2019 Water Quality Monitoring Report

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Authors and Contributors

Monitoring and Assessment Unit Hydrologists – Ben Bruening, Heather Johnson, Michael MacDonald, Scott Matteson, Katie Rassmussen, Matt Ribikawskis, Brennon Schaefer, Dylan Timm, and David Tollefson.

Monitoring and Assessment Unit Supervisor - Bill VanRyswyk

Editor – Heather Johnson

Minnesota Department of Agriculture
Pesticide and Fertilizer Management Division
Monitoring and Assessment Unit

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Executive Summary
Minnesota Department of Agriculture 2019 Annual Monitoring Report*

Ambient Groundwater Monitoring

The Minnesota Department of Agriculture (MDA) collected 611 pesticide samples from 166 ambient groundwater monitoring sites (monitoring wells, springs, and private drinking water wells) in 2019. These sites represent the MDA's long-term groundwater monitoring network from agricultural and urban locations around the state.

- Forty-seven different pesticides or pesticide degradates were detected out of the 166 pesticide analytes that were analyzed by the MDA Laboratory.
- The total concentration of cyanazine and its degradates exceeded the drinking water Health Risk Limit (HRL) of 1,000 ng/L in one sample collected from a spring in Goodhue County with a measured total concentration of 1,035.9 ng/L.
- Metolachlor ESA was the most frequently detected pesticide analyte.
- Glyphosate and its degradate AMPA were not detected in the 167 samples that were analyzed.
- Six neonicotinoid insecticides and two neonicotinoid insecticide degradates were analyzed in the groundwater samples.
  - Imidacloprid was detected in the urban area for the first time since 2011. This is the only neonicotinoid that has been detected in urban groundwater.
  - Detection frequencies of clothianidin, imidacloprid, and thiamethoxam ranged from 10 to 18%.
- Eleven pesticides were analyzed for the first time in 2019.
  - Cyanazine acid, cyanazine amide, and deethylcyanazine acid were detected in 2%, 2%, and 4%, of samples collected statewide, respectively.
  - Acifluorfen, afidopyropen, deethylcyanazine, deethylcyanazine amide, flutianil, flutianil OC 56574, flutianil OC 56635, and pydiflumetofen were not detected.

Private Well Pesticide Sampling

As part of the Private Well Pesticide Sampling (PWPS) Project, the MDA collected 1,103 pesticide samples from private wells in 23 counties in 2019. PWPS samples were analyzed by a contract laboratory for pesticides and nitrate. The PWPS Project is a companion program to the MDA Township Testing Program which focuses on nitrate.

- At least one pesticide was detected in 72% of wells sampled.
- As many as 16 different pesticide compounds were detected in a single well.
- Metolachlor ESA was the most frequently detected pesticide analyte.
- Four neonicotinoid insecticides were detected infrequently: clothianidin (3%), dinotefuran (<1%), imidacloprid (2%), and thiamethoxam (<1%).
- Twenty-nine wells indicated total cyanazine concentration above the HRL of 1,000 ng/L. Detections above the HRL occurred in Scott (17), Olmsted (4), Houston (3), Wright (2), Chippewa (2), and Pipestone (1) counties. No other pesticide was detected above a HRL in 2019.

In a separate study that targeted wells in Dakota County with previous detections of cyanazine degradates, 14 out of 84 private wells indicated total cyanazine concentrations above the HRL.

Ambient Surface Water Monitoring

The MDA's ambient surface water monitoring focuses on pesticide sample collection from rivers and streams around the state. In 2019, 1,161 pesticide samples were collected from 55 river or stream monitoring locations for up to166 pesticide analytes.

- Sixty-nine different pesticides or pesticide degradates were detected.
  - Thirty-nine were detected in 10% or less of the samples.
  - Twelve were detected in 50% to 97% of the samples.
- The most commonly detected parent pesticide compounds were the herbicides 2,4-D, metolachlor, and atrazine detected in 85%, 79%, and 67% of samples, respectively.
- Three neonicotinoid insecticides, clothianidin, imidacloprid, and thiamethoxam, were detected in 30%, 27%, and 11% of samples, respectively.
- One hundred thirty-eight detections were above an applicable numeric water quality reference value, including acetochlor (11), atrazine (2), chlorpyrifos (3), clothianidin (62), dichlorvos (1), imidacloprid (58), and metolachlor (1).
  - Where state water quality standards are available, the Minnesota Pollution Control Agency (MPCA) will assess these detections, as well as the duration of concentration, for any applicable violations of standards.
  - Pesticides without state standards in the above list (clothianidin, dichlorvos and imidacloprid) are compared to U.S. Environmental Protection Agency (USEPA) aquatic life benchmarks.
- Glyphosate was detected in 10% of samples, and the maximum glyphosate detection (5,880 ng/L) was <1% of the lowest water quality reference value.
- Acifluorfen and deethylcyanazine acid were detected for the first time in Minnesota surface water in 3% and 15% of samples, respectively.
- Six pesticide samples were collected from one lake and eight pesticide analytes were detected at concentrations well below the applicable water quality reference values.
- Forty-three pesticide samples were collected from four rainfall monitoring locations, and 20 pesticide compounds were detected.

Special Monitoring Studies and Additional Data Analysis

- Seventy pesticide samples were collected from three small watersheds with the Root River Pesticide Study.
  - Seven pesticide were detected, with one detection each of acetochlor, atrazine, and metolachlor over a numeric reference value.
- Pesticide water quality monitoring results from Fish Creek, an urban stream, were presented separately due to concerns related to elevated concentrations and pesticide use in the watershed. The MDA continues to investigate possible sources of the detected pesticides.
- The MDA completed a review of all river and stream pesticide water quality data relative to the drinking water HRLs established by the Minnesota Department of Health (MDH). While most river and stream locations are not used or protected as drinking water sources, this analysis does provide useful background for consideration of downstream or regional uses that may include drinking water.
  - It is important to keep in mind that drinking water reference values assume a long-term exposure period. Elevated pesticide concentrations in surface waterbodies are often short lived, with pesticide concentrations falling within days or weeks.
  - From 2014-2019, between 1,685 and 4,197 samples were evaluated. Results indicated six different pesticides were detected over HRLs in 61 samples. Most detections were confirmed to be below the HRL in a few days or weeks.

*Suggested Citation: Minnesota Department of Agriculture 2019 Water Quality Monitoring Report: https://www.mda.state.mn.us/pesticide-fertilizer/water-monitoring-reports-and-resources

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Abbreviations

µg/L	Micrograms per liter (equivalent to one part per billion of water sample or ppb)
AMPA	aminomethylphosphonic acid
BCS	Bayer Crop Sciences
BMP	Best management practice
CAS	Chemical abstract service
CWTU	Clean Water Technical Unit
DFM	Discovery Farms Minnesota
DOP	Dissolved orthophosphorus
EFED	Environmental Fate and Effects Division
EFI	Equal Flow Incremented
GC-MS/MS	Gas chromatography with tandem mass spectrometry
HBV	Health Based Value
HRL	Health Risk Limit
LC-MS/MS	Liquid chromatography with tandem mass spectrometry
MAU	Monitoring and Assessment Unit
MCL	Maximum contaminant level
MDA	Minnesota Department of Agriculture
MDH	Minnesota Department of Health
mg/L	milligram per liter or parts per million
MN DNR	Minnesota Department of Natural Resources
MPCA	Minnesota Pollution Control Agency
MRL	Method reporting limit
ng/L	Nanograms per liter (equivalent to one parts per trillion or ppt)
NLA	National Lakes Assessment
OGRL	Organic Geochemistry Research Laboratory
OPP	Office of Pesticide Programs (USEPA)
QA/QC	Quality Assurance/Quality Control
PFMD	Pesticide and Fertilizer Management Division
PMP	Pesticide Management Plan
PMPC	Pesticide Management Plan Committee
PMR	Pesticide Monitoring Region
PWPS	Private Well Pesticide Sampling
RA	Rapid assessment
RAA	Risk assessment advice
RRFSP	Root River Field to Stream Partnership
TP	Total phosphorus
TSS	Total suspended solids
TTP	Township Testing Program
USGS	United States Geological Survey
USEPA	United States Environmental Protection Agency

Definitions

- Analytes - Individual compounds, each with a defined Chemistry Abstract Service (CAS) number, which are being identified and quantified by the laboratory.
- Acute toxicity - As defined in Minnesota Rules Chapter 7050 means a stimulus severe enough to rapidly induce a response. In toxicity tests, a response is normally observed in 96 hours or less. Acute effects are often measured in terms of mortality or other debilitating effects, represented as LC50s or EC50s, and expressed as concentrations of mass per unit volume, percent effluent, or toxic units.
- Chronic Standard, Criterion or Advisory Value - The highest water concentration of a chemical to which organisms can be exposed without causing chronic toxicity to the organisms in question. Established for individual chemicals, based on toxicity to aquatic life ("toxicity-based") and based on toxicity to human life ("human health-based"), when sufficient information exists to establish one or both of these numbers. The more stringent of the two numbers is used as the chronic standard, criterion or advisory value for purposes of implementation of Minnesota Rules Chapter 7050. The underlying exposure assumptions (e.g., timeframes for exposure comparisons) and applicability of any numbers are established by the MPCA and may vary depending on the state classification of the water body, the nature of the data comparisons being made, and the regulatory status of the number being used for comparison.
- Common Detection - An official state designation made by the MDA Commissioner of Agriculture and is defined as "detection of a pollutant that is not due to misuse or unusual or unique circumstances but is likely the result of normal use of a product or practice."
- Degradate - A compound formed as part of the process when a pesticide is broken down or metabolized in the environment.
- Detection – When a pesticide analyte has a concentration that is able to be quantified (*i.e.*, concentration above the Method Reporting Limit).
- Detection frequency - The frequency of detection of an individual pesticide that was computed as the number of samples with a detection of an individual pesticide divided by the number of samples in which the pesticide was analyzed and then multiplied by 100.
- Health Based Value (HBV) - is the concentration of a groundwater contaminant that can be consumed daily with little or no risk to health. HBVs are derived using the same algorithm as HRLs; however, they have not been promulgated as rules, have not undergone peer review, and may be based on less data and/or subject to greater uncertainty than HRLs. An HBV is expressed as a concentration in micrograms per liter (µg/L).
- Health Risk Limit (HRL) - A health risk limit (HRL) is the concentration of a groundwater contaminant, or a mixture of contaminants, that can be consumed with little or no risk to health and which has been promulgated under rule. A HRL is expressed as a concentration in micrograms per liter (µg/L).

- Herbicide - A pesticide designed to control or destroy plants, weeds or grasses.
- Fungicide - A pesticide used to control, deter, or destroy fungi.
- Insecticide - A pesticide used to kill or prevent the growth of insects.
- Impaired - A body of water is considered to be this if it fails to meet one or more water quality standards. Minnesota water quality standards protect lakes, rivers, streams, and wetlands by defining how much of a pollutant (bacteria, nutrients, turbidity, mercury, etc.) can be in water before it is no longer drinkable, swimmable, fishable, or useable in other, designated ways (called “beneficial uses”). Waters that do not meet their designated uses (drinkable, swimmable, fishable, etc.) because of water quality standard violations are impaired.
- Location - A distinct place where a water sample was collected. This term has been utilized throughout this Report as a general descriptor to characterize where surface water samples were collected from and as a way to differentiate between the groundwater and surface water programs.
- Maximum - The largest value observed in a data set.
- Maximum Contaminant Level (MCL) - A value established by the United States Environmental Protection Agency (USEPA) as the maximum amount of a chemical allowed in a federally regulated public water supply, considering health, economic or other factors, including technological factors such as treatment cost and feasibility.
- Median - The value for which 50 percent of the data, when arranged in order of magnitude, lie on each side.
- Method Reporting Limit (MRL) - Represents the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.
- Percentile - A measure used to indicate the value at which or below a given percentage of data falls on a scale of one hundred.
- Pesticide - Substances intended to repel, kill, or control any species designated a "pest", including weeds, insects, rodents, fungi, bacteria, or other organisms. The family of pesticides includes herbicides, insecticides, rodenticides, fungicides, and bactericides.
- Pollutant - A chemical or substance for which a health risk limit has been adopted.
- Reference value - An all-encompassing term that includes applicable water quality benchmarks, guidance values, or standards established by state and/or federal agencies.
- Sample - Each individual analysis performed at the laboratory.
- Sample collection event - A field visit resulting in the collection of a water quality sample(s).
- Site - Refers to a general place where water samples were collected. This term has been utilized throughout this Report as a general descriptor to characterize where groundwater samples were collected from and as a way to differentiate between the groundwater and surface water programs.

- Surface Water Pesticide of Concern - Official designation used by the Commissioner of Agriculture to identify a pesticide with detection(s) of a pesticide in surface water at concentrations of concern relative to a water quality standard, water quality criterion or water quality advisory value (i.e., a “reference value”), not due to misuse or unusual or unique circumstances, but likely to be the result of normal use of product or practice.
- Water quality standard exceedance - A detection of a compound that exceeds both the concentration and duration referenced in a water quality standard. The Minnesota Pollution Control Agency (MPCA) makes water quality standard exceedance determinations.
- Water quality standard violation - A water quality standard is violated when two chronic water quality standard exceedances occur within a three year period, or when one maximum water quality standard exceedance is documented for a given water body. The MPCA makes water quality standard violation determinations.

Section 1: Introduction

2019 Water Quality Monitoring Report

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This annual report presents groundwater and surface water pesticide data collected by the Minnesota Department of Agriculture (MDA) Pesticide and Fertilizer Division (PFMD) Monitoring and Assessment Unit (MAU). Water quality results for 2019 are presented along with summaries of historical pesticide data. This report also presents pesticide and nutrient water quality data summaries from several special projects conducted, or assisted, by the MAU in 2019. Finally, monitoring results for select nutrients and total suspended solids collected during the pesticide sample collection event are presented.

1.1 Program history

In 1985, the MDA and the Minnesota Department of Health (MDH) undertook a cooperative survey of groundwater for pesticides and nitrate-nitrogen in areas of agricultural land use considered susceptible to contamination (outwash sands and karst bedrock areas). This survey found that some of the pesticides commonly applied to fields in agricultural production (normal use) were present in groundwater at detectable concentrations. The most frequently detected pesticides were the herbicides atrazine and alachlor (Klaseus, Buzicky, and Schneider, 1988). A second survey, performed by the MDH in 1986, targeted primarily private (farm) drinking water wells, and showed similar results (Klaseus and Hines, 1989).

In 1987, the Minnesota Legislature amended the Minnesota Pesticide Control Law (Chapter 18B of Minnesota State Statutes). Minnesota Statute 18B.04(a) requires: *"The commissioner shall:*

> *(1) determine the impact of pesticides on the environment, including the impacts on surface water and groundwater in this state;*
>
> *(2) develop best management practices involving pesticide distribution, storage, handling, use, and disposal; and*
>
> *(3) cooperate with and assist other state agencies and local governments to protect public health, pollinators, and the environment from harmful exposure to pesticides."*

In response to this charge, the MDA initiated a groundwater pesticide monitoring program in 1987, and the surface water pesticide monitoring program began in 1991.

In 1989, the Comprehensive Groundwater Protection Act (Chapter 103H of Minnesota State Statutes) expanded groundwater protection responsibilities of the MDA by including specific direction regarding monitoring for agricultural chemicals and the management of those chemicals when they were found to impact groundwater. The Comprehensive Groundwater Protection Act mandated the development of a State Pesticide Management Plan, with water quality monitoring data required to act as the primary informational tool for guiding management decisions within that plan.

1.2 Overall program purpose

Ambient water quality monitoring is conducted by the MAU for the purpose of evaluating the impact from the routine application of agricultural chemicals on groundwater and surface water in Minnesota. The data collected is used to identify compounds and/or places where concentrations may exceed established water quality benchmarks, guidance values, and/or standards, collectively referred to as reference values. These data are also used to identify trends related to the detection frequency and concentration of specific agricultural chemicals found in the waters of Minnesota. The data can also prompt the development of best management practices (BMPs), as aid in evaluating the effectiveness of BMPs, for those specific compound(s). The groundwater and surface water monitoring networks have evolved over the years to meet the needs of Minnesota. The vast majority of the water quality data collected is public information and is available by request or through the MDA Monitoring and Assessment website.

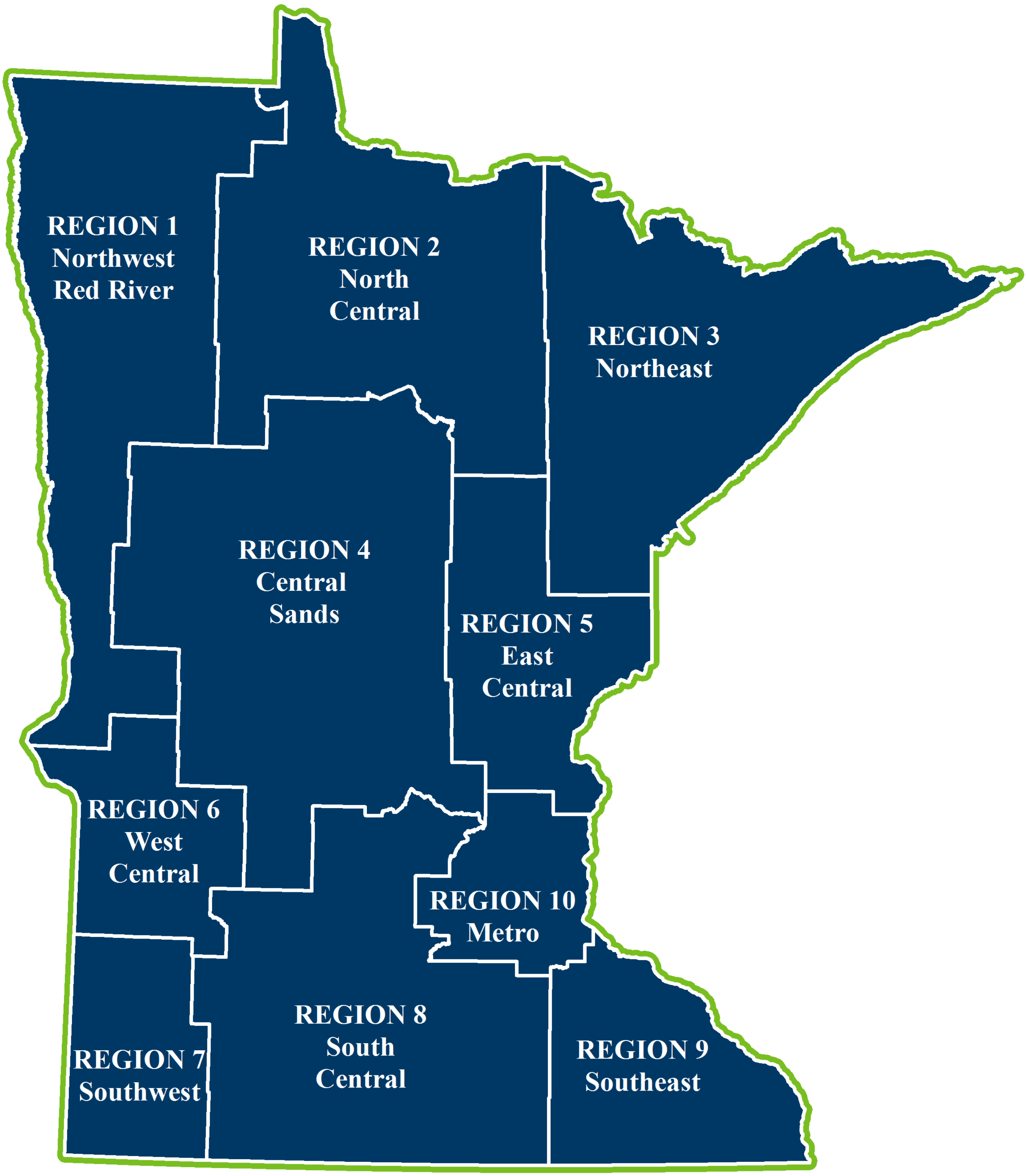
1.3 Program elements

Groundwater was monitored by collecting samples primarily from networks of wells established by the MDA, with additional samples being collected from private wells and naturally occurring springs, for the purpose of characterizing long-term trends in specific aquifers. Surface water was monitored by collecting samples primarily from rivers and streams, with additional samples being collected from lakes, rainfall, and wetlands. Samples were analyzed by the MDA Laboratory Services Division (MDA Laboratory) by using well-established laboratory methods. Occasionally there were departures from these monitoring and analytical approaches as the MDA explored new ways to achieve its mandates and enhance its capabilities.

1.4 Pesticide Monitoring Regions

The MDA has developed a regional water quality monitoring design that is based on Pesticide Monitoring Regions (PMRs). The PMRs established geographical areas for the purposes of collecting, analyzing, and reporting water quality monitoring data (Figure 1-0). Minnesota was divided into 10 PMRs on the basis of agricultural practices and hydrologic/geologic characteristics. The PMRs follow county boundaries, but are intended to generally represent different hydrologic regions in Minnesota.

Figure 1-0. MDA's Pesticide Monitoring Regions (PMRs).



1.5 Changes to program activities

This section highlights changes made to the groundwater and surface water monitoring programs that were completed in 2019, or are proposed for the 2020 monitoring season.

For more information on location-specific program changes, please refer to the associated annual surface water and groundwater work plans on the [MDA Monitoring and Assessment website.]()

1.5.1 Groundwater

The MDA replaced wells at six sites within PMR 4 in 2019, that previously had two or three wells, due to the presence of tree roots that restricted sample collection. A single well, with a longer screen, was installed to straddle the water table at each site. The new wells were within 500 feet of the original wells and installed away from the trees. One of the new wells was sampled in the fall of 2019. All the new wells will be sampled in 2020, as outlined in the Groundwater Quality Monitoring 2020 Annual Work Plan.

The MDA did not have permission to sample a domestic well in southeastern Minnesota due to change in property ownership in 2019. The MDA will seek permission to sample the well in 2020 or may find a replacement well to add to the PMR 9 network if access isn't allowed.

A well located in Redwood County (Unique well number 733725) could not be sampled in 2019. In the spring, access to the site was prevented because of high water and road construction. In the fall, it was discovered that the inner well casing had been damaged, possibly when water from flooding during springtime entered the protective well casing and froze, distorting the inner PVC casing so that a bailer could not fit. This well will be sealed in 2020 and a nearby DNR observation well (Unique well number 708361) will replace it in MDA's PMR 8 network.

A site containing a nested well pair in Otter Tail County was not sampled as scheduled in the fall. Site 56-F8 (wells 623613 and 623614) were both dry. Since the wells at this site have historically had water limitations, the MDA will look to seal and replace these wells in the future for the PMR 4 network.

1.5.2 Surface water

The 2019 surface water monitoring activities were similar to 2018. However, the MDA did add an urban rainfall monitoring location in downtown St. Paul in 2019. This location complements three rainfall locations in agricultural regions of Minnesota. With regards to data analysis, it should also be noted that the MDA is presenting all water quality data collected at Fish Creek, a small urban watershed in Ramsey County, independently from the rest of the network results. It was found that results from Fish Creek were substantially different from other monitored urban watersheds, likely due to the presence of a point source within the watershed. As such, Fish Creek data will be summarized and presented separately in Section 4.6.

The MDA is planning minimal changes to the ambient surface water monitoring network in 2020. The changes to note include discontinuing monitoring at Lawrence Creek (PMR 5) and the Pine River

(PMR 4), and adding monitoring at Nine Mile Creek (Urban) and the Shell River (PMR 4). The Root River Pesticide Study will discontinue monitoring at Bridge Creek and Crystal Creek, and expand monitoring in the Headwaters to include GC-MS/MS, LC-MS/MS and glyphosate LC-MS/MS methods. This realignment of resources will allow the MDA to greatly expand the number of pesticides analyzed in the Headwaters watershed to gain a better understanding of pesticide transport.

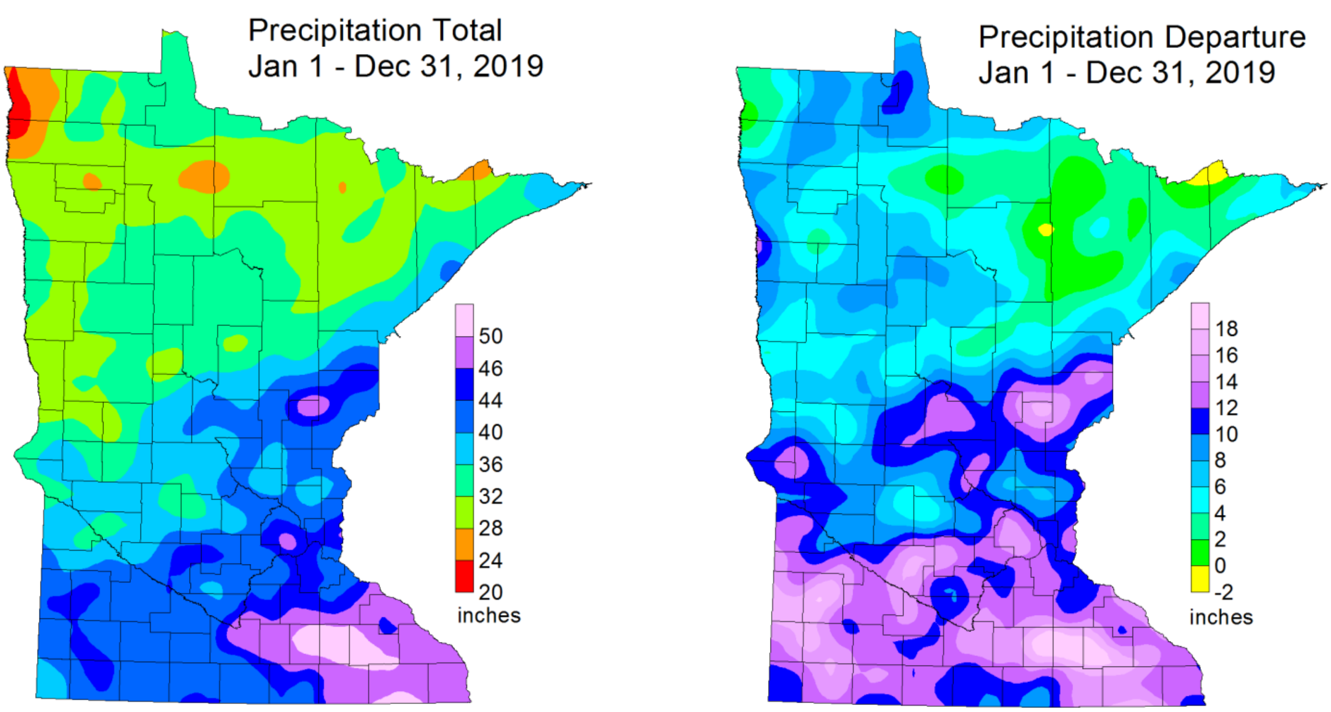
1.5.3 Cyanazine

In 2019, the MDA included the analysis of cyanazine degradates in its ambient groundwater, surface water, and Private Well Pesticide Sampling (PWPS) programs, providing data from monitoring locations throughout the state. In addition, the MDA collected samples from 84 private well locations in Dakota County that had previous detections of cyanazine related compounds, as found by monitoring performed by Dakota County Environmental Resources Department. Results and summaries for all cyanazine related sampling efforts performed in 2019 by the MDA can be found in Section 5.

1.6 Recent precipitation patterns

There is often a relationship between pesticide concentrations measured in groundwater and surface water samples and precipitation patterns in a given year. Pesticide movement from the location of the application to the broader environment is often related to the individual pesticide properties, as well as the timing and magnitude of precipitation events with respect to pesticide application periods. Statewide total annual precipitation and annual precipitation departure from normal (1981-2010) summary maps, as reported by the State Climatology Office, are shown in Figure 1-1.

Figure 1-1. Statewide total annual 2019 precipitation and annual 2019 precipitation departure from normal (1981-2010).



1.7 Chemical analytes and 2019 detection summary

Water quality samples were analyzed at the MDA Lab for pesticides and inorganic compounds, which were referred to as "analytes" throughout this report. The gas chromatography with tandem mass spectrometry (GC-MS/MS) method, liquid chromatography with tandem mass spectrometry (LC-MS/MS) method and glyphosate LC-MS/MS method were used to analyze the water quality samples for pesticides. The GC-MS/MS and LC-MS/MS pesticide analyses were reported in nanograms per liter (ng/L), which is equivalent to parts per trillion. The glyphosate LC-MS/MS method is used to analyze for glyphosate and a glyphosate degradate, aminomethlyphosphonic acid (AMPA). Glyphosate and AMPA were reported in micrograms per liter (µg/L), which is equivalent to parts per billion, from the MDA Laboratory. All pesticide results have been presented in ng/L in this report for consistency. All results for inorganic compounds (nutrients and total suspended solids) were reported and presented in milligram per liter (mg/L), which is equivalent to parts per million.

Due to limited resources, the MDA carefully selects which agricultural chemicals are targeted for analysis in its monitoring program by following a protocol for the addition and removal of analytes from the target analyte list. The target analyte list includes many of the most commonly used pesticide products and associated degradates. The protocol specifies that a pesticide may be included in MDA's target analyte list based on several factors, including:

- Pesticides that have been used, or are planned to be used, in Minnesota or neighboring states;
- Pesticides that have environmental fate characteristics or use patterns that could potentially result in adverse water resource impacts;
- Pesticides that have occurrence data from non-MDA water quality monitoring reports of relevance to Minnesota;
- Pesticides that have a laboratory analytical method that can achieve reasonable results; and
- Pesticides that generally have available reference values or risk guidance for human health and aquatic life toxicity from the Minnesota Pollution Control Agency (MPCA), the MDH, and/or the United States Environmental Protection Agency (USEPA).

The MDA has formed an advisory committee with the MDH and the MPCA to coordinate efforts to identify pesticides and their degradates that are a priority for monitoring. The goal is to prioritize chemicals that are most likely to reach ground and surface water, as well as those that may pose a risk to human health or non-target organisms.

The MAU compared pesticide water quality results to established water quality benchmarks, guidance values, and/or standards, collectively referred to as reference values. These reference values were published by various state and federal agencies and were reviewed by the MDA Pesticide Technical Unit. Reference values for groundwater and surface water presented throughout this report provide context for the detected concentrations. Reference values are presented in Table 2-0 for groundwater and in Table 3-0 for surface water.

All pesticides analyzed by the MDA Laboratory in 2019, as well as their detection status in groundwater or surface water, are listed in Table 1-0. The pesticide type shown in Table 1-0 was provided as a

general reference and may not represent all pesticide uses. Eleven pesticide analytes were added to the LC-MS/MS method in 2019, including: acifluorfen, afidopyropen, cyanazine acid, cyanazine amide, deethylcyanazine acid, deethylcyanazine amide, deethylcyanazine, flutianil, flutianil OC 56574, flutianil OC 56635, and pydiflumetofen. The atrazine degradate, didealkylatrazine, had been reported as DEDI atrazine since 2010. The MDA decided to present the data as didealkylatrazine starting in 2019 to align with the most widely recognized name.

The 2019 detection frequencies presented in the groundwater and surface water summary tables of this report were calculated using the Method Reporting Limits (MRLs) presented in Table 1-0 for each compound. Long-term detection frequencies were calculated using the highest historical MRL for each compound in the period of analysis (noted on figures), unless noted otherwise. As a result, long-term detection frequencies were directly comparable for each specific compound. Please note that directly comparing 2019 detection frequencies between different compounds with different MRLs should be approached with caution as the MRL is likely to impact the detection frequency.

In addition, most pesticide samples were collected along with select nutrients (nitrate-nitrogen, total phosphorus (TP), dissolved orthophosphorus (DOP)) and/or total suspended solids (TSS) at the same time. These analytes were reported in milligrams per liter (mg/L). The MRL and analytical method for each analysis is provided in Table 1-1.

Additional information pertaining to chemical abstracts service (CAS) registry numbers can be found in Appendix 1. For a historic listing of all pesticides detected by the MDA in groundwater, surface water and rainfall, see Appendix 2. Groundwater and surface water program annual summaries can be found in Appendix 3.

Table 1-0. 2019 list of target pesticide and pesticide degradate detection status in groundwater and surface water with associated MRLs.

Common Name	Type	2019 Analyte Detected in Groundwater	2019 Analyte Detected in Surface Water	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
2,4,5-T	Herbicide				50
2,4,5-TP	Herbicide				50
2,4-D	Herbicide	X	X		8.3
2,4-DB	Herbicide				20
Acetamiprid	Insecticide				25
Acetochlor	Herbicide	X	X	30	
Acetochlor ESA	Herbicide Degradate	X	X		30
Acetochlor OXA	Herbicide Degradate	X	X		33.3
Acifluorfen*	Herbicide		X		25
Afidopyropen*	Insecticide				50
Alachlor	Herbicide	X		30	
Alachlor ESA	Herbicide Degradate	X	X		41.6
Alachlor OXA	Herbicide Degradate	X	X		33.3
Aldicarb Sulfone	Insecticide Degradate				15
Aldicarb Sulfoxide	Insecticide Degradate				50
Aminopyralid	Herbicide	X	X		25
Atrazine	Herbicide	X	X	30	
Deisopropylatrazine	Herbicide Degradate	X	X		25
Desethylatrazine	Herbicide Degradate	X	X	50	
Didealkylatrazine	Herbicide Degradate	X	X		50
Hydroxyatrazine	Herbicide Degradate	X	X		6.7
Azoxystrobin	Fungicide		X		10
Benfluralin	Herbicide			25	
Bensulfuron-methyl	Herbicide				16.7
Bensulide	Herbicide				250
Bentazon	Herbicide	X	X		5
Benzovindiflupyr	Fungicide		X		50
Bicyclopyrone	Herbicide		X		10
Bicyclopyrone SYN503870	Herbicide Degradate				100
Bifenthrin	Insecticide			20	
Boscalid	Fungicide				50
Bromacil	Herbicide	X	X		30
Bromoxynil	Herbicide		X		25
Carbaryl	Insecticide				25
Carbendazim	Fungicide		X		10
Carbofuran	Insecticide				13.3
Chlorantraniliprole	Insecticide		X		50

Common Name	Type	2019 Analyte Detected in Groundwater	2019 Analyte Detected in Surface Water	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Chlorimuron-ethyl	Herbicide				20
Chlorothalonil	Fungicide			50	
Chlorpyrifos	Insecticide		X	40	
Chlorpyrifos Oxon	Insecticide Degradate				40
Clethodim Sulfone	Herbicide Degradate		X		100
Clethodim Sulfoxide	Herbicide Degradate		X		50
Clomazone	Herbicide			15	
Clopyralid	Herbicide	X	X		41.6
Clothianidin	Insecticide	X	X		25
Cyanazine	Herbicide				25
Cyanazine Acid*	Herbicide Degradate	X			10
Cyanazine Amide*	Herbicide Degradate	X			10
Deethylcyanazine Acid*	Herbicide Degradate	X	X		25
Deethylcyanazine Amide*	Herbicide Degradate				25
Deethylcyanzine*	Herbicide Degradate				25
Cyantraniliprole	Insecticide				100
Cyfluthrin	Insecticide			100	
Diazinon	Insecticide			30	
Diazinon Oxon	Insecticide Degradate			75	
Dicamba	Herbicide	X	X		50
Dichlobenil	Herbicide		X	5	
Dichlorprop	Herbicide				50
Dichlorvos	Insecticide		X	15	
Dicrotophos	Insecticide				25
Difenoconazole	Fungicide				25
Dimethenamid	Herbicide	X	X	15	
Dimethenamid ESA	Herbicide Degradate	X	X		6.7
Dimethenamid OXA	Herbicide Degradate	X	X		10
Dimethoate	Insecticide				50
Dinotefuran	Insecticide				25
Disulfoton	Insecticide			60	
Disulfoton Sulfone	Insecticide Degradate				20
Diuron	Herbicide		X		13.3
EPTC	Herbicide		X	10	
Esfenvalerate	Insecticide			150	
Ethalfluralin	Herbicide			50	
Ethofumesate	Herbicide		X	50	
Flufenacet OXA	Herbicide Degradate				8.3
Flumetsulam	Herbicide	X	X		50

Common Name	Type	2019 Analyte Detected in Groundwater	2019 Analyte Detected in Surface Water	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Flupyradifurone	Insecticide				10
Flutianil*	Fungicide				25
Flutianil OC 56574*	Fungicide Degradate				50
Flutianil OC 56635*	Fungicide Degradate				25
Flutriafol	Fungicide		X		10
Fluxapyroxad	Fungicide		X		10
Fomesafen	Herbicide	X	X		50
Fonofos	Insecticide			15	
Glyphosate	Herbicide		X		1,020
Aminomethylphosphonic acid (AMPA)	Herbicide Degradate				5,090
Halauxifen-methyl	Herbicide				10
Halauxifen Acid	Herbicide Degradate				25
Halosulfuron-methyl	Herbicide				30
Hexazinone	Herbicide				10
Imazamethabenz-methyl	Herbicide				5
Imazamethabenz Acid	Herbicide Degradate				10
Imazamox	Herbicide	X	X		13.3
Imazapic	Herbicide		X		10
Imazapyr	Herbicide	X	X		8.3
Imazaquin	Herbicide				16.7
Imazethapyr	Herbicide	X	X		6.7
Imidacloprid	Insecticide	X	X		5
Imidacloprid Olefin	Insecticide Degradate				50
Imidacloprid Urea	Insecticide Degradate				50
Isoxaflutole	Herbicide				40
Isoxaflutole DKN	Herbicide Degradate	X			50
lambda-Cyhalothrin	Insecticide			75	
Linuron	Herbicide				20
Malathion	Insecticide			50	
Mandestrobin	Fungicide				25
MCPA	Herbicide	X	X		5
MCPB	Herbicide				20
MCPP	Herbicide	X	X		50
Mesotrione	Herbicide		X		50
Metalaxyl	Fungicide	X	X		8.3
Methoxychlor	Insecticide			50	
Metolachlor	Herbicide	X	X	25	
Metolachlor ESA	Herbicide Degradate	X	X		10

Common Name	Type	2019 Analyte Detected in Groundwater	2019 Analyte Detected in Surface Water	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Metolachlor OXA	Herbicide Degradate	X	X		10
Metribuzin	Herbicide	X	X	75	
Metribuzin DA	Herbicide Degradate	X	X		25
Metribuzin DADK	Herbicide Degradate	X			500
Metribuzin DK	Herbicide Degradate				500
Metsulfuron-methyl	Herbicide	X	X		23.3
Momfluorothrin	Insecticide				50
Myclobutanil	Fungicide				10
Nicosulfuron	Herbicide				26.6
Norflurazon	Herbicide				20
Norflurazon-desmethyl	Herbicide Degradate				50
Oxadiazon	Herbicide			75	
Oxathiapiprolin	Fungicide				100
Oxydemeton-methyl	Insecticide				20
Parathion-methyl	Insecticide			100	
Parathion-methyl oxon	Insecticide Degradate				25
Pendimethalin	Herbicide			75	
Phorate	Insecticide			25	
Picloram	Herbicide	X			41.6
Picoxystrobin	Fungicide				50
Prometon	Herbicide		X	100	
Prometryn	Herbicide		X		3.3
Propachlor	Herbicide			30	
Propachlor ESA	Herbicide Degradate				30
Propachlor OXA	Herbicide Degradate				10
Propazine	Herbicide		X	25	
Propiconazole	Fungicide		X		10
Pydiflumetofen*	Fungicide				25
Pyraclostrobin	Fungicide				25
Pyroxasulfone	Herbicide		X		50
Saflufenacil	Herbicide	X	X		15
Sedaxane	Fungicide				75
Siduron	Herbicide				6.7
Simazine	Herbicide			75	
Sulfentrazone	Herbicide	X	X		50
Sulfometuron-methyl	Herbicide		X		8.3
Tebuconazole	Fungicide		X		10
Tebupirimfos	Insecticide			30	
Tembotrione	Herbicide	X	X		50

Common Name	Type	2019 Analyte Detected in Groundwater	2019 Analyte Detected in Surface Water	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Terbufos	Insecticide			30	
Tetraconazole	Fungicide		X		10
Thiacloprid	Insecticide				50
Thiamethoxam	Insecticide	X	X		25
Thifensulfuron-methyl	Herbicide				16.7
Thiobencarb	Herbicide				8.3
Tolfenpyrad	Insecticide			100	
Tolpyralate	Herbicide				50
Triallate	Herbicide			50	
Triasulfuron	Herbicide				23.3
Triclopyr	Herbicide	X	X		50
Trifluralin	Herbicide			50	
zeta-Cypermethrin	Insecticide			500	

**New analytes added in 2019.*

Table 1-1. Inorganic (nutrients and total suspended solids) analyte list.

