequent intervals with the goal of identifying spike duration and levels. Ideally, targeted sampling would occur at multiple intervals throughout the day for several days around pesticide spikes, but this is unrealistic given the variability of pesticide spikes and limited budget. Thus, targeted sampling was performed at six sites in 2014 which had notable pesticide detections in previous years (*Table 6*). Targeted samples were collected two to three times per month from mid-June through August. Targeted sampling will be revised in the future as additional data is gathered and pesticide spikes become more predictable.

Results of targeted sampling events for pesticides with a history of high detections were further reviewed. It is impossible to determine the pesticide contribution to surface water (i.e. how frequently and from where as an initial source), but if levels approach or exceed an ALB, it would be extremely beneficial to determine how long levels persist at or near an ALB.

Acetochlor was quantifiably detected at three sites where targeted sampling occurred: the Goose River at Hillsoboro, ND; the Bois de Sioux near Doran, MN; and the Wild Rice River near Abercrombie, ND.

In 2014, at the Goose River at Hillsboro, ND samples were collected on April 24, May 20, July 7, July 9, July 28, August 6, September 3, and October 14. Acetochlor was detected at 0.3 ppb on

July 9 and was not detected at any other dates. At the Goose River at Hillsboro, acetochlor levels were not present for long periods of time.

In 2014, at the Bois de Sioux near Doran, MN samples were collected April 28, May 20, June 17, July 10, July 22, July 29, August 27, September 4, and October 21. Acetochlor was detected at 1.2 ppb on April 28, 3.3 ppb on May 20, 1 ppb on June 17, 0.15 ppb on July 10, and was not detected at any other sampling dates. At the Bois de Sioux near Doran, MN, targeted sampling did not coincide with acetochlor spikes, and it is impossible to determine if the levels detected were spikes or persistent levels.

In 2014, at the Wild Rice River near Abercrombie, ND samples were collected April 29, May 20, June 17, July 10, July 22, July 29, August 26, September 4, and October 22. Acetochlor was detected at 0.67 ppb on April 29, 4.3 ppb on June 17, was present below the reporting limit on July10, and was not detected at any other sampling dates. At the Wild Rice River near Abercrombie, ND, targeted sampling did not coincide with acetochlor detections and acetochlor detections appear to be spikes that did not persist longer than one to two months.

Atrazine was quantifiably detected at all sites where targeted sampling occurred and was detected at levels at 20% or more of an ALB at the Red River at Fargo; the Bois de Sioux near Doran, MN; the Maple River below Mapleton, ND; and the Wild Rice River near Abercrombie, ND.

In 2014, at the Red River at Fargo, samples were collected on April 24; May 20; July 9, July 14; July 29; August 6; September 3; and October 14. Atrazine was detected at 0.064 ppb on April 24; 0.05 ppb on May 20; 0.34 ppb on July 9; 0.23 ppb on July 14; 0.11 ppb on July 29; 0.062 on August 6; 0.047 on September 3; and 0.022 ppb on October 14. At the Red River at Fargo, atrazine levels were low throughout the sampling season and when a spike was detected it dissipated or was broken down in a relatively short period of time.

In 2014, at the Bois de Sioux near Doran, MN samples were collected April 28; May 20; June 17; July 10; July 22; July 29; August 27; September 4; and October 21. Atrazine was detected at 0.12 ppb on April 28; 0.38 ppb on May 20; 0.54 ppb on June 17; 0.33 ppb on July 10; 0.31 ppb on July 22; 0.17 on July 29; 0.04 ppb on August 27; 0.069 ppb on September 4; and 0.018 on October 21. At the Bois de Sioux near Doran, MN, targeted sampling indicated that atrazine levels are relatively constant May through August.

In 2014, at the Maple River near Mapleton, ND samples were collected April 30; May 21; June 16; July 10; July 21; July 29; August 25; September 4; and October 20. Atrazine was detected at 0.2 ppb on April 30; 0.075 ppb on May 20; 0.8 ppb on June 16; 1.1 ppb on July 10; 0.51 ppb July 21; at 0.29 ppb on July 29; 0.074 ppb on August 25; 0.071 ppb on September 4; and 0.028 ppb on October 20. At the Maple River near Mapleton, ND, atrazine levels varied but appeared to degrade or dissociate relatively quickly after a spike (1.1 ppb to 0.51 ppb in 11 days and 0.51ppb to 0.29 ppb in 8 days).

In 2014, at the Wild Rice River near Abercrombie, ND samples were collected April 29; May 20; June 17; July 10; July 22; July 29; August 26; September 4; and October 22. Atrazine was detected at 0.15 ppb on April 29; 0.11 ppb on May 20; 1.7 ppb on June 17; 0.93 ppb on July 10; 0.95 on July 22; 0.54 on July 29; 0.19 on August 26; 0.16 on September 4; and 0.12 on October 22. At the Wild Rice River near Abercrombie, ND, sampling indicated atrazine levels spike in June and levels persisted below the spike into July.

Metolachlor was quantifiably detected at all sites where targeted sampling occurred and was detected at levels at 20% or more of an ALB at the Bois de Sioux near Doran, MN; the Maple River below Mapleton, ND; and the Wild Rice River near Abercrombie, ND.

In 2014, at the Bois de Sioux near Doran, MN samples were collected April 28; May 20; June 17; July 10; July 22; July 29; August 27; September 4; and October 21. Metolachlor was detected at 0.042 ppb on April 28; 0.25 ppb on May 20; 0.77 ppb on June 17; 0.26 ppb on July 10; 0.15 ppb on July 22; 0.11 ppb on July 29; present below the reporting limit on August 27; and 0.023 ppb on September 24. At the Bois de Sioux near Doran, MN, targeted sampling indicated that metolachlor spikes were relatively short lived.

In 2014, at the Maple River near Mapleton, ND samples were collected April 30; May 21; June 16; July 10; July 21; July 29; August 25; September 4; and October 20. Metolachlor was detected at 0.041 ppb on April 30; 0.016 ppb on May 21; 0.14 ppb on June 16; 0.32 ppb on July 10; 0.31 ppb July 21; and at 0.13 on July 29. At the Maple River near Mapleton, ND, metolachlor levels appeared to spike in early to mid-July and the dissociate or degrade in a few weeks.