Compound	Analytical Method	MRL (mg/L)
Nitrate-nitrogen	APHA 4500-NO3(F)	0.20
Dissolved orthophosphorus	USEPA 365.1	0.005
Total phosphorus	USEPA 365.1	0.005
Total suspended solids	APHA 2540-D	0.10

Section 2: Groundwater Monitoring Results

2019 Water Quality Monitoring Report

Section 2: Groundwater Monitoring Results

The MDA began monitoring groundwater in November 1985 and redesigned the program in 1998. New wells were installed in 1999, and the MDA began sampling the redesigned monitoring network in January 2000. The network was designed for the purpose of tracking trends over time. The current program was established around the goal of providing the information necessary to manage pesticide use for water quality protection on a regional basis. All monitoring sites were established to evaluate pesticide impacts to the most vulnerable groundwater conditions in their associated PMR and were considered sensitive to contamination from activities at the land surface. PMRs 2 and 3 are not currently monitored for groundwater due to relatively low use of agricultural chemicals in these heavily forested regions.

PMR 4 was the first region in the state to be monitored as part of the redesigned network, and it contains the majority of the sites in the program. Groundwater sampling began in PMR 4 in 2000, when analysis for the parent common detection pesticides (acetochlor, alachlor, atrazine, metolachlor and metribuzin) began, as well as two degradates of atrazine (desethylatrazine and deisopropylatrazine) and three degradates of metribuzin (DA, DADK, and DK). Analysis for the degradates of alachlor, acetochlor, and metolachlor began in 2002. Analysis of didealkylatrazine and hydroxyatrazine, began in 2010. Sampling began in PMRs 1, 6, and 7 in 2004, in PMR 8 in 2006, and in PMR 5 in 2007. In 2019, 166 compounds were analyzed by the MDA Laboratory, which included the common detection pesticides.

Common detection is an official state designation made by the Commissioner of Agriculture and is defined as "detection of a pollutant that is not due to misuse or unusual or unique circumstances but is likely to be the result of normal use of a product or a practice" (Minn. Stat. § 103H.005, Subd. 5). Acetochlor, alachlor, atrazine, metolachlor and metribuzin are the current groundwater common detection pesticides. A complete explanation of common detection is presented in Section 2.3.

PMR 9 groundwater has been sampled via naturally occurring springs and domestic drinking water wells. Three MN DNR fish hatchery springs were first sampled through the redesigned monitoring network in 2000, while regional spring sampling began in 2006. The PMR 9 regional springs dataset represents a broader geographical distribution and a better reflection of shallow hydrogeologic conditions than the initial data, which only came from samples collected at the MN DNR fish hatchery springs. Private drinking water wells in the PMR 9 region were first sampled in 2009 and were selected to represent the upper-most aquifer in the area. Private wells were targeted for monitoring due to the high cost of monitoring well installation in the bedrock aquifers of PMR 9.

In 2004, the MDA began a cooperative effort with the MPCA to sample wells within urban/suburban land use areas or developing urban settings. In this report, these areas are all identified as urban. Historically, sampling for urban use pesticides was conducted in urban areas within the geographic bounds of several PMRs. Beginning in 2017, all urban groundwater samples were collected from monitoring wells within PMR 10.

Appendix 4 contains the 2019 groundwater quality results, which are available online at the MDA Monitoring and Assessment webpage and through the National Water Quality Monitoring Council Portal.

All groundwater sample collection events in 2019 included GC-MS/MS, LC-MS/MS, and nitrate-nitrogen (nitrate) analysis. All sites received at least one glyphosate LC-MS/MS analysis as well.

Data from the Private Well Pesticide Sampling (PWPS) Project are not included in this section. A summary of the latest results from the PWPS Project can be found in Section 4.5. Complete project information can be found online for the Private Well Pesticide Sampling Project.

2.1 2019 Groundwater pesticide sampling summary

Groundwater samples were collected from 166 sites across Minnesota (Figure 2-0).

- 142 were shallow monitoring wells, including 20 urban wells.
- 13 were naturally occurring springs.
- 11 were private drinking water wells.

In total, 222 sample collection events resulted in 222 GC-MS/MS, 222 LC-MS/MS, 167 glyphosate LC-MS/MS and 201 nitrate samples collected from the groundwater monitoring sites (Table 2-0). There were samples from three springs collected in February that were analyzed with the laboratory analytical methods used in 2018, which did not include the eleven new compounds for 2019. They were also analyzed with the 2018 MRL for imidacloprid (10 ng/L). The samples collected from these sites in August did include the new compounds and had the lower MRL for imidacloprid (5 ng/L).

In summary:

- Forty-seven different pesticides or pesticide degradates were detected.
- Metolachlor ESA was the most frequently detected analyte.
- Glyphosate and AMPA (a degradate of glyphosate) were not detected in groundwater (167 samples).
- Eleven pesticides were analyzed for the first time in 2019.
    - Cyanazine acid, cyanazine amide, and deethylcyanazine acid were detected in 2%, 2%, and 4% of samples collected statewide, respectively.
    - Acifluorfen, afidopyropen, deethylcyanazine, deethylcyanazine amide, flutianil, flutianil OC 56574, flutianil OC 56635, and pydiflumetofen were not detected.
- The total concentration of cyanazine and its degradates exceeded the drinking water Health Risk Limit (HRL) of 1,000 ng/L in one sample collected from a spring in Goodhue County. This was the only exceedance of a drinking water reference value in the ambient groundwater monitoring.

Figure 2-0. 2019 MDA groundwater sampling sites.

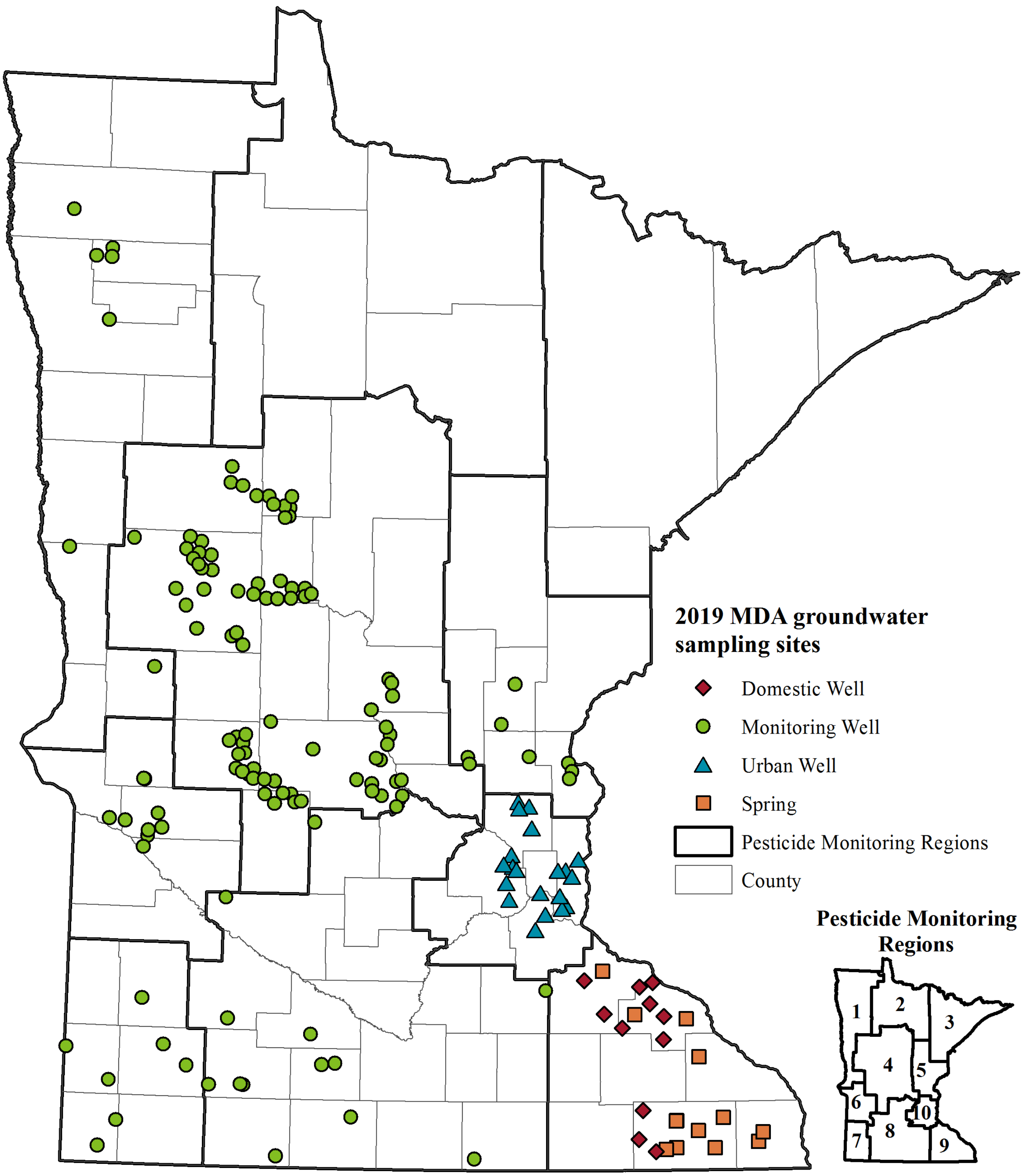


Table 2-0. 2019 summary of groundwater monitoring results and reference values.

Pesticide Analyte	Sampled Analyzed	Number of Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type	PMRs with Detection
2,4,5-T	222	0	0	<50	10,000	RA$_{14}$	none
2,4,5-TP	222	0	0	<50	50,000	HRL$_{MCL}$	none
2,4-D	222	**6**	**3**	**354**	30,000	HRL$_{18}$	**1,6,7,9,U**
2,4-DB	222	0	0	<20	5,000	RA$_{14}$	none
Acetamiprid	222	0	0	<25	100,000	RA$_{14}$	none
Acetochlor	222	**8**	**4**	**295**	20,000	HRL$_{18}$	**1,5,8,9**
Acetochlor ESA	222	**92**	**41**	**11,100**	300,000	HRL$_{18}$	**1,4,5,6,7,8,9,U**
Acetochlor OXA	222	**25**	**11**	**4,410**	90,000	HRL$_{18}$	**1,4,5,7,8,9**
Acifluorfen	219	0	0	<50	5,000*	RA$_{20}$ (for sodium acifluorfen)	none
Afidopyropen	219	0	0	< 50	1,000	RA$_{19}$	none
Alachlor	222	**1**	**<1**	**54.5**	9,000	HRL$_{18}$	**9**
Alachlor ESA	222	**60**	**27**	**936**	50,000	RAA$_{16}$	**4,5,6,7,8,9,U**
Alachlor OXA	222	**6**	**3**	**147**	50,000	RAA$_{16}$	**4,7,9,U**
Aldicarb Sulfone	222	0	0	<15	3,000	RA$_{14}$	none
Aldicarb Sulfoxide	222	0	0	<50	2,000	RA$_{14}$	none
Aminopyralid	222	**16**	**7**	**513**	800,000	RA$_{16}$	**1,4,6,7,8,9,U**
Atrazine	222	**30**	**14**	**204**	3,000	HRL$_{MCL}$	**1,4,6,7,9**
Didealkylatrazine	222	**39**	**18**	**379**	3,000*	Parent	**1,4,6,7,9**
Deisopropyl atrazine	222	**10**	**5**	**82.0**	3,000*	Parent	**1,4,7,9**
Desethylatrazine	222	**36**	**16**	**270**	3,000*	Parent	**1,4,5,7,8,9**
Hydroxyatrazine	222	**36**	**16**	**76.2**	20,000	RA$_{14}$	**4,7,9,U**
Azoxystrobin	222	0	0	<10	300,000	RA$_{14}$	none
Benfluralin	222	0	0	<25	8,000	RA$_{14}$	none
Bensulfuron-methyl	222	0	0	<16.7	50,000	RA$_{14}$	none
Bensulide	222	0	0	<250	10,000	RA$_{16}$	none
Bentazon	222	**33**	**15**	**1,940**	30,000	HRL$_{15}$	**1,4,6,9**
Benzovindiflupyr	222	0	0	<50	80,000	RA$_{16}$	none
Bicyclopyrone	222	0	0	<10	400	RA$_{15}$	none
Bicyclopyrone SYN503870	222	0	0	<100	400*	Parent	none
Bifenthrin	222	0	0	<20	2,000	RA$_{14}$	none
Boscalid	222	0	0	<50	300,000	RA$_{14}$	none
Bromacil	222	**2**	**1**	**1,060**	30,000	RA$_{14}$	**U**
Bromoxynil	222	0	0	<25	700	RA$_{14}$	none
Carbaryl	222	0	0	<25	10,000	RA$_{14}$	none
Carbendazim	222	0	0	<10	9,000	RA$_{14}$	none
Carbofuran	222	0	0	<13.3	100	RA$_{14}$	none
Chlorantraniliprole	222	0	0	<50	1,000,000	RA$_{14}$	none
Chlorimuron-ethyl	222	0	0	<20	20,000	RA$_{14}$	none
Chlorothalonil	222	0	0	<50	6,000	RA$_{14}$	none
Chlorpyrifos	222	0	0	<40	600	HBV$_{13}$	none
Chlorpyrifos Oxon	222	0	0	<40	400	RAA$_{13}$	none
Clethodim sulfone	222	0	0	<100	300,000*	RA$_{18}$ (for Clethodim)	none

Pesticide Analyte	Sampled Analyzed	Number of Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type	PMRs with Detection
Clethodim sulfoxide	222	0	0	<50	300,000*	RA_{18} (for Clethodim)	none
Clomazone	222	0	0	<15	70,000	RA_{14}	none
Clopyralid	222	**3**	**1**	**208**	200,000	RA_{14}	**4,8**
Clothianidin	222	**40**	**18**	**1,460**	200,000	HRL_{18}	**4,5,7,8,9**
Cyanazine	222	0	0	<25	1,000	HRL_{18}	none
Cyanazine acid	219	**5**	**2**	**26.2**	1,000*	Parent	**9**
Cyanazine amide	219	**5**	**2**	**30.6**	1,000*	Parent	**9**
Deethylcyanazine	219	0	0	<25	1,000*	Parent	none
Deethylcyanazine acid	219	**9**	**4**	**653**	1,000*	Parent	**6,9**
Deethylcyanazine amide	219	0	0	<25	1,000*	Parent	none
Cyantraniliprole	222	0	0	<100	2,000	RA_{15}	none
Cyfluthrin	222	0	0	<100	6,000	RA_{14}	none
Diazinon	222	0	0	<30	80	RA_{14}	none
Diazinon Oxon	222	0	0	<75	80*	Parent	none
Dicamba	222	**2**	**1**	**228**	700,000	RA_{14}	**4,6**
Dichlobenil	222	0	0	<5	40,000	RA_{14}	none
Dichlorprop	222	0	0	<50	60,000	RA_{14}	none
Dichlorvos	222	0	0	<15	1,000	RA_{14}	none
Dicrotophos	222	0	0	<25	30	RA_{14}	none
Difenoconazole	222	0	0	<25	10,000	RA_{14}	none
Dimethenamid	222	**1**	**<1**	**25.9**	300,000	HRL_{15}	**4**
Dimethenamid ESA	222	**36**	**16**	**910**	300,000	RAA_{13}	**1,4,7,8,9**
Dimethenamid OXA	222	**9**	**4**	**410**	300,000	RAA_{13}	**1,4**
Dimethoate	222	0	0	<50	3,000	RA_{14}	none
Dinotefuran	222	0	0	<25	5,000	RA_{14}	none
Disulfoton	222	0	0	<60	300	RA_{14}	none
Disulfoton Sulfone	222	0	0	<20	300*	Parent	none
Diuron	222	0	0	<13.3	2,000	RA_{14}	none
EPTC	222	0	0	<10	40,000	HRL_{18}	none
Esfenvalerate	222	0	0	<150	2,000	RA_{14}	none
Ethalfluralin	222	0	0	<50	1,000	RA_{14}	none
Ethofumesate	222	0	0	<50	800,000	RA_{14}	none
Flufenacet OXA	222	0	0	<8.3	2,000	RA_{14}	none
Flumetsulam	222	**13**	**6**	**274**	400,000	RA_{14}	**4,7,8**
Flupyradifurone	222	0	0	<10	20,000	RA_{16}	none
Flutianil	219	0	0	<25	Insufficient data	Insufficient data	none
Flutianil OC 56574	219	0	0	<50	Insufficient data	Insufficient data	none
Flutianil OC 56635	219	0	0	<25	Insufficient data	Insufficient data	none
Flutriafol	222	0	0	<10	10,000	RA_{14}	none
Fluxapyroxad	222	0	0	<10	30,000	RA_{16}	none
Fomesafen	222	**30**	**14**	**2,960**	20,000	HBV_{20}	**1,4,7,8**
Fonofos	222	0	0	<15	500	RA_{14}	none
Glyphosate	167	0	0	<1,020	500,000	HBV_{17}	none

Pesticide Analyte	Sampled Analyzed	Number of Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type	PMRs with Detection
AMPA	167	0	0	<5,100	1,000,000	HBV$_{17}$	none
Halauxifen-methyl	222	0	0	<10	40,000	RA$_{18}$	none
Halauxifen Acid	222	0	0	<25	300,000	RA$_{18}$	none
Halosulfuron-methyl	222	0	0	<30	20,000	RA$_{14}$	none
Hexazinone	222	0	0	<10	10,000	RA$_{14}$	none
Imazamethabenz-methyl	222	0	0	<5	60,000	RA$_{14}$	none
Imazamethabenz Acid	222	0	0	<10	60,000*	Parent	none
Imazamox	222	**18**	**8**	**106**	20,000,000	RA$_{14}$	**4**
Imazapic	222	0	0	<10	30,000	RA$_{14}$	none
Imazapyr	222	**7**	**3**	**461**	900,000	RA$_{14}$	**1,6,9,U**
Imazaquin	222	0	0	<16.7	60,000	RA$_{14}$	none
Imazethapyr	222	**6**	**3**	**50.9**	900,000	RA$_{14}$	**5,6,7,9**
Imidacloprid	222	**22**	**10**	**165**	3,000	HBV$_{19}$	**4,5,U**
Imidacloprid Olefin	222	0	0	<50	3,000*	Parent	none
Imidacloprid Urea	222	0	0	<50	3,000*	Parent	none
Isoxaflutole	222	0	0	<40	7,000	RA$_{14}$	none
Isoxaflutole DKN	222	**3**	**1**	**165**	7,000*	Parent	**7**
lambda-Cyhalothrin	222	0	0	<75	200	RA$_{14}$	none
Linuron	222	0	0	<20	2,000	RA$_{14}$	none
Malathion	222	0	0	<50	90,000	RA$_{14}$	none
Mandestrobin	222	0	0	<25	300,000	RA$_{18}$	none
MCPA	222	**1**	**<1**	**8.27**	7,000	RA$_{14}$	**6**
MCPB	222	0	0	<20	7,000	RA$_{14}$	none
MCPP	222	**2**	**1**	**304**	4,000	RA$_{14}$	**U**
Mesotrione	222	0	0	< 50	5,000	RA$_{14}$	none
Metalaxyl	222	**6**	**3**	**30.2**	20,000	RA$_{14}$	**4**
Methoxychlor	222	0	0	<50	10,000	RA$_{14}$	none
Metolachlor	222	**22**	**10**	**711**	300,000	HRL$_{11}$	**1,4,5,7,9**
Metolachlor ESA	222	**183**	**82**	**12,500**	800,000	HRL$_{11}$	**1,4,5,6,7,8,9,U**
Metolachlor OXA	222	**107**	**48**	**7,400**	800,000	HRL$_{11}$	**1,4,5,6,7,8,9,U**
Metribuzin	222	**5**	**2**	**174**	10,000	HRL$_{13}$	**4**
Metribuzin DA	222	**7**	**3**	**229**	10,000	RAA$_{12}$	**4,7**
Metribuzin DADK	222	**3**	**1**	**782**	10,000	RAA$_{12}$	**4**
Metribuzin DK	222	0	0	<500	10,000	RAA$_{12}$	none
Metsulfuron-methyl	222	**2**	**1**	**85.2**	400,000	RA$_{14}$	**4,8**
Momfluorothrin	222	0	0	<50	100,000	RA$_{18}$	none
Myclobutanil	222	0	0	<10	40,000	RA$_{14}$	none
Nicosulfuron	222	0	0	<26.6	300,000	RA$_{14}$	none
Norflurazon	222	0	0	<20	4,000	RA$_{14}$	none
Norflurazon-desmethyl	222	0	0	<50	4,000*	Parent	none
Oxadiazon	222	0	0	<75	1,000	RA$_{14}$	none
Oxathiapiprolin	222	0	0	<100	6,000,000	RA$_{18}$	none
Oxydemeton-methyl	222	0	0	<20	300	RA$_{14}$	none

Pesticide Analyte	Sampled Analyzed	Number of Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type	PMRs with Detection
Parathion-methyl	222	0	0	<100	80	RA_{14}	none
Parathion-methyl Oxon	222	0	0	<25	80*	Parent	none
Pendimethalin	222	0	0	<75	40,000	RA_{14}	none
Phorate	222	0	0	<25	1,000	RA_{14}	none
Picloram	222	**1**	**<1**	**3,460**	300,000	RA_{14}	**U**
Picoxystrobin	222	0	0	<50	10,000	RA_{15}	none
Prometon	222	0	0	<100	10,000	RA_{14}	none
Prometryn	222	0	0	<3.3	100,000	RA_{14}	none
Propachlor	222	0	0	<30	3,000	RA_{14}	none
Propachlor ESA	222	0	0	<30	3,000*	Parent	none
Propachlor OXA	222	0	0	<10	3,000*	Parent	none
Propazine	222	0	0	<25	1,000[1]	HRL_{18} (for cyanazine)	none
Propiconazole	222	0	0	<10	90,000	RA_{14}	none
Pydiflumetofen	219	0	0	< 25	8,000	RA_{18}	none
Pyraclostrobin	222	0	0	<25	100,000	HBV_{16}	none
Pyroxasulfone	222	0	0	<50	5,000	RA_{14}	none
Saflufenacil	222	**17**	**8**	**1,000**	40,000	RA_{14}	**4,5,9**
Sedaxane	222	0	0	<75	200,000	RA_{16}	none
Siduron	222	0	0	<6.7	200,000	RA_{14}	none
Simazine	222	0	0	<75	4,000	HRL_{MCL}	none
Sulfentrazone	222	**21**	**9**	**4,810**	200,000	RA_{18}	**1,4,6,7,8,9**
Sulfometuron-methyl	222	0	0	<8.3	100,000	RA_{14}	none
Tebuconazole	222	0	0	<10	30,000	RA_{14}	none
Tebupirimfos	222	0	0	<30	70	RA_{14}	none
Tembotrione	222	**1**	**<1**	**88.0**	600	RA_{14}	**6**
Terbufos	222	0	0	<30	100	RA_{14}	none
Tetraconazole	222	0	0	<10	30,000	RA_{14}	none
Thiacloprid	222	0	0	<50	20,000	RA_{16}	none
Thiamethoxam	222	**22**	**10**	**2,180**	200,000	HRL_{18}	**4**
Thifensulfuron-methyl	222	0	0	<16.7	70,000	RA_{14}	none
Thiobencarb	222	0	0	<8.3	20,000	RA_{14}	none
Tolfenpyrad	222	0	0	<100	10,000	RA_{16}	none
Tolpyralate	222	0	0	<50	20,000	RA_{18}	none
Triallate	222	0	0	<50	10,000	RA_{14}	none
Triasulfuron	222	0	0	<23.3	10,000	RA_{14}	none
Triclopyr	222	**2**	**1**	**80.2**	80,000	RA_{14}	**4,9**
Trifluralin	222	0	0	<50	9,000	RA_{14}	none
zeta-Cypermethrin	222	0	0	<500	50,000	RA_{14}	none

<u>Key to value types and symbols in groundwater reference values</u>

The values selected were discussed with MDH while preparing this report, and appropriate human health-based groundwater guidance may change pending MDH evaluation of toxicity information.

As defined in the Minnesota Pesticide Management Plan, the MDA seeks a published chronic reference value in the absence of an MCL, HRL, HBV, RAA, or RA. If available, the MDA will use the USEPA Office of Water's Health Advisory value. Further, the lowest published reference value will be utilized for comparison to the results, but an HRL or MCL value will take preference over other values if listed.

Human health-based groundwater reference values:

HBV – Health Based Value (chronic), a non-promulgated value established by the MDH in the year indicated.

HRL – Health Risk Limit (chronic), a promulgated value established by the MDH in the year indicated or set in 2007 to the USEPA Maximum Contaminant Level (MCL) as required by state law.

MCL – Maximum Contaminant Level, established by the USEPA for the regulation of public water supplies.

RAA – Risk Assessment Advice (chronic), a non-promulgated value established by the MDH in the year indicated.

RA – Rapid Assessment (chronic), a non-promulgated value established by the MDH in the year indicated. The MDH conducts rapid assessments by using the most current USEPA data on a given chemical. Rapid assessments were developed using assumptions that were potentially more protective than the nuanced and careful selection of doses and exposures that are made in the course of a full, in-depth chemical review that is carried out to develop HRL, RAA, and HBVs.

* – In the absence of compound-specific toxicological information for pesticide degradates, the MDH conservatively assumes by default that a pesticide degradate has the same toxicological effect as the pesticide parent compound and is as potent.

[1] – In the absence of compound-specific toxicological information for propazine, the MDA conservatively assumes that the HRL for cyanazine, a chemical in the same family as propazine, represents the same toxicological effect as propazine.

Insufficient data – An RA was requested from the MDH but, at this time, there was insufficient data available to allow the MDH to make a recommendation on a reference value.

Please visit the MDH website for the most current and detailed descriptions of the MDH health-based reference values for groundwater.

The USEPA maintains the current drinking water standards advisories and human health benchmarks for pesticides and other contaminants.

For all other reference values, health effects information is available from the MDA or the MDH. Guidance can also be found at MDH website for evaluating concurrent exposures to multiple chemicals.

2.1.1 2019 Quality Assurance/Quality Control summary

There were 74 pesticide related quality assurance/quality control (QA/QC) and 27 nitrate related QA/QC samples collected along with the 611 routine pesticide and 201 routine nitrate samples during the 2019 monitoring season. All QA/QC samples were planned prior to the start of the monitoring season and analyzed by the MDA Laboratory. The MDA sets a target of 10% of groundwater samples to be collected as QA/QC samples, which includes blanks (5%) and replicates/duplicates (5%).

In 2019, the QA/QC samples represented 12% of the routine groundwater pesticide samples collected. These included 35 field replicates/duplicates, 19 field blanks, 12 field equipment blanks, and 8 field equipment post-lab cleaning blanks. There were no detections in the blank samples. Field replicates were compared by the MDA staff against their respective paired routine sample, and all analyte concentrations were determined to be within acceptable ranges of variability. In addition, the MDA Laboratory completed QA/QC measures that included in-lab sample blanks, spike and spike duplicates with each batch of samples analyzed that is reviewed prior to the release of the water quality data.

2.2 Trend analysis

Detection frequency, median concentration, and 90th percentile concentrations trend analysis for select pesticides and their degradates were conducted by the MDA MAU. This work was conducted for each PMR on a semi-annual basis. For this report, the trend analysis was conducted on the pesticide data collected from 2010 through 2019. In previous years, the trend analysis was conducted on the entire data record. This modification was motivated in part by changes to the laboratory analytical methods which occurred in 2010 and resulted in lower MRLs for some pesticide compounds. This time period (2010-2019) also better represents more current agricultural practices and conditions throughout the state. This information was also used to generate all of the graphs presented in Section 2.

All trend analyses were performed using the two-sided Mann-Kendall test, with an indication of statistical significance based upon the 90% confidence level. Discussion of these results can be found in Section 2.3.1 through Section 2.3.5, where trend summary maps have been included to display the results from the trend analysis for the median and 90th percentile concentrations, as well as detection frequency, for the common detection pesticides and several of their degradates by PMR. Output from the trend test analyses that were performed, along with trend summary tables, can be found in Appendix 5a.

Impact of changing method reporting limits (MRLs) on trend analysis.
The existence of multiple analytical reporting limits over time for a single compound complicates trend analysis. To ensure comparability of results over time requires censoring (or restricting) the entire data set at the highest historic MRL for each compound during the time frame of evaluation. All trend analyses were conducted from data where concentrations below the highest MRL were set to zero (*i.e.*, non-detect), thereby allowing unbiased time-trend evaluations across all concentration data. It should also be noted that trends were only assessed for calculated percentile concentration values for pesticides and degradates with more than three detections above the highest historical MRL.

Because current trend analysis methods employed by the MDA require censoring data that was once included in the calculation of annual detection frequency, and because MRL values change and vary among different pesticides, detection frequency comparisons among pesticides is not advised. Generally, it is more useful to compare detection frequency over time for individual pesticide compounds.

Two categories of "no trend" are presented in the following trend summaries. The first category is indicated as "*Trend not able to be calculated*." This means that the compound was not detected in more than 3 samples, or a calculated percentile value was below the highest historical MRL in the PMR. The second category, "*Trend not statistically significant,*" means that there was a trend present but not statistically significant.

2.3 Analysis of the common detection pesticides

Common detection is an official designation made by the Commissioner of Agriculture and is defined as "detection of a pollutant that is not due to misuse or unusual or unique circumstances but is likely to be the result of normal use of a product or a practice" (Minn. Stat. § 103H.005, Subd. 5). The process of designating a common detection pesticide is described in the Minnesota Pesticide Management Plan (PMP). Pesticides, and select degradates, that have been designated as "common detection" receive heightened scrutiny from the MDA during reporting of monitoring results. Acetochlor, alachlor, atrazine, metolachlor, and metribuzin are the current groundwater common detection pesticides. Atrazine, metolachlor and metribuzin were designated in 2002 and acetochlor and alachlor were designated in 2003. Alachlor was removed as a registered pesticide in Minnesota in 2016. Figure 2-1 displays the number of common detection pesticides (any parent or degradate) detected at each monitoring site in 2019.

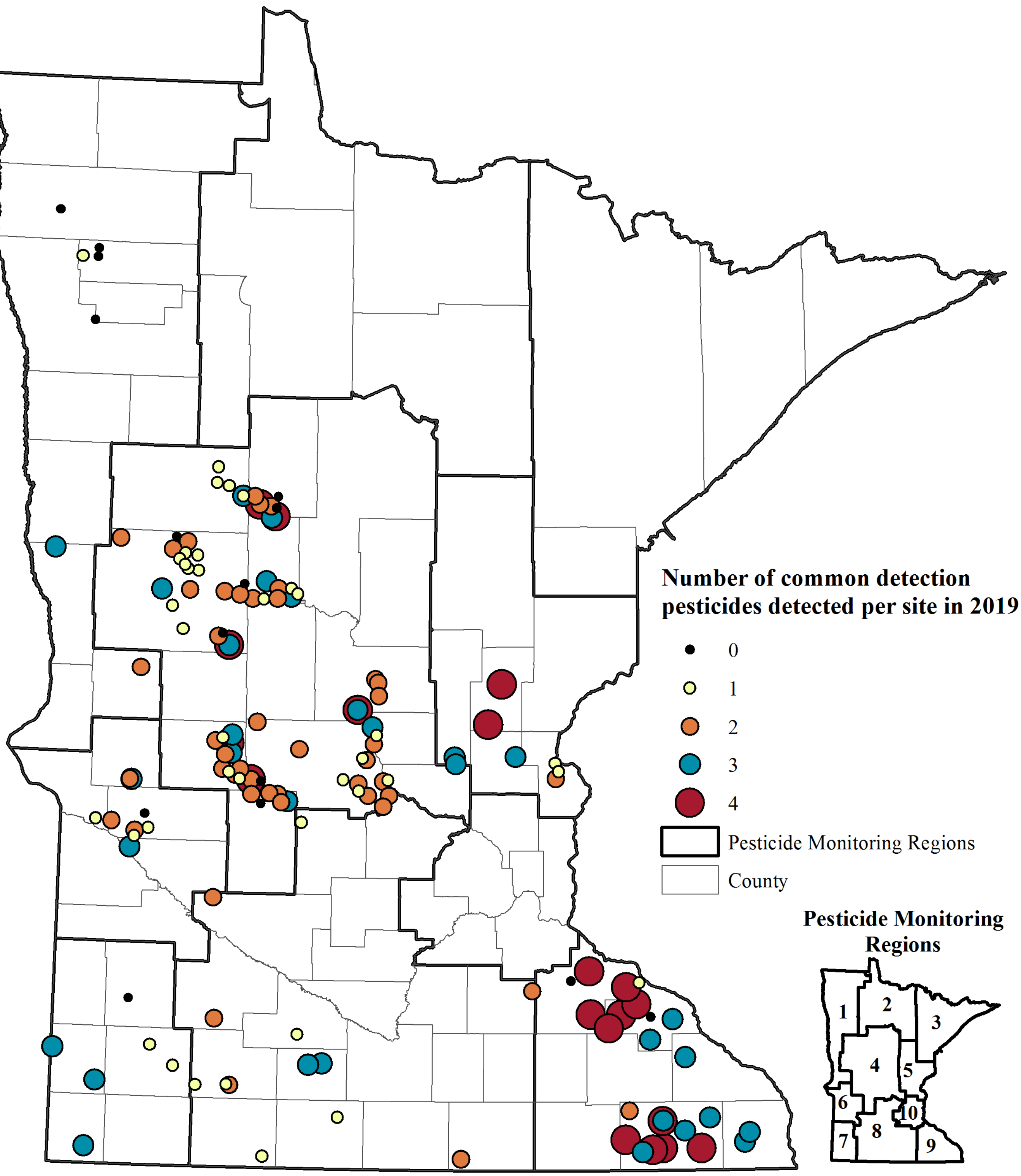
The MDA groundwater monitoring program is designed to determine the detection frequency, magnitude of pesticide concentrations, and changes in pesticide detections and concentrations, both spatially and temporally. Various analyses were performed, and summaries were prepared, for this report to meet these objectives, specifically for the common detection pesticides. Maps were prepared to display the spatial variability in pesticide detections across Minnesota. Tables are utilized to present the 2019 pesticide concentration data (median, 90^{th} percentile, and maximum values) and detection frequencies.

Concentration data over time is presented through the use of graphical displays of median and 90^{th} percentile concentration values and detection frequencies from 2010 through 2019. Long-term time series graphs, that display data dating back to before 2010, can be found in Appendix 5b. Maximum values are not included in the concentration time series graphics because their magnitude can mask trends in the other statistics that better represent the dataset and because they represent a single concentration value that is not representative of general conditions and the wider sample population. PMR-specific graphics are only provided when there are enough results at greater than non-detect values to see a pattern and to evaluate a trend, as found in the trend summary maps in Section 2.3.1 through 2.3.5. Dashed lines representing a 4^{th} order polynomial smooth for each of the data groups are displayed in the graphs for both detection frequency and for concentration (median and 90^{th} percentile values).

The polynomial smooth is a nonparametric curve fitting method, which generates a line representing the general tendency of the data over time based upon the data itself rather than being constrained by assumptions associated with fitting a specific equation to the data. This is particularly useful for data that

does not conform to standard statistical distributions, such as the water quality pesticide data that the MAU collects and analyzes. The order of the smoothing polynomial in the method routine is selected by the analyst to generate a line that is determined to provide the “best fit.” The generated line can be utilized for visual assessment of the data to investigate if there are any general patterns or trends in the data that would otherwise be difficult to see (Helsel and Hirsch, 2002).

Figure 2-1. Number of common detection pesticides (parent or degradate) detected in groundwater samples per site in 2019.



2.3.1 Acetochlor results

Figure 2-2 displays the distribution of sites where acetochlor and/or acetochlor degradates (acetochlor ESA and acetochlor OXA) were detected during the 2019 sampling season. Summary statistics from groundwater monitoring results for acetochlor and acetochlor degradates are presented in Table 2-1. In Table 2-1, the category "Number of samples with a compound detected" represents the count of samples with any form of acetochlor and/or acetochlor degradates detected.

Figure 2-3 shows the acetochlor and acetochlor degradate trend analysis maps for 2010 through 2019 for the median and 90th percentile concentrations and the detection frequency. Time series graphics for the median and 90th percentile concentrations and detection frequency of acetochlor degradates are shown in Figures 2-4 through 2-6. Both the trend analysis and time series graphics were based on the same pesticide data sets collected from 2010 through 2019 and can be directly compared. It should be noted that PMR-specific graphics are only provided when there are enough results at greater than non-detect values to see a pattern and to evaluate a trend (either concentration or detection frequency), as found in the trend summary map. Long-term time series graphs can be found in Appendix 5b.

- 2019 acetochlor and acetochlor degradates summary statistics (Table 2-1)
    - An acetochlor degradate was detected in every monitored PMR.
    - Acetochlor was detected in PMRs 1, 5, 8, and 9.
    - Acetochlor ESA was the most common form of acetochlor detected and had the greatest 90th percentile concentration of any acetochlor compound in each PMR.

- 2010 through 2019 trend analysis (Figure 2-3)
    - Median concentration trend findings for acetochlor and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Acetochlor ESA in PMRs 7, 8, and 9.
            - Acetochlor OXA in PMR 7.
        - A decreasing trend was calculated for:
            - Acetochlor ESA in PMR 5.
    - 90th percentile concentration trend findings for acetochlor and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Acetochlor in PMR 5.
            - Acetochlor ESA in PMRs 4, 6, 7, and 9.
            - Acetochlor OXA in PMRs 1, 4, 5, 6, 7, and 9.
        - An increasing trend was calculated for:
            - Acetochlor ESA in PMRs 1 and 8.
            - Acetochlor OXA in PMR 8.
        - A decreasing trend was calculated for:
            - Acetochlor ESA in PMR 5.
    - Detection frequency trend findings for acetochlor and acetochlor degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Acetochlor in PMRs 1, 4, 5, 7, 8, and 9.
            - Acetochlor ESA in PMRs 1, 5, 6, 7, 8, and 9.

- Acetochlor OXA in PMRs 1, 4, 6, 7, 8, and 9.

- An increasing trend was calculated for:
  - Acetochlor ESA in PMR 4.
  - Acetochlor OXA in PMR 5.

Figure 2-2. Pesticide Monitoring Regions and groundwater monitoring sites with acetochlor and/or acetochlor degradate detections in 2019.

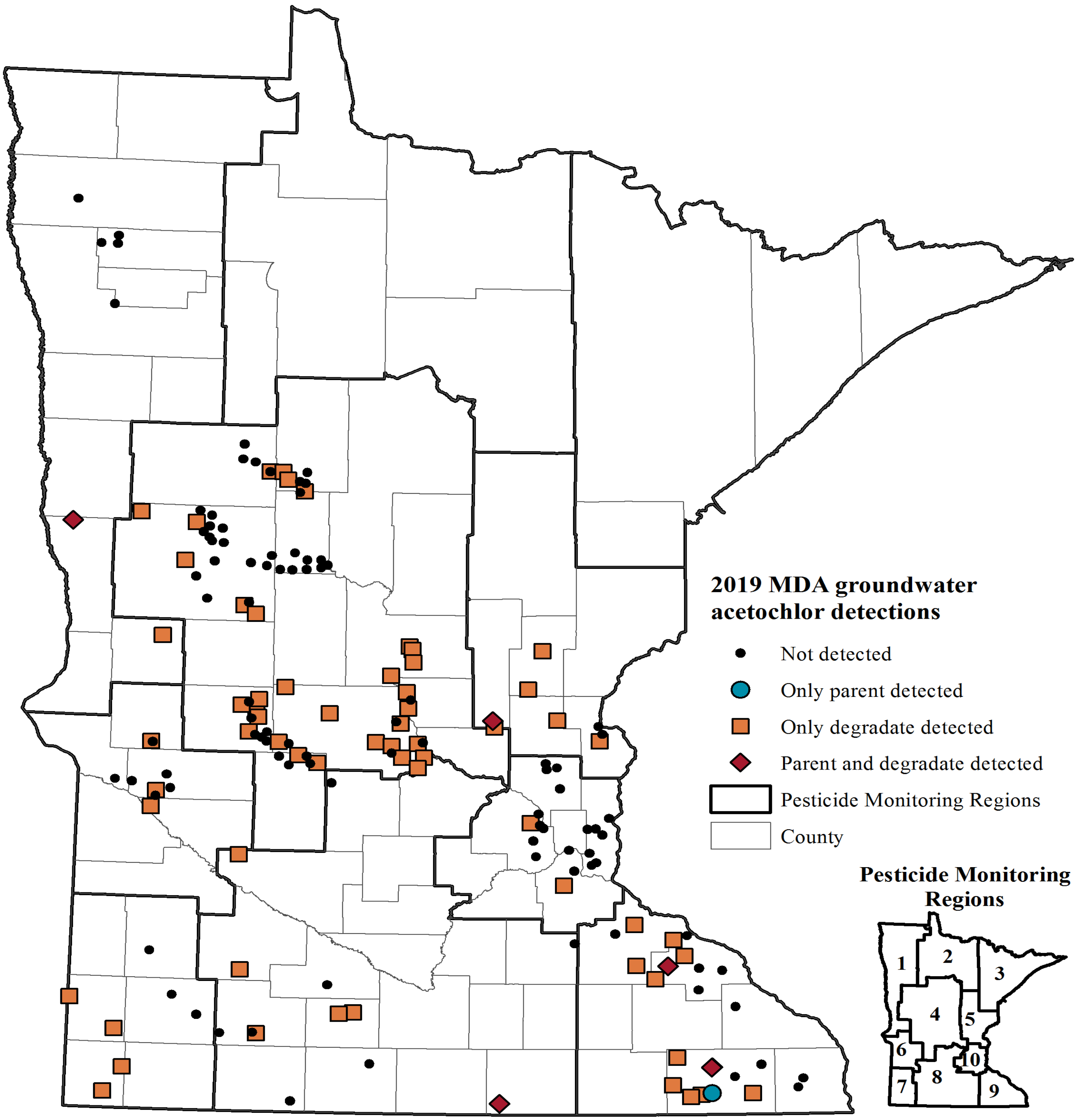


Table 2-1. 2019 data summary of acetochlor and acetochlor degradates in MDA groundwater samples.

Analyte	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)*	90^{th} Percentile (ng/L)*	Maximum (ng/L)*
PMR 1						
Acetochlor	14	**2**	**14**	<30	<30	**74.7**
Acetochlor ESA	14	**4**	**29**	<30	**816**	**1,270**
Acetochlor OXA	14	**2**	**14**	<33.3	**721**	**1,400**
Number of samples with a compound detected	14	**4**	**29**	-	-	-
PMR 4						
Acetochlor	78	0	0	<30	<30	<30
Acetochlor ESA	78	**33**	**42**	<30	**611**	**4,900**
Acetochlor OXA	78	**7**	**9**	<33.3	<33.3	**411**
Number of samples with a compound detected	78	**33**	**42**	-	-	-
PMR 5						
Acetochlor	16	**1**	**6**	<30	<30	**53.1**
Acetochlor ESA	16	**11**	**69**	**58.5**	**1,651**	**11,100**
Acetochlor OXA	16	**2**	**13**	<33.3	<33.3	**4,410**
Number of samples with a compound detected	16	**11**	**69**	-	-	-
PMR 6						
Acetochlor	17	0	0	<30	<30	<30
Acetochlor ESA	17	**5**	**29**	<30	**75.8**	**152**
Acetochlor OXA	17	0	0	<33.3	<33.3	<33.3
Number of samples with a compound detected	17	**5**	**29**	-	-	-
PMR 7						
Acetochlor	14	0	0	<30	<30	<30
Acetochlor ESA	14	**8**	**57**	**120**	**632**	**823**
Acetochlor OXA	14	**5**	**36**	<33.3	**210**	**252**
Number of samples with a compound detected	14	**8**	**57**	-	-	-
PMR 8						
Acetochlor	26	**1**	**4**	<30	<30	**62.3**
Acetochlor ESA	26	**11**	**42**	<30	**1,194**	**2,290**
Acetochlor OXA	26	**7**	**27**	<33.3	**127**	**875**
Number of samples with a compound detected	26	**11**	**42**	-	-	-
PMR 9						
Acetochlor	37	**4**	**11**	<30	<30	**295**
Acetochlor ESA	37	**18**	**49**	<30	**125**	**424**
Acetochlor OXA	37	**2**	**5**	<33.3	<33.3	**108**
Number of samples with a compound detected	37	**19**	**51**	-	-	-

**Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*
-Acetochlor degradates are not additive with the parent, so concentration statistics were not calculated for total acetochlor.

Figure 2-3. 2010 through 2019 acetochlor and acetochlor degradates median and 90th percentile concentrations and detection frequency trend maps.

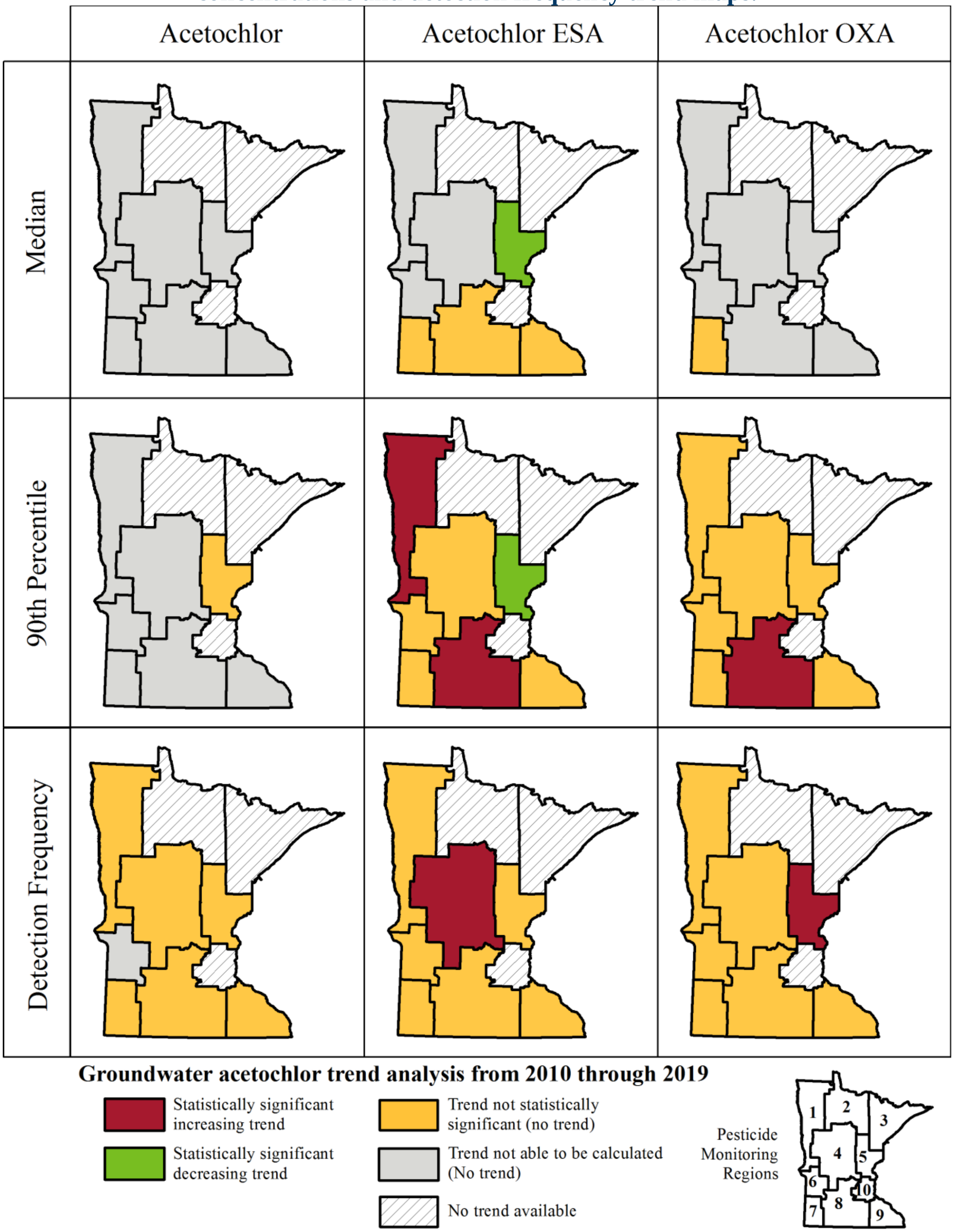


Figure 2-4. 2010 through 2019 acetochlor concentration results and detection frequencies for MDA PMRs 1, 4, 5, 7, 8, and 9.

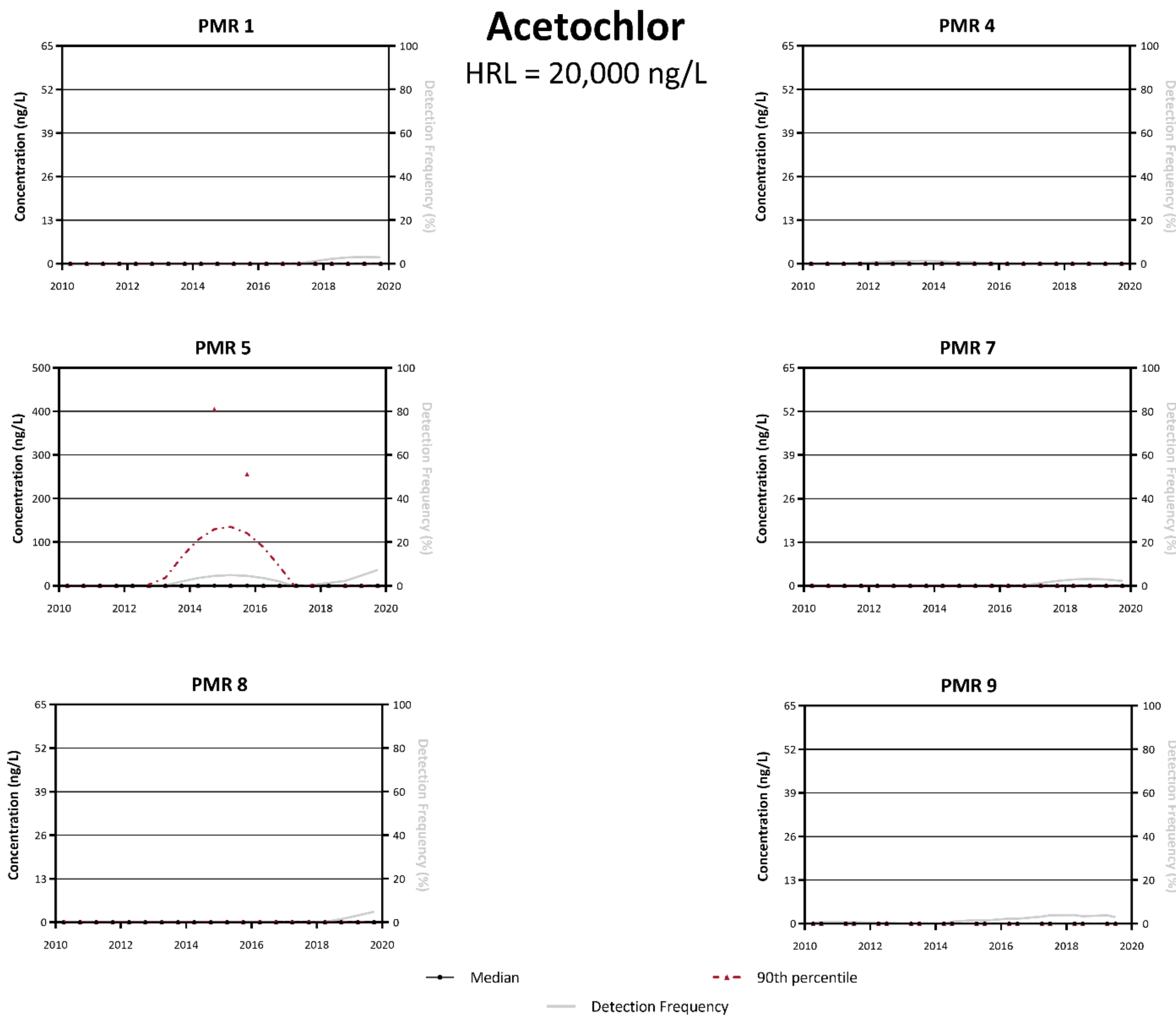


Figure 2-5. 2010 through 2019 acetochlor ESA concentration results and detection frequencies for all monitored PMRs.

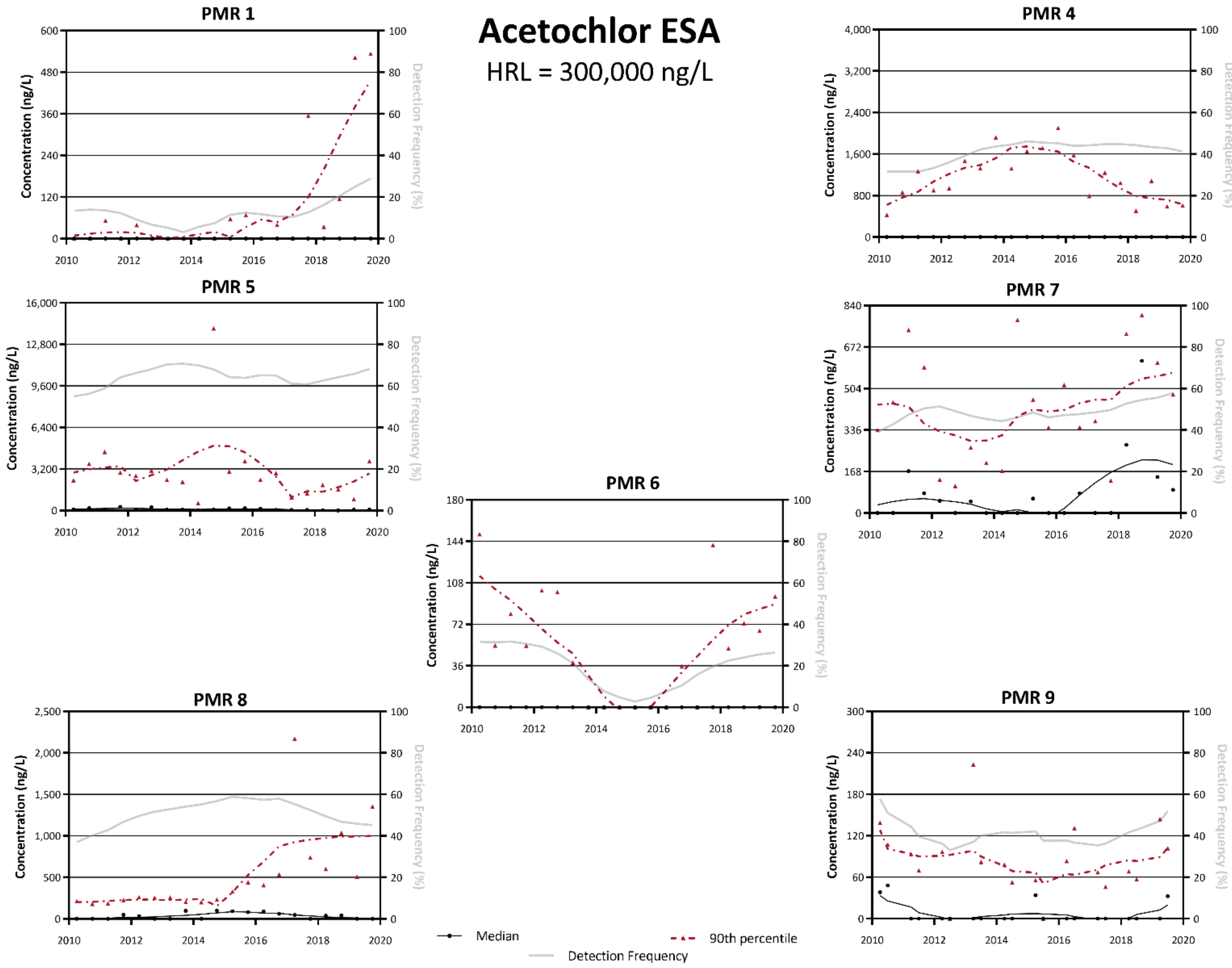
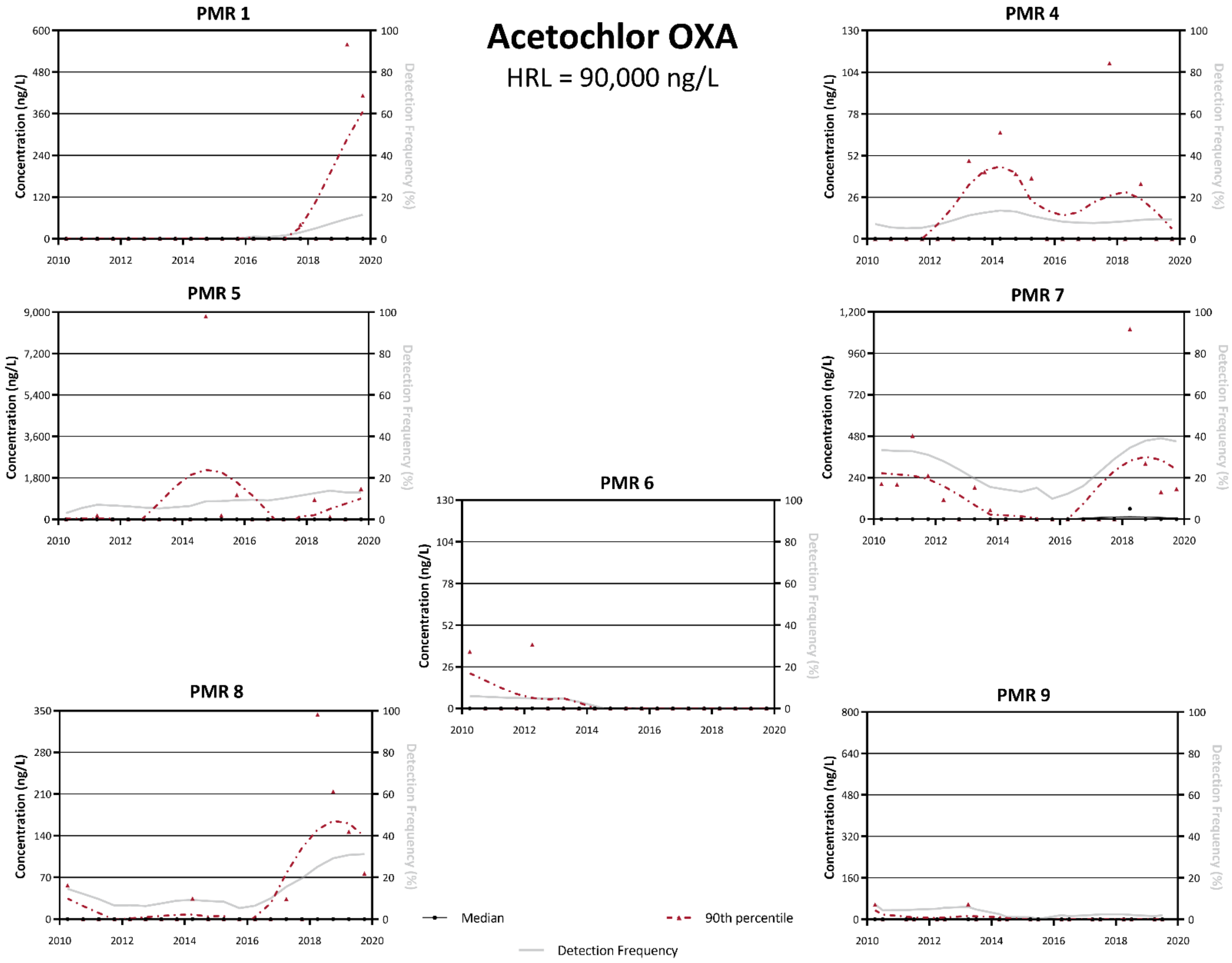


Figure 2-6. 2010 through 2019 acetochlor OXA concentration results and detection frequencies for all monitored PMRs.



2.3.2 Alachlor results

Figure 2-7 presents the distribution of sites where alachlor and/or alachlor degradates (alachlor ESA and alachlor OXA) were detected during the 2019 sampling season. Summary statistics from groundwater monitoring results for alachlor and alachlor degradates are located in Table 2-2. In Table 2-2, the category "Number of samples with a compound detected" represents the number of samples with any form of alachlor and/or alachlor degradates detected.

Figure 2-8 shows the alachlor and alachlor degradate trend analysis maps for 2010 through 2019 for the median and 90th percentile concentrations and the detection frequency. Time series graphics for the concentration and detection frequency of alachlor degradates are presented in Figures 2-9 and 2-10. Both the trend analysis and time series graphics were based on the same pesticide data sets collected from 2010 through 2019 and can be directly compared. It should be noted that PMR-specific graphics are only provided when there are enough results at greater than non-detect values to see a pattern and to evaluate a trend (either concentration or detection frequency), as found in the trend summary map. Long-term time series graphs can be found in Appendix 5b.

- Alachlor was removed as a registered pesticide in Minnesota in 2016.
- 2019 alachlor and alachlor degradates summary statistics (Table 2-2)
    - Alachlor was only detected in PMR 9.
    - Alachlor ESA was detected in all regions except PMR 1.
    - Alachlor ESA median concentrations were below the MRL in all regions except PMR 9.
    - Alachlor OXA median concentrations were below the MRL in every PMR.
    - Alachlor ESA was the most common form of alachlor detected and had the greatest concentrations compared to alachlor and alachlor OXA.
- 2010 through 2019 trend analysis (Figure 2-8)
    - Median concentration trend findings for alachlor and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Alachlor ESA in PMRs 5 and 6.
        - A decreasing trend was calculated for:
            - Alachlor ESA in PMR 9.
    - 90th percentile concentration trend findings for alachlor and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Alachlor ESA in PMRs 7 and 8.
        - A decreasing trend was calculated for:
            - Alachlor ESA in PMRs 4, 5, 6, and 9.
    - Detection frequency trend findings for alachlor and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Alachlor ESA in PMRs 1, 5, 7, 8, and 9.
            - Alachlor OXA in PMRs 4, 5, and 7.
        - A decreasing trend was calculated for:
            - Alachlor ESA in PMRs 4, 6, and 9.

Figure 2-7. Pesticide Monitoring Regions and groundwater monitoring sites with alachlor and/or alachlor degradate detections in 2019.

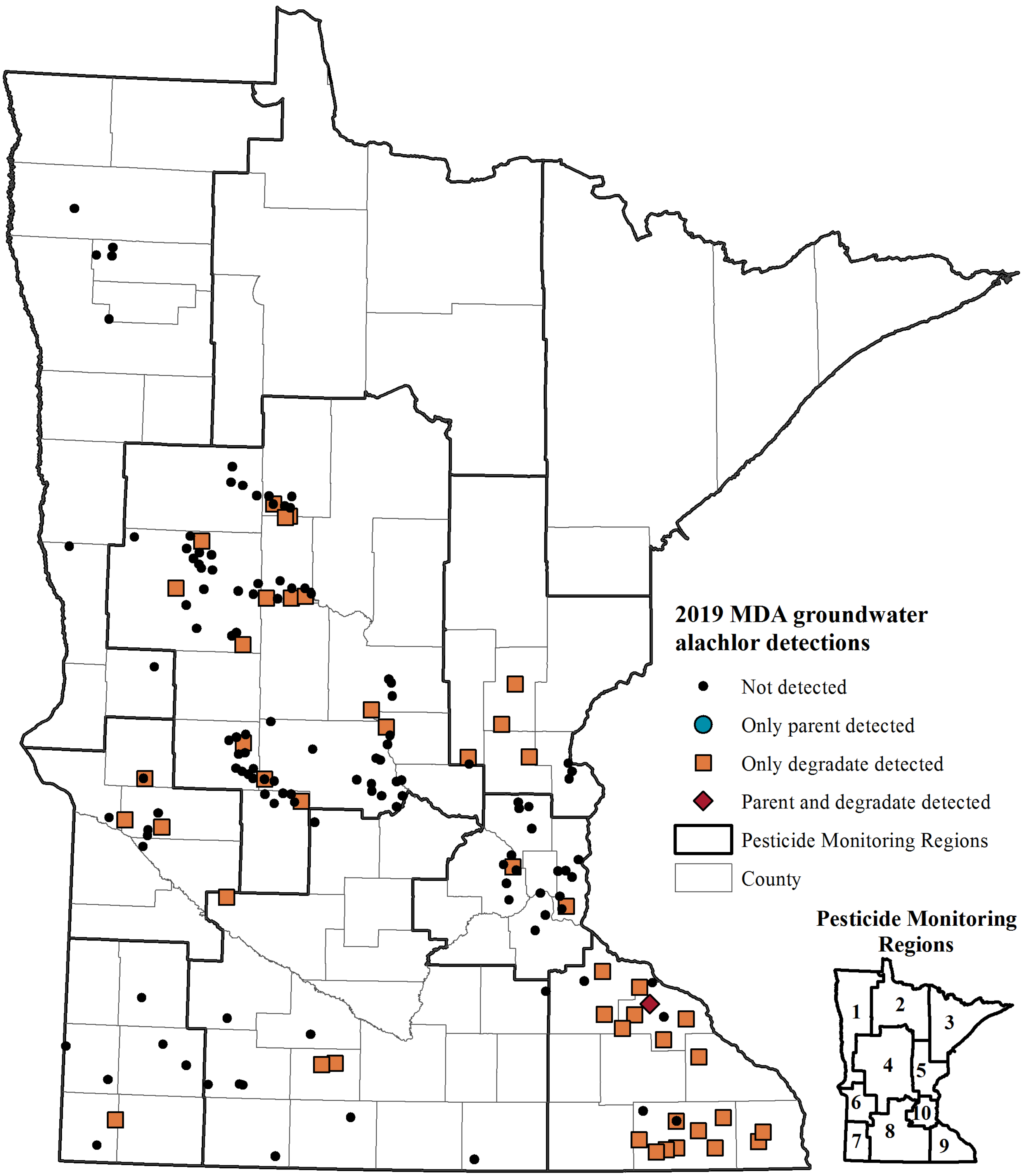


Table 2-2. 2019 data summary of alachlor and alachlor degradates in MDA groundwater samples.

Analyte	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)*	90th Percentile (ng/L)*	Maximum (ng/L)*
PMR 1						
Alachlor	14	0	0	<30	<30	<30
Alachlor ESA	14	0	0	<41.6	<41.6	<41.6
Alachlor OXA	14	0	0	<33.3	<33.3	<33.3
Number of samples with a compound detected	14	0	0	-	-	-
PMR 4						
Alachlor	78	0	0	<30	<30	<30
Alachlor ESA	78	**13**	**17**	<41.6	**91.7**	**884**
Alachlor OXA	78	**1**	**1**	<33.3	<33.3	**147**
Number of samples with a compound detected	78	**13**	**17**	-	-	-
PMR 5						
Alachlor	16	0	0	<30	<30	<30
Alachlor ESA	16	**6**	**38**	<41.6	**206**	**412**
Alachlor OXA	16	0	0	<33.3	<33.3	<33.3
Number of samples with a compound detected	16	**6**	**38**	-	-	-
PMR 6						
Alachlor	17	0	0	<30	<30	<30
Alachlor ESA	17	**5**	**29**	<41.6	**136**	**184**
Alachlor OXA	17	0	0	<33.3	<33.3	<33.3
Number of samples with a compound detected	17	**5**	**29**	-	-	-
PMR 7						
Alachlor	14	0	0	<30	<30	<30
Alachlor ESA	14	**2**	**14**	<41.6	**112**	**172**
Alachlor OXA	14	**2**	**14**	<33.3	**39.2**	**66.1**
Number of samples with a compound detected	14	**2**	**14**	-	-	-
PMR 8						
Alachlor	26	0	0	<30	<30	<30
Alachlor ESA	26	**5**	**19**	<41.6	**198**	**586**
Alachlor OXA	26	0	0	<33.3	<33.3	<33.3
Number of samples with a compound detected	26	**5**	**19**	-	-	-
PMR 9						
Alachlor	37	**1**	**3**	<30	<30	**54.5**
Alachlor ESA	37	**28**	**76**	**149**	**579**	**936**
Alachlor OXA	37	**2**	**5**	<33.3	<33.3	**76.8**
Number of samples with a compound detected	37	**28**	**76**	-	-	-

**Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*
-Alachlor degradates are not additive with the parent, so concentration statistics were not calculated for total alachlor.

Figure 2-8. 2010 through 2019 alachlor and alachlor degradates median and 90th percentile concentrations and detection frequency trend maps.

Figure 2-9. 2010 through 2019 alachlor ESA concentration results and detection frequencies for all monitored PMRs.

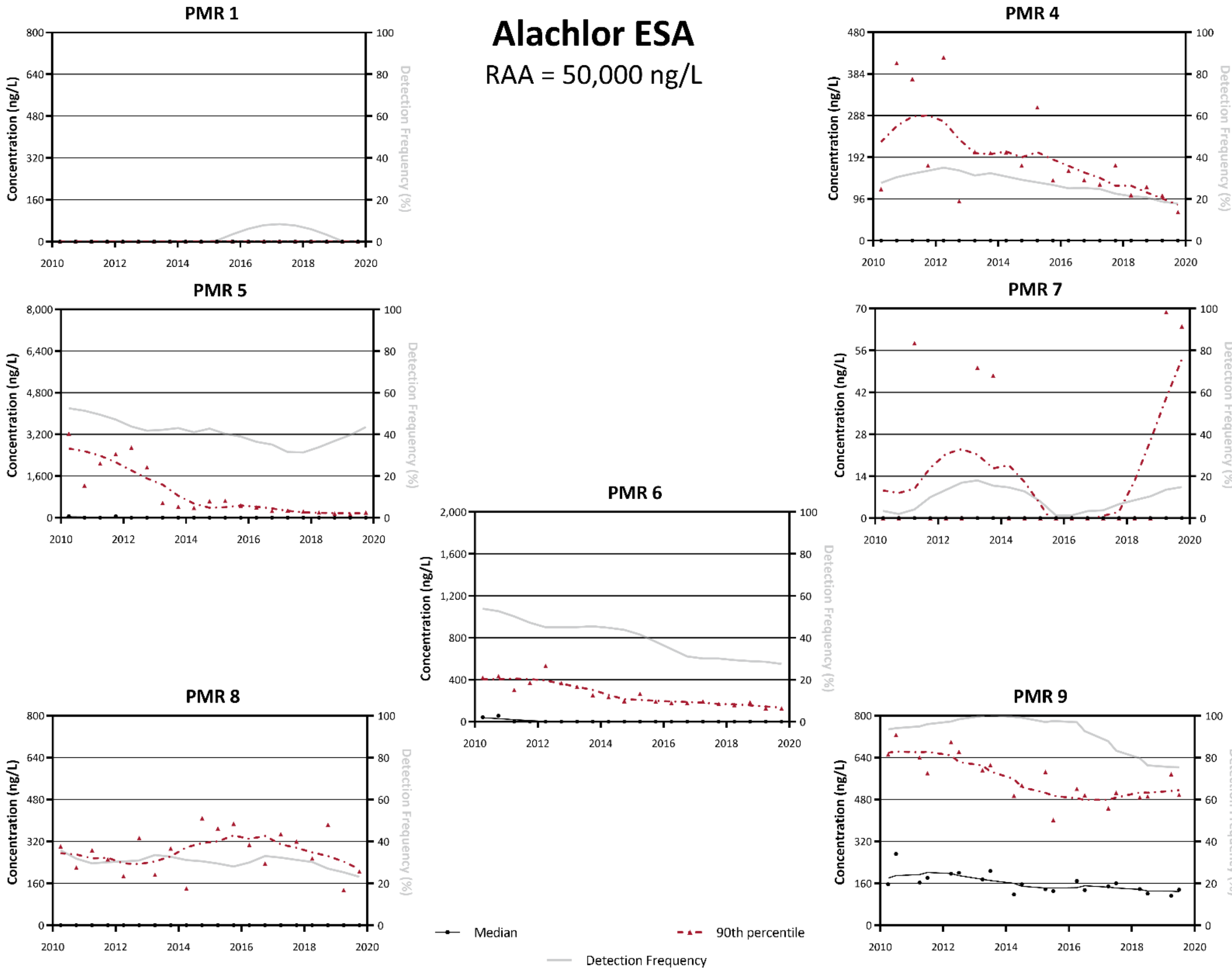
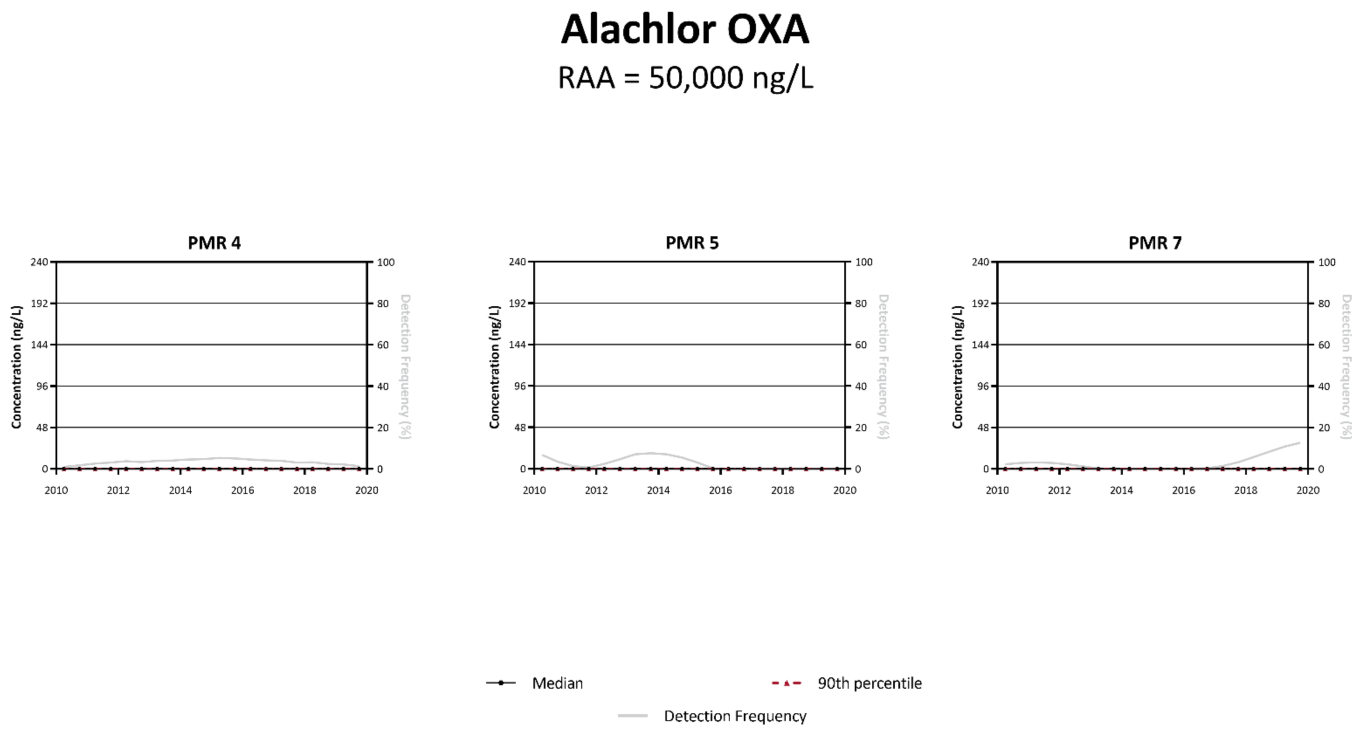


Figure 2-10. 2010 through 2019 alachlor OXA concentration results and detection frequencies for PMRs 4, 5, and 7.



2.3.3 Atrazine results

Figure 2-11 presents the distribution of sites where atrazine and/or atrazine degradates (didealkylatrazine, deisopropylatrazine, desethylatrazine, and hydroxyatrazine) were detected during the 2019 sampling season. Summary statistics from groundwater monitoring results for atrazine and atrazine degradates are presented in Table 2-3. In Table 2-3, the category "Number of samples with a compound detected" represents the count of samples with any form of atrazine and/or atrazine degradates detected.

Figure 2-12 shows the atrazine and atrazine degradate trend analysis maps for 2010 through 2019 for the median and 90th percentile concentrations and the detection frequency. Time series graphics for the concentration and detection frequency of atrazine and atrazine degradates are presented in Figures 2-13 through 2-17. Both the trend analysis and time series graphics were based on the same pesticide data sets collected from 2010 through 2019 and can be directly compared. It should be noted that PMR-specific graphics are only provided when there are enough results at greater than non-detect values to see a pattern and to evaluate a trend (either concentration or detection frequency), as found in the trend summary map. Long-term time series graphs can be found in Appendix 5b.

- 2019 atrazine and atrazine degradates summary statistics (Table 2-3)
    - Atrazine, or an atrazine degradate(s), was detected in every monitored PMR.
        - Atrazine was detected in PMRs 1, 4, 6, 7, and 9.
        - Deisopropylatrazine was detected in PMRs 1, 4, 7, and 9.
        - Desethylatrazine was detected in PMRs 1, 4, 5, 7, 8, and 9.
        - Didealkylatrazine was detected in PMRs 1, 4, 6, 7, and 9.
        - Hydroxyatrazine was detected in PMRs 4, 7, and 9.
    - The median concentrations for atrazine and atrazine degradates were below the MRLs in all regions except PMR 9 (atrazine, desethylatrazine, didealkylatrazine, and hydroxyatrazine).
    - Didealkylatrazine had the greatest maximum concentration among all atrazine compounds in PMRs 4, 6. and 9.
    - Desethylatrazine had the greatest maximum concentration among all atrazine compounds in PMRs 1, 5, and 8.
    - Atrazine had the greatest maximum concentration among all atrazine compounds in PMR 7.
- 2010 through 2019 trend analysis (Figure 2-12)
    - Median concentration trend findings for atrazine and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Atrazine in PMR 9.
            - Desethylatrazine in PMRs 4, 5, and 9.
            - Hydroxyatrazine in PMR 9.
        - An increasing trend was calculated for:
            - Didealkylatrazine in PMR 9.
    - 90th percentile concentration trend findings for atrazine and its degradates:

        - A trend that was not statistically significant (no trend) was calculated for:
            - Atrazine in PMRs 1 and 9.
            - Desethylatrazine in PMRs 1, 6, 7, 8, and 9.
            - Didealkylatrazine in PMRs 4, 5, 6, 7, and 9.
            - Hydroxyatrazine in PMRs 4, 5, 7, and 9.
        - An increasing trend was calculated for:
            - Atrazine in PMR 7.
            - Didealkylatrazine in PMR 1.
        - A decreasing trend was calculated for:
            - Desethylatrazine in PMRs 4 and 5.
    - Detection frequency trend findings for atrazine and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for:
            - Atrazine in PMRs 6 and 7.
            - Desethylatrazine in PMRs 5, 6, 7, and 8.
            - Deisopropylatrazine in PMRs 1 and 4.
            - Didealkylatrazine in PMRs 4, 5, and 8.
            - Hydroxyatrazine in PMRs 1, 4, 7, and 9.
        - A decreasing trend was calculated for:
            - Atrazine in PMRs 1, 4, 5, and 9.
            - Desethylatrazine in PMRs 1, 4, and 9.
            - Hydroxyatrazine in PMRs 5 and 8.
        - An increasing trend was calculated for:
            - Didealkylatrazine in PMRs 1, 6, 7, and 9.