In 2014, at the Wild Rice River near Abercrombie, ND samples were collected April 29; May 20; June 17; July 10; July 22; July 29; August 26; September 4; and October 22. Metolachlor was detected at 0.022 ppb on April 29; 0.011 ppb on May 20; 0.93 ppb on June 17; 0.092 ppb on July 10; 0.028 ppb on July 22; 0.016 ppb on July 29; present below the reporting limit on August 26; and 0.0086 ppb on September 4. At the Wild Rice River near Abercrombie, ND, metolachlor levels appeared to spike in June and degrade or dissociate quickly.

| *Table 6.* Targeted sampling results for pesticides that have been historically detected in a high percentage of samples. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **380156 Goose River at Hillsboro, ND** | Sample collection date | | | | | | | |
| Pesticide | 4/24/14 | 5/20/14 | 7/7/14 | 7/9/14 | 7/28/14 | 8/6/14 | 9/3/14 | 10/14/14 |
| Acetochlor | ND | ND | ND | 0.3 | ND | ND | ND | ND |
| Acetochlor ESA | 0.034 | 0.077 | 0.13 | 0.44 | 0.028 | 0 .038 | 0.03 | 0.039 |
| Acetochlor OA | 0.027 | 0.065 | 0.34 | 1.6 | 0.067 | 0 .088 | 0.048 | 0.068 |
| Atrazine | 0.028 | 0.02 | 0.13 | 0.18 | 0.037 | 0 .070 | 0.047 | 0.0082 |
| Deethyl atrazine | 0.01 | 0.0081 | 0.04 | 0.047 | 0.0076 | 0 .030 | 0.036 | 0.0024 |
| Deethyl deisopropyl atrazine | ND | ND | ND | ND | ND | ND | ND | ND |
| Deisopropyl atrazine | Q | Q | 0.014 | 0.019 | Q | Q | Q | ND |
| Hydroxy atrazine | 0.0082 | 0.0074 | 0.02 | 0.059 | 0.012 | 0 .018 | 0.017 | 0.0083 |
| Metolachlor | 0.011 | NA | 0.11 | 0.038 | Q | 0 .13 | Q | Q |
| Metolachlor ESA | 0.017 | 0.04 | 0.05 | 0.054 | 0.026 | 0 .048 | 0.037 | 0.013 |
| Metolachlor OA | Q | 0.023 | 0.021 | Q | Q | 0 .029 | Q | Q |
| **385414 Red River at Fargo, ND** | Sample collection date | | | | | | | |
| Pesticide | 4/24/14 | 5/20/14 | 7/9/14 | 7/14/14 | 7/29/14 | 8/6/14 | 9/3/14 | 10/14/14 |
| Acetochlor | ND | Q | Q | Q | ND | ND | ND | ND |
| Acetochlor ESA | 0.047 | 0.33 | 0.25 | 0.29 | 0.2 | 0 .055 | 0.15 | 0.023 |
| Acetochlor OA | 0.062 | 0.25 | 0.87 | 0.9 | 0.59 | 0 .13 | 0.3 | 0.054 |
| Atrazine | 0.064 | 0.05 | 0.34 | 0.23 | 0.11 | 0 .062 | 0.047 | 0.022 |
| Deethyl atrazine | 0.023 | 0.028 | 0.097 | 0.078 | 0.043 | 0 .031 | 0.03 | 0.009 |
| Deethyl deisopropyl atrazine | ND | ND | ND | ND | ND | ND | ND | ND |
| Deisopropyl atrazine | Q | Q | 0.03 | 0.051 | 0.032 | Q | Q | Q |
| Hydroxy atrazine | 0.019 | 0.037 | 0.11 | 0.07 | 0.056 | 0 .023 | 0.065 | 0.011 |
| Metolachlor | Q | NA | 0.12 | 0.11 | 0.035 | Q | 0.011 | ND |
| Metolachlor ESA | 0.045 | 0.11 | 0.21 | 0.13 | 0.095 | 0 .074 | 0.11 | 0.069 |
| Metolachlor OA | Q | 0.04 | 0.093 | 0.044 | 0.041 | 0 .028 | 0.047 | Q |

Highlighted cells with black text indicate result was notable but below an ALB.
Highlighted cells with red text indicate result was at or above an ALB.

| *Table 6 (continued).* Targeted sampling results for pesticides that have been historically detected in a high percentage of samples. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Bois de Sioux near Doran, MN** | Sample collection date | | | | | | | | |
| Pesticide | 4/28/14 | 5/20/14 | 6/17/14 | 7/10/14 | 7/22/14 | 7/29/14 | 8/27/14 | 9/4/14 | 10/21/14 |
| Acetochlor | 1.2 | 3.3 | 1 | 0.15 | ND | ND | ND | ND | ND |
| Acetochlor ESA | 1 | 0.45 | 2.8 | 0.65 | 0.64 | 0.48 | 0.34 | 0.3 | 0.64 |
| Acetochlor OA | 0.82 | 0.35 | 4.6 | 2 | 2.1 | 1.5 | 1.3 | 0.7 | 0.87 |
| Atrazine | 0.12 | 0.38 | 0.54 | 0.33 | 0.31 | 0.17 | 0.04 | 0.069 | 0.018 |
| Deethyl atrazine | 0.057 | 0.060 | 0.087 | 0.084 | 0.095 | 0.056 | 0.017 | 0.036 | 0.015 |
| Deethyl deisopropyl atrazine | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Deisopropyl atrazine | 0.020 | 0.020 | 0.029 | 0.029 | 0.049 | 0.037 | Q | Q | ND |
| Hydroxy atrazine | 0.037 | 0.067 | 0.062 | 0.11 | 0.11 | 0.14 | 0.16 | 0.13 | 0.1 |
| Metolachlor | 0.042 | 0.25 | 0.77 | 0.26 | 0.15 | 0.11 | Q | 0.023 | ND |
| Metolachlor ESA | 0.23 | 0.091 | 0.30 | 0.23 | 0.21 | 0.2 | 0.11 | 0.2 | 0.16 |
| Metolachlor OA | 0.074 | 0.027 | 0.11 | 0.068 | 0.062 | 0.063 | 0.056 | 0.088 | Q |
| **Maple River below Mapleton, ND** | Sample collection date | | | | | | | | |
| Pesticide | 4/30/14 | 5/21/14 | 6/16/14 | 7/10/14 | 7/21/14 | 7/29/14 | 8/25/14 | 9/4/14 | 10/20/14 |
| Acetochlor | Q | ND | Q | Q | ND | ND | ND | ND | ND |
| Acetochlor ESA | 0.25 | 0.18 | 0.23 | 0.38 | 0.12 | 0.076 | 0.044 | 0.073 | 0.026 |
| Acetochlor OA | 0.21 | 0.14 | 0.2 | 1.1 | 0.45 | 0.29 | 0.09 | 0.17 | 0.018 |
| Atrazine | 0.2 | 0.075 | 0.8 | 1.1 | 0.51 | 0.29 | 0.074 | 0.071 | 0.028 |
| Deethyl atrazine | 0.13 | 0.046 | 0.13 | 0.27 | 0.16 | 0.084 | 0.049 | 0.044 | 0.0045 |
| Deethyl deisopropyl atrazine | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Deisopropyl atrazine | 0.041 | 0.015 | 0.046 | 0.09 | 0.1 | 0.049 | 0.011 | 0.012 | ND |
| Hydroxy atrazine | 0.084 | 0.062 | 0.097 | 0.099 | 0.11 | 0.098 | 0.09 | 0.06 | 0.049 |
| Metolachlor | 0.041 | 0.016 | 0.14 | 0.32 | 0.31 | 0.13 | 0.013 | Q | Q |
| Metolachlor ESA | 0.14 | 0.14 | 0.076 | 0.14 | 0.23 | 0.17 | 0.16 | 0.079 | 0.068 |
| Metolachlor OA | 0.061 | 0.051 | 0.035 | 0.048 | 0.21 | 0.078 | 0.064 | 0.036 | 0.036 |