Figure 2-11. Pesticide Monitoring Regions and groundwater monitoring sites with atrazine and/or atrazine degradate detections in 2019.

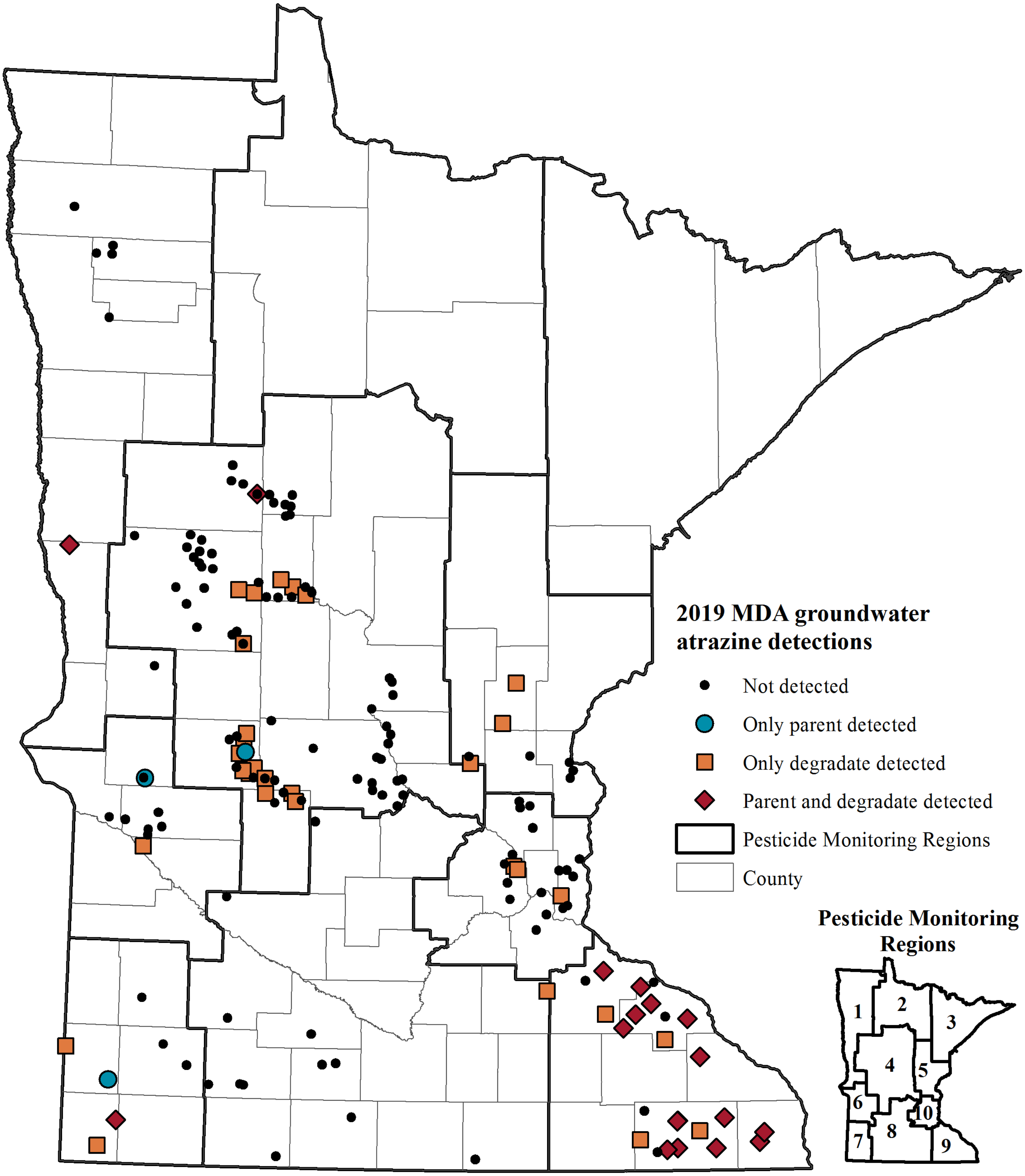


Table 2-3. 2019 data summary of atrazine and atrazine degradates in MDA groundwater samples.

Analyte	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)*	90th Percentile (ng/L)*	Maximum (ng/L)*
PMR 1						
Atrazine	14	**2**	**14**	<30	<30	**43.7**
Deisopropylatrazine	14	**1**	**7**	<25	<25	**30.7**
Desethylatrazine	14	**2**	**14**	<50	**51.7**	**102**
Didealkylatrazine	14	**1**	**7**	<50	<50	**78.6**
Atrazine +Degradates	14	**2**	**14**	<50	**74.8**	**255**
Hydroxyatrazine[1]	14	0	0	<6.7	<6.7	<6.7
PMR 4						
Atrazine	78	**2**	**3**	<30	<30	**83.8**
Deisopropylatrazine	78	**1**	**1**	<25	<25	**67.7**
Desethylatrazine	78	**3**	**4**	<50	<50	**74.4**
Didealkylatrazine	78	**5**	**6**	<50	<50	**180**
Atrazine +Degradates	78	**7**	**9**	<50	<50	**406**
Hydroxyatrazine[1]	78	**9**	**12**	<6.7	**7.21**	**34.7**
PMR 5						
Atrazine	16	0	0	<30	<30	<30
Deisopropylatrazine	16	0	0	<25	<25	<25
Desethylatrazine	16	**3**	**19**	<50	**55.6**	**67.4**
Didealkylatrazine	16	0	0	<50	<50	<50
Atrazine +Degradates	16	**3**	**19**	<50	**55.6**	**67.4**
Hydroxyatrazine[1]	16	0	0	<6.7	<6.7	<6.7
PMR 6						
Atrazine	17	**1**	**6**	<30	<30	**65.3**
Deisopropylatrazine	17	0	0	<25	<25	<25
Desethylatrazine	17	0	0	<50	<50	<50
Didealkylatrazine	17	**2**	**12**	<50	**51.6**	**164**
Atrazine +Degradates	17	**3**	**18**	<50	**51.6**	**229**
Hydroxyatrazine[1]	17	0	0	<6.7	<6.7	<6.7
PMR 7						
Atrazine	14	**3**	**21**	<30	**86.4**	**204**
Deisopropylatrazine	14	**2**	**14**	<25	<25	**30.6**
Desethylatrazine	14	**2**	**14**	<50	**59.2**	**124**
Didealkylatrazine	14	**3**	**21**	<50	**60.9**	**82.3**
Atrazine +Degradates	14	**5**	**36**	<50	**207**	**441**
Hydroxyatrazine[1]	14	**5**	**36**	<6.7	**59.6**	**76.2**
PMR 8						
Atrazine	26	0	0	<30	<30	<30
Deisopropylatrazine	26	0	0	<25	<25	<25
Desethylatrazine	26	**2**	**8**	<50	<50	**73.6**
Didealkylatrazine	26	0	0	<50	<50	<50
Atrazine +Degradates	26	**2**	**8**	<50	<50	**73.6**
Hydroxyatrazine[1]	26	0	0	<6.7	<6.7	<6.7
PMR 9						
Atrazine	37	**22**	**59**	**34.7**	**68.6**	**185**
Deisopropylatrazine	37	**6**	**16**	<25	**31.0**	**82.0**
Desethylatrazine	37	**24**	**65**	**79.3**	**134**	**270**
Didealkylatrazine	37	**28**	**76**	**88.9**	**186**	**379**
Atrazine +Degradates	37	**30**	**81**	**203**	**420**	**916**
Hydroxyatrazine[1]	37	**19**	**51**	**7.17**	**15.6**	**21.1**

**Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*
[1]Hydroxyatrazine is not additive like the other atrazine degradates when evaluating health risk. It was not included in the Atrazine+ Degradate summation.

Figure 2-12. 2010 through 2019 atrazine and atrazine degradates median and 90th percentile concentrations and detection frequency trend maps.

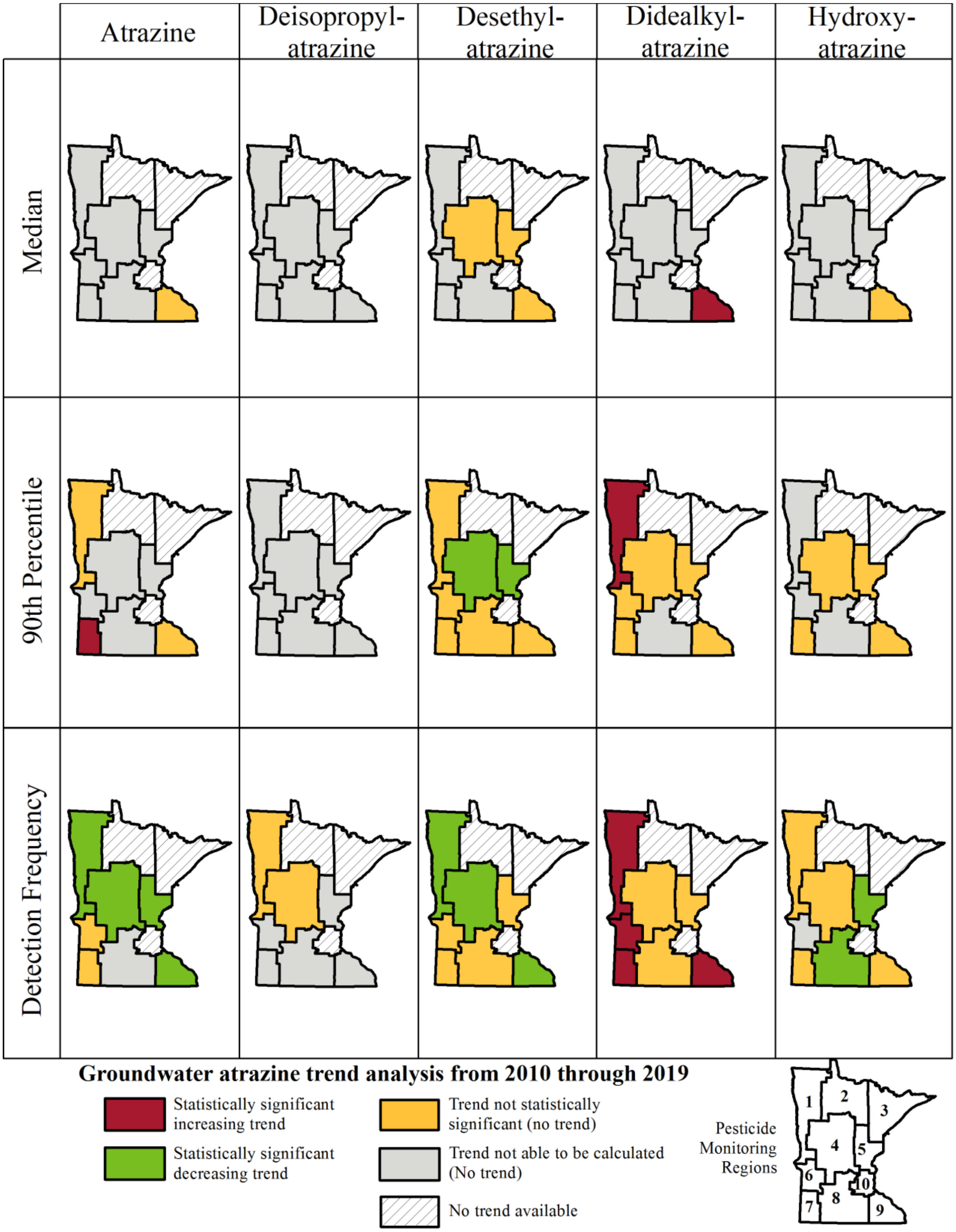


Figure 2-13. 2010 through 2019 atrazine concentration results and detection frequencies for PMRs 1, 4, 5, 6, 7, and 9.

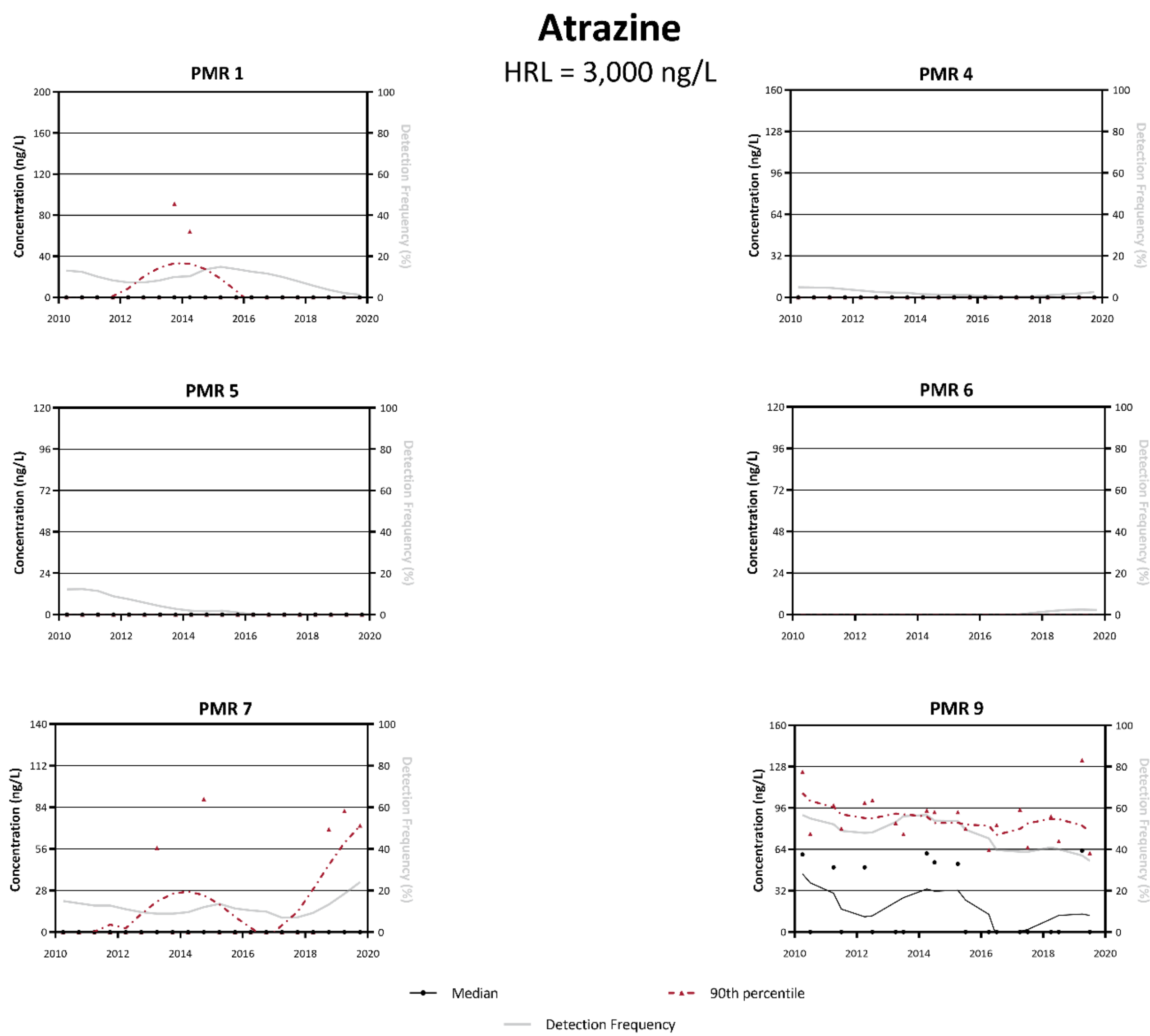


Figure 2-14. 2010 through 2019 didealkylatrazine concentration results and detection frequencies for all monitored PMRs.

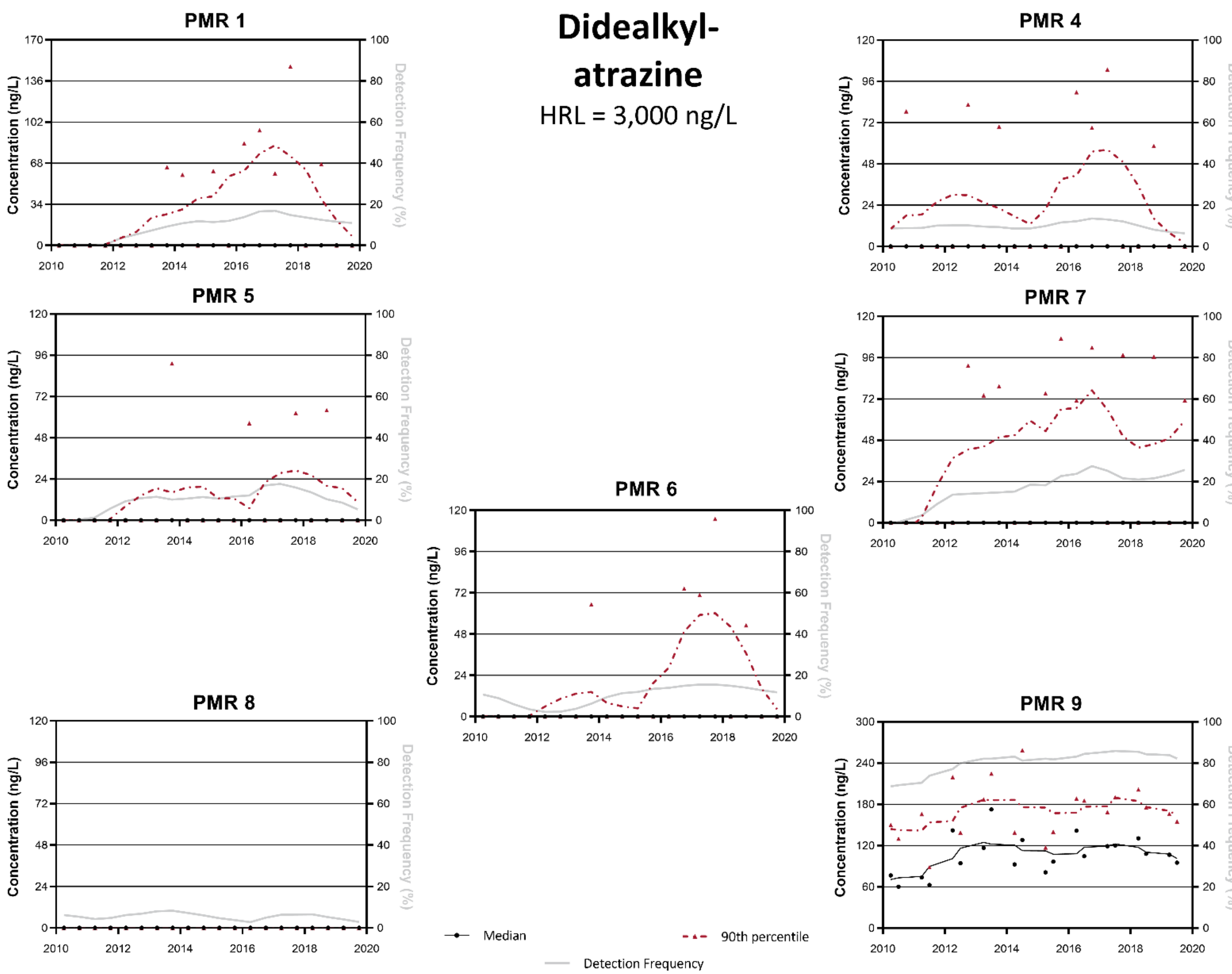


Figure 2-15. 2010 through 2019 deisopropylatrazine concentration results and detection frequencies for PMRs 1 and 4.

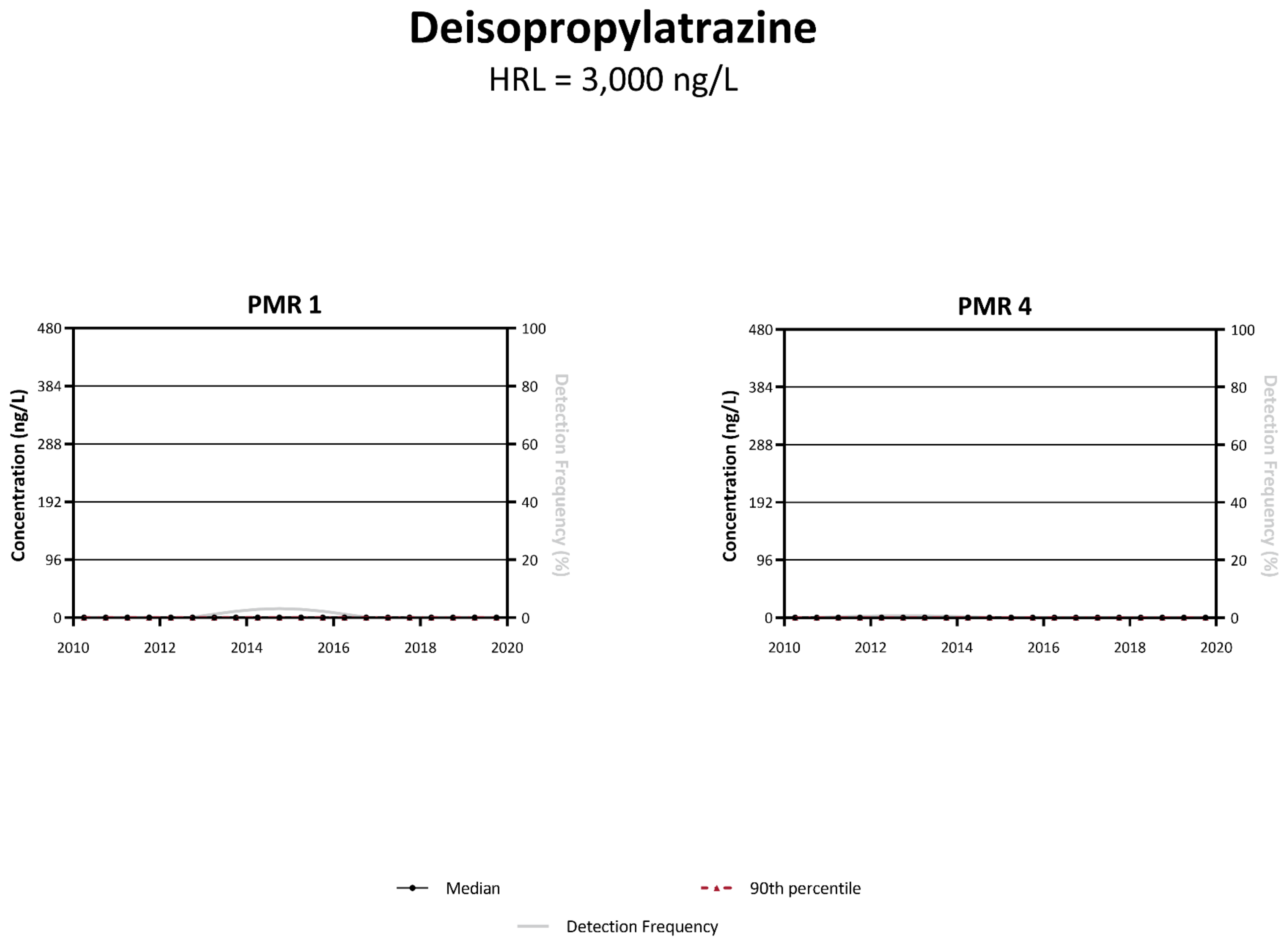


Figure 2-16. 2010 through 2019 desethylatrazine concentration results and detection frequencies for all monitored PMRs.

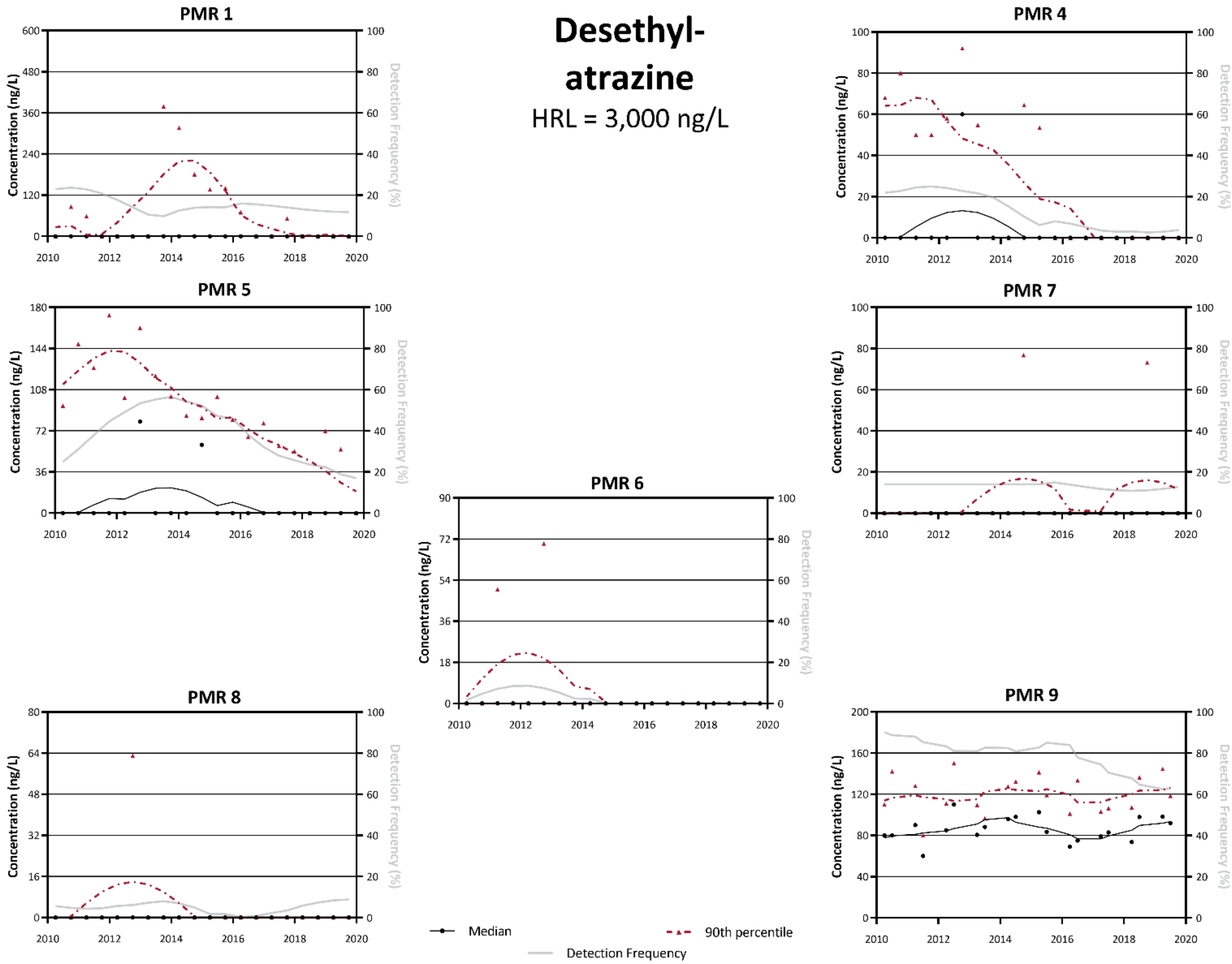
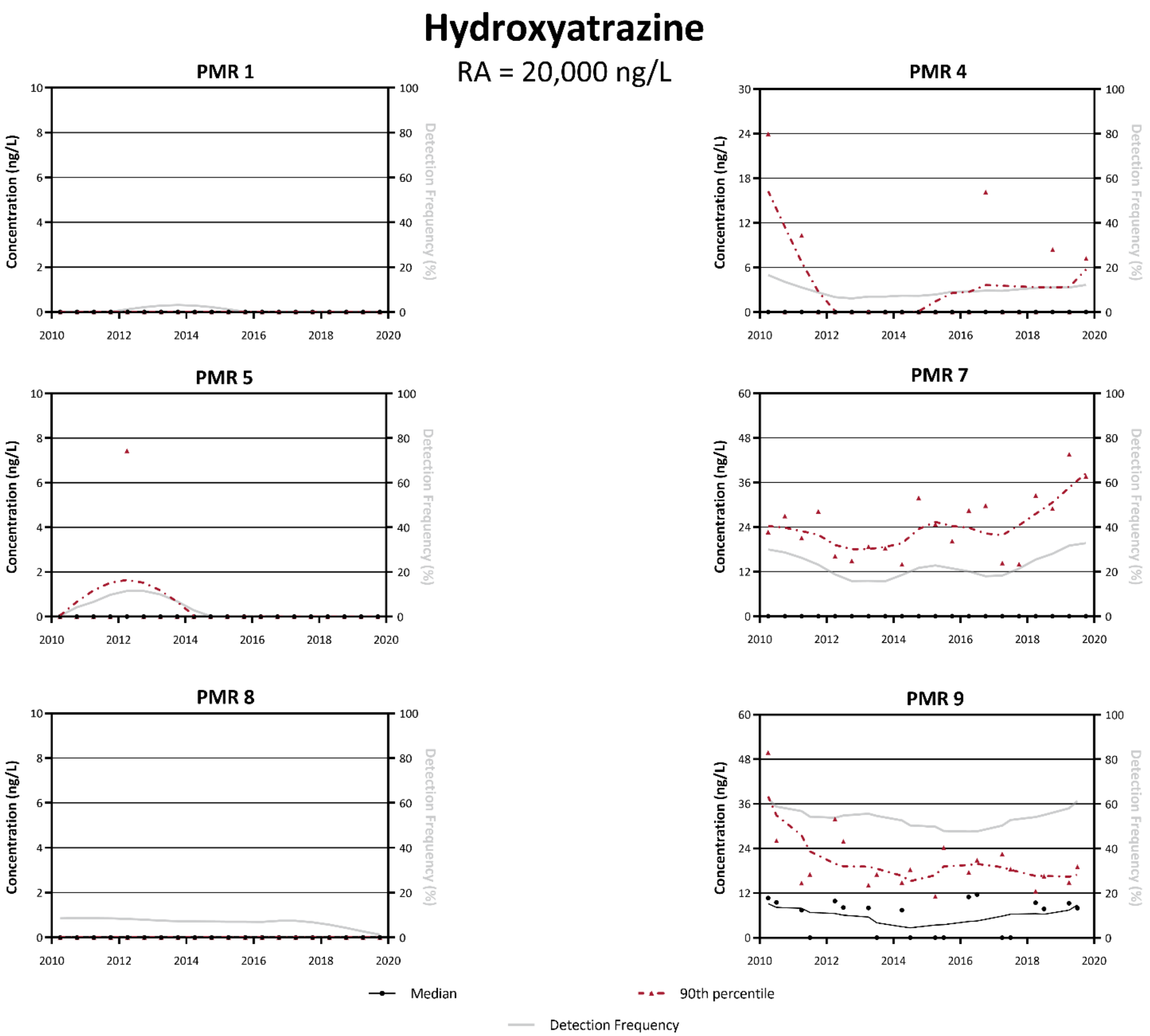


Figure 2-17. 2010 through 2019 hydroxyatrazine concentration results and detection frequencies for PMRs 1, 4, 5, 7, 8, and 9.



2.3.4 Metolachlor results

Figure 2-18 presents the monitoring site distribution where metolachlor and/or metolachlor degradates (metolachlor ESA and metolachlor OXA) were detected during the 2019 sampling season. Summary statistics from groundwater metolachlor and metolachlor degradates monitoring results are located in Table 2-4. In Table 2-4, the category "Number of samples with a compound detected" represents the number of samples with any form of metolachlor and/or metolachlor degradates detected.

Figure 2-19 shows the metolachlor, and metolachlor degradates, trend analysis maps for 2010 through 2019 for the median and 90th percentile concentrations and the detection frequency. Time series graphics for the concentration and detection frequency of metolachlor degradates are presented in Figures 2-20 through 2-22. Both the trend analysis and time series graphics were based on the same pesticide data sets collected from 2010 through 2019 and can be directly compared. It should be noted that PMR-specific graphics are only provided when there are enough results at greater than non-detect values to see a pattern and to evaluate a trend (either concentration or detection frequency), as found in the trend summary map. Long-term time series graphs can be found in Appendix 5b.

- 2019 metolachlor and metolachlor degradates summary statistics (Table 2-4)
  - Metolachlor was found in PMRs 1, 4, 5, 7, and 9.
  - Metolachlor ESA and metolachlor OXA were detected in all PMRs.
  - Metolachlor ESA had the greatest median, 90th percentile, and maximum concentrations among the metolachlor compounds in PMRs 4, 5, 6, 7, 8, and 9.
- 2010 through 2019 trend analysis (Figure 2-19)
  - Median concentration trend findings for metolachlor and its degradates:
    - A trend that was not statistically significant (no trend) was calculated for:
      - Metolachlor ESA in PMRs 4 and 5.
      - Metolachlor OXA in PMRs 4, 5, 7, and 9.
    - A decreasing trend was calculated for:
      - Metolachlor ESA in PMRs 6 and 8.
    - An increasing trend was calculated for:
      - Metolachlor ESA in PMRs 7 and 9.
  - 90th percentile concentration trend findings for metolachlor and its degradates:
    - A trend that was not statistically significant (no trend) was calculated for:
      - Metolachlor in PMRs 1, 5, 7, and 9.
      - Metolachlor ESA in PMRs 1, 4, 7, and 9.
      - Metolachlor OXA in PMRs 6 and 7.
    - An increasing trend was calculated for:
      - Metolachlor ESA in PMRs 5, 6, and 8.
      - Metolachlor OXA in PMRs 1, 4, 5, 8, and 9.
  - Detection frequency trend findings for metolachlor and its degradates:
    - A trend that was not statistically significant (no trend) was calculated for:
      - Metolachlor in PMRs 1, 4, 5, 7, and 9.

    - Metolachlor ESA in PMRs 1, 4, 5, 6, 7, and 8.
    - Metolachlor OXA in PMRs 1, 4, 5, 6, and 7.
- An increasing trend was calculated for:
    - Metolachlor ESA in PMR 9.
    - Metolachlor OXA in PMRs 8 and 9.

Figure 2-18. Pesticide Monitoring Regions and groundwater monitoring sites with metolachlor and/or metolachlor degradate detections in 2019.

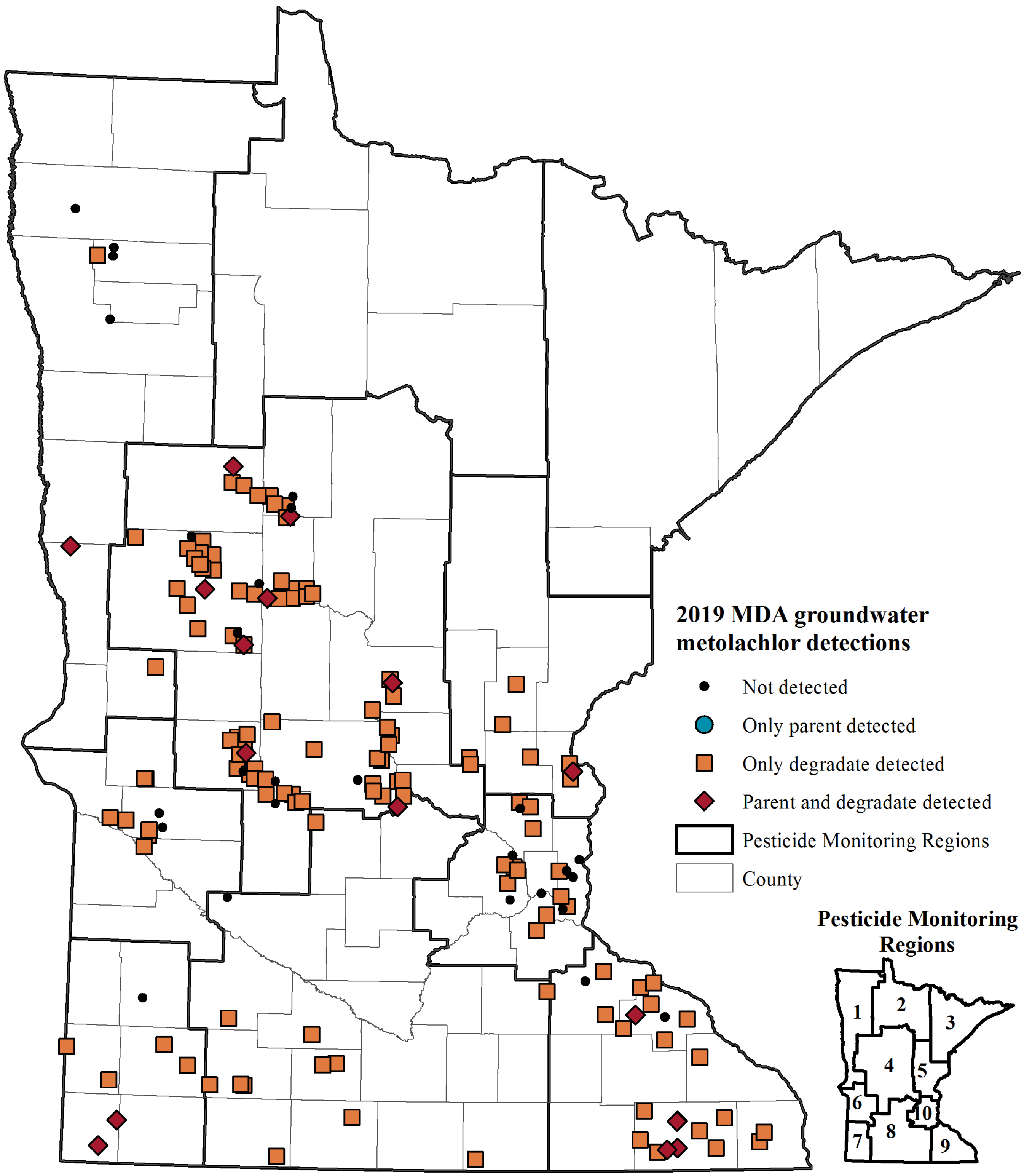


Table 2-4. 2019 data summary of metolachlor and metolachlor degradates in MDA groundwater samples.

Analyte	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)*	90th Percentile (ng/L)*	Maximum (ng/L)*
PMR 1						
Metolachlor	14	**2**	**14**	<25	**326**	**637**
Metolachlor ESA	14	**5**	**36**	<10	**350**	**796**
Metolachlor OXA	14	**2**	**14**	<10	**127**	**328**
Number of samples with a compound detected	14	**5**	**36**	-	-	-
PMR 4						
Metolachlor	78	**9**	**12**	<25	**26.3**	**711**
Metolachlor ESA	78	**69**	**88**	**324**	**4,949**	**12,500**
Metolachlor OXA	78	**43**	**55**	**17.4**	**1,356**	**7,400**
Number of samples with a compound detected	78	**69**	**88**	-	-	-
PMR 5						
Metolachlor	16	**1**	**6**	<25	<25	**127**
Metolachlor ESA	16	**16**	**100**	**510**	**5,055**	**9,610**
Metolachlor OXA	16	**12**	**75**	**35.7**	**1,726**	**3,720**
Number of samples with a compound detected	16	**16**	**100**	-	-	-
PMR 6						
Metolachlor	17	0	0	<25	<25	<25
Metolachlor ESA	17	**12**	**71**	**29.4**	**495**	**1,010**
Metolachlor OXA	17	**4**	**24**	<10	**21.4**	**41.2**
Number of samples with a compound detected	17	**12**	**71**	-	-	-
PMR 7						
Metolachlor	14	**2**	**14**	<25	**26.3**	**49.1**
Metolachlor ESA	14	**12**	**86**	**355**	**1,276**	**2,290**
Metolachlor OXA	14	**7**	**50**	**37.4**	**564**	**922**
Number of samples with a compound detected	14	**12**	**86**	-	-	-
PMR 8						
Metolachlor	26	0	0	<25	<25	<25
Metolachlor ESA	26	**24**	**92**	**61.3**	**2,785**	**4,340**
Metolachlor OXA	26	**9**	**35**	<10	**256**	**1,790**
Number of samples with a compound detected	26	**24**	**92**	-	-	-
PMR 9						
Metolachlor	37	**8**	**22**	<25	**57.2**	**348**
Metolachlor ESA	37	**35**	**95**	**524**	**1,646**	**2,340**
Metolachlor OXA	37	**24**	**65**	**17.3**	**130**	**212**
Number of samples with a compound detected	37	**35**	**95**	-	-	-

**Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*
-Metolachlor degradates are not additive with the parent, so concentration statistics were not calculated for total metolachlor.

Figure 2-19. 2010 through 2019 metolachlor and metolachlor degradates median concentration and detection frequency trend maps.

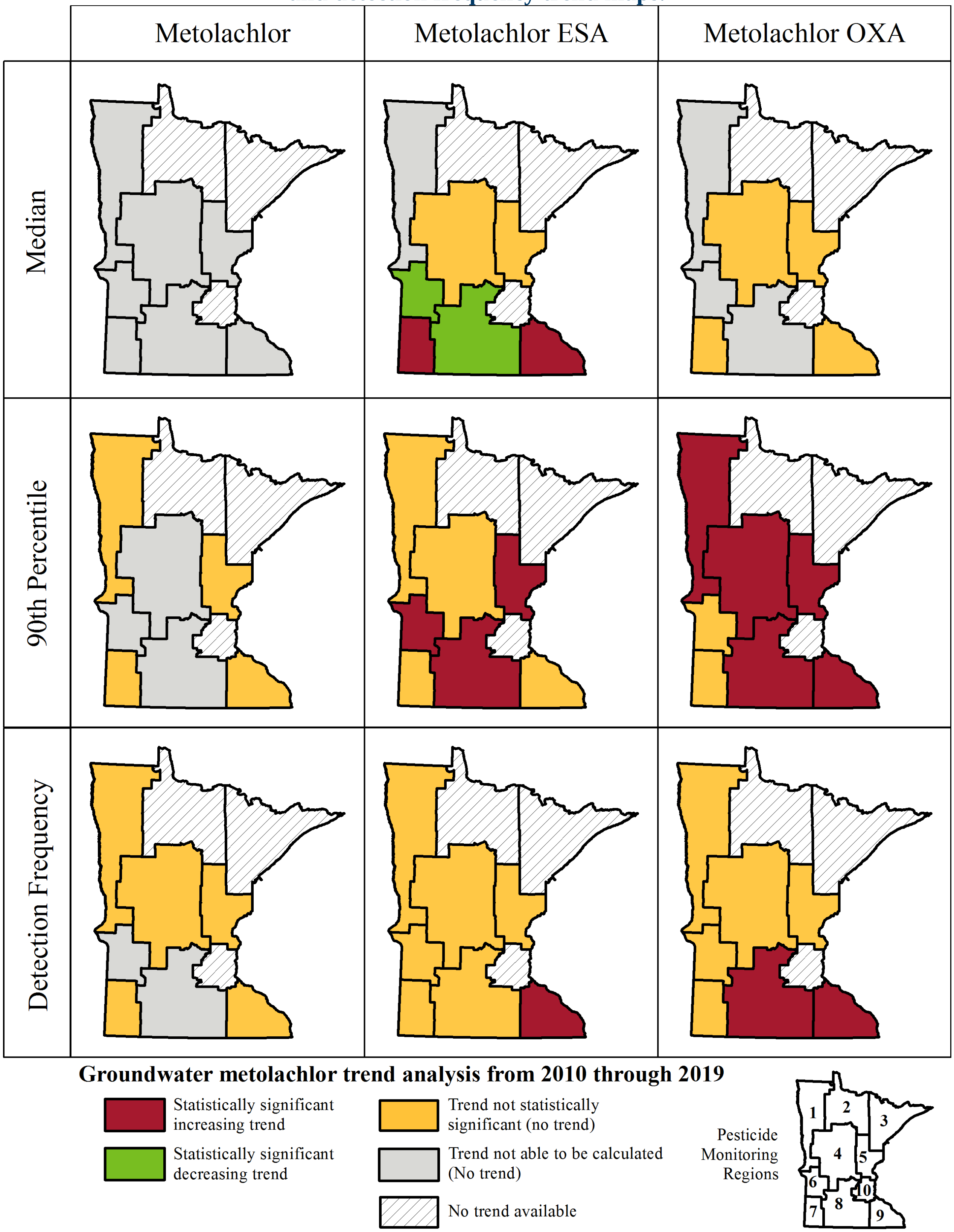


Figure 2-20. 2010 through 2019 metolachlor concentration results and detection frequencies for PMRs 1, 4, 5, 7, and 9.

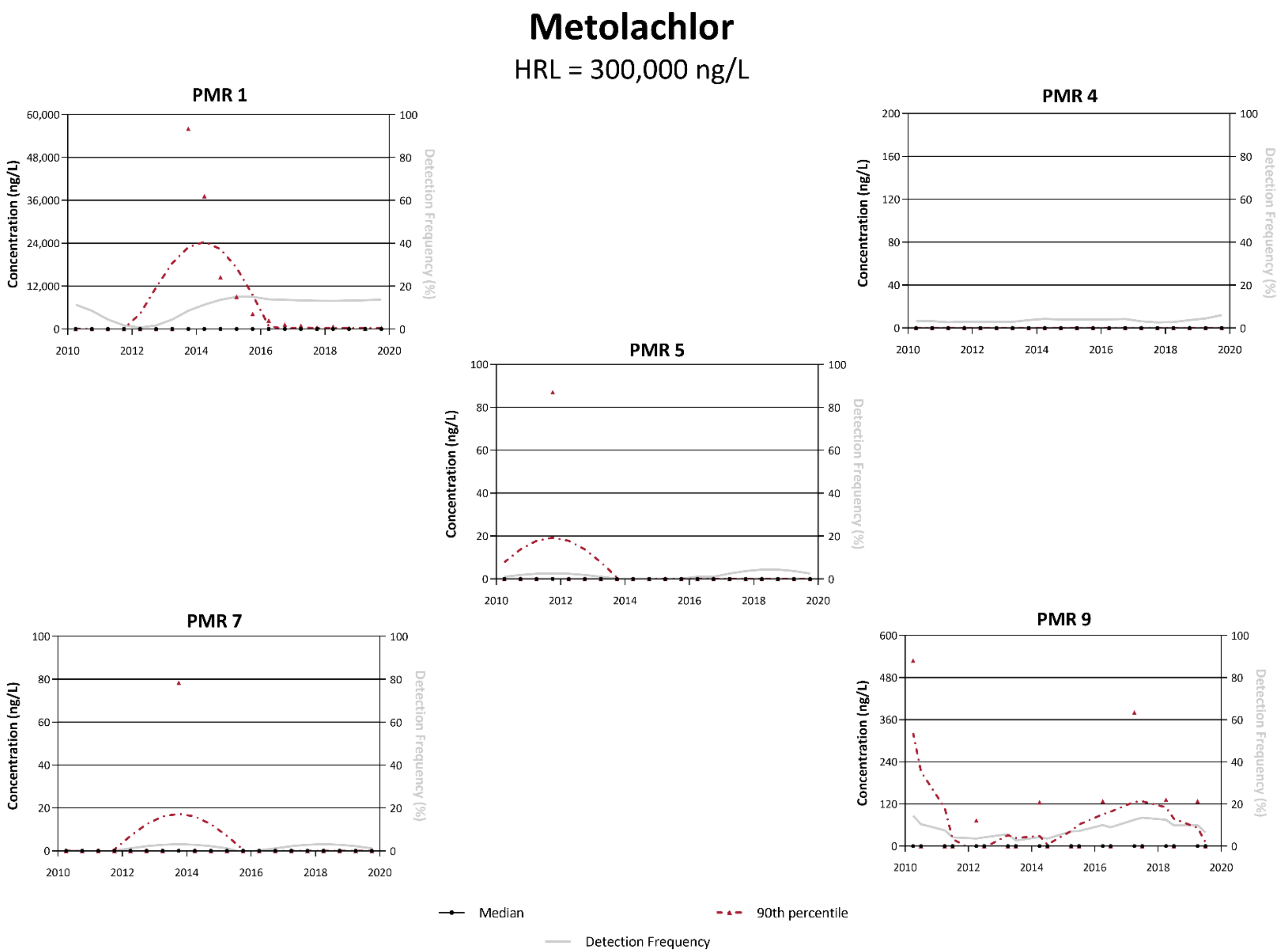


Figure 2-21. 2010 through 2019 metolachlor ESA concentration results and detection frequencies for all monitored PMRs.

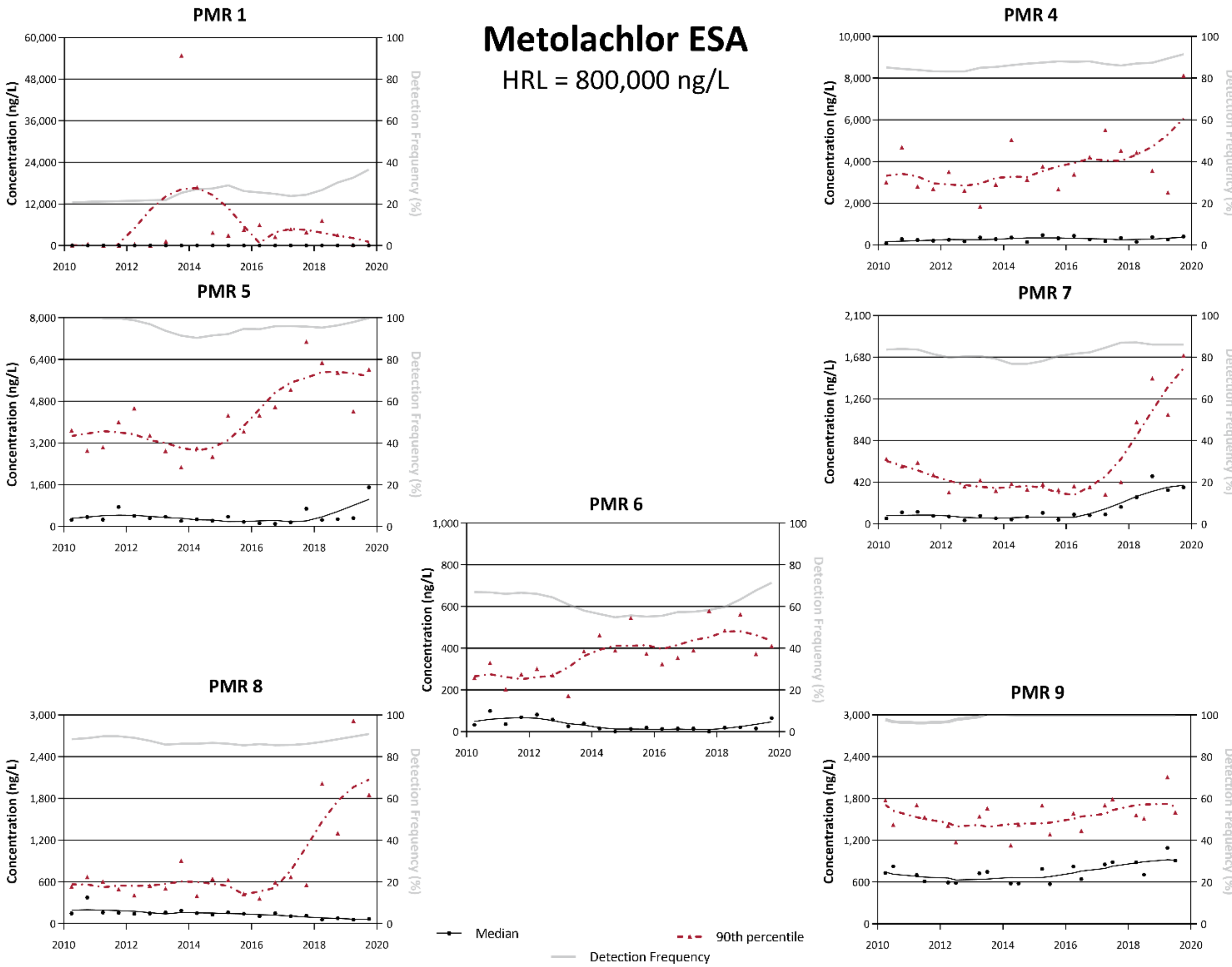
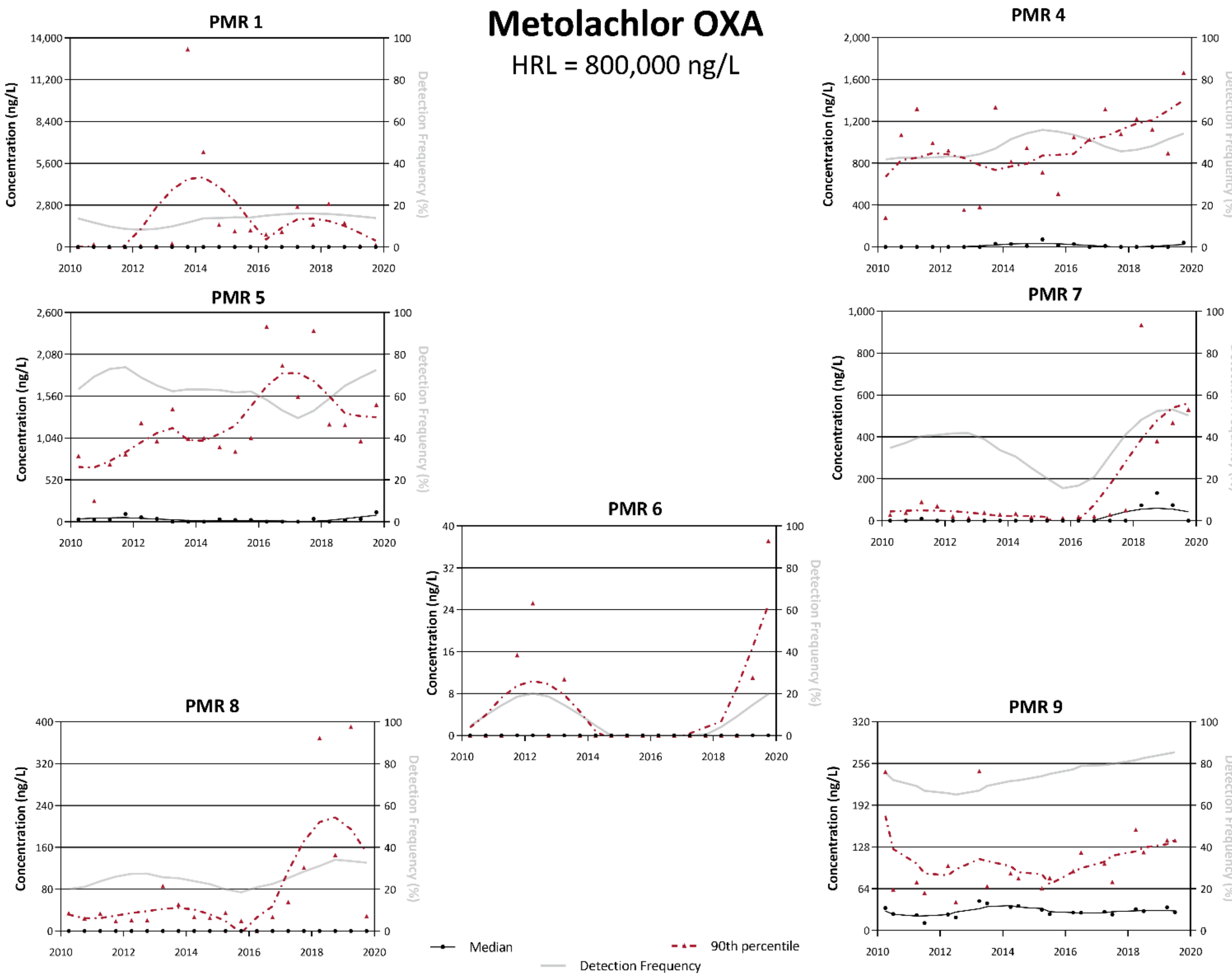


Figure 2-22. 2010 through 2019 metolachlor OXA concentration results and detection frequencies for all monitored PMRs.



2.3.5 Metribuzin results

Figure 2-23 shows the distribution of monitoring sites where metribuzin and/or metribuzin degradates (metribuzin DA, metribuzin DADK, and metribuzin DK) were detected during the 2019 sampling season. Summary statistics from groundwater monitoring results for metribuzin and metribuzin degradates are located in Table 2-5. In Table 2-5, the category "Number of samples with a compound detected" represents the number of samples with any form of metribuzin and/or metribuzin degradates detected.

Figure 2-24 shows the metribuzin and metribuzin degradate trend analysis map from 2010 through 2019 for the median and 90th percentile concentrations and the detection frequency. Time series graphics for the concentration and detection frequency of metribuzin degradates are located in Figure 2-25. Both the trend analysis and time series graphics were based on the same pesticide data sets collected from 2010 through 2019 and can be directly compared. It should be noted that PMR-specific graphics are only provided when there are enough results at greater than non-detect values to see a pattern and to evaluate a trend (either concentration or detection frequency), as found in the trend summary map. Long-term time series graphs can be found in Appendix 5b.

Metribuzin and/or metribuzin degradates have been detected four times in monitoring wells outside of PMR 4 (metribuzin in PMR 5 in 2008; metribuzin DA in PMR 8 in 2017 and 2018, as well as in PMR 7 in 2019). The concentrations of the detections for these metribuzin compounds were slightly above their respective MRLs. As such, trend analysis and time series figure generation were not completed for PMRs 1, 5, 6, 7, 8, and 9. The principal findings from the 2019 data and trend summaries below are only for PMR 4.

- 2019 metribuzin and metribuzin degradates summary statistics (Table 2-5)
    - Metribuzin DA was the most common form of metribuzin detected.
    - Metribuzin DADK had the greatest maximum concentration among the metribuzin compounds.
- 2010 through 2019 trend analysis (Figure 2-24)
    - Median concentration trend findings for metribuzin and its degradates:
        - A trend was not able to be calculated for all forms of metribuzin.
    - 90th percentile concentration trend findings for metribuzin and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for metribuzin DADK.
    - Detection frequency trend findings for metribuzin and its degradates:
        - A trend that was not statistically significant (no trend) was calculated for metribuzin and metribuzin DK.
        - A decreasing trend was calculated for metribuzin DADK.

Figure 2-23. Pesticide Monitoring Regions and groundwater sites with metribuzin and/or metribuzin degradate detections in 2019.

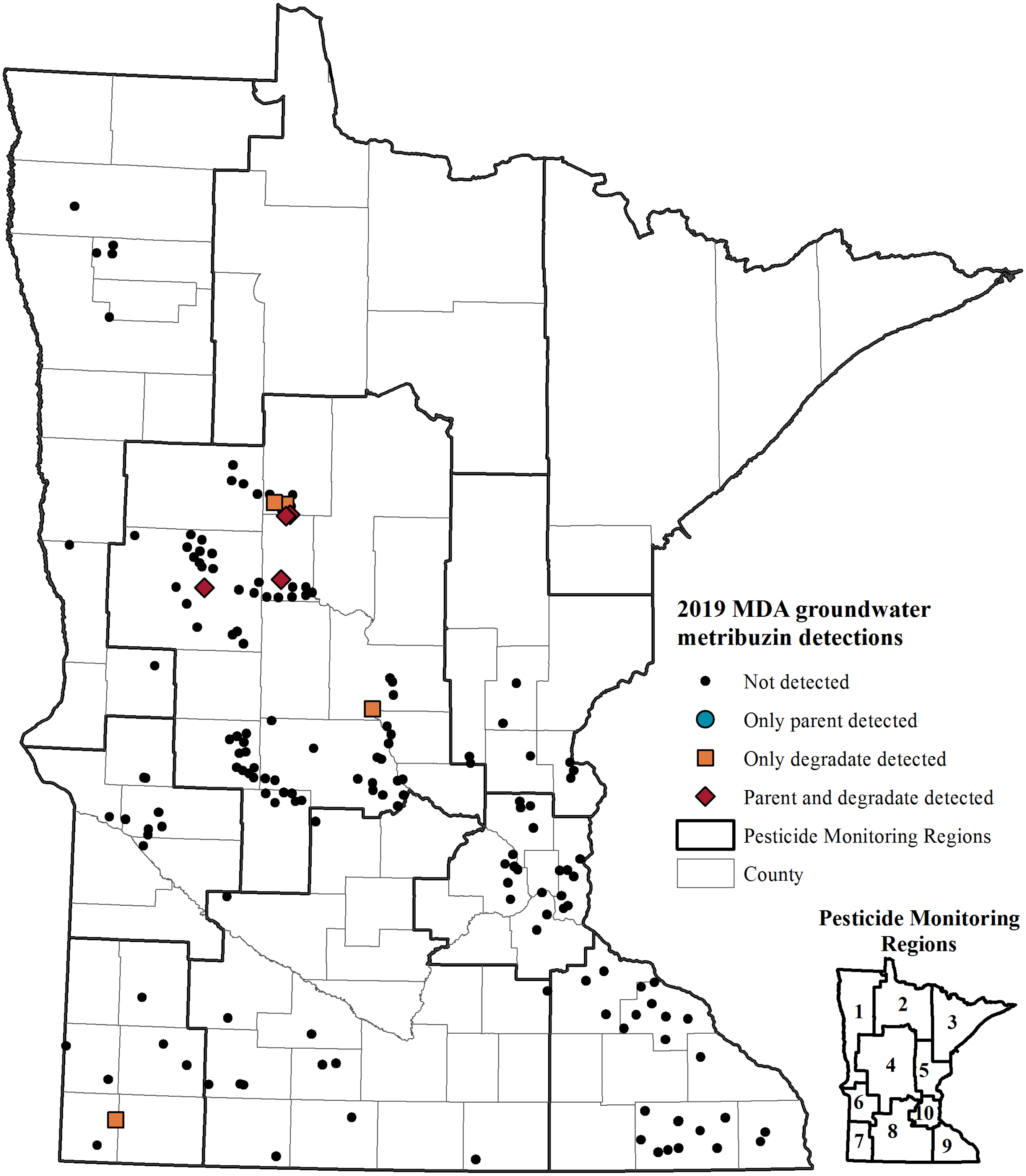


Table 2-5. 2019 data summary of metribuzin and metribuzin degradates in MDA groundwater samples.

Analyte	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)*	90th Percentile (ng/L)*	Maximum (ng/L)*
PMR 1						
Metribuzin	14	0	0	<75	<75	<75
Metribuzin DA	14	0	0	<25	<25	<25
Metribuzin DADK	14	0	0	<500	<500	<500
Metribuzin DK	14	0	0	<500	<500	<500
Metribuzin + Degradates	14	0	0	<500	<500	<500
PMR 4						
Metribuzin	78	**5**	**6**	<75	<75	**174**
Metribuzin DA	78	**6**	**8**	<25	<25	**229**
Metribuzin DADK	78	**3**	**4**	<500	<500	**782**
Metribuzin DK	78	0	0	<500	<500	<500
Metribuzin + Degradates	78	**6**	**8**	<500	<500	**1,185**
PMR 5						
Metribuzin	16	0	0	<75	<75	<75
Metribuzin DA	16	0	0	<25	<25	<25
Metribuzin DADK	16	0	0	<500	<500	<500
Metribuzin DK	16	0	0	<500	<500	<500
Metribuzin + Degradates	16	0	0	<500	<500	<500
PMR 6						
Metribuzin	17	0	0	<75	<75	<75
Metribuzin DA	17	0	0	<25	<25	<25
Metribuzin DADK	17	0	0	<500	<500	<500
Metribuzin DK	17	0	0	<500	<500	<500
Metribuzin + Degradates	17	0	0	<500	<500	<500
PMR 7						
Metribuzin	14	0	0	<75	<75	<75
Metribuzin DA	14	**1**	**7**	<25	<25	**27.6**
Metribuzin DADK	14	0	0	<500	<500	<500
Metribuzin DK	14	0	0	<500	<500	<500
Metribuzin + Degradates	14	**1**	**7**	<500	<500	**27.6**
PMR 8						
Metribuzin	26	0	0	<75	<75	<75
Metribuzin DA	26	0	0	<25	<25	<25
Metribuzin DADK	26	0	0	<500	<500	<500
Metribuzin DK	26	0	0	<500	<500	<500
Metribuzin + Degradates	26	0	0	<500	<500	<500
PMR 9						
Metribuzin	37	0	0	<75	<75	<75
Metribuzin DA	37	0	0	<25	<25	<25
Metribuzin DADK	37	0	0	<500	<500	<500
Metribuzin DK	37	0	0	<500	<500	<500
Metribuzin + Degradates	37	0	0	<500	<500	<500

**Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*

Figure 2-24. 2010 through 2019 metribuzin and metribuzin degradate median concentration and detection frequency trend maps.

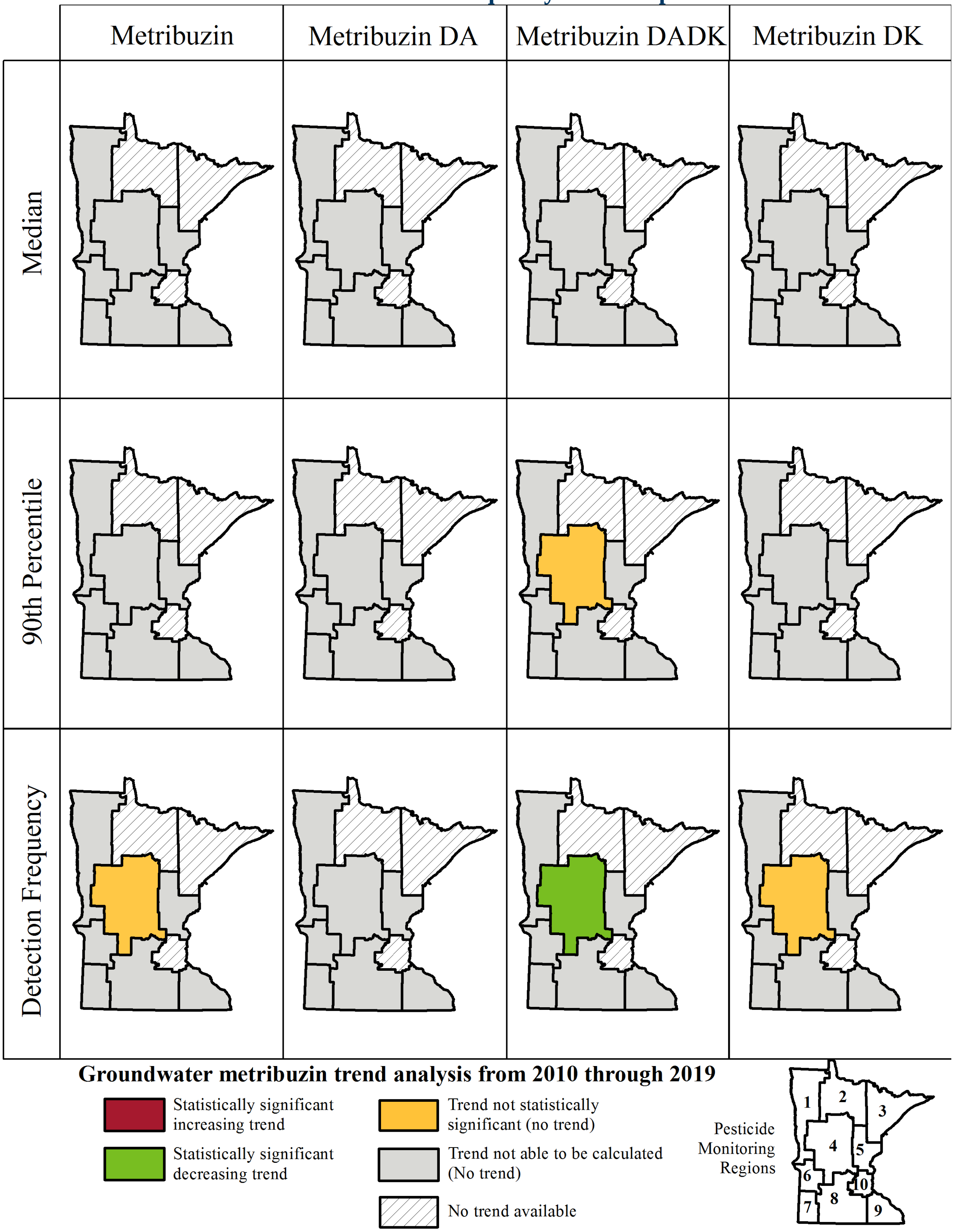
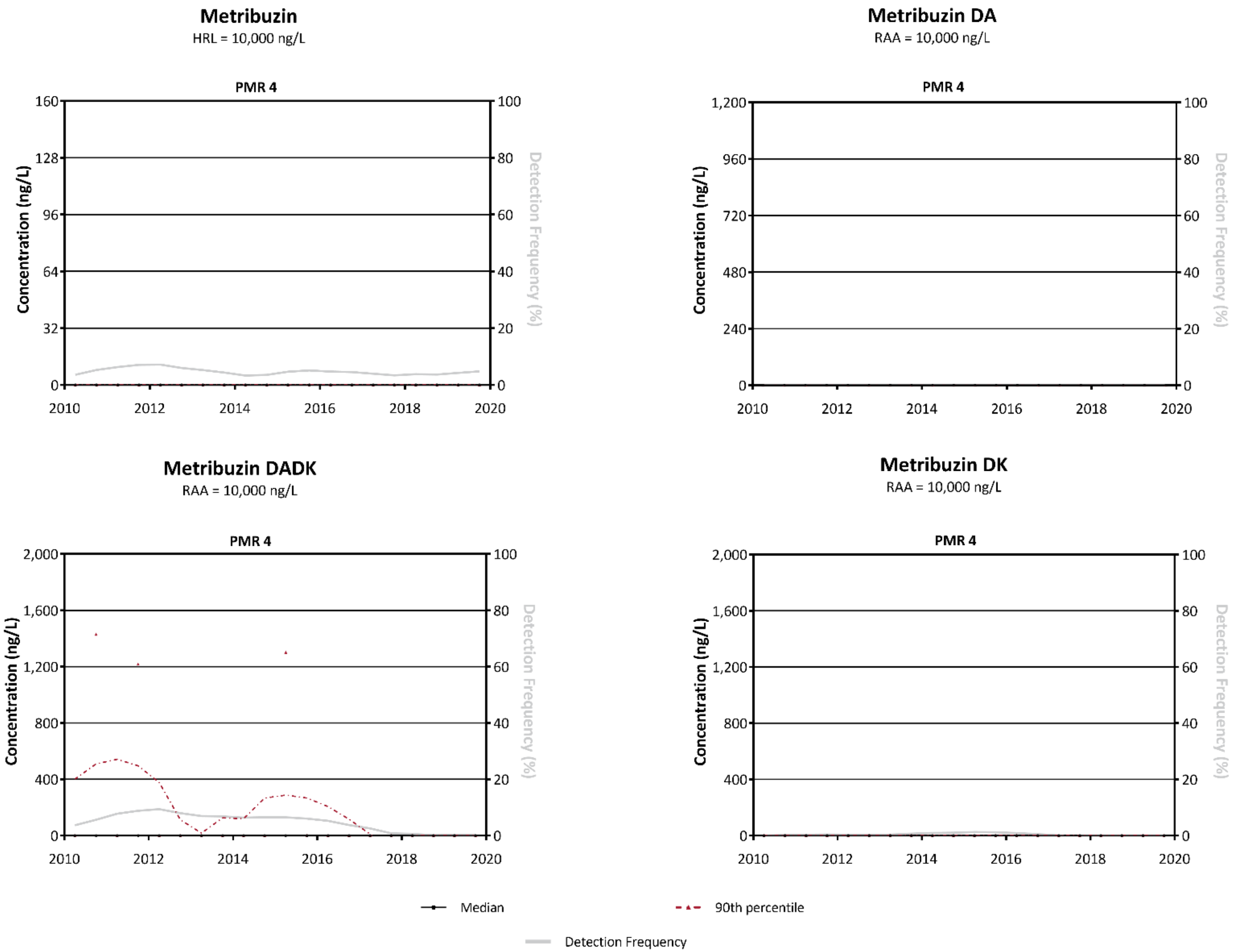


Figure 2-25. 2010 through 2019 metribuzin degradates concentration results and detection frequencies for MDA PMR 4.



2.4 Analysis of additional pesticides

This section provides additional data analysis for pesticides because they had detection frequencies greater than 15% in PMR 4 in 2019. The pesticides included (parent and degradates, where appropriate) are: bentazon, clothianidin, dimethenamid, fomesafen, imazamox, imidacloprid, saflufenacil, and thiamethoxam. PMR 4 is an area of increased concern due to the vulnerability to shallow groundwater from agricultural production on sandy soils. Three of the compounds (clothianidin, imidacloprid, and thiamethoxam) are neonicotinoids that are also of concern because of the potential impact to pollinators. Compounds may be added to or removed from this section depending on the detection frequency for the year in question. In 2019, saflufenacil was added to this analysis. Please note, none of these compounds are in common detection pesticides status.

Detection frequencies and maximum concentration information for all monitoring PMRs is found in Table 2-6. It should be noted that these summaries are only based upon monitoring data from the shallow monitoring wells (deep well data from PMR 4 are not included), to allow for comparison among PMRs. Table 2-7 displays the trend analysis results from the 2010 through 2019 median and 90th percentile concentrations and the detection frequency for these compounds from PMR 4. Output from the trend test analyses that were performed can be found in Appendix 5a.

Time series graphics for the concentration and detection frequency of these compounds are located in Figures 2-26 through 2-32. All of these compounds (except clothianidin, fomesafen and imidacloprid degradates) have been analyzed by the MDA since 2010, so all graphics were generated at that starting point. Note that the MRL values differ across pesticides, therefore direct comparisons of detection frequency between pesticides is discouraged. It is appropriate to compare detection frequency over time for individual pesticides.

The principal findings for all of the compounds from PMR 4 include:

- None of the other pesticide compounds described in this section exceeded available groundwater health-based reference values.
- Median concentration trend findings for these compounds:
    - The trend on the median concentration was not able to be calculated for all compounds.
- 90th percentile concentration trend findings for these compounds:
    - A trend that was not statistically significant was calculated for dimethenamid OXA, imazamox, and imidacloprid.
    - An increasing trend was calculated for bentazon, clothianidin, dimethenamid ESA, saflufenacil, and thiamethoxam.
- Detection frequency trend findings for these compounds:
    - A trend that was not statistically significant was calculated for dimethenamid OXA and imidacloprid.

- An increasing trend was calculated for bentazon, clothianidin, dimethenamid ESA, imazamox, saflufenacil, and thiamethoxam.

Table 2-6. Detection frequencies and maximum concentrations for additional pesticides in groundwater samples.

	2019			
	Total Samples	**Detections**	**Detection Frequency (%)**	**Maximum Concentration (ng/L)**
PMR 1				
Bentazon	14	**1**	**7**	**25.2**
Clothianidin	14	0	0	<25
Dimethenamid	14	0	0	<15
Dimethenamid ESA	14	**2**	**14**	**68.9**
Dimethenamid OXA	14	**2**	**14**	**39.7**
Dimethenamid + Degradates	14	**2**	**14**	**109**
Fomesafen	14	**3**	**21**	**161**
Imazamox	14	0	0	<13.3
Imidacloprid	14	0	0	<5
Imidacloprid-olefin	14	0	0	<50
Imidacloprid-urea	14	0	0	<50
Saflufenacil	14	0	0	<15
Thiamethoxam	14	0	0	<25
PMR 4				
Bentazon	78	**25**	**32**	**1,940**
Clothianidin	78	**32**	**41**	**1,460**
Dimethenamid	78	**1**	**1**	**25.9**
Dimethenamid ESA	78	**27**	**35**	**910**
Dimethenamid OXA	78	**7**	**9**	**410**
Dimethenamid + Degradates	78	**27**	**35**	**1,320**
Fomesafen	78	**22**	**28**	**2,960**
Imazamox	78	**18**	**23**	**106**
Imidacloprid	78	**20**	**26**	**165**
Imidacloprid-olefin	78	0	0	<50
Imidacloprid-urea	78	0	0	<50
Saflufenacil	78	**14**	**18**	**1,000**
Thiamethoxam	78	**22**	**28**	**2,180**
PMR 5				
Bentazon	16	0	0	<5
Clothianidin	16	**1**	**6**	**80.7**
Dimethenamid	16	0	0	<15
Dimethenamid ESA	16	0	0	<6.7
Dimethenamid OXA	16	0	0	<10
Dimethenamid + Degradates	16	0	0	<15
Fomesafen	16	0	0	<50
Imazamox	16	0	0	<13.3
Imidacloprid	16	**1**	**6**	**5.22**
Imidacloprid-olefin	16	0	0	<50
Imidacloprid-urea	16	0	0	<50
Saflufenacil	16	**1**	**6**	**57.2**
Thiamethoxam	16	0	0	<25
PMR 6				
Bentazon	17	**5**	**29**	**99.2**
Clothianidin	17	0	0	<25
Dimethenamid	17	0	0	<15
Dimethenamid ESA	17	0	0	<6.7
Dimethenamid OXA	17	0	0	<10
Dimethenamid + Degradates	17	0	0	<15
Fomesafen	17	0	0	< 50

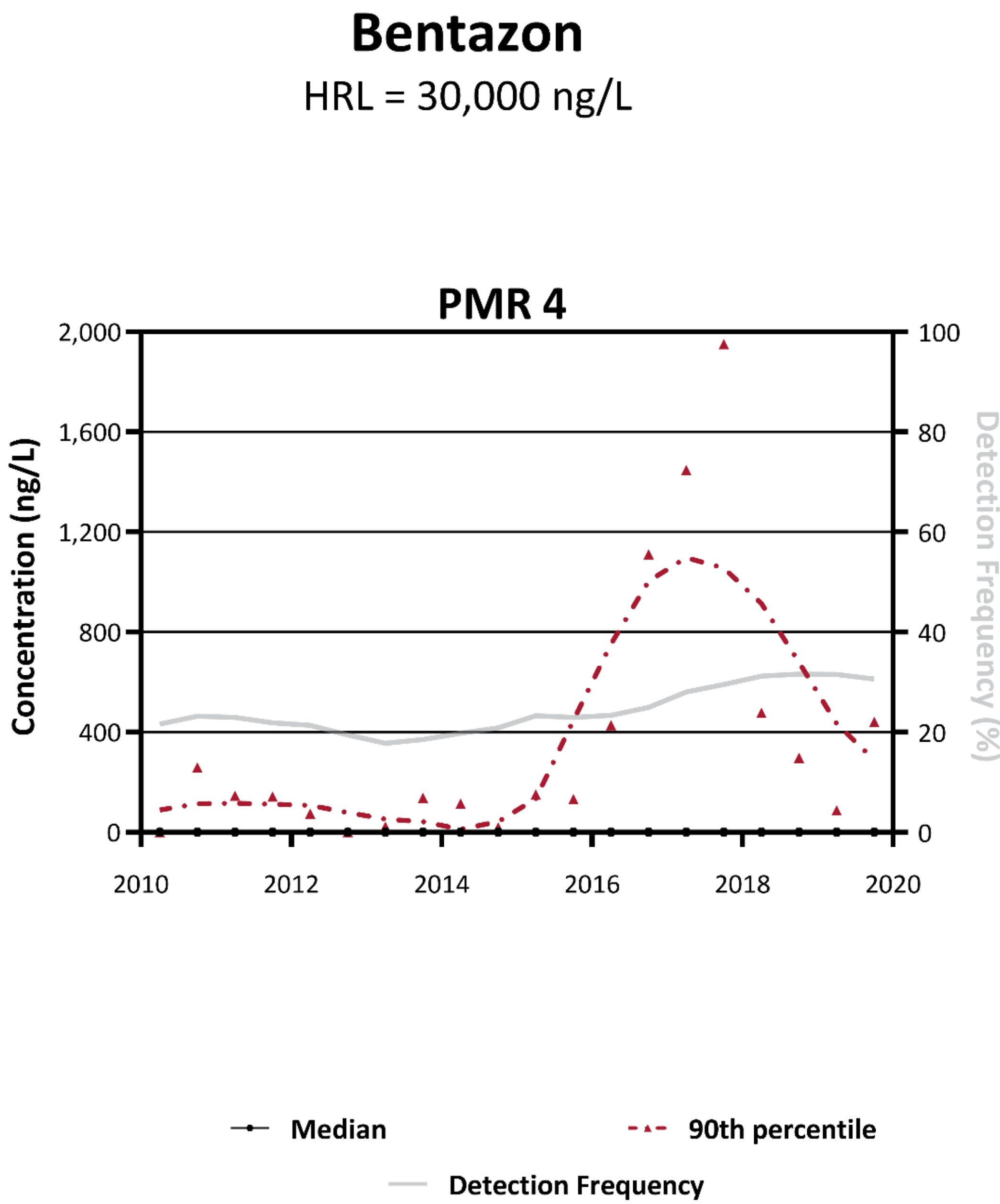
	2019			
	Total Samples	**Detections**	**Detection Frequency (%)**	**Maximum Concentration (ng/L)**
Imazamox	17	0	0	<13.3
Imidacloprid	17	0	0	<5
Imidacloprid-olefin	17	0	0	<50
Imidacloprid-urea	17	0	0	<50
Saflufenacil	17	0	0	<15
Thiamethoxam	17	0	0	<25
PMR 7				
Bentazon	14	0	0	<5
Clothianidin	14	**2**	**14**	**43.0**
Dimethenamid	14	0	0	<15
Dimethenamid ESA	14	**2**	**14**	**8.35**
Dimethenamid OXA	14	0	0	<10
Dimethenamid + Degradates	14	**2**	**14**	**8.35**
Fomesafen	14	**2**	**14**	**253**
Imazamox	14	0	0	<13.3
Imidacloprid	14	0	0	<5
Imidacloprid-olefin	14	0	0	<50
Imidacloprid-urea	14	0	0	<50
Saflufenacil	14	0	0	<15
Thiamethoxam	14	0	0	<25
PMR 8				
Bentazon	26	0	0	<5
Clothianidin	26	**2**	**8**	**55.3**
Dimethenamid	26	0	0	<15
Dimethenamid ESA	26	**2**	**8**	**18.3**
Dimethenamid OXA	26	0	0	<10
Dimethenamid + Degradates	26	**2**	**8**	**18.3**
Fomesafen	26	**3**	**12**	**403**
Imazamox	26	0	0	<13.3
Imidacloprid	26	0	0	<5
Imidacloprid-olefin	26	0	0	<50
Imidacloprid-urea	26	0	0	<50
Saflufenacil	26	0	0	<15
Thiamethoxam	26	0	0	<25
PMR 9				
Bentazon	37	**2**	**5**	**251**
Clothianidin	37	**3**	**8**	**42.2**
Dimethenamid	37	0	0	<15
Dimethenamid ESA	37	**3**	**8**	**26.8**
Dimethenamid OXA	37	0	0	<10
Dimethenamid + Degradates	37	**3**	**8**	**26.8**
Fomesafen	37	0	0	< 50
Imazamox	37	0	0	<13.3
Imidacloprid	37	0	0	<5
Imidacloprid-olefin	37	0	0	<50
Imidacloprid-urea	37	0	0	<50
Saflufenacil	37	**2**	**5**	**36.6**
Thiamethoxam	37	0	0	<25

Table 2-7. Median, 90th percentile, and detection frequency trend analysis results for additional pesticides from 2010-2019 groundwater sampling.