Highlighted cells with black text indicate result was notable but below an ALB.
Highlighted cells with red text indicate result was at or above an ALB.

| *Table 6 (continued).* Targeted sampling results for pesticides that have been historically detected in a high percentage of samples. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Wild Rice River near Abercrombie, ND** | Sample collection date | | | | | | | | |
| Pesticide | 4/29/14 | 5/20/14 | 6/17/14 | 7/10/14 | 7/22/14 | 7/29/14 | 8/26/14 | 9/4/14 | 10/22/14 |
| Acetochlor | 0.67 | ND | 4.3 | Q | ND | ND | ND | ND | ND |
| Acetochlor ESA | 0.78 | 0.43 | 2.4 | 0.3 | 0.15 | 0.1 | 0.1 | 0.089 | 0.18 |
| Acetochlor OA | 0.72 | 0.3 | 3.9 | 0.9 | 0.54 | 0.35 | 0.26 | 0.24 | 0.23 |
| Atrazine | 0.15 | 0.11 | 1.7 | 0.93 | 0.95 | 0.54 | 0.19 | 0.16 | 0.12 |
| Azoxystrobin | NA | ND | 0.01 | Q | ND | Q | ND | ND | ND |
| Deethyl atrazine | 0.082 | 0.046 | 0.11 | 0.27 | 0.17 | 0.1 | 0.07 | 0.068 | 0.034 |
| Deethyl deisopropyl atrazine | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Deisopropyl atrazine | 0.03 | 0.018 | 0.033 | 0.086 | 0.11 | 0.054 | 0.015 | 0.015 | Q |
| Hydroxy atrazine | 0.07 | 0.092 | 0.094 | 0.21 | 0.2 | 0.17 | 0.15 | 0.15 | 0.1 |
| Metolachlor | 0.022 | 0.011 | 0.93 | 0.092 | 0.028 | 0.016 | Q | 0.0086 | ND |
| Metolachlor ESA | 0.073 | 0.12 | 0.089 | 0.11 | 0.067 | 0.045 | 0.044 | 0.055 | 0.049 |
| Metolachlor OA | 0.033 | 0.031 | 0.033 | 0.041 | 0.029 | 0.028 | 0.022 | 0.025 | Q |
| **Souris River near Verendrye, ND** | Sample collection date | | | | | | | | |
| Pesticide | 4/29/14 | 5/29/14 | 6/17/14 | 7/9/14 | 7/22/14 | 7/28/14 | 8/20/14 | 9/4/14 | 10/7/14 |
| Acetochlor | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Acetochlor ESA | ND | Q | Q | Q | ND | ND | ND | ND | ND |
| Acetochlor OA | ND | ND | ND | Q | ND | ND | ND | Q | ND |
| Atrazine | 0.013 | 0.034 | 0.018 | 0.029 | 0.02 | 0.024 | 0.0083 | 0.0049 | 0.0045 |
| Deethyl atrazine | 0.0041 | 0.0066 | 0.0045 | 0.0055 | 0.0046 | 0.0049 | 0.0035 | 0.0028 | 0.0026 |
| Deethyl deisopropyl atrazine | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Deisopropyl atrazine | Q | Q | ND | Q | Q | Q | ND | ND | ND |
| Hydroxy atrazine | Q | Q | Q | Q | Q | Q | Q | 0.0041 | Q |
| Metolachlor | ND | ND | 0.011 | 0.008 | Q | Q | ND | ND | ND |
| Metolachlor ESA | ND | Q | Q | 0.005 | 0.0051 | 0.0048 | Q | 0.0066 | ND |
| Metolachlor OA | ND | ND | ND | ND | ND | ND | ND | Q | ND |

Highlighted cells with black text indicate result was notable but below an ALB.
Highlighted cells with red text indicate result was at or above an ALB.

*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, and field studies, as well as 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*

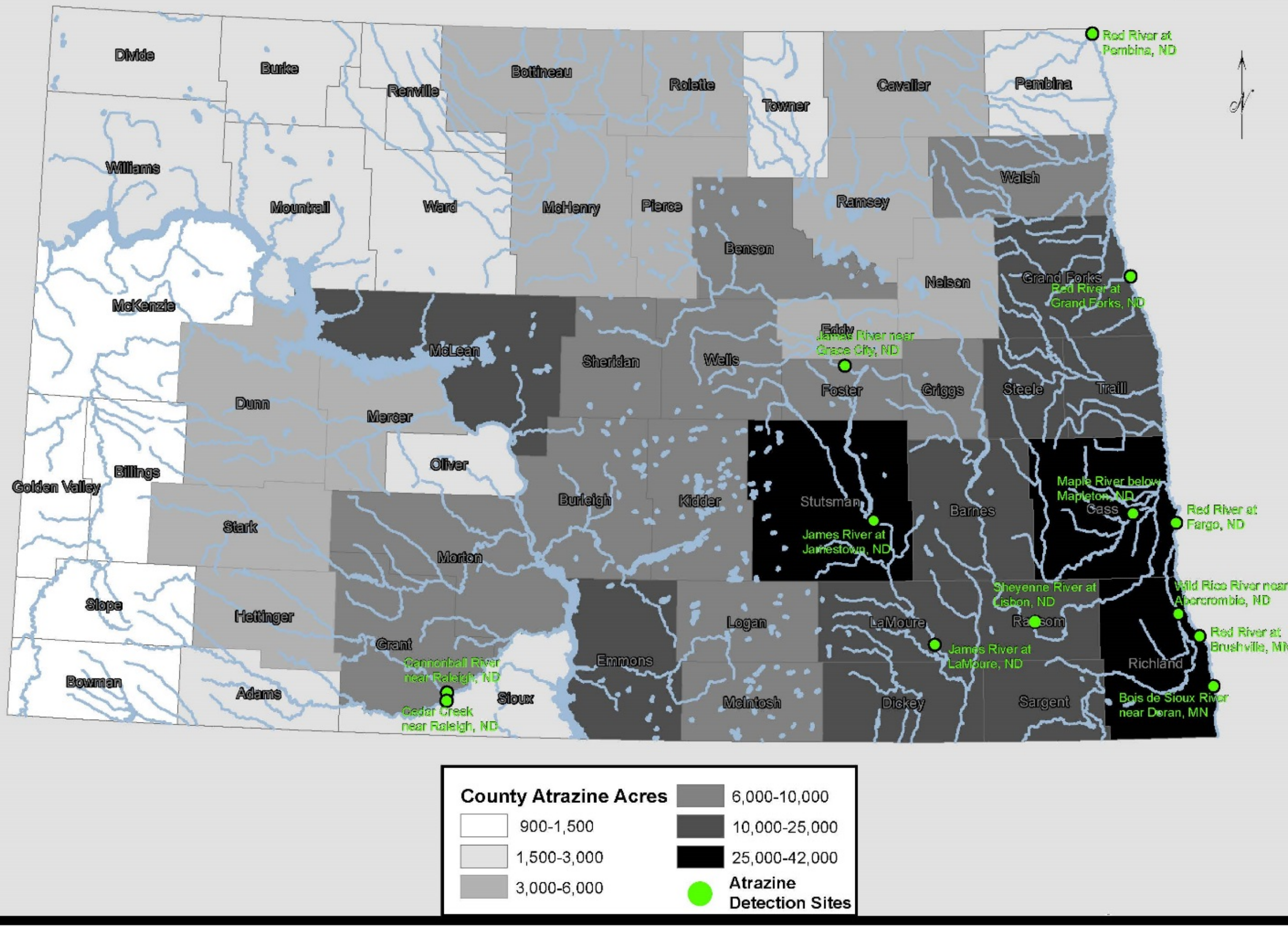
Detections were compared to pesticide use throughout the state. The information is derived from a comprehensive survey of North Dakota farm operators on 2012 practices published by North Dakota State University Extension (Zollinger et al. 2013) and county estimate data collected by USDA's National Agricultural 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 quantifiably detected in 99% (192) and present in the remaining 1% (2) of samples in 2014. Of those detections, 27 of them were at 20% or more of an ALB. Atrazine was detected three times at levels meeting or exceeding the ALB of 1 ppb. Specifically, atrazine was detected at 1.7 ppb in the Wild Rice River on June 17, 2014; at 1.1 ppb in the Maple River on July 10, 2014; and at 1.3 ppb in the James River at Jamestown on July 22, 2014. Most atrazine detections at 20% or more of the lowest ALB were in counties with high atrazine estimated use (Figure 7).

The lowest EPA established ALB for atrazine is 1 ppb for acute aquatic non-vascular plant toxicity. The toxicity value is based on an $EC_{50}$ (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 atrazine concentration detected in 2014 was 1.7 ppb, exceeding the ALB value by 1.7 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 10 days and exceed 1 ppb continuously. The drinking water MCL for atrazine is 3 ppb. The highest concentration detected is approximately 1.8 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.

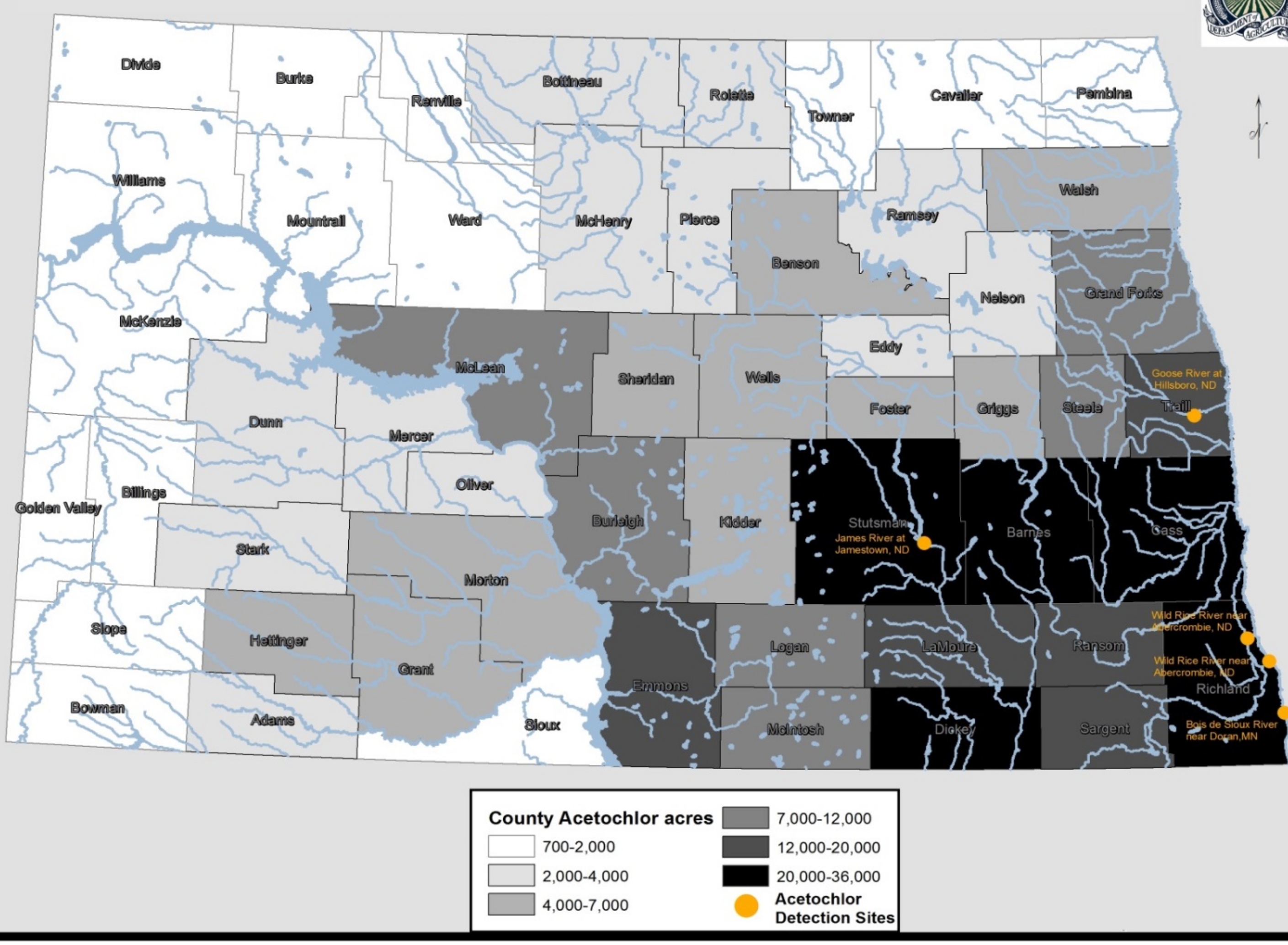
*Figure 4.* **Sampling locations where atrazine was detected at 20% or more of lowest EPA ALB.**



*Acetochlor*

Acetochlor is an herbicide used on corn and soybeans and was 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 ten times at five sites in 2014. Four of the sites were in counties with high levels of estimated acetochlor use (Figure 6). Acetochlor breakdown products were detected or present in about 64% of samples. The lowest EPA established ALB for acetochlor is 1.43 ppb for acute aquatic non-vascular plant toxicity. The toxicity value is based on an $EC_{50}$ (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 in 2014 was 4.3 ppb, which is three times higher than the ALB. This indicates risk to aquatic non-vascular plant communities. Further review of the data shows that samples collected after acetochlor spikes were below the ALB of 1.43. Targeted sampling indicated acetochlor levels did not persist, which indicates any risk posed to aquatic ecosystems is a short term risk. There is no EPA established drinking water standard for acetochlor.