	Bentazon	Clothianidin	Dimethenamid ESA	Dimethenamid OXA	Imazamox	Imidacloprid	Saflufenacil	Thiamethoxam
Median	—	—	—	—	—	—	—	—
90th Percentile	↑	↑	↑	↔	↔	↔	↑	↑
Detection Frequency	↑	↑	↑	↔	↑	↔	↑	↑

↑ = statistically significant increasing trend.
↓ = statistically significant decreasing trend.
↔ = trend not statistically significant (no trend).
— = trend not able to be calculated (no trend).

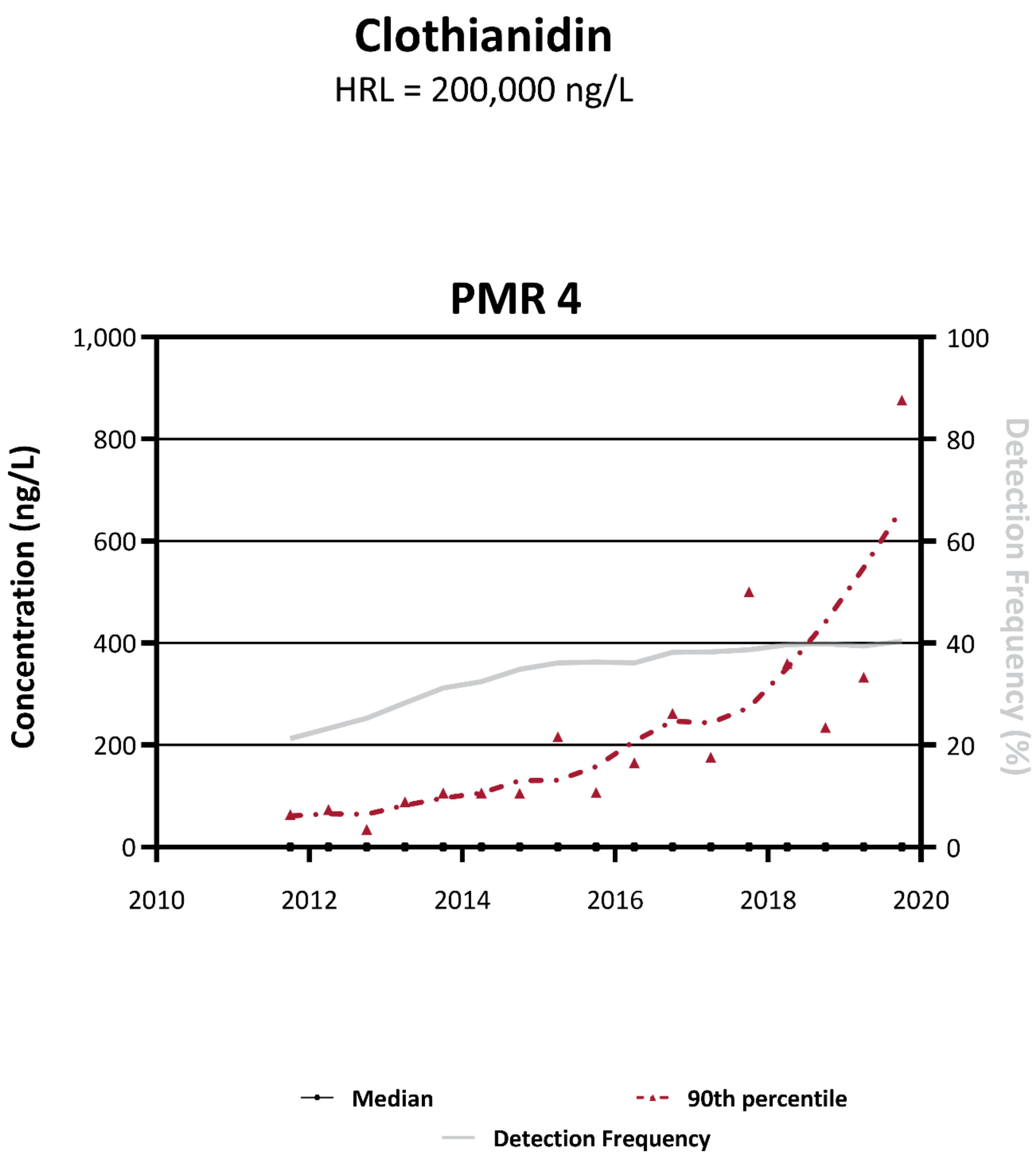
Figure 2-26. Bentazon concentration and detection frequency over time for MDA PMR 4.



Bentazon

- The highest maximum concentration (1,940 ng/L) occurred in PMR 4 followed by PMR 9 at 251 ng/L.
- Bentazon was detected in PMRs 1, 4, 6, and 9 and these PMRs had detection frequencies of 7%, 32%, 29%, and 5%, respectively.
- Within PMR 4, there was a statistically significant increasing trend in the 90th percentile concentration and the detection frequency.

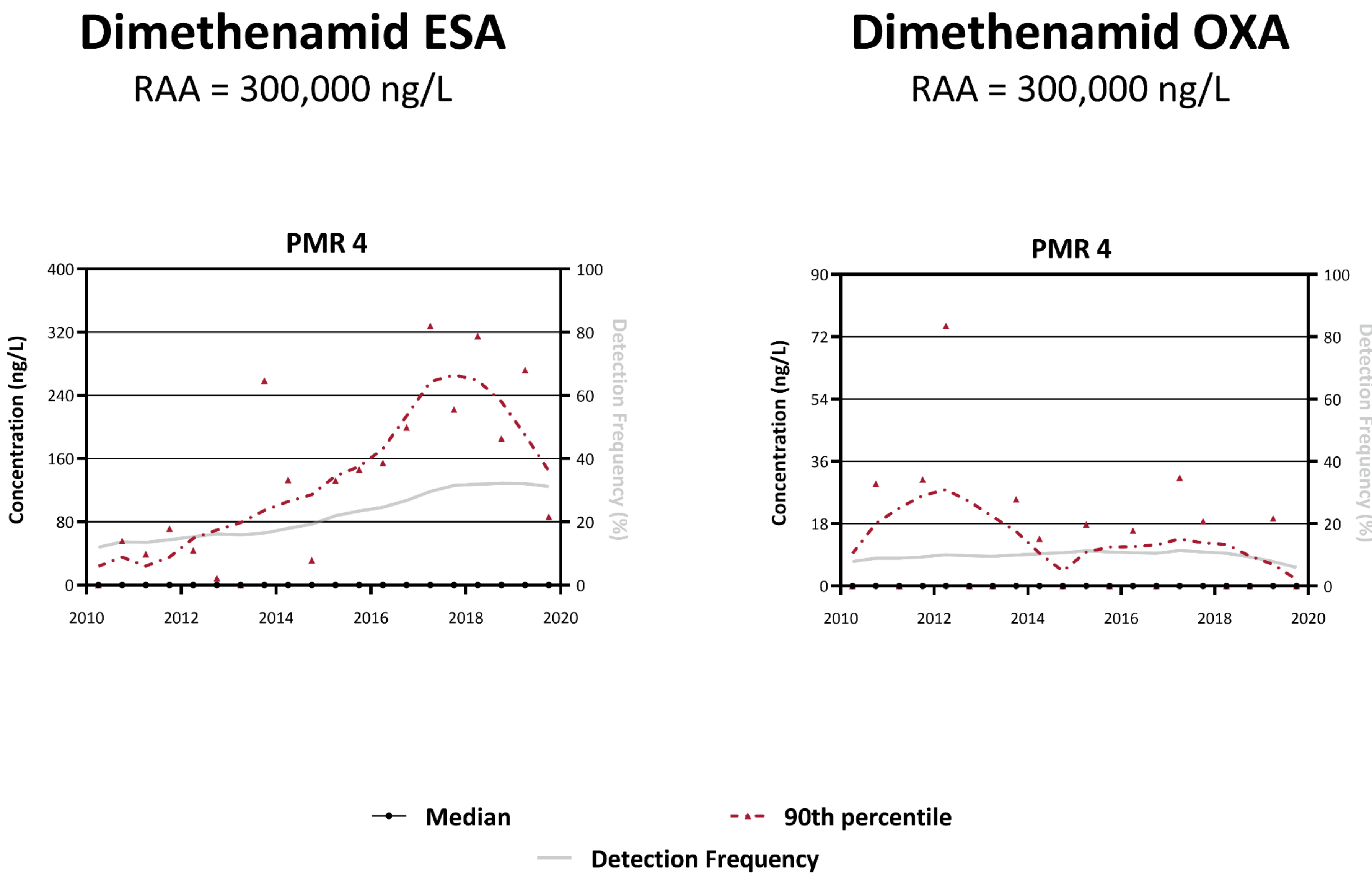
Figure 2-27. Clothianidin concentration and detection frequency over time for MDA PMR 4.



Clothianidin

- The highest maximum concentration was found in PMR 4 at 1,460 ng/L followed by PMR 5 (80.7 ng/L).
- Clothianidin was detected in PMRs 4, 5, 7, 8, and 9, and these PMRs had detection frequencies of 41%, 6%, 14%, 8%, and 8%, respectively.
- Within PMR 4, there was a statistically significant increasing trend in the 90th percentile concentration and the detection frequency.

Figure 2-28. Dimethenamid degradates, concentrations, and detection frequency over time for MDA PMR 4.



Dimethenamid

- Dimethenamid was detected in one sample in PMR 4 (25.9 ng/L).
- Dimethenamid has seldom been detected in the PMR 4 shallow monitoring wells since 2010, so there was insufficient data to conduct a trend analysis.

Dimethenamid ESA

- PMR 4 had the highest maximum concentration (910 ng/L) followed by PMR 1 (68.9 ng/L).
- Dimethenamid ESA was detected in PMRs 1, 4, 7, 8, and 9, and these PMRs had detection frequencies of 14%, 35%, 14%, 8%, and 8%, respectively.
- Within PMR 4, there was a statistically significant increasing trend in the 90^{th} percentile concentration and the detection frequency.

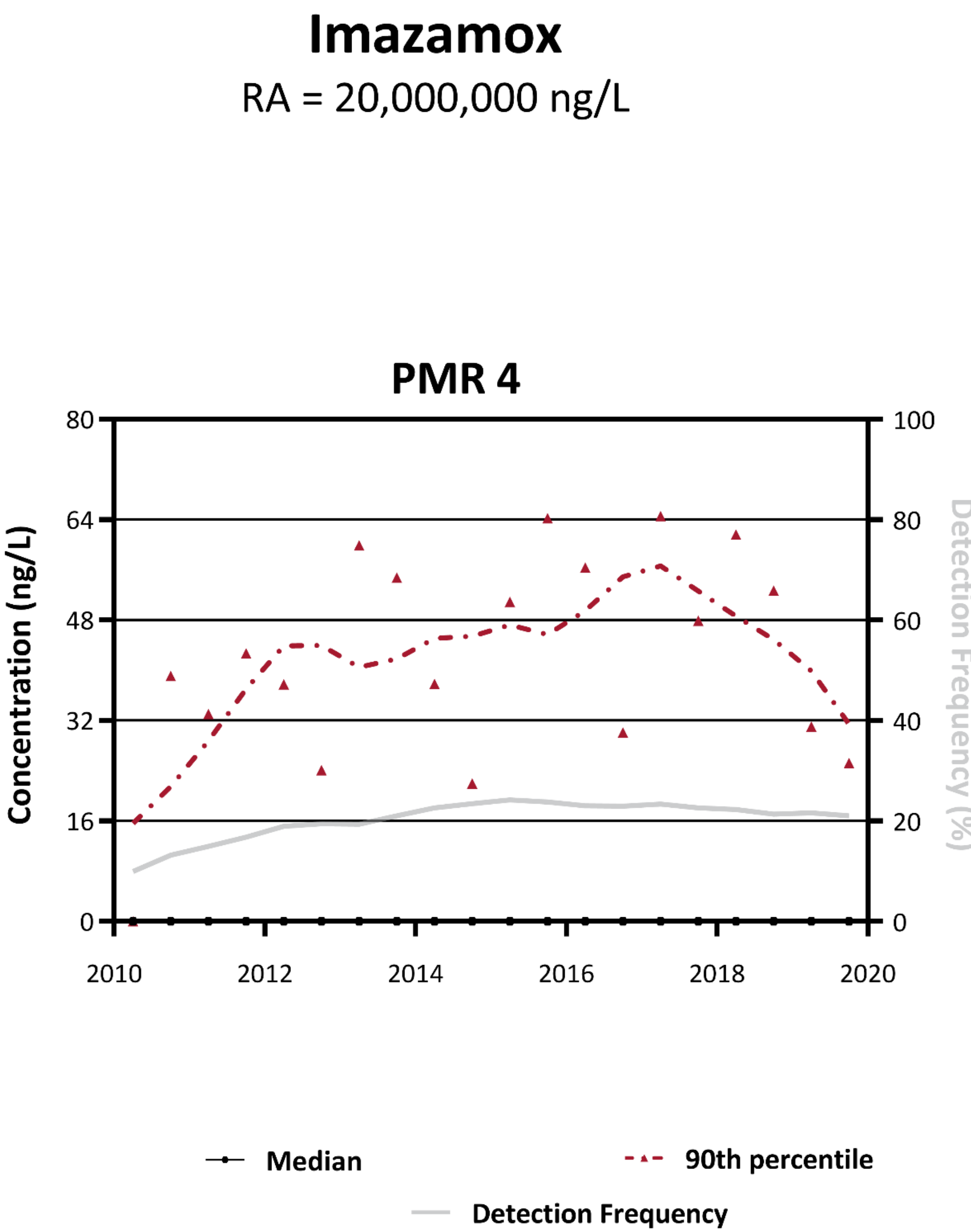
Dimethenamid OXA

- Dimethenamid OXA was only detected in PMRs 1 and 4.
    - PMR 1 had a maximum concentration of 39.7 ng/L, and in PMR 4 it was 410 ng/L.
    - The detection frequency was 14% and 9%, respectively.
- Within PMR 4, a trend was calculated to not be statistically significant for the 90^{th} percentile concentration and the detection frequency.

Fomesafen

- The highest maximum concentration came from PMR 4 (2,960 ng/L) followed by PMR 8 (403 ng/L).
- Fomesafen was detected in PMRs 1, 4, 7, and 8, and these PMRs had detection frequencies of 21%, 28%, 14%, and 12%, respectively.
- Fomesafen was first analyzed time in 2018 by the MDA Laboratory, so the time series graphic generation and a trend analysis was not performed because there is only two years of data. These will be performed and evaluated next year, when there is enough data for these analyses.

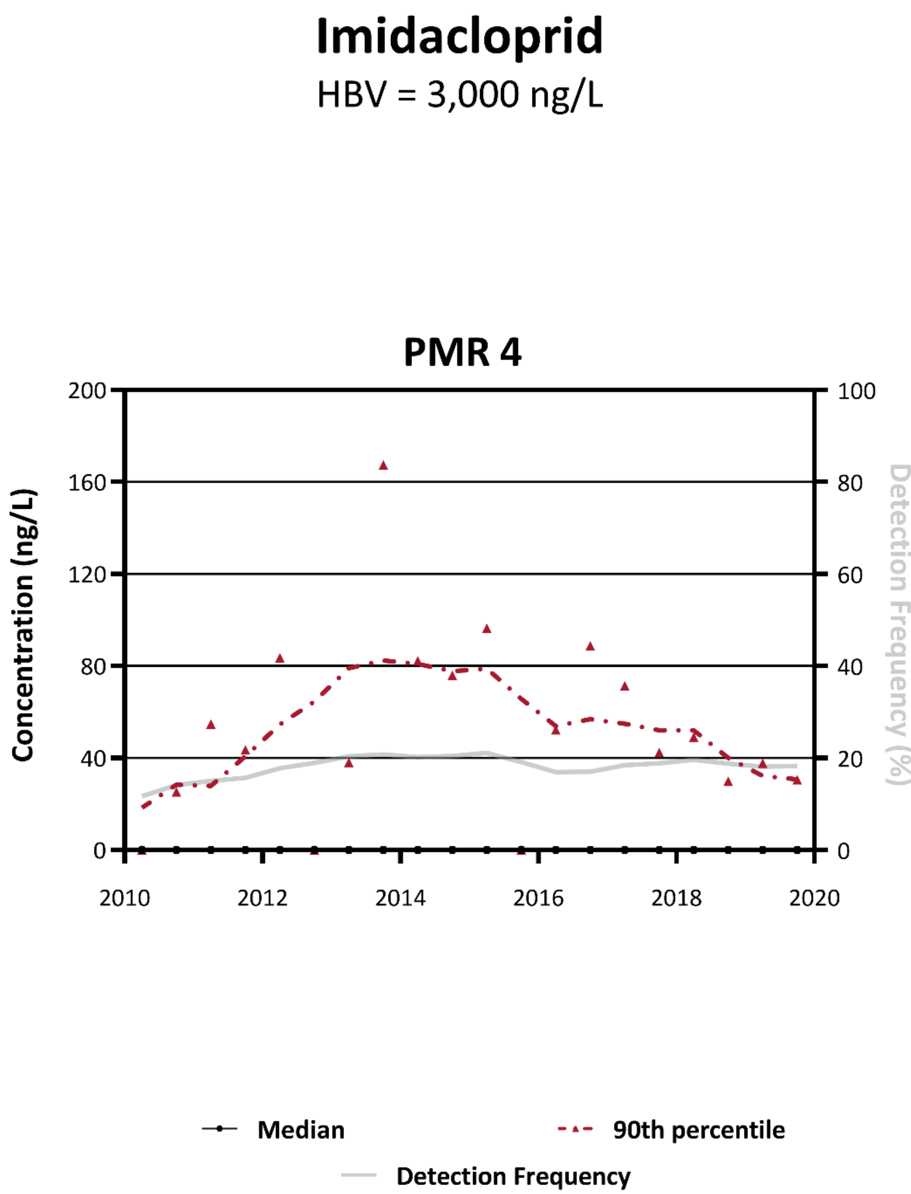
Figure 2-29. Imazamox concentration and detection frequency over time for MDA PMR 4.



Imazamox

- Imazamox was only detected in PMR 4, with a maximum concentration of 106 ng/L and a detection frequency of 23%.
- A trend that was not statistically significant was calculated for the 90th percentile concentration, while a statistically significant increasing trend was calculated for the detection frequency.

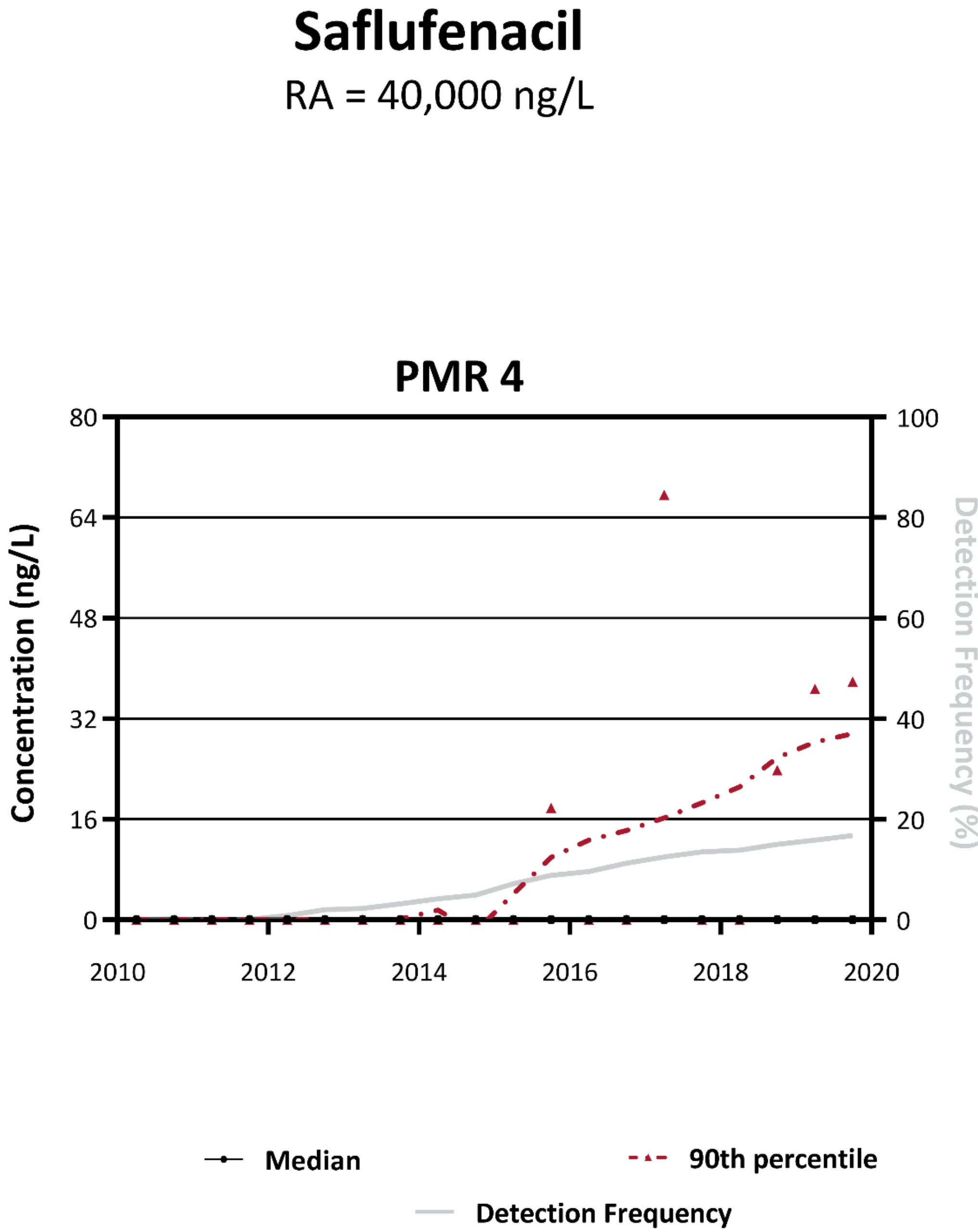
Figure 2-30. Imidacloprid concentration and detection frequency over time for MDA PMR 4.



Imidacloprid

- Imidacloprid was only detected in PMRs 4 and 5.
  - PMR 4 had a maximum concentration of 165 ng/L, and in PMR 5 it was 5.22 ng/L.
  - The detection frequency was 26% and 6%, respectively.
- Within PMR 4, a trend was calculated to not be statistically significant for the 90^{th} percentile concentration and the detection frequency.
- Neither of the imidacloprid degradates (imidacloprid-olefin nor imidacloprid-urea) were detected in any groundwater samples.

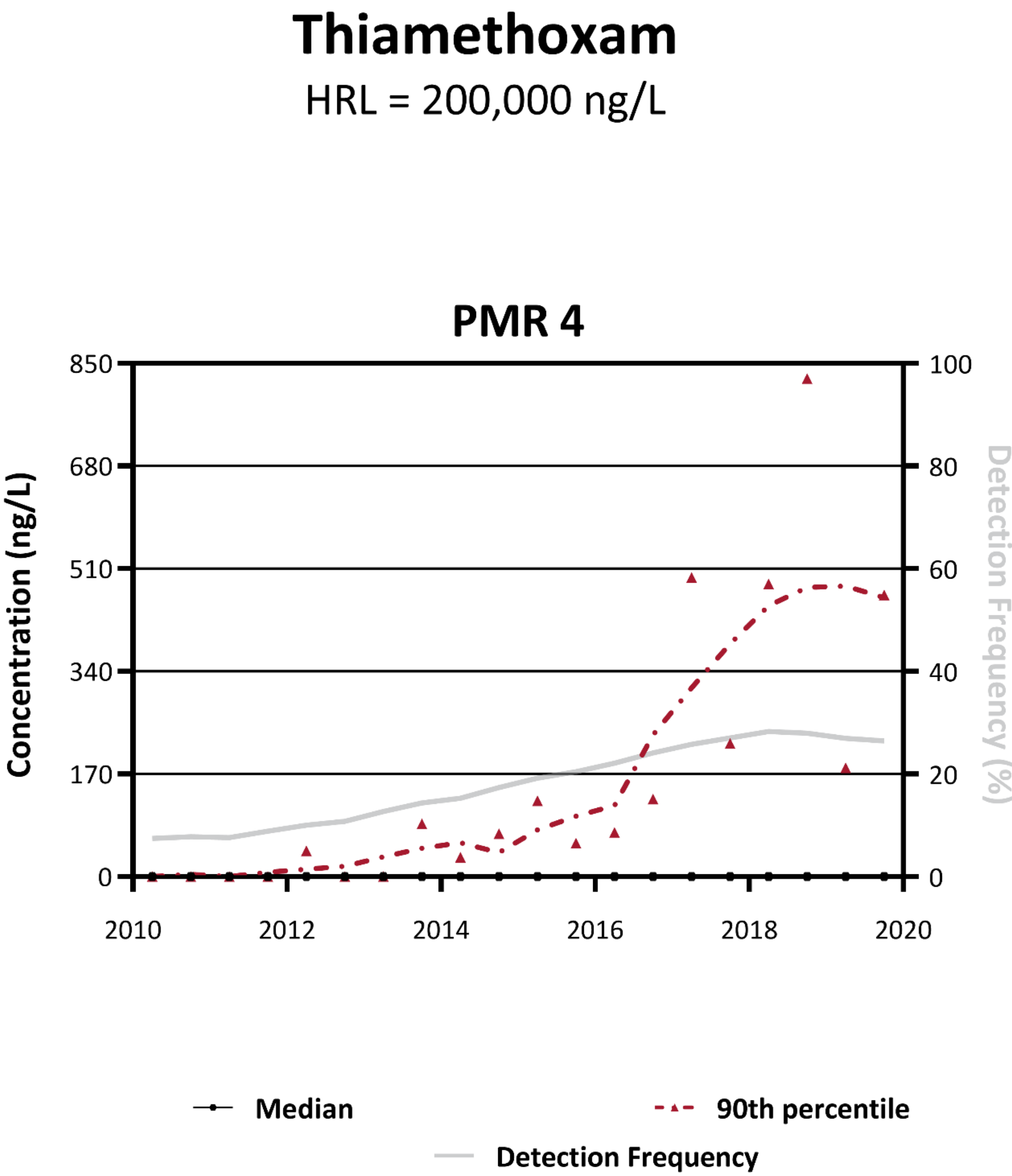
Figure 2-31. Saflufenacil concentration and detection frequency over time for MDA PMR 4.



Saflufenacil

- The highest maximum concentration was found in PMR 4 at 1,000 ng/L followed by PMR 5 (57.2 ng/L).
- Saflufenacil was detected in PMRs 4, 5, and 9, and these PMRs had detection frequencies of 18%, 6% and 5%, respectively.
- Within PMR 4, there was a statistically significant increasing trend in the 90th percentile concentration and the detection frequency.

Figure 2-32. Thiamethoxam concentration and detection frequency over time for MDA PMR 4.



Thiamethoxam

- Thiamethoxam was only detected in PMR 4, with a maximum concentration of 2,180 ng/L and a detection frequency of 28%.
- A statistically significant increasing trend was calculated for the 90th percentile concentration and the detection frequency.

2.5 Groundwater neonicotinoid results

Neonicotinoids were first analyzed by the MDA Laboratory in samples in 2010. In 2019, the MDA Laboratory analyzed water samples for six neonicotinoid parent pesticides and two degradates: the parent pesticides acetamiprid, imidacloprid, and thiamethoxam (analysis began in 2010), clothianidin (analysis began in mid-2011), dinotefuran (analysis began in 2012), thiacloprid (analysis began in 2014), and the degradates imidacloprid-urea and imidacloprid-olefin (analysis began in 2017). All of these insecticide compounds were analyzed utilizing the LC/MS-MS method and have MRLs ranging from 5 to 50 ng/L.

Statewide neonicotinoid results from MDA's groundwater monitoring network for 2019 are presented in Table 2-8. Table 2-9 presents a summary of the neonicotinoid results from 2010 through 2019. The 2019 summary was based upon results from only the shallow monitoring wells, while all monitoring well data (including deep well data from PMR 4) was included in the long-term data summary. Further, the imidacloprid results for the 2019 summary are indicative of the new MRL for imidacloprid (5.0 ng/L). The imidacloprid data used in the long-term data summary were censored to the highest historical MRL of 20 ng/L that was used prior to 2018. Although never detected, the acetamiprid data were also censored to reflect the highest historical MRL of 25 ng/L (in 2010, the MRL was 15 ng/L).

Groundwater neonicotinoid detection summary findings include:

- In 2019, the MDA collected 222 groundwater samples that were analyzed for six parent neonicotinoid insecticides and two imidacloprid degradates.
- The 2019 statewide detection frequencies for clothianidin, imidacloprid, and thiamethoxam were 18%, 10%, and 10%, respectively.
- The maximum concentration in 2019 for the three detected neonicotinoids was for thiamethoxam (2,180 ng/L).
- Acetamiprid, dinotefuran, imidacloprid-urea, imidacloprid-olefin, and thiacloprid have not been detected in Minnesota groundwater.
- Clothianidin, imidacloprid, and thiamethoxam have been detected in groundwater from agricultural areas each year since analysis.
- Imidacloprid was detected in the urban area for the first time since 2011 (6.55 ng/L). This is the only neonicotinoid that has been detected in urban groundwater.
- All detections have been below applicable human health-based drinking water reference values.

Table 2-8. Groundwater neonicotinoid monitoring results for 2019.

Land Use	Neonicotinoid Analyte	Total Samples	Detections	Detection Frequency (%)	Maximum (ng/L)
Agricultural	Acetamiprid	202	0	0	<25
	Clothianidin	202	**40**	**20**	**1,460**
	Dinotefuran	202	0	0	<25
	Imidacloprid	202	**21**	**10**	**165**
	Imidacloprid-olefin	202	0	0	<50
	Imidacloprid-urea	202	0	0	<50
	Thiacloprid	202	0	0	<50
	Thiamethoxam	202	**22**	**11**	**2,180**
Urban	Acetamiprid	20	0	0	<25
	Clothianidin	20	0	0	<25
	Dinotefuran	20	0	0	<25
	Imidacloprid	20	**1**	**5**	**6.55**
	Imidacloprid-olefin	20	0	0	<50
	Imidacloprid-urea	20	0	0	<50
	Thiacloprid	20	0	0	<50
	Thiamethoxam	20	0	0	<25
All	Acetamiprid	222	0	0	<25
	Clothianidin	222	**40**	**18**	**1,460**
	Dinotefuran	222	0	0	<25
	Imidacloprid	222	**22**	**10**	**165**
	Imidacloprid-olefin	222	0	0	<50
	Imidacloprid-urea	222	0	0	<50
	Thiacloprid	222	0	0	<50
	Thiamethoxam	222	**22**	**10**	**2,180**

Table 2-9. Groundwater neonicotinoids results summary, 2010-2019.

Neonicotinoid Analyte	Agricultural				Urban				All				Year Analysis Started	Years with a detection	Censored MRL
	Total Samples	Detections	Detection Frequency (%)	Maximum (ng/L)	Total Samples	Detections	Detection Frequency (%)	Maximum (ng/L)	Total Samples	Detections	Detection Frequency (%)	Maximum (ng/L)			
Acetamiprid*	2,375	0	0	< 25	199	0	0	< 25	2,574	0	0	< 25	2010	-	25
Clothianidin	2,004	**312**	**16**	**1,610**	179	0	0	< 25	2,183	**312**	**14**	**1,610**	2011	2011-2019	25
Dinotefuran	1,882	0	0	< 25	159	0	0	< 25	2,041	0	0	< 25	2012	-	25
Imidacloprid*	2,375	**183**	**8**	**2,260**	199	**1**	**<1**	**28.0**	2,574	**184**	**7**	**2,260**	2010	2010-2019	20
Imidacloprid-olefin	668	0	0	< 50	59	0	0	< 50	727	0	0	< 50	2017	-	50
Imidacloprid-urea	668	0	0	< 50	59	0	0	< 50	727	0	0	< 50	2017	-	50
Thiacloprid	1,381	0	0	< 50	119	0	0	< 50	1,500	0	0	< 50	2014	-	50
Thiamethoxam	2,375	**178**	**7**	**6,340**	199	0	0	< 25	2,574	**178**	**7**	**6,340**	2010	2010-2019	25

*These compounds have been censored to reflect the highest historical MRL used by the laboratory.

2.6 Monitoring results from the well nests in PMR 4

In 2010, the MDA MAU installed eight wells at existing monitoring sites in PMR 4 (Figure 2-33) to create well nests, or a site with a shallow well (or sometimes two) and a deep well, both in the water table aquifer. The original shallow wells at each site were screened across the water table, while the screens of the deeper wells were installed 10 to 15 feet deeper into the aquifer. The deep wells were distributed across PMR 4 at sites with a history of higher pesticide concentrations compared to other wells in PMR 4. The purpose of the deep wells was to determine if pesticides were impacting deeper portions of the unconfined surficial aquifer. Samples were collected from both the shallow and deep wells during the routine spring and fall sampling periods.

Historically, each well nest was sampled twice a year, once in the spring and once in the fall during the regular sampling season. In 2019, because of MDA Laboratory capacity, sampling at seven of the eight wells nests was reduced to once a year. The sites were randomly assigned a sampling period, similar to the other sites in PMR 4. Samples were collected from both the shallow and deep well. One site (80-B1) was sampled in both the spring and the fall, as it has historically had elevated concentrations of a number of different compounds. The extra sampling event was used as a check on the concentrations at the site. While the wells were sampled in both the spring and the fall at this site, only the data from the spring sampling event is considered as the “routine” sample, since this was the first sampling event at the site. The nature of the second sample precludes it from being included herein.

Results from the 2019 well nest sampling are presented in Table 2-10. Only those compounds that were detected at two or more well nests are presented in the table. Selecting compounds that were detected in two or more wells nests provides a clearer picture of potential patterns between the shallow and deep wells.

The data from the shallow wells is used in the analysis presented throughout this report, as the characteristics of these shallow wells (i.e., being screened across the water table) matches the other wells in MDA’s ambient groundwater monitoring network in PMR 4. The data from the deep wells is only presented in this section and the long-term evaluation of neonicotinoids in Section 2.5.

Figure 2-33. Placement of shallow and deep well nests within the MDA's groundwater monitoring network.

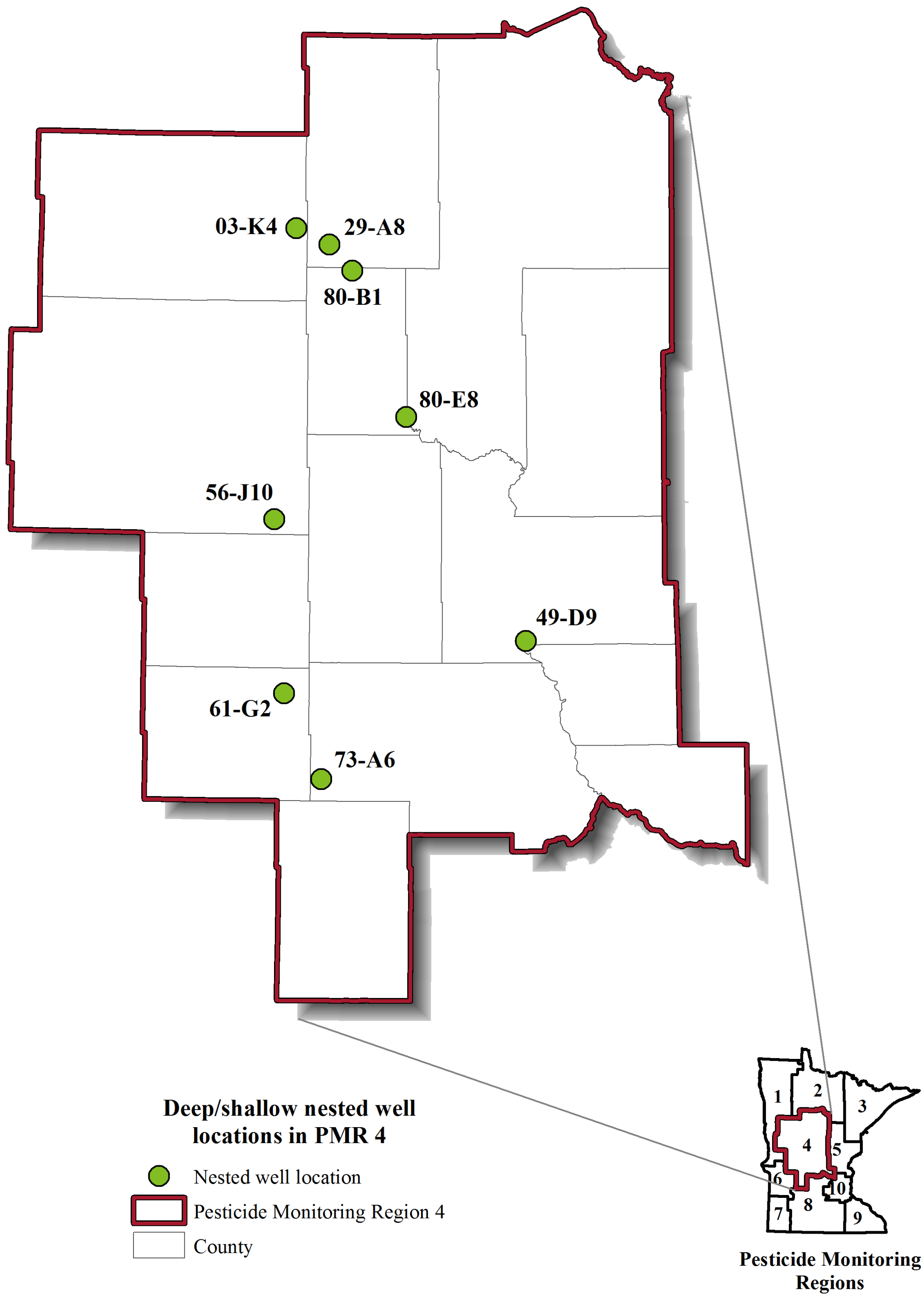


Table 2-10. 2019 pesticide sample results in ng/L for chemicals with detections in two or more of the well nests in MDA PMR 4.