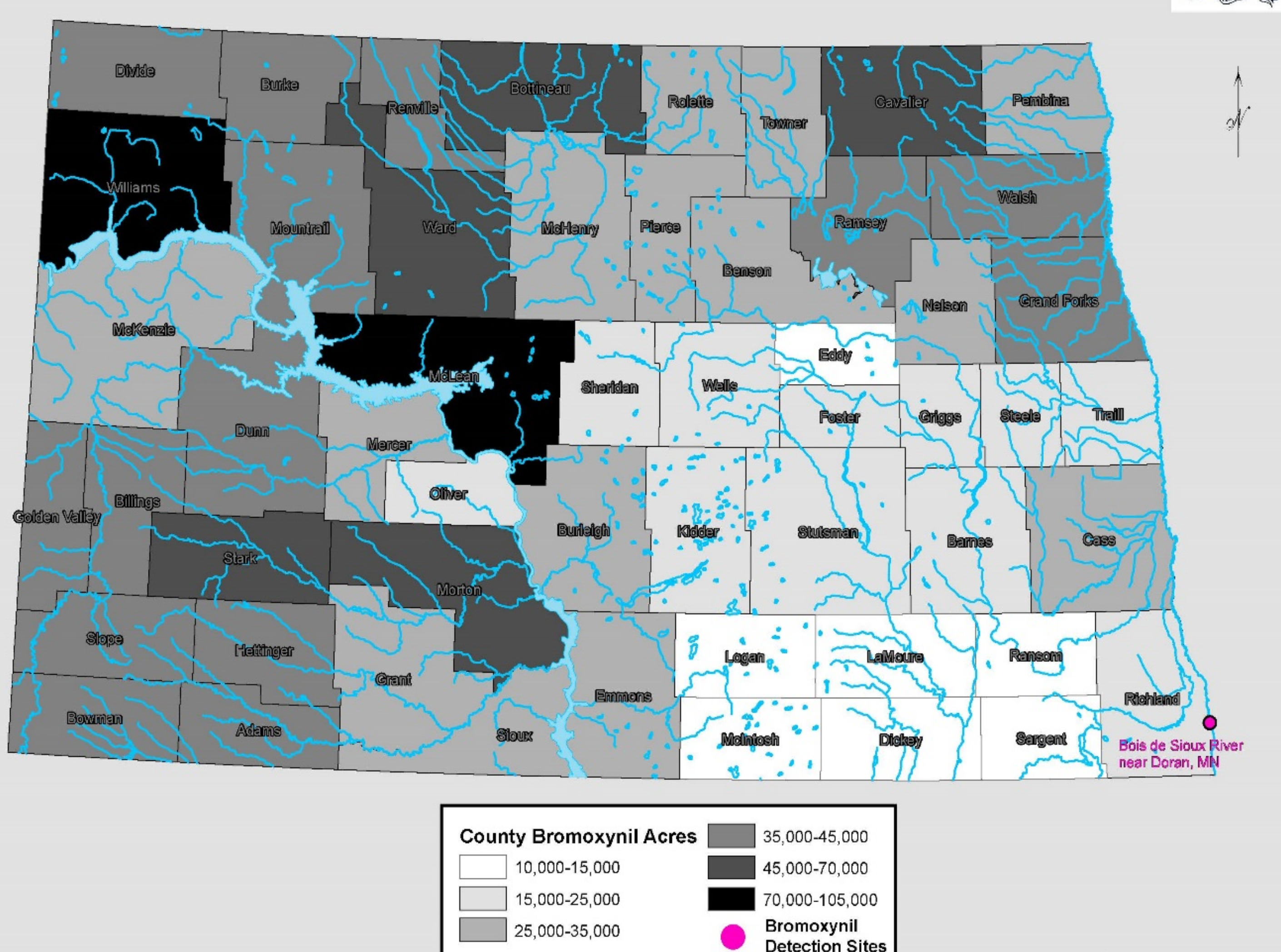
***Figure 5.* Sampling locations where acetochlor was detected at 20% or more of lowest EPA ALB.**



*Bromoxynil*

Bromoxynil is typically used as a post-emergent herbicide to control broadleafs on cereals, corn, and dry beans in North Dakota. It was applied to approximately 28,900 acres as a stand-alone product and to an additional 2,340,000 acres in mixtures in 2012. (Zollinger et al. 2013). Bromoxynil was present in approximately 24% of samples, one of which was at 20% or more of an ALB. This detection was not in a county of high estimated use (Figure 7). The lowest published toxicity endpoint for bromoxynil is the no observed adverse effect concentration (NOAEC) for freshwater invertebrates (Federoff and Gelmann 2013) at 2.5 ppb. 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 bromoxynil.

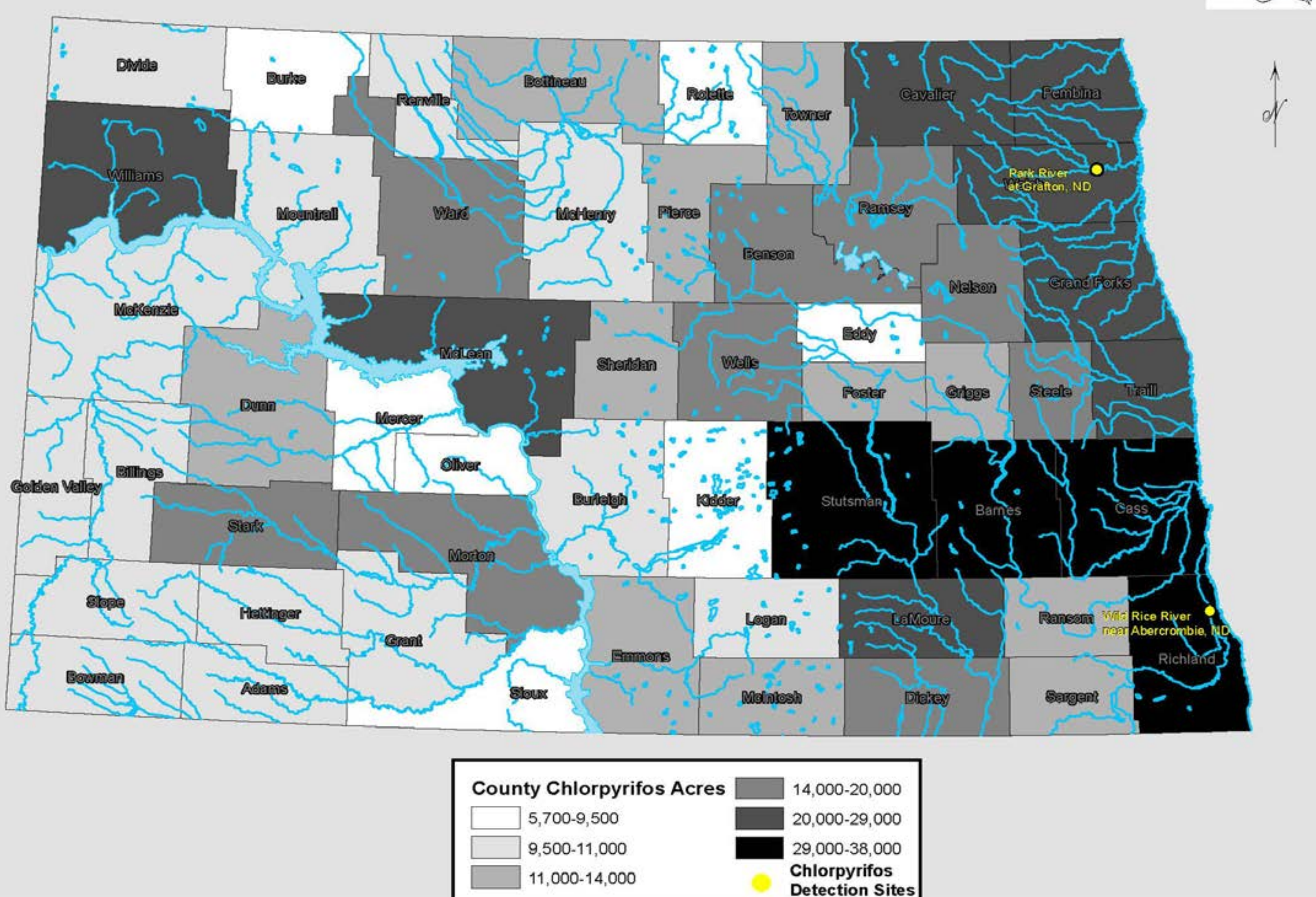
***Figure 6.*** **Sampling locations where bromoxynil was detected at 20% or more of lowest EPA ALB.**



*Chlorpyrifos*

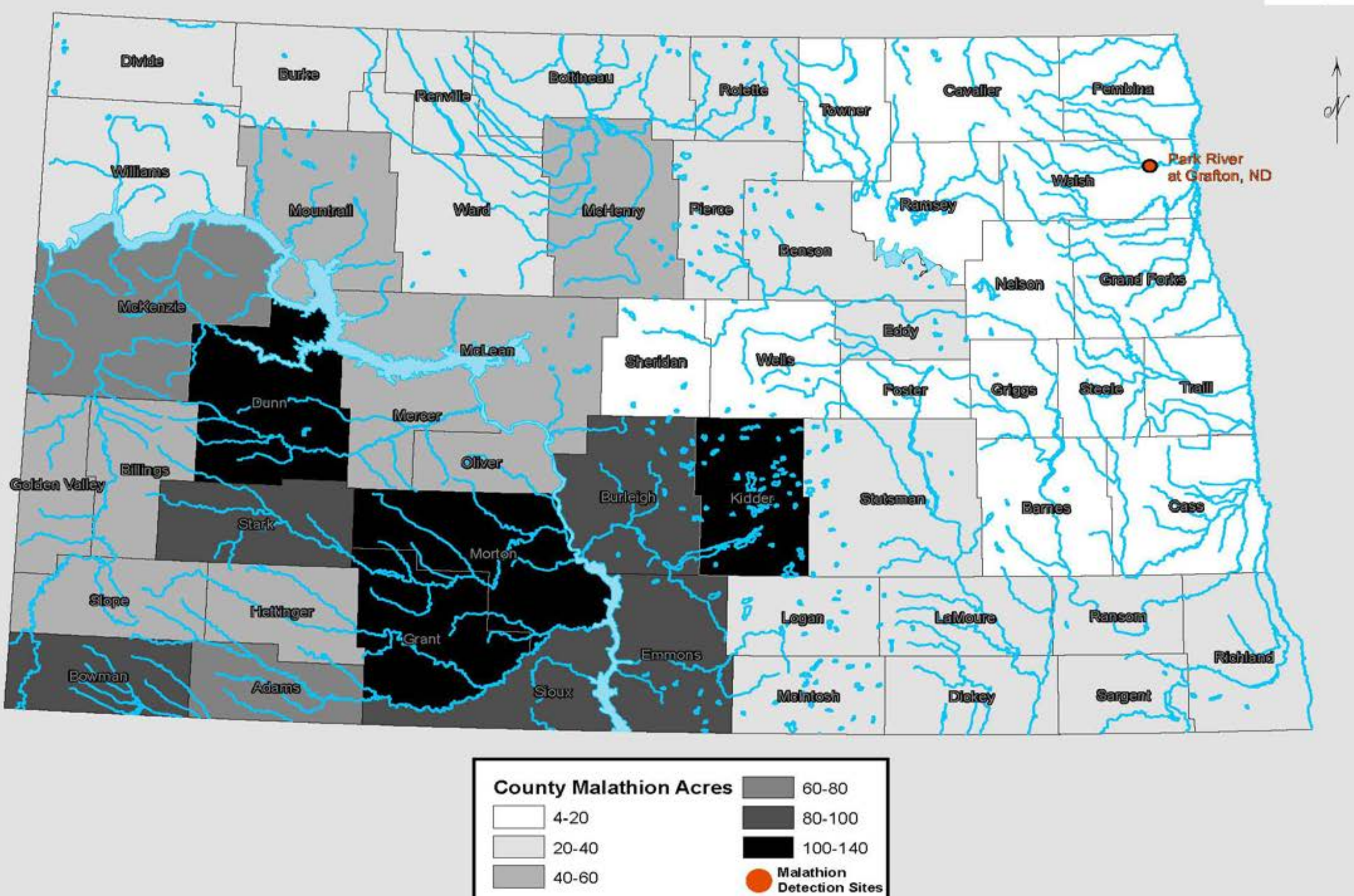
Chlorpyrifos is used to control insect pests on various crops grown in North Dakota. It was applied to approximately 934,000 acres as a stand-alone product and to an additional 9,800 acres in mixtures in 2012. (Zollinger et al. 2013). Chlorpyrifos was present in approximately 8% of samples, two of which were at 20% or more of an ALB. Both detections were in counties of high estimated use (Figure 8). The lowest toxicity endpoint is the no observed adverse effect concentration (NOAEC) is 0.04 ppb for chronic freshwater invertebrates (Chlorpyrifos RED 2000). Further review indicates the lowest observed adverse effect concentration (LOAEC) is 0.08 ppb, which greatly reduced survival and offspring production in *Daphnia magna*. The highest concentration detected was 0.092 ppb which is 1.15 times higher than the LOAEC. Samples collected before chlorpyrifos spikes did not indicate an ALB had been exceeded and samples were not collected after the spike in a short enough timeframe to indicate spike duration. A very small percentage of samples indicated chlorpyrifos may pose a risk to aquatic ecosystems in 2013. Monitoring will continue in the future to further assess risk. There is no EPA established drinking water standard for chlorpyrifos.