Site	03-K4		29-A8		49-D9		56-J10		61-G2		73-A6		80-B1		80-E8	
Collection season	Spring		Spring		Spring		Fall		Spring		Spring		Spring		Fall	
Well depth	Shallow	Deep	Shallow	Deep	Shallow	Deep	Shallow	Deep	Shallow	Deep	Shallow	Deep	Shallow	Deep	Shallow	Deep
Acetochlor ESA	**92.2**	<30	**134**	**620**	**673**	**315**	**1,090**	**745**	**379**	**97.6**	**109**	**117**	<30	<30	<30	<30
Acetochlor OXA	<33.3	<33.3	<33.3	**41.8**	<33.3	**82.5**	<33.3	<33.3	<33.3	<33.3	<33.3	<33.3	<33.3	<33.3	<33.3	<33.3
Alachlor ESA	<41.6	<41.6	<41.6	**72.8**	**154**	**1,040**	**126**	**157**	<41.6	<41.6	<41.6	**221**	**884**	**977**	<41.6	<41.6
Alachlor OXA	<33.3	<33.3	<33.3	<33.3	<33.3	**66.0**	<33.3	<33.3	<33.3	<33.3	<33.3	<33.3	**147**	**124**	<33.3	<33.3
Bentazon	**6.62**	**11.3**	**22.0**	**356**	**11.9**	<5	**1,940**	**1,420**	**14.9**	**198**	**1,610**	**5,320**	**22.0**	**1,400**	**151**	<5
Clothianidin	**177**	<25	**111**	**29.4**	**368**	**52.3**	**123**	**137**	<25	<25	**227**	**52.9**	**369**	**495**	**1,460**	<25
Didealkylatrazine	<50	<50	<50	<50	<50	<50	<50	**51.2**	**77.0**	**91.7**	<50	**56.5**	<50	<50	<50	<50
Dimethenamid ESA	**319**	<6.7	**66.9**	**6.93**	<6.7	<6.7	**80.6**	<6.7	<6.7	<6.7	**74.2**	**229**	**910**	**500**	**38.9**	<6.7
Dimethenamid OXA	**63.2**	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	**410**	**652**	<10	<10
Flumetsulam	<50	<50	<50	<50	**274**	<50	<50	<50	**122**	<50	<50	<50	<50	<50	<50	<50
Fomesafen	**484**	<50	<50	<50	**1,000**	**139**	<50	<50	<50	<50	**423**	**155**	**264**	<50	**2,960**	<50
Imazamox	<13.3	<13.3	<13.3	**37.9**	<13.3	<13.3	**106**	**29.8**	<13.3	<13.3	**97.3**	**70.3**	**54.4**	**50.3**	<13.3	<13.3
Imidacloprid	**38.4**	<5	**54.1**	**7.03**	**16.5**	**21.9**	<5	<5	<5	<5	<5	<5	**90.1**	**124**	**165**	<5
Metalaxyl	**12.4**	<8.3	<8.3	**16.6**	**8.86**	**136**	<8.3	<8.3	<8.3	<8.3	<8.3	<8.3	**12.8**	**291**	<8.3	<8.3
Metolachlor ESA	**2,590**	**50.3**	**61.9**	**412**	**6,880**	**8,180**	**10,900**	**6,050**	**2,550**	**3,480**	**293**	**1,860**	**2,310**	**1,250**	**12,500**	**884**
Metolachlor OXA	**1,320**	<10	**10.7**	**147**	**2,230**	**5,050**	**1,350**	**516**	<10	**28.8**	<10	**68.1**	**2,180**	**918**	**6,800**	**265**
Metribuzin DA	<25	<25	<25	<25	<25	**175**	<25	<25	<25	<25	<25	<25	**70.2**	**839**	<25	<25
Metribuzin DADK	<500	<500	<500	**732**	<500	**583**	<500	<500	<500	<500	<500	<500	<500	**1,530**	<500	<500
Saflufenacil	<15	<15	**97.3**	<15	**33.6**	<15	**49.1**	<15	<15	<15	**22.1**	**28.6**	<15	<15	**317**	<15
Thiamethoxam	**454**	<25	**156**	<25	**35.7**	**59.8**	<25	<25	<25	<25	**397**	<25	**1,130**	**1,720**	**462**	<25

Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the MDA Laboratory.
Refer to Table 2-0 of this report for the source of each reference value and for more information regarding these values.

2.7 Urban groundwater pesticide sampling

In 2019, pesticide water quality samples were collected by MPCA staff from 20 urban wells in MPCA's ongoing monitoring program. The wells were water table aquifer wells from the MPCA's monitoring well network. The MDA works with the MPCA to ensure the wells meet the MDA's monitoring requirements.

All 20 wells were located in the Twin Cities metro area within PMR 10. The MDA does not currently have any monitoring locations in agricultural areas of PMR 10. Figure 2-34 displays the well sites and the number of compounds detected in each well. Table 2-11 is a summary of results for pesticide compounds that were detected in the 2019 urban groundwater samples. General findings were:

- Metolachlor ESA was the most frequently detected pesticide in the urban samples (10 out of 20 samples).
- Ten of the 13 compounds detected in samples from the urban wells were also found in agricultural areas.
    - The detection frequency for the common detection pesticides, described previously, are generally less in the urban wells when compared to the agricultural monitoring regions.
    - Bromacil, MCPP, and picloram were only detected in urban groundwater.
- Four compounds were only detected once in the urban groundwater samples.
- Maximum concentrations were low compared to groundwater reference values (Table 2-0).

Figure 2-34. 2019 MDA urban groundwater monitoring sites and number of detected pesticide compounds at each site.

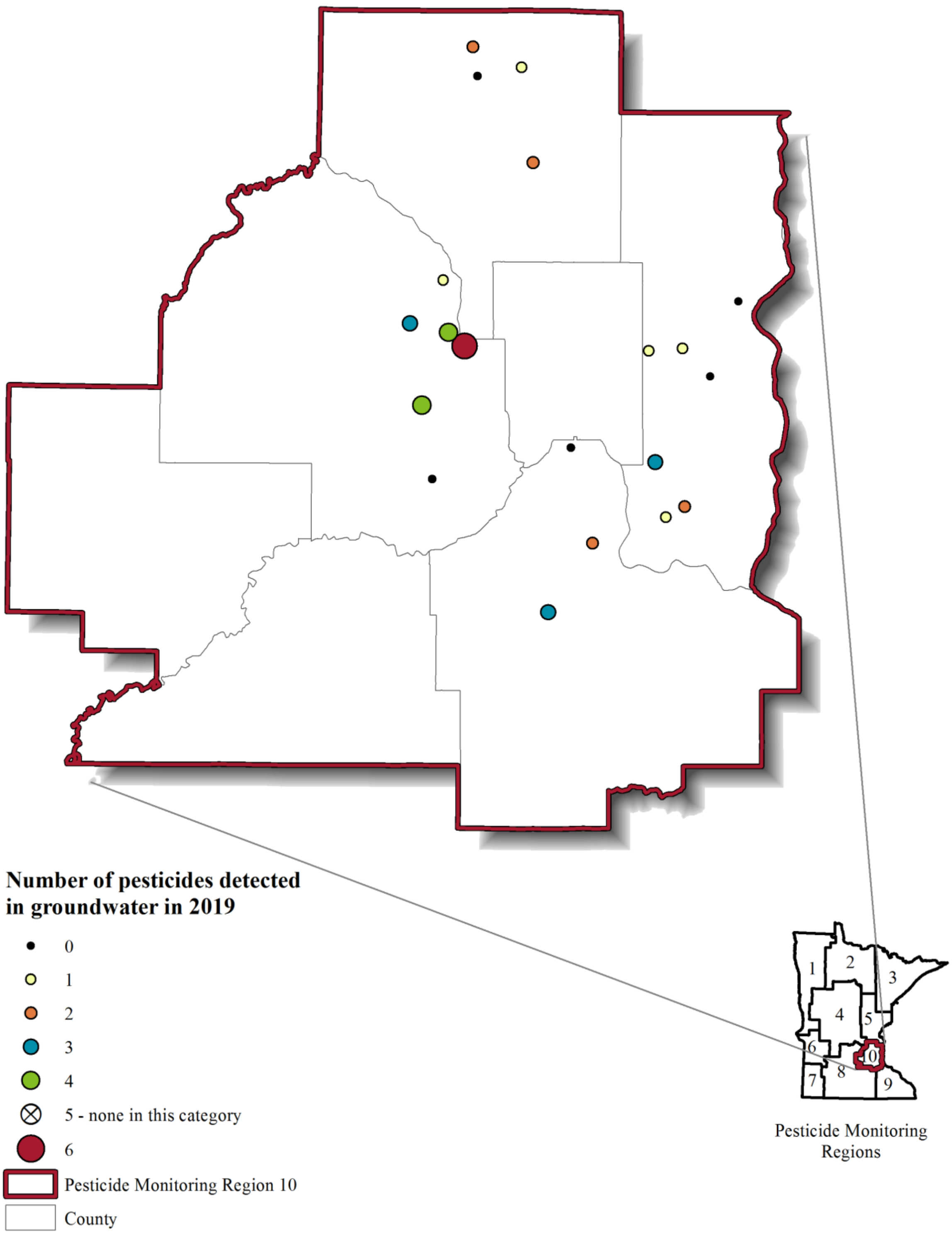


Table 2-11. 2019 MDA urban groundwater pesticide sampling results.

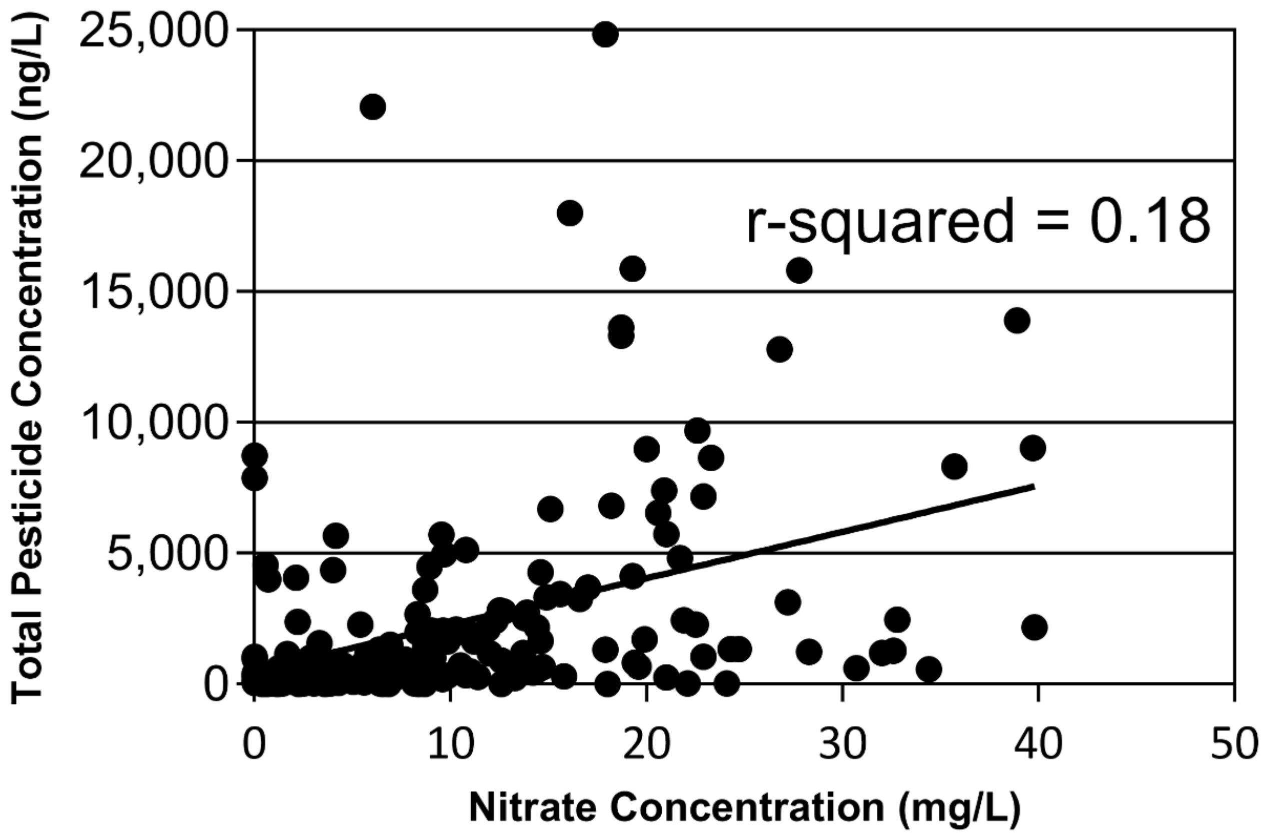
Pesticide Analyte	2019					
	Total Samples	Detections	Detection Frequency (%)	Maximum Concentration (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type
2,4-D	20	**2**	**10**	**228**	30,000	HRL_{18}
Acetochlor ESA	20	**2**	**10**	**47.7**	300,000	HRL_{18}
Alachlor ESA	20	**1**	**5**	**216**	50,000	RAA_{16}
Alachlor OXA	20	**1**	**5**	**35.8**	50,000	RAA_{16}
Aminopyralid	20	**2**	**10**	**84.0**	800,000	RA_{16}
Bromacil	20	**2**	**10**	**1,060**	30,000	RA_{14}
Hydroxyatrazine	20	**3**	**15**	**19.1**	20,000	RA_{14}
Imazapyr	20	**3**	**15**	**461**	900,000	RA_{14}
Imidacloprid	20	**1**	**5**	**6.55**	3,000	HBV_{19}
MCPP	20	**2**	**10**	**304**	4,000	RA_{14}
Metolachlor ESA	20	**10**	**50**	**399**	800,000	HRL_{11}
Metolachlor OXA	20	**6**	**30**	**61.1**	800,000	HRL_{11}
Picloram	20	**1**	**5**	**3,460**	300,000	RA_{14}

2.8 Nitrate and pesticide co-occurrence

The MDA staff collected a nitrate sample whenever pesticide samples were collected at all groundwater sites, except from the urban wells. Nitrate data were censored to the highest historical MRL (0.4 mg/L), due to the MDA Laboratory lowering their MRL for nitrate analysis in 2017. Censoring these data allows for direct comparisons over time and consistency in data analysis.

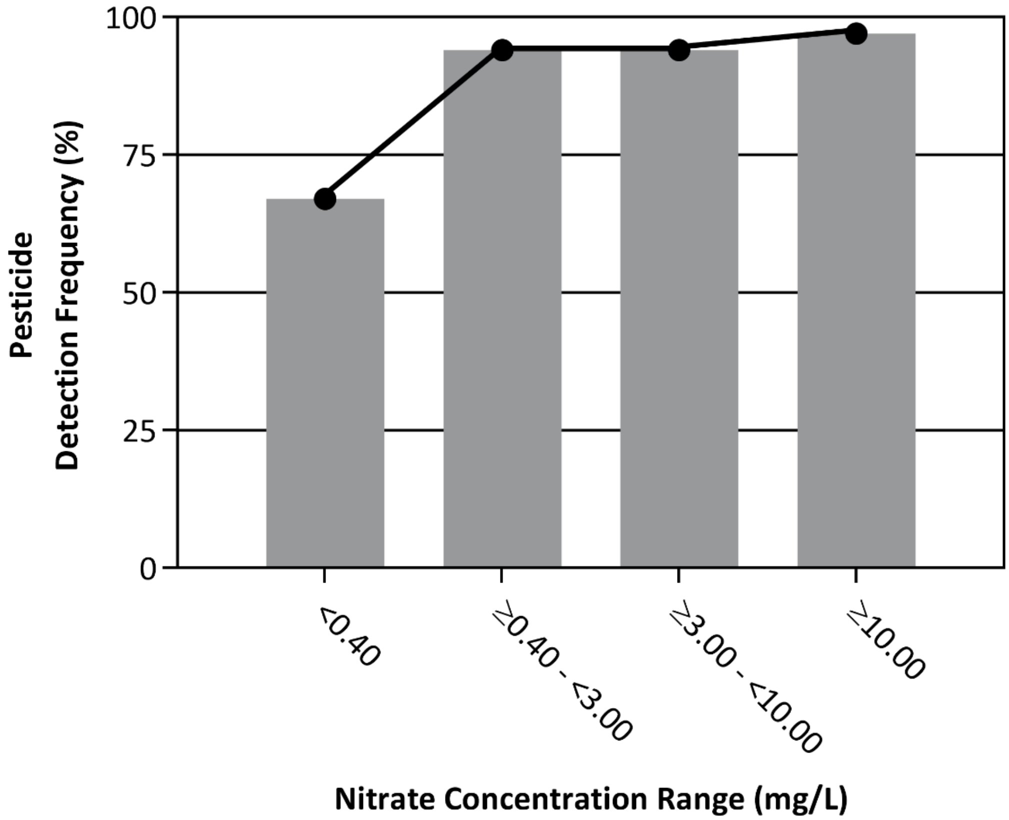
Nitrate presence and concentration in groundwater may indicate impacts from land use and vulnerability from surface contamination caused by human activities (MDA, 2006). The relationship between total pesticide concentration and nitrate concentration for the 2019 MDA groundwater sampling data is displayed in Figure 2-35 as the solid line. There is a general relationship between total pesticide concentration and nitrate concentration, where total pesticide concentration increases when nitrate concentration increases. This is a weak positive relationship (r-squared = 0.18), however, and should not be used to predict actual total pesticide concentration based on nitrate concentrations. There were instances where samples had elevated nitrate concentrations with no pesticide detections. Conversely, there were also instances of samples with no or low nitrate concentrations where pesticides were detected.

Figure 2-35. Relationship between nitrate and total pesticide concentrations from 2019 MDA groundwater sampling.



The general classification of nitrate levels used as guidance in Minnesota for evaluating human impact on nitrate concentrations in groundwater, as discussed later in Section 6.1, was utilized to evaluate the detection probability of pesticides (Figure 2-36). This graphic suggests that pesticides have an increasing likelihood of being detected when nitrate concentrations exceed 0.40 mg/L.

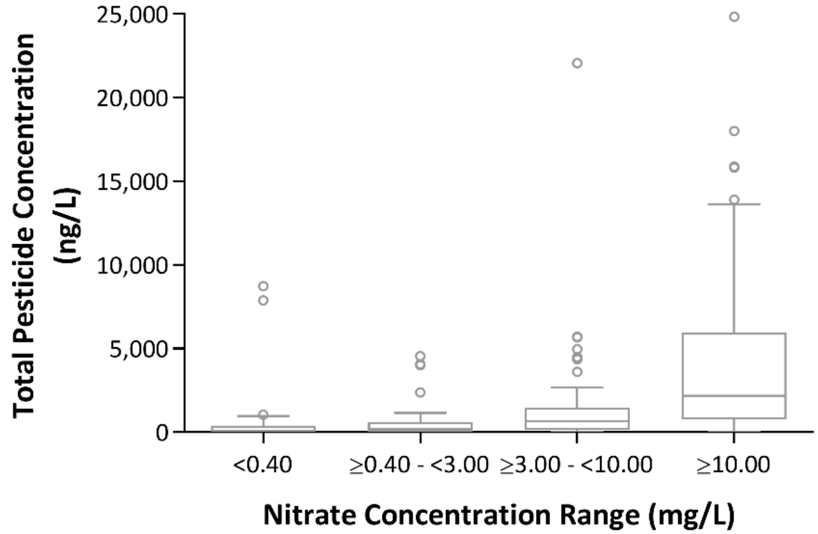
Figure 2-36. 2019 pesticide detection probability in shallow groundwater based on nitrate concentration ranges.



It was found that total pesticide concentration, and the number of pesticides detected in the MDA's shallow monitoring wells, increases as nitrate concentration exceeds 3.00 mg/L (Figures 2-37 and 2-38, respectively). As indicated in these figures:

- The variability in the total pesticide concentration increased as the detected nitrate concentration exceeded 3.00 mg/L.
- When nitrate concentrations exceeded 10.00 mg/L, it was more likely that the total pesticide concentrations exceeded 5,000 ng/L.
- The likelihood of detecting five or more pesticides in a sample increased when nitrate concentrations exceeded 3.00 mg/L.

Figure 2-37. Total pesticide concentration and median pesticide concentration based on nitrate concentration ranges from the 2019 MDA groundwater data.



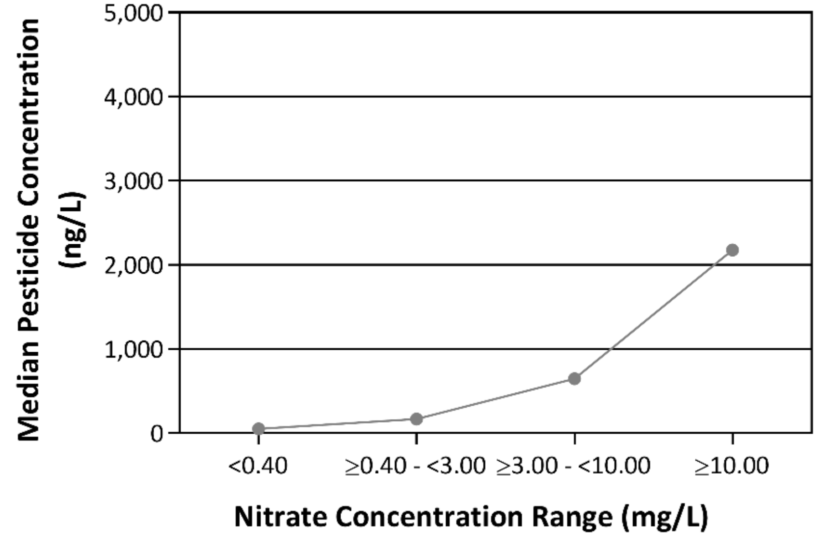
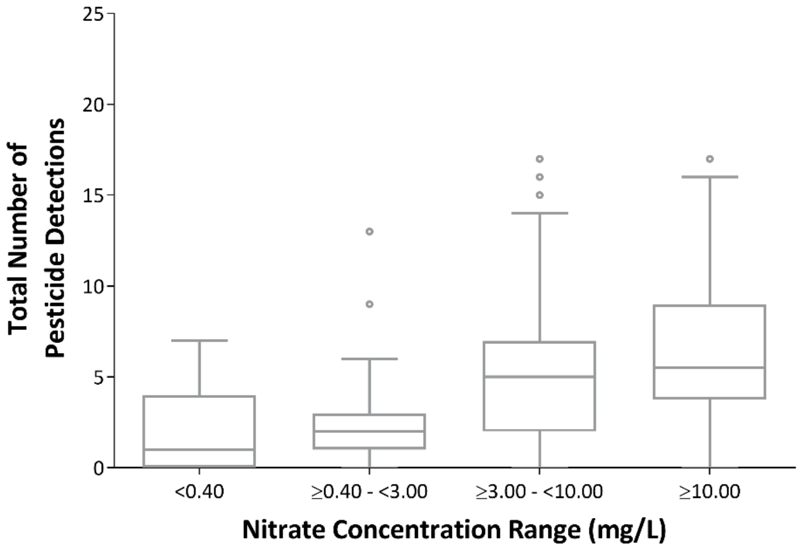
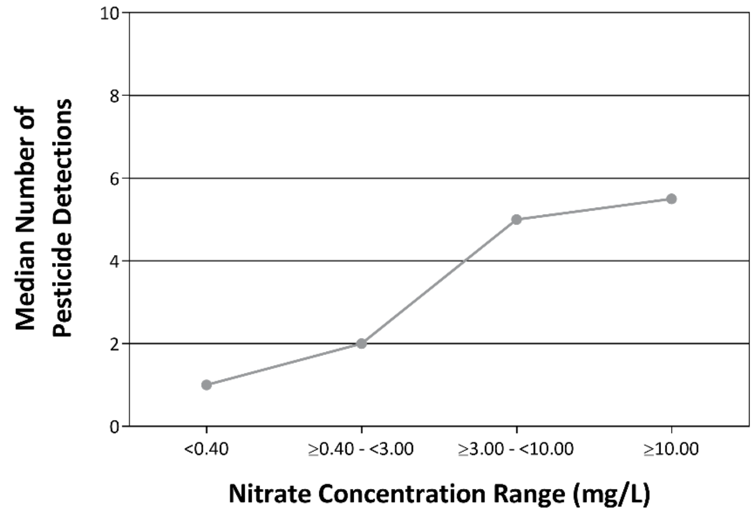


Figure 2-38. Total number of pesticide detections and median number of pesticide detections based on nitrate concentration ranges from the 2019 MDA groundwater data.





Section 3: Surface Water Monitoring Results

2019 Water Quality Monitoring Report

Section 3: Surface Water Monitoring Results

In 2006, the MDA began monitoring surface water from agricultural and urban watersheds utilizing a tier structure defined and described in the 2007 MDA Surface Water Quality Monitoring Design Document. Within the tier structure, there were three different levels of monitoring intensity.

- Tier 1 locations were distributed across the state and grab samples were collected eight times from May 1st through August 31st, targeting storm flow conditions if they occurred. The objective was to provide a general assessment of water quality during peak pesticide runoff and detection periods from watersheds throughout the state.
- Tier 2 locations were distributed across the state and included the same sampling regime as Tier 1 with the addition of a second "follow-up" grab sample if the sample was collected during storm flow conditions. This monitoring provided a duration component, to evaluate the length of time a pesticide concentration persists at a certain level.
- Tier 3 locations were located at specific watersheds in south central, southeast, and northwest Minnesota and were sampled using an equal-time increment (ETI) auto sampler to collect a sample over several days during storm flow conditions along with grab samples between stormflow events. This sampling regime provided a duration component to the pesticide concentration data collected during storm flow conditions.

Since 2015, the MDA added a third August sample collection period at Enhanced Tier 2 locations that had a chlorpyrifos detection within the previous five years.

A summary of the 2019 MDA Tier 1 through Tier 3 surface water monitoring location names and physical characteristics is provided in Appendix 7. The 2019 surface water quality data are provided in Appendix 8 (available only online at the MDA Monitoring and Assessment webpage). Appendix 9 contains site codes and sampling history for all current and historic MDA monitoring locations. Previously published reports and design documents are available at the MDA Monitoring and Assessment webpage. The MDA water quality data is also available for download through the National Water Quality Monitoring Council Portal.

Sample collection events at surface water locations included a variety of analytical methods, including GC-MS/MS, LC-MS/MS, glyphosate LC-MS/MS, nutrient, and sediment methods. Please refer to the annual work plan for more information regarding specific monitoring details at each location. Throughout this section, the word "sample" has been used to refer to each individual analysis performed at the MDA Laboratory.

Field staff described stream flow conditions during sample collections as being either base flow or storm flow. Base flow conditions represented stable, lower flow, or, in some cases, a falling stream level and were often associated with higher stream transparency. Storm flow conditions represented increased stream level (*i.e.,* increased flow) and generally have lower stream transparency. Storm flow conditions occurred most frequently following periods of rainfall generated runoff or snowmelt and are typically

the periods when most elevated herbicide concentrations occur. The stream condition designations were used to analyze the results for providing a more thorough interpretation of the pesticide water quality data and to aid in assessing transport mechanisms related when and how pesticides were entering Minnesota surface waters.

The MDA also conducted pesticide water quality monitoring through projects that are not a part of the routine river and stream tier monitoring program. This included annual rainfall monitoring for pesticides (see Section 3.7) and survey monitoring of lakes, wetlands or rivers/streams on a rotating schedule, often in cooperation with other state and federal agencies, but were not this year. The MDA also conducts intensive pesticide water quality monitoring with the Root River Pesticide Study (see Section 4.2).

3.1 2019 Pesticide monitoring season summary

During the 2019 monitoring season:

- 101 pesticide samples were collected from eight Tier 1 and one Urban Tier 1 locations.
- 806 pesticide samples were collected from 19 Tier 2, 17 Enhanced Tier 2, and three Urban Tier 2 locations.
- 254 pesticide samples were collected from seven Tier 3 locations.
- 43 pesticide samples were collected from four rainfall-monitoring locations.
- 6 pesticide samples were collected from Double Lake.

3.1.1 2019 Maximum pesticide detections in rivers and streams and reference values

Table 3-0 presents the 2019 river and stream maximum detections and the lowest applicable pesticide water quality reference value. In general, Minnesota Rule Chap. 7050 water quality standards supersede other reference values because they have been reviewed and promulgated for their applicability to Minnesota's water resources and because of their potential use in making water body impairment decisions under the federal Clean Water Act. For pesticides without a Minnesota standard, the lowest USEPA Office of Pesticide Program (OPP) aquatic life benchmark is presented. In the absence of a Minnesota standard and USEPA OPP aquatic life benchmark, the MDA calculated a value from the toxicity data provided in USEPA risk assessment documents. Table 3-0 only includes a comparison of the numeric component of the associated reference value, without consideration for the duration component of the reference value as a conservative approach to protect aquatic life. The MPCA will assess these detections to determine if a violation of the standard occurred, which would lead to a waterbody impairment. All river and stream data are presented in Table 3-0. A review of the 2019 data collected at Class 1B and 2A waters and those associated human health-based reference values are presented in Section 3.1.2. Additional information and reference values are presented in Appendix 10.

There were 69 different pesticides or pesticide degradates detected from the routine tier river and stream monitoring in 2019. Please refer to Table 3-0 for water quality reference values when reviewing the 2019 surface water data.

Table 3-0. 2019 summary of river and stream maximum detections and lowest applicable pesticide water quality reference values.

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Surface Water Reference Value Type	PMRs with Detection (U=Urban)
2,4,5-T	380	0	0	<50	—	—	None
2,4,5-TP	380	0	0	<50	—	—	None
2,4-D	380	323	85	10,900	79,200	USEPA OPP Chronic (f)	1,3,4,5,6,7,8,9,10,U
2,4-DB	380	0	0	<20	1,000,000	USEPA OPP Acute (f)	None
Acetamiprid	380	0	0	<25	2,100	USEPA OPP Chronic (i)	None
Acetochlor	689	345	50	58,000	3,600	Minn. 7050 Chronic T	1,4,5,6,7,8,9,10,U
Acetochlor ESA	380	317	83	3,440	9,900,000	USEPA OPP Chronic (n)	1,4,5,6,7,8,9,10,U
Acetochlor OXA	380	294	77	4,300	—	—	1,4,5,6,7,8,9,10,U
Acifluorfen	373	10	3	226	>355,000	USEPA OPP Chronic (n)	6,8,10
Afidopyropen	373	0	0	<50	123	Calculated from EFED Chronic (i)	None
Alachlor	689	0	0	<30	59,000	Minn. 7050 Chronic T	None
Alachlor ESA	380	199	52	589	3,600,000	USEPA OPP Chronic (n)	4,5,6,8,9,10,U
Alachlor OXA	380	2	1	39.1	>47,500,000	USEPA OPP Acute (i)	8
Aldicarb Sulfone	380	0	0	<15	140,000	USEPA OPP Acute (i)	None
Aldicarb Sulfoxide	380	0	0	<50	21,500	USEPA OPP Acute (i)	None
Aminopyralid	380	17	4	151	1,360,000	USEPA OPP Chronic (f)	7,9
Atrazine	689	463	67	7,230	10,000	Minn. 7050 Chronic T	1,4,5,6,7,8,9,10,U
Deisopropylatrazine	380	61	16	158	2,500,000	USEPA OPP Chronic (n)	1,6,7,8,9,10,U
Desethylatrazine	689	226	33	518	1,000,000	USEPA OPP Chronic (n)	1,4,5,6,7,8,9,10,U
Didealkylatrazine	380	135	36	262	>50,000,000	USEPA OPP Acute (f)(i)	1,6,7,8,9,10,U
Hydroxyatrazine	380	368	97	220	>1,500,000	USEPA OPP Acute (f)	1,4,5,6,7,8,9,10,U
Azoxystrobin	380	31	8	1,910	44,000	USEPA OPP Chronic (i)	1,8,9,10,U
Benfluralin	689	0	0	<25	1,900	USEPA OPP Chronic (f)	None
Bensulfuron-methyl	380	0	0	<16.7	7,800	USEPA OPP Chronic (n)	None
Bensulide	380	0	0	<250	11,000	USEPA OPP Chronic (i)	None
Bentazon	380	73	19	3,120	4,500,000	USEPA OPP Chronic (n)	1,6,7,8,9,10,U
Benzovindiflupyr	380	1	<1	158	950	USEPA OPP Chronic (f)	9
Bicyclopyrone	380	18	5	56.9	13,000	USEPA OPP Chronic (v)	8,9,10
Bicyclopyrone SYN503870	380	0	0	<100	—	—	None
Bifenthrin	689	0	0	<20	1.3	USEPA OPP Chronic (i)	None
Boscalid	380	0	0	<50	116,000	USEPA OPP Chronic (f)	None
Bromacil	380	4	1	60.4	6,800	USEPA OPP Chronic (n)	1,6,7,8
Bromoxynil	380	1	<1	31.3	2,500	USEPA OPP Chronic (i)	8
Carbaryl	380	0	0	<25	500	USEPA OPP Chronic (i)	None
Carbendazim	380	11	3	205	990	USEPA OPP Chronic (f)	1,6,8,U
Carbofuran	380	0	0	<13.3	750	USEPA OPP Chronic (i)	None
Chlorantraniliprole	380	1	<1	55.2	4,470	USEPA OPP Chronic (i)	8
Chlorimuron-ethyl	380	0	0	<20	270	USEPA OPP Chronic (v)	None
Chlorothalonil	689	0	0	<50	600	USEPA OPP Chronic (i)	None
Chlorpyrifos	689	3	<1	70.2	41	Minn. 7050 Chronic T	1,6,8
Chlorpyrifos Oxon	380	0	0	<40	—	—	None
Clethodim sulfone	380	2	1	190	—	—	1,10
Clethodim sulfoxide	380	23	6	336	—	—	1,6,8,9,10
Clomazone	689	0	0	<15	167,000	USEPA OPP Chronic (n)	None
Clopyralid	380	130	34	4,590	6,900,000	USEPA OPP Chronic (n)	1,4,6,7,8,9,10,U
Clothianidin	380	114	30	201	50	USEPA OPP Chronic (i)	1,6,7,8,9,10
Cyanazine	380	0	0	<25	—	—	None
Cyanazine Acid	373	0	0	<10	—	—	None

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Surface Water Reference Value Type	PMRs with Detection (U=Urban)
Cyanazine Amide	373	0	0	<10	—	—	None
Deethylcyanazine	373	0	0	<25	—	—	None
Deethylcyanazine Acid	373	55	15	104	—	—	1,6,7,8
Deethylcyanazine Amide	373	0	0	<25	—	—	None
Cyantraniliprole	380	0	0	<100	6,560	USEPA OPP Chronic (i)	None
Cyfluthrin	689	0	0	<100	7.4	USEPA OPP Chronic (i)	None
Diazinon	689	0	0	<30	170	USEPA OPP Chronic (i)	None
Diazinon Oxon	689	0	0	<75	—	—	None
Dicamba	380	97	26	9,580	61,000	USEPA OPP Chronic (n)	1,6,7,8,9,10,U
Dichlobenil	689	11	2	584	30,000	USEPA OPP Chronic (v)	U
Dichlorprop	380	0	0	<50	77,000	USEPA OPP Chronic (n)	None
Dichlorvos	689	1	<1	116	5.8	USEPA OPP Chronic (i)	U
Dicrotophos	380	0	0	<25	1,700	USEPA OPP Chronic (i)	None
Difenoconazole	380	0	0	<25	860	USEPA OPP Chronic (f)	None
Dimethenamid	689	237	34	3,100	8,900	USEPA OPP Chronic (v)	1,4,6,7,8,9,10,U
Dimethenamid ESA	380	279	73	988	—	—	1,4,5,6,7,8,9,10,U
Dimethenamid OXA	380	154	41	710	—	—	1,4,6,7,8,9,10,U
Dimethoate	380	0	0	<50	500	USEPA OPP Chronic (i)	None
Dinotefuran	380	0	0	<20	6,360,000	USEPA OPP Chronic (f)	None
Disulfoton	689	0	0	<60	10	USEPA OPP Chronic (i)	None
Disulfoton Sulfone	380	0	0	<20	140	USEPA OPP Chronic (i)	None
Diuron	380	5	1	26.2	2,400	USEPA OPP Chronic (n)	9,U
EPTC	689	5	1	123	40,000	USEPA OPP Chronic (f)	1,6
Esfenvalerate	689	0	0	<150	17	USEPA OPP Chronic (i)	None
Ethalfluralin	689	0	0	<50	400	USEPA OPP Chronic (f)	None
Ethofumesate	689	40	6	3,510	300,000	USEPA OPP Chronic (i)	1,6,8,10
Flufenacet OXA	380	0	0	<8.3	—	—	None
Flumetsulam	380	103	27	1,240	3,100	USEPA OPP Chronic (v)	1,6,7,8,9,10,U
Flupyradifurone	380	0	0	<10	3,300	Calculated from EFED Chronic (i)	None
Flutianil	373	0	0	<25	2,240	Calculated from EFED Chronic(f)	None
Flutianil OC 56574	373	0	0	<50	—	—	None
Flutianil OC 56635	373	0	0	<25	>48,400,000	Calculated from EFED Acute (i)	None
Flutriafol	380	3	1	31.7	310,000	USEPA OPP Chronic (i)	8,9
Fluxapyroxad	380	8	2	27.1	22,000	Calculated from EFED Chronic (f)	1,9
Fomesafen	380	162	43	2,130	92,000	USEPA OPP Chronic (n)	1,6,7,8,9,10,U
Fonofos	689	0	0	<15	—	—	None
Glyphosate	92	9	10	5,880	11,900,000	USEPA OPP Chronic (v)	1,6,8,9,10,U
AMPA	92	0	0	<5,100	249,500,000	USEPA OPP Acute (f)	None
Halauxifen-methyl	380	0	0	<10	135	USEPA OPP Chronic (v)	None
Halauxifen acid	380	0	0	<25	580	USEPA OPP Chronic (v)	None
Halosulfuron-methyl	380	0	0	<30	42	USEPA OPP Chronic (v)	None
Hexazinone	380	0	0	<10	7,000	USEPA OPP Chronic (n)	None
Imazamethabenz-methyl	380	0	0	<5	—	—	None
Imazamethabenz Acid	380	0	0	<10	—	—	None
Imazamox	380	2	1	91.3	8,000	USEPA OPP Chronic (v)	1
Imazapic	380	5	1	20.5	6,220	USEPA OPP Chronic (v)	8,U
Imazapyr	380	25	7	118	18,000	USEPA OPP Chronic (v)	1,9,10,U
Imazaquin	380	0	0	<16.7	140,000,000	USEPA OPP Acute (f)(i)	None
Imazethapyr	380	173	46	240	8,100	USEPA OPP Chronic (v)	1,4,6,7,8,9,10,U
Imidacloprid	380	103	27	32	10	USEPA OPP Chronic (i)	1,6,7,8,9,10,U
Imidacloprid-olefin	380	0	0	<50	—	—	None