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



*Malathion*
Malathion is used to control insect pests on a small percentage of alfalfa acres in North Dakota. It was applied to approximately 900 acres as a stand-alone product in 2012. (Zollinger et al. 2013). Malathion was present in two samples in 2014, one of which was at 20% or more of an ALB. The detection was not in a county of high estimated use (Figure 9). The lowest toxicity endpoint is the no observed adverse effect concentration (NOAEC) and is 0.035 ppb for chronic freshwater invertebrates (Risks of Malathion Use to the Federally Threatened Delta Smelt (*Hypomesus transpacificus*) and California Tiger Salamander (*Ambystoma californiense*), Central California Distinct Population Segment, and the Federally Endangered California Tiger Salamander, Santa Barbara County and Sonoma County Distinct Population Segments, 2010). This value is estimated using a ratio for the most sensitive species, a water flea (*Simocephalus serrulatus*). The highest detection was 0.023 ppb or 1.5 times less than the lowest estimated NOAEC value. Samples collected before the malathion spike did not indicate an ALB had been exceeded and samples were not collected after the spike in a short enough timeframe to indicate spike duration. Monitoring will continue in the future to further assess risk. There is no EPA established drinking water standard for malathion.

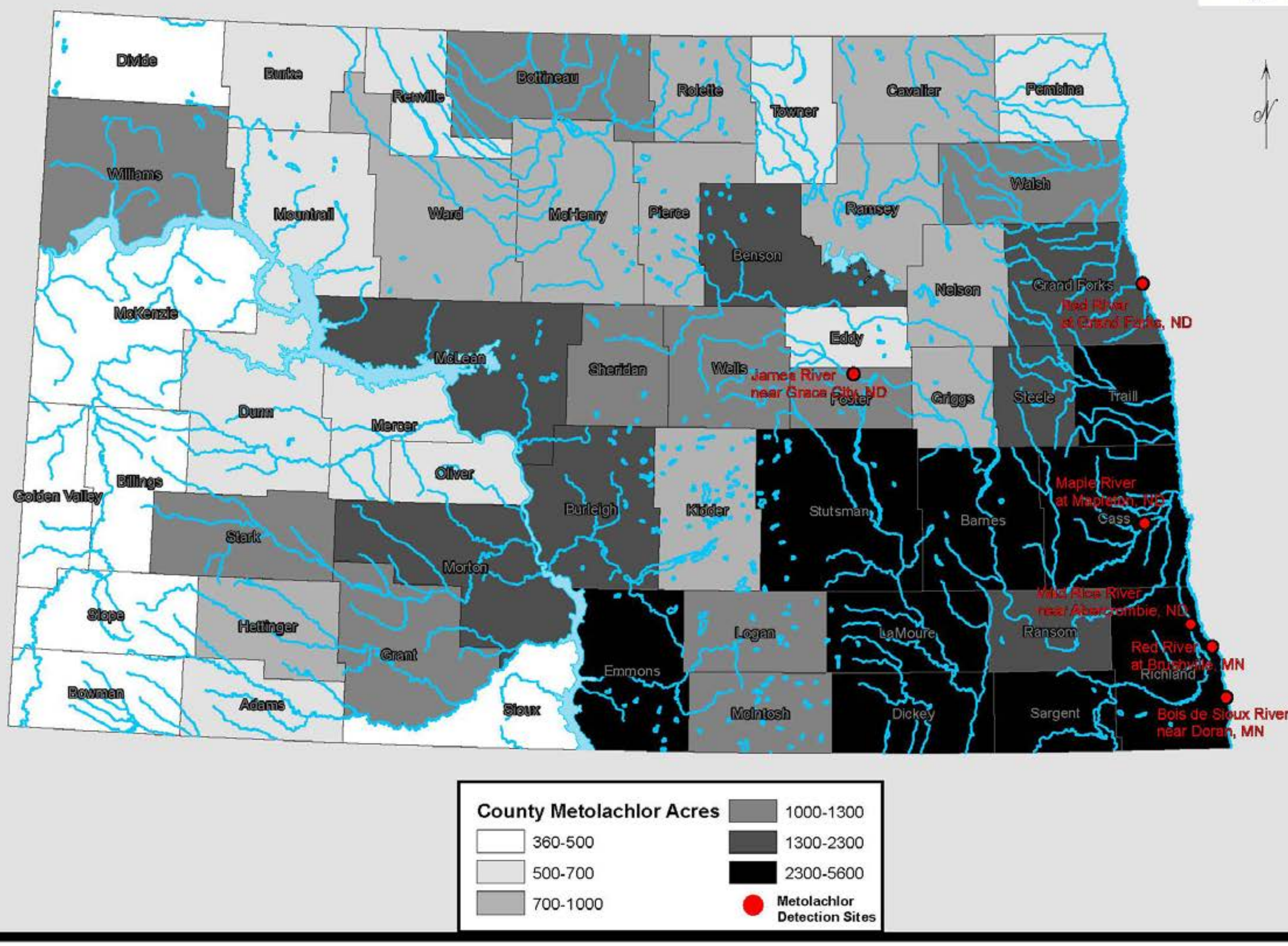
***Figure 8.*** **Sampling locations where malathion was detected at 20% or more of lowest EPA ALB.**



*Metolachlor*

Metolachlor is used on corn, wheat, and a small percentage of barley in North Dakota for grass and broadleaf weed control. The majority of metolachlor use is in the form of s-metolachlor mixed with atrazine and mesotrione or mixed with glyphosate and mesotrione. These mixes were applied to an estimated 63,200 acres in North Dakota in 2012 (Zollinger et al. 2013). Metolachlor and metolachlor degradates were detected or present in as high as 72% of samples in 2014. Metolachlor was detected at 20% or more of an ALB six times in 2014, all in counties with high estimates of metolachlor use (Figure 10). 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 2014 monitoring study indicate that pesticides are not being found in North Dakota rivers and streams at levels posing a risk of unreasonable adverse effects to human health or the environment. Results further illustrate that current regulatory approaches are effective in mitigating the risk of pesticide contamination of surface water. Sampling frequency and laboratory analysis is continuously evolving, and as a result there were 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, 2013, and 2014 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 and 2014. This is not surprising as 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 came 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 may 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 2014 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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*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 2014 | | | |
|---|---|---|---|
| **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 | F | 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 2014 | | | |
|---|---|---|---|
| **Analyte** | **Common Trade Names*** | **Type** | **Reporting Limit (ppb)** |
| **Diuron** | Direx, Karmex | H | 0.00530 |
| **Fluoroethyldiaminotriazine (FDAT)** | degradate | D | 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 |
| **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 | 0.00520 |
| **NOA 447204 (Pinoxaden metablolite)** | degradate | D | 0.01000 |
| **Norflurazon** | Solicam | H | 0.02000 |

| List of analytes 2014 | | | |
|---|---|---|---|
| **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 |
| **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 |

*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) |
| **James River at Jamestown, ND** | 380013 | 7/22/2014 | Acetochlor | 0.35 | 1.43 |
| **James River at Jamestown, ND** | 380013 | 7/22/2014 | Atrazine | 1.3 | 1.00 |
| **James River at Jamestown, ND** | 380013 | 8/19/2014 | Atrazine | 0.74 | 1.00 |
| **James River nr Grace City, ND** | 384130 | 6/18/2014 | Atrazine | 0.21 | 1.00 |
| **James River nr Grace City, ND** | 384130 | 6/18/2014 | Metolachlor | 0.31 | 1.00 |
| **James River nr Grace City, ND** | 384130 | 8/18/2014 | Atrazine | 0.28 | 1.00 |
| **James River at Lamoure, ND** | 380012 | 7/22/2014 | Atrazine | 0.82 | 1.00 |
| **James River at Lamoure, ND** | 380012 | 8/19/2014 | Atrazine | 0.71 | 1.00 |
| **Goose River at Hillsboro, ND** | 380156 | 7/9/2014 | Acetochlor | 0.3 | 1.43 |
| **Red River at Fargo, ND** | 385414 | 7/9/2014 | Atrazine | 0.34 | 1.00 |
| **Red River at Fargo, ND** | 385414 | 7/14/2014 | Atrazine | 0.23 | 1.00 |
| **Red River at Pembina, ND** | 384157 | 7/15/2014 | Atrazine | 0.27 | 1.00 |
| **Sheyenne River at Lisbon, ND** | 385168 | 7/22/2014 | Atrazine | 0.22 | 1.00 |
| **Red River at Grand Forks, ND** | 384156 | 7/10/2014 | Metolachlor | 0.36 | 1.00 |
| **Red River at Grand Forks, ND** | 384156 | 7/10/2014 | Atrazine | 0.3 | 1.00 |
| **Park River at Grafton, ND** | 380157 | 8/13/2014 | Chlorpyrifos | 0.092 | 0.04 |
| **Park River at Grafton, ND** | 380157 | 8/13/2014 | Malathion | 0.023 | 0.04 |
| **Cedar Creek nr Raleigh, ND** | 380077 | 7/8/2014 | Atrazine | 0.3 | 1.00 |
| **Cannonball River nr Raleigh, ND** | 380105 | 7/8/2014 | Atrazine | 0.23 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 4/28/2014 | Acetochlor | 1.2 | 1.43 |
| **Bois de Sioux River near Doran, MN** | 385055 | 5/20/2014 | Acetochlor | 3.3 | 1.43 |
| **Bois de Sioux River near Doran, MN** | 385055 | 6/17/2014 | Acetochlor | 1 | 1.43 |
| **Bois de Sioux River near Doran, MN** | 385055 | 5/20/2014 | Atrazine | 0.38 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 6/17/2014 | Atrazine | 0.54 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 7/10/2014 | Atrazine | 0.33 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 7/22/2014 | Atrazine | 0.31 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 6/17/2014 | Bromoxynil | 0.53 | 2.50 |
| **Bois de Sioux River near Doran, MN** | 385055 | 5/20/2014 | Metolachlor | 0.25 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 6/17/2014 | Metolachlor | 0.77 | 1.00 |
| **Bois de Sioux River near Doran, MN** | 385055 | 7/10/2014 | Metolachlor | 0.26 | 1.00 |
| **Maple River below Mapleton, ND** | 384155 | 4/30/2014 | Atrazine | 0.2 | 1.00 |
| **Maple River below Mapleton, ND** | 384155 | 6/16/2014 | Atrazine | 0.8 | 1.00 |
| **Maple River below Mapleton, ND** | 384155 | 7/10/2014 | Atrazine | 1.1 | 1.00 |
| **Maple River below Mapleton, ND** | 384155 | 7/21/2014 | Atrazine | 0.51 | 1.00 |

| Detections that were 20% or more of an aquatic life benchmark | | | | | |
|---|---|---|---|---|---|
| **Site Name** | Site ID | Sample Date | Analyte | Level (ppb) | ALB (ppb) |
| **Maple River below Mapleton, ND** | 384155 | 7/29/2014 | Atrazine | 0.29 | 1.00 |
| **Maple River below Mapleton, ND** | 384155 | 7/10/2014 | Metolachlor | 0.32 | 1.00 |
| **Maple River below Mapleton, ND** | 384155 | 7/21/2014 | Metolachlor | 0.31 | 1.00 |
| **Red River at Brushville, MN** | 380083 | 4/28/2014 | Acetochlor | 0.77 | 1.43 |
| **Red River at Brushville, MN** | 380083 | 5/20/2014 | Acetochlor | 0.91 | 1.43 |
| **Red River at Brushville, MN** | 380083 | 6/17/2014 | Acetochlor | 1.7 | 1.43 |
| **Red River at Brushville, MN** | 380083 | 6/17/2014 | Atrazine | 0.57 | 1.00 |
| **Red River at Brushville, MN** | 380083 | 6/18/2014 | Metolachlor | 0.51 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 4/29/2014 | Acetochlor | 0.67 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 6/17/2014 | Acetochlor | 4.3 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 6/17/2014 | Atrazine | 1.7 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 7/10/2014 | Atrazine | 0.93 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 7/22/2014 | Atrazine | 0.95 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 7/29/2014 | Atrazine | 0.54 | 1.00 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 8/26/2014 | Chlorpyrifos | 0.036 | 0.04 |
| **Wild Rice River near Abercrombie, ND** | 380031 | 6/17/2014 | Metolachlor | 0.93 | 1.00 |