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Surface Water Reference Value Type	PMRs with Detection (U=Urban)
Imidacloprid-urea	380	0	0	<50	>47,400,000	USEPA OPP Acute (i)	None
Isoxaflutole	380	0	0	<40	4,900	USEPA OPP Chronic (v)	None
Isoxaflutole DKN	380	0	0	<50	75,000	USEPA OPP Chronic (v)	None
Lambda-Cyhalothrin	689	0	0	<75	2	USEPA OPP Chronic (i)	None
Linuron	380	0	0	<20	90	USEPA OPP Chronic (i)	None
Malathion	689	0	0	<50	49	USEPA OPP Acute (i)	None
Mandestrobin	380	0	0	<25	60,000	Calculated from EFED Chronic (n)	None
MCPA	380	51	13	701	20,000	USEPA OPP Chronic (v)	1,4,6,7,8,9,10,U
MCPB	380	0	0	<20	210,000	USEPA OPP Chronic (v)	None
MCPP	380	15	4	222	14,000	USEPA OPP Chronic (n)	U
Mesotrione	380	40	11	468	17,700	USEPA OPP Chronic (v)	1,6,7,8,9,10
Metalaxyl	380	2	1	14.9	100,000	USEPA OPP Chronic (i)	8,10
Methoxychlor	689	0	0	<50	700	USEPA OPP Acute (i)	None
Metolachlor	689	543	79	23,100	23,000	Minn. 7050 Chronic T	1,4,5,6,7,8,9,10,U
Metolachlor ESA	380	340	89	7,930	24,000,000	USEPA OPP Acute (f)	1,4,5,6,7,8,9,10,U
Metolachlor OXA	380	341	90	1,680	7,700,000	USEPA OPP Acute (i)	1,4,5,6,7,8,9,10,U
Metribuzin	689	44	6	810	8,100	USEPA OPP Chronic (n)	1,6,7,8,9
Metribuzin DA	380	32	8	159	–	–	6,7,8,9
Metribuzin DADK	380	0	0	<500	–	–	None
Metribuzin DK	380	0	0	<500	–	–	None
Metsulfuron-methyl	380	4	1	60.3	360	USEPA OPP Chronic (v)	9,10,U
Momfluorothrin	380	0	0	<50	600	USEPA OPP Acute (f)	None
Myclobutanil	380	0	0	<10	830,000	USEPA OPP Chronic (n)	None
Nicosulfuron	380	0	0	<26.6	43,000,000	USEPA OPP Chronic (i)	None
Norflurazon	380	0	0	<20	9,700	USEPA OPP Chronic (n)	None
Norflurazon-desmethyl	380	0	0	<50	–	–	None
Oxadiazon	689	0	0	<75	5,200	USEPA OPP Chronic (n)	None
Oxathiapiprolin	380	0	0	<100	>140,000	USEPA OPP Chronic (n)	None
Oxydemeton-methyl	380	0	0	<20	5,000	USEPA OPP Chronic (f)	None
Parathion-methyl	689	0	0	<100	250	USEPA OPP Chronic (i)	None
Parathion-methyl Oxon	380	0	0	<25	–	–	None
Pendimethalin	689	0	0	<75	5,200	USEPA OPP Chronic (n)	None
Phorate	689	0	0	<25	210	USEPA OPP Chronic (i)	None
Picloram	380	0	0	<41.6	550,000	USEPA OPP Chronic (f)	None
Picoxystrobin	380	0	0	<50	1,000	USEPA OPP Chronic (i)	None
Prometon	689	6	1	360	98,000	USEPA OPP Chronic (n)	6
Prometryn	380	1	<1	4.31	1,040	USEPA OPP Chronic (n)	U
Propachlor	689	0	0	<30	13,500	USEPA OPP Chronic (n)	None
Propachlor ESA	380	0	0	<30	–	–	None
Propachlor OXA	380	0	0	<10	–	–	None
Propazine	689	16	2	75.1	24,800	USEPA OPP Chronic (n)	1,6,7,8,9
Propiconazole	380	26	7	727	21,000	USEPA OPP Chronic (n)	1,8,9,10,U
Pydiflumetofen	373	0	0	<25	42,000	Calculated from EFED Chronic (i)	None
Pyraclostrobin	380	0	0	<25	1,500	USEPA OPP Chronic (n)	None
Pyroxasulfone	380	24	6	302	380	Calculated from EFED Chronic (n)	1,7,8,9
Saflufenacil	380	131	34	512	42,000	USEPA OPP Chronic (n)	1,4,6,7,8,9,10,U
Sedaxane	380	0	0	<75	110,000	Calculated from EFED Chronic (f)	None
Siduron	380	0	0	<6.7	6,000	USEPA OPP Chronic (i)	None
Simazine	689	0	0	<75	6,000	USEPA OPP Chronic (n)	None
Sulfentrazone	380	194	51	2,710	28,800	USEPA OPP Chronic (v)	1,6,7,8,9,10,U
Sulfometuron-methyl	380	8	2	51.3	450	USEPA OPP Chronic (v)	U

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Surface Water Reference Value Type	PMRs with Detection (U=Urban)
Tebuconazole	380	13	3	45.6	11,000	USEPA OPP Chronic (f)	1,8,U
Tebupirimfos	689	0	0	<30	11	USEPA OPP Chronic (i)	None
Tembotrione	380	21	6	505	5,200	USEPA OPP Chronic (v)	1,6,8,9,10
Terbufos	689	0	0	<30	30	USEPA OPP Chronic (i)	None
Tetraconazole	380	4	1	16.8	190,000	USEPA OPP Chronic (i)	1,6,8
Thiacloprid	380	0	0	<50	970	USEPA OPP Chronic (i)	None
Thiamethoxam	380	43	11	241	740	USEPA OPP Chronic (i)	1,6,8,9,10
Thifensulfuron-methyl	380	0	0	<16.7	1,590	USEPA OPP Chronic (v)	None
Thiobencarb	380	0	0	<8.3	1,000	USEPA OPP Chronic (i)	None
Tolfenpyrad	689	0	0	<100	81.5	USEPA OPP Acute (f)	None
Tolpyralate	380	0	0	<50	6,670	USEPA OPP Chronic (v)	None
Triallate	689	0	0	<50	14,000	USEPA OPP Chronic (i)	None
Triasulfuron	380	0	0	<23.3	190,000	USEPA OPP Chronic (v)	None
Triclopyr	380	23	6	2,310	26,000	USEPA OPP Chronic (f)	1,6,7,8,9,U
Trifluralin	689	0	0	<50	1,900	USEPA OPP Chronic (f)	None
zeta-Cypermethrin	689	0	0	<500	0.59	USEPA OPP Chronic (i)	None

Key to value types and symbols for surface water reference values in Table 3-0.
In general, Minnesota Rule Chap. 7050 water quality standards supersede other reference values because they have been reviewed and promulgated for their applicability to Minnesota's water resources, and because of their potential use in making water body impairment decisions under the federal Clean Water Act.

Reference Values are given for all target pesticide analytes when available. Some analytes do not have an established reference value from the sources listed below.

Minn. 7050 - Standard established in Minn. Rule Chap. 7050.

USEPA OPP - Aquatic life benchmarks based on toxicity values derived from data available to the USEPA's OPP supporting registration of the pesticide are provided only when a Minnesota Rule Chap. 7050 value is not available. Current values posted by the USEPA's OPP may differ from those of previous MDA reports. See USEPA's website for more detailed information and definitions.

Calculated from EFED - In the absence of an applicable USEPA/OPP reference value(s) for a pesticide compound, the MDA calculated the value from USEPA/OPP toxicity data from the EPA's Environmental Fate and Effects Division (EFED).

— – For some analytes, reference values have not been developed, identified or evaluated.
(f) – reference value for fish.
(i) – reference value for invertebrates.
(n) – reference value for nonvascular plants.
(v) – reference value for vascular plants.
T – Chronic Standard values are toxicity-based for aquatic organisms and protective for an exposure duration of 4 days.

3.1.2 2019 Class 2A and 2Bd Waters comparison to Health Based Values

As part of MDA's river and stream network, six rivers or streams are protected as cold water aquatic life and/or are protected for drinking water (Class 1B, 2A, and 2Bd waters) including location(s) in PMRs 1, 5, 8, and 9. Minnesota Rule Chap. 7050 water quality standards provides additional standards for these waters. Twelve pesticide analytes have additional standards (Appendix 10). Of these twelve pesticide analytes, only 2,4-D and atrazine were detected in 2019 at the Class 2A and 2Bd waters. 2,4-D was detected in 71% of the 66 samples collected from these Class 2A and 2Bd waters and the maximum detection was 1,940 ng/L (approximately 3% of the human health-based Minnesota chronic standard). Atrazine was detected in 66% of the 86 samples collected from these Class 2A and 2Bd waters. Atrazine was detected above the 3,400 ng/L human health-based Minnesota chronic standard twice in PMR 9. The MPCA will assess these detections to determine if an exceedance of the standard occurred.

3.1.3 2019 Quality Assurance/Quality Control summary

Quality assurance/quality control (QA/QC) samples were collected and analyzed as a part of the routine surface water pesticide samples collected. All QA/QC samples were planned prior to the start of the season and analyzed by the MDA Laboratory using GC-MS/MS, LC-MS/MS, and/or glyphosate LC-MS/MS methods. The MDA sets a target of 10% of the total surface water samples collected for each analytical method, to be analyzed as QA/QC samples, which includes blanks and replicates/duplicates.

There were 128 QA/QC samples collected (11% of the routine 1,210 surface water pesticide samples) which included 30 equipment blanks, 32 field blanks and 66 field replicates/duplicates. There were no pesticide detections in the equipment blank or field blank samples. Field replicates/duplicates were compared by MDA staff against their respective paired routine sample and all analyte concentrations were determined to be within their acceptable ranges of variability. The MDA Laboratory also completed internal QA/QC measures that included sample blanks, spikes and spike duplicates with each batch of samples analyzed that are reviewed before the release of the data.

All QA/QC data were excluded from the data analysis of this report; however, the QA/QC data are available in Appendix 8.

3.1.4 2019 Pesticide detections equal to or greater than 50% of a reference value

The MDA uses the Minnesota Administrative Rules (Minn. Rule Chap. 7050) and USEPA Office of Pesticide Program (OPP) aquatic life benchmarks to determine the lowest appropriate reference value(s) to compare against the data. Surface water detections equal to or greater than 50% of the lowest applicable numeric reference value are tracked (Table 3-1). All surface water pesticide data are reviewed annually by the MPCA for water quality assessment purposes, to identify impaired waters, and to determine if additional review or development of a pesticide water quality standard(s) is needed. A pesticide concentration that has been measured above the numeric reference value is assessed by the MPCA for the duration, or the length of time the concentration persisted in the waterbody, to determine if an "exceedance" above the reference value occurred. For most chronic exposure standards, four days

is typically the duration of interest. For acute and maximum exposure, a single concentration value from a grab sample can be compared to the reference value.

Acetochlor, atrazine, chlorpyrifos, clothianidin, dichlorvos, imidacloprid, metolachlor and pyroxasulfone had detections equal to or greater than 50% of an applicable surface water numeric reference value in 2019 (Table 3-1).

Table 3-1. 2019 river and stream detections equal to or greater than 50% of an applicable numeric reference value.

Pesticide	Reference Value (ng/L)	Samples	Detections	Detections ≥ 50% and Below the Numeric Reference Value	Detections ≥ Numeric Reference Value	PMR with Detection(s) ≥ 50% of Reference Value (U=Urban)	Locations with Detection(s) ≥ 50% of Reference Value
Acetochlor	3,600	689	345	21	11	1,6,7,8,9,10	20
Atrazine*	3,400	86	57	1	2	9	2
Atrazine	10,000	603	406	4	0	6,7,9	4
Chlorpyrifos	41	689	3	0	3	1,6,8	3
Clothianidin	50	380	114	52	62	1,6,7,8,9,10	22
Dichlorvos	5.8	689	1	0	1	U	1
Imidacloprid	10	380	103	45	58	1,6,7,8,9,10,U	25
Metolachlor	23,000	689	543	2	1	6,7	2
Pyroxasulfone	380	380	24	2	0	8,9	2

**Applies only to Class 2A and 2Bd waterbodies.*

The principal findings from Table 3-1 include:

- No pesticide detections in 2019 exceeded an acute or maximum reference value. All detections presented in Table 3-1 are compared to the lowest applicable chronic reference value.
- Acetochlor
    - One sample from PMR 6 and 10 samples from five locations in PMR 8 had acetochlor concentrations greater than the numeric MPCA 3,600 ng/L chronic standard.
    - Twenty-one samples from PMR 1 (two locations), PMR 6 (two locations), PMR 7 (one location), PMR 8 (five locations), PMR 9 (three locations) and PMR 10 (two locations) had acetochlor concentrations greater than 50%, but below the numeric MPCA 3,600 ng/L chronic standard.
- Atrazine
    - 3,400 ng/L human-health based standard (Class 2A and 2Bd waters only):
        - Two samples collected from one location in PMR 9 had an atrazine concentration greater than the chronic numeric 3,400 ng/L human-health based standard.
        - One sample collected in PMR 9 had an atrazine concentration greater than 50%, but below the chronic numeric 3,400 ng/L human-health based standard.
    - 10,000 ng/L aquatic life standard:
        - Four samples collected from PMR 6 (one location), PMR 7 (one location) and PMR 9 (two locations) had atrazine concentrations greater than 50%, but below the numeric Minnesota Rule Ch. 7050 chronic standard.

- Chlorpyrifos
    - Three samples from PMRs 1, 6, and 8 had chlorpyrifos concentrations greater than the numeric Minnesota Rule Ch. 7050 41 ng/L chronic standard but below the Minnesota Rule Ch. 7050 83 ng/L maximum standard.
- Clothianidin
    - Sixty-two samples from PMR 6 (two locations), PMR 7 (one location), PMR 8 (five locations), PMR 9 (six locations) and PMR 10 (one location) had clothianidin concentrations greater than the numeric chronic USEPA OPP 50 ng/L reference value.
    - Fifty-two samples from PMR 1 (two locations), PMR 6 (two locations), PMR 7 (two locations), PMR 8 (six locations), PMR 9 (five locations), and PMR 10 (three locations) had clothianidin concentrations greater than 50%, but below the numeric chronic USEPA OPP 50 ng/L reference value.
- Dichlorvos
    - One sample collected from an urban location had a dichlorvos concentration greater than the numeric USEPA OPP 5.8 ng/L benchmark value.
- Imidacloprid
    - Fifty-eight samples from PMR 1 (three locations), PMR 6 (two locations), PMR 7 (one location), PMR 8 (six locations), PMR 9 (six locations), PMR 10 (three locations) and two urban locations had imidacloprid concentrations greater than the numeric chronic USEPA OPP 10 ng/L reference value.
    - Forty-five samples from PMR 1 (three locations), PMR 6 (two locations), PMR 7 (one location), PMR 8 (six locations), PMR 9 (five locations), PMR 10 (three locations) and four urban locations had imidacloprid concentrations greater than 50%, but below the numeric chronic USEPA OPP 10 ng/L reference value.
- Metolachlor
    - One sample collected from PMR 6 had a metolachlor concentration greater than the numeric MPCA 23,000 ng/L chronic standard.
    - One sample each collected from PMRs 6 and 7 had metolachlor concentrations greater than 50%, but below the numeric MPCA 23,000 ng/L chronic standard.
- Pyroxasulfone
    - One sample each collected from PMRs 8 and 9 had a pyroxasulfone concentration greater than 50%, but below the 380 ng/L numeric reference value calculated from EFED documents.

3.1.5 Pesticide water quality impairments

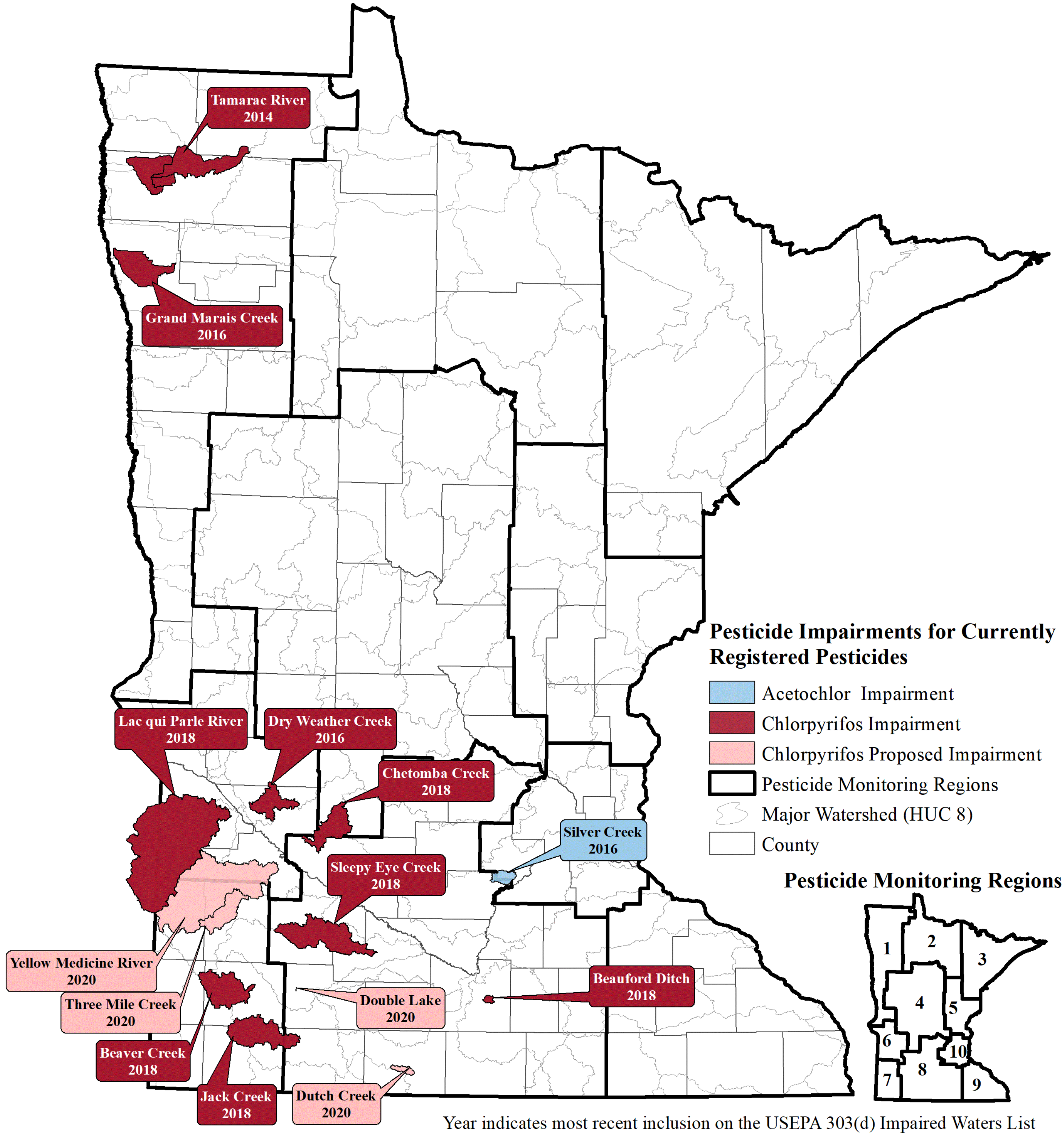
There are fourteen waterbodies in Minnesota that are either designated, or proposed to be designated, by the MPCA as impaired on the USEPA 303(d) Impaired Waters List for currently registered pesticides. These listings result from the MPCA assessments of the MDA surface water pesticide data (Table 3-2 and Figure 3-0). The 2019 MDA pesticide water quality data will be reviewed by MPCA as part of the 2022 USEPA 303(d) Impaired Waters List assessment process.

Table 3-2. Minnesota pesticide impairments for currently registered pesticides.

Pesticide	Impaired Waters List Year	Stream	County	Violation that Resulted in Impairment
Acetochlor	2016	Silver Creek	Carver	chronic (3,600 ng/L) Minnesota water quality standard
Chlorpyrifos	2018	Beauford Ditch	Blue Earth	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2018	Beaver Creek	Murray	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2018	Chetomba Creek	Renville	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2020	Double Lake	Cottonwood	chronic (41 ng/L) Minnesota water quality standard
Chlorpyrifos	2016	Dry Weather Creek	Chippewa	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2020	Dutch Creek	Martin	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2014/2016	Grand Marais Creek	Polk	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2018	Jack Creek	Jackson	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2018	Lac qui Parle River	Lac qui Parle	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2018	Sleepy Eye Creek	Redwood	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2014	Tamarac River	Marshall	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2020	Three Mile Creek	Lyon	maximum (83 ng/L) Minnesota water quality standard
Chlorpyrifos	2020	Yellow Medicine River	Yellow Medicine	maximum (83 ng/L) Minnesota water quality standard

Three waterbodies have been removed from the USEPA 303(d) Impaired Waters List for currently registered pesticides. The Le Sueur River and Beauford Ditch were designated as impaired for acetochlor in 2008 and were removed from the USEPA 303(d) Impaired Waters List in 2014. Seven Mile Creek was designated as impaired on the 2012 Impaired Waters List for chlorpyrifos and was removed from the USEPA 303(d) Impaired Waters List in 2018. Removal from the USEPA 303(d) Impaired Waters List typically occurs after several years of water quality monitoring without pesticide detections above the applicable standards.

Figure 3-0. Minnesota pesticide water quality impairments for currently registered pesticides.



3.1.6 Newly detected pesticides in Minnesota surface water

The MDA MAU works closely with the MDA Pesticide Technical Unit to identify pesticide compounds that have the potential to affect Minnesota water resources. If analytical methods are available, these compounds may be added to the analyte list. Section 1.7 provides additional information on the selection of pesticide analytes, as well as the pesticide compounds added to the analyte list in 2019.

- Acifluorfen
  - First registered with USEPA in 1980.
  - MDA began analysis in 2019.
    - Ten detections from five locations in PMR 6 (one location), PMR 8 (three locations) and PMR 10 (one location).
    - Statewide detection frequency was 3%.
    - The maximum detection (226 ng/L) occurred in PMR 10 and was less than <0.1% of the USEPA aquatic life benchmark.
- Deethylcyanazine acid
  - Deethylcyanazine acid is a cyanazine degradate. The herbicide cyanazine was first registered with the USEPA in 1971 and was widely used on corn until all use stopped in 2002, when the registration of this pesticide was voluntarily cancelled.
  - MDA began analysis in 2019.
    - Fifty-five detections from six locations in PMR 1 (one location), PMR 6 (two locations), PMR 7 (one location) and PMR 8 (two locations).
    - Statewide detection frequency was 15%.
    - The maximum detection (104 ng/L) occurred in PMR 6.
      - There are no established reference values for deethylcyanazine acid in surface water.
    - Additional analysis of cyanazine compounds are presented in Section 5.

3.2 Tier river and stream pesticide monitoring

Samples were collected at the 55 tier river and stream locations as shown in Figure 3-1. Additional information related to the characteristics and monitoring history of each sample location is available in Appendix 7. Figure 3-1 also presents past monitoring locations (1991 through 2018) to provide context for data collected prior to 2019.

3.2.1 Tier 1 and Tier 2 monitoring overview

The primary objective was to collect grab samples from each location during major storm events, once in each of the eight two-week sample collection periods from May 1st to August 31st. If no storm events occurred during a given period, a base flow grab sample was collected near the end of the two-week period. If a storm event occurred, each Enhanced Tier 2, Tier 2, and Urban Tier 2 location has a follow-up sample collected between 24 and 96 hours after the first sample.

An Enhanced Tier 2 location was a location that has had a chlorpyrifos detection(s) in the previous five years. The Enhanced Tier 2 locations had one additional sample collection period in August to collect samples when chlorpyrifos is typically applied.

Sample collection events at Tier 1, Tier 2 and Enhanced Tier 2 location included GC-MS/MS pesticide analysis, and at least one location per agricultural PMR included LC-MS/MS and/or glyphosate LC-MS/MS pesticide analysis. LC-MS/MS and glyphosate LC-MS/MS analyses were targeted to surface water locations that served as municipal drinking water sources, and/or generally exhibited elevated GC-MS/MS pesticide concentrations compared to other locations in the PMR. Sample collection events at Urban Tier 1 and Urban Tier 2 locations included both GC-MS/MS and LC-MS/MS pesticide analysis. Glyphosate LC-MS/MS analysis was conducted at two urban locations.

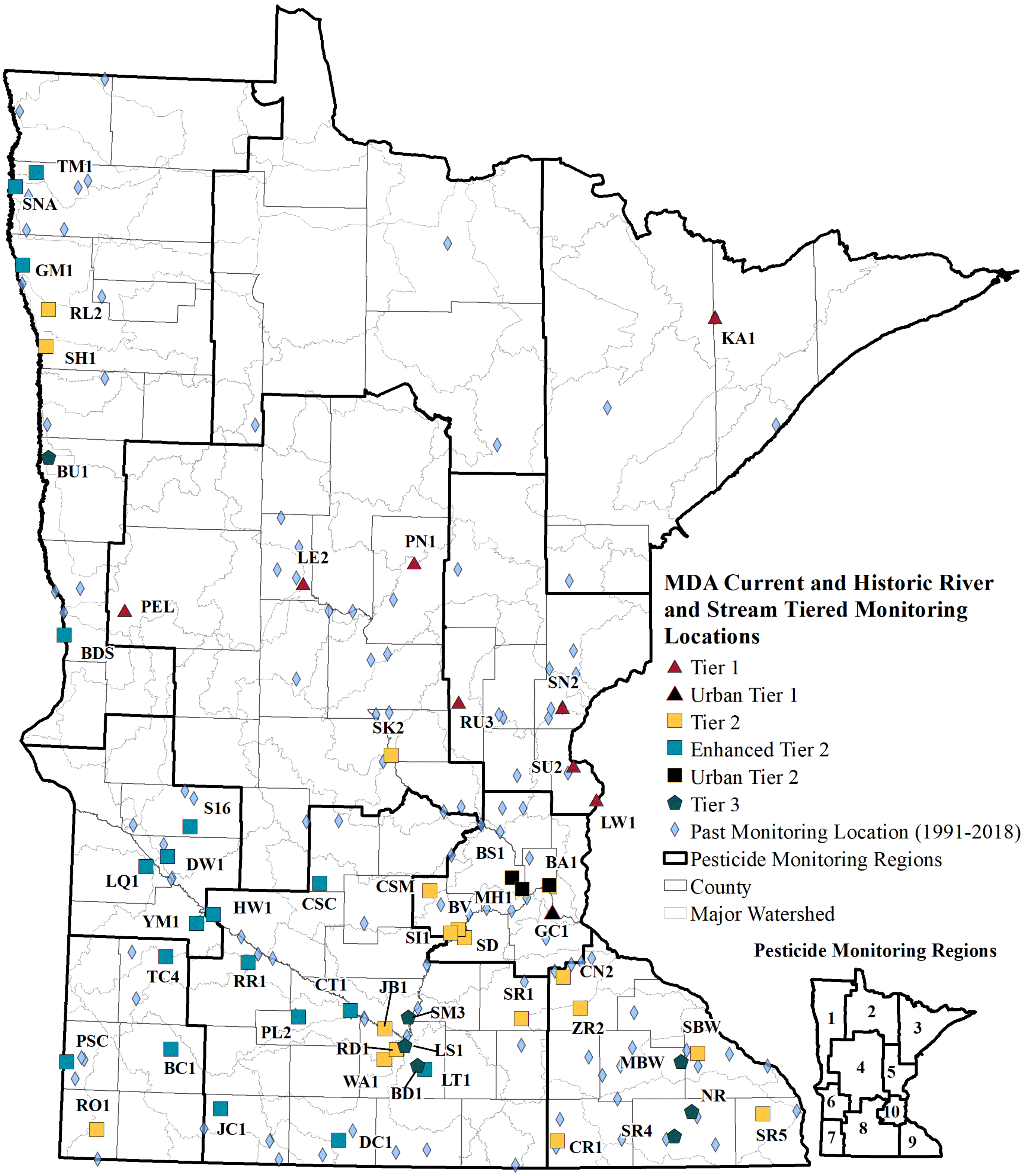
Nitrate-nitrogen, dissolved orthophosphate, and total phosphorus samples were collected and analyzed with all pesticide samples. The MDA Laboratory conducted all analyses, and a summary of the results can be found in Section 6.

3.2.2 Tier 3 monitoring overview

Tier 3 locations are the most intensively monitored watersheds in the MDA tier monitoring network and were established in watersheds with a history of elevated pesticide detections that had the possibility to result in water quality impairments. Since 2006, the MDA has collected ETI composite samples during storm flow conditions from mid-April through August at Tier 3 locations so that the data is readily comparable to 4-day duration-based chronic water quality standards or reference values. Grab samples are also collected during base flow periods. Sampling frequency is reduced from September through mid-April.

All samples collected at Tier 3 locations included GC-MS/MS pesticide analysis. LC-MS/MS and glyphosate LC-MS/MS analyses were conducted on samples collected during storm flow conditions. Inorganic analyte sampling, which included the nutrients nitrate-nitrogen, dissolved orthophosphate, total phosphorus, and total suspended solids (at select locations), were also collected. The summary of results for the inorganic analyte sampling can be found in Section 6.

Figure 3-1. 2019 and past MDA river and stream tier monitoring locations.



3.2.3 2019 Tier river and stream pesticide monitoring results

Table 3-3 presents the 2019 water quality results for pesticide analytes detected at a tier river or stream location. During the 2019 season, there were 85 samples collected at the Tier 1 locations and 16 samples at the Urban Tier 1 location. There were 342 samples collected at the Tier 2 locations, 374 samples at the Enhanced Tier 2 locations, and 90 samples at the Urban Tier 2 locations. At the Tier 3 locations, 254 samples were collected. Of the 1,161 samples presented in Table 3-3, 1,015 samples were grab samples, and 146 samples were multi-day composite samples. The flow condition of the stream during the sample collection event is also included.

Key data findings for this data analysis include:

- Sixty-nine of the 166 pesticide analytes were detected at least once.
  - Thirty-nine of the 69 detected pesticide analytes were detected in less than 10% of the samples.
  - The most commonly detected parent pesticides were the herbicide compounds 2,4-D, metolachlor, and atrazine. They were detected in 85%, 79%, and 67% of samples, respectively.
  - Various degradates of the herbicides acetochlor, alachlor, atrazine, dimethenamid, and metolachlor were detected more frequently than their respective parent compounds.
- Acetochlor, atrazine, chlorpyrifos, clothianidin, dichlorvos, imidacloprid, metolachlor, and pyroxasulfone all had detections equal to or greater than 50% of an applicable numeric reference value in 2019.
  - Of the 265 total detections equal to or greater than 50% of an applicable numeric reference value in 2019, 44 were herbicide detections, and 221 were insecticide detections.
    - Ninety-eight percent of the herbicide detections and 83% of insecticide detections, were equal to or greater than 50% of an applicable numeric reference value occurred in storm flow.
- Glyphosate was detected in 10% of all samples (15% of storm flow samples).
- Dicamba was detected in 26% of all samples (33% of storm flow samples).
- Three neonicotinoid insecticides (clothianidin, imidacloprid, and thiamethoxam) were detected in 30, 27, and 11% of samples, respectively.
  - Clothianidin was detected 114 times.
    - 52 detections were greater than or equal to 50% of the numeric USEPA OPP 50 ng/L benchmark.
    - 62 detections were greater than the numeric USEPA OPP 50 ng/L benchmark.
  - Imidacloprid was detected 103 times.
    - 45 detections were greater than or equal to 50% of the numeric USEPA OPP 10 ng/L benchmark.
    - 58 detections were greater than the numeric USEPA OPP 10 ng/L benchmark.
  - All 43 thiamethoxam detections were less than 50% of the numeric USEPA OPP 740 ng/L benchmark.

- Analysis for acifluorfen and deethylcyanazine acid began in 2019, and both were detected.
    - Acifluorfen was detected in 3% of samples.
    - Deethylcyanazine acid was detected in 15% of samples.
- Herbicides and herbicide degradates were most frequently detected; however, most detections were well below the applicable water quality reference values.
- Insecticides were detected less frequently than herbicides and herbicide degradates, however, the frequency of detection for concentrations greater than 50% of the applicable reference value were higher for insecticides compared to herbicides and herbicide degradates.
- Fungicides were detected less frequently than insecticides or herbicides. There were no fungicide detections that were greater than 50% of the applicable reference value.
- Samples collected during storm flow conditions generally exhibited higher pesticide detection frequencies and concentrations than samples collected during base flow conditions.

Table 3-3. 2019 Tier river and stream location pesticide results.

River and Stream Detected Compounds	All Samples					Base flow						Storm flow					
	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum (ng/L)	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum* (ng/L)	Samples ≥50% of Reference Value	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum* (ng/L)	Samples ≥50% of Reference Value
2,4-D	380	323	85	70.0	10,900	147	110	75	37.0	10,900	0	233	213	91	90.0	7,310	0
Acetochlor	689	345	50	30.0	58,000	297	70	24	<30	2,270	1	392	275	70	111	58,000	31
Acetochlor ESA	380	317	83	423	3,440	147	112	76	303	2,530	0	233	205	88	518	3,440	0
Acetochlor OXA	380	294	77	242	4,300	147	97	66	118	3,200	--	233	197	85	280	4,300	--
Acifluorfen	373	10	3	<25	226	140	2	1	<25	54.0	0	233	8	3	<25	226	0
Alachlor ESA	380	199	52	45	589	147	71	48	<41.6	589	0	233	128	55	47.0	423	0
Alachlor OXA	380	2	1	<33.3	39.1	147	0	0	<33.3	<33.3	0	233	2	1	<33.3	39.1	0
Aminopyralid	380	17	4	<25	151	147	5	3	<25	36.5	0	233	12	5	<25	151	0
Atrazine	689	463	67	48.0	7,230	297	173	58	36.0	2,180	0	392	290	74	68.0	7,230	7
Deisopropylatrazine	380	61	16	<25	158	147	10	7	<25	77.6	0	233	51	22	<25	158	0
Desethylatrazine	689	226	33	<50	518	297	69	23	<50	212	0	392	157	40	<50	518	0
Hydroxyatrazine	380	368	97	37	220	147	139	95	31.0	209	0	233	229	98	42.0	220	0
Didealkylatrazine	380	135	36	<50	262	147	37	25	<50	117	0	233	98	42	<50	262	0
Azoxystrobin	380	31	8	<10	1,910	147	11	7	<10	117	0	233	20	9	<10	1,910	0
Bentazon	380	73	19	<5	3,120	147	30	20	<5	138	0	233	43	18	<5	3,120	0
Benzovindiflupyr	380	1	<1	<50	158	147	0	0	<50	<50	0	233	1	<1	<50	158	0
Bicyclopyrone	380	18	5	<10	56.9	147	3	2	<10	16.1	0	233	15	6	<10	56.9	0
Bromacil	380	4	1	<30	60.4	147	0	0	<30	<30	0	233	4	2	<30	60.4	0
Bromoxynil	380	1	<1	<25	31.3	147	0	0	<25	<25	0	233	1	<1	<25	31.3	0
Carbendazim	380	11	3	<10	205	147	5	3	<10	31.5	0	233	6	3	<10	205	0
Chlorantraniliprole	380	1	<1	<50	55.2	147	0	0	<50	<50	0	233	1	<1	<50	55.2	0
Chlorpyrifos	689	3	<1	<40	70.2	297	1	<1	<40	70.2	1	392	2	1	<40	56.6	2
Clethodim sulfone	380	2	1	<100	190	147	0	0	<100	<100	0	233	2	1	<100	190	0
Clethodim sulfoxide	380	23	6	<50	336	147	5	3	<50	336	0	233	18	8	<50	323	0
Clopyralid	380	130	34	<41.6	4,590	147	31	21	<41.6	679	0	233	99	42	<41.6	4,590	0
Clothianidin	380	114	30	<25	201	147	16	11	<25	74.4	16	233	98	42	<25	201	98

River and Stream Detected Compounds	All Samples					Base flow						Storm flow					
	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum (ng/L)	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum* (ng/L)	Samples ≥50% of Reference Value	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum* (ng/L)	Samples ≥50% of Reference Value
Deethylcyanazine	373	55	15	<25	104	140	17	12	<25	104	0	233	38	16	<25	102	0
Dicamba	380	97	26	<50	9,580	147	21	14	<50	2,600	0	233	76	33	<50	9,580	0
Dichlobenil	689	11	2	<5	584	297	7	2	<5	47.7	0	392	4	1	<5	584	0
Dichlorvos	689	1	<1	<15	116	297	0	0	<15	<15	0	392	1	<1	<15	116	1
Dimethenamid	689	237	34	<15	3,100	297	54	18	<15	928	0	392	183	47	<15	3,100	0
Dimethenamid ESA	380	279	73	20	988	147	94	64	14.0	411	--	233	185	79	23	988	--
Dimethenamid OXA	380	154	41	<10	710	147	47	32	<10	217	--	233	107	46	<10	710	--
Diuron	380	5	1	<13.3	26.2	147	2	1	<13.3	20.2	0	233	3	1	<13.3	26.2	0
EPTC	689	5	1	<10	123	297	2	1	<10	123	0	392	3	1	<10	32.5	0
Ethofumesate	689	40	6	<50	3,510	297	7	2	<50	518	0	392	33	8	<50	3,510	0
Flumetsulam	380	103	27	<50	1,240	147	30	20	<50	344	0	233	73	31	<50	1,240	0
Flutriafol	380	3	1	<10	31.7	147	0	0	<10	<10	0	233	3	1	<10	31.7	0
Fluxapyroxad	380	8	2	<10	27.1	147	1	1	<10	11.3	0	233	7	3	<10	27.1	0
Fomesafen	380	162	43	<50	2,130	147	41	28	<50	1,890	0	233	121	52	56.0	2,130	0
Glyphosate	92	9	10	<1.02	5.88	38	1	3	<1.02	1.54	0	54	8	15	<1.02	5.88	0
Imazamox	380	2	1	<13.3	91.3	147	0	0	<13.3	<13.3	0	233	2	1	<13.3	91.3	0
Imazapic	380	5	1	<10	20.5	147	2	1	<10	20.5	0	233	3	1	<10	19.6	0
Imazapyr	380	25	7	<8.3	118	147	10	7	<8.3	118	0	233	15	6	<8.3	52.0	0
Imazethapyr	380	173	46	<6.7	240	147	46	31	<6.7	151	0	233	127	55	8.00	240	0
Imidacloprid	380	103	27	<5	32.0	147	20	14	<5	27.8	20	233	83	36	<5	32.0	83
MCPA	380	51	13	<5	701	147	21	14	<5	205	0	233	30	13	<5	701	0
MCPP	380	15	4	<50	222	147	6	4	<50	176	0	233	9	4	<50	222	0
Mesotrione	380	40	11	<50	468	147	5	3	<50	192	0	233	35	15	<50	468	0
Metalaxyl	380	2	1	<8.3	14.9	147	0	0	<8.3	<8.3	0	233	2	1	<8.3	14.9	0
Metolachlor	689	543	79	93	23,100	297	196	66	46.0	5,750	0	392	347	89	205	23,100	3
Metolachlor ESA	380	340	89	959	7,930	147	124	84	801	4,030	0	233	216	93	1,090	7,930	0
Metolachlor OXA	380	341	90	221	1,680	147	124	84	160	1,130	0	233	217	93	263	1,680	0
Metribuzin	689	44	6	<75	810	297	5	2	<75	244	0	392	39	10	<75	810	0

River and Stream Detected Compounds	All Samples					Base flow						Storm flow					
	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum (ng/L)	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum* (ng/L)	Samples ≥50% of Reference Value	Total Samples	Detections	Detection Frequency (%)	Median* (ng/L)	Maximum* (ng/L)	Samples ≥50% of Reference Value
Metribuzin DA	380	32	8	<25	159	147	7	5	<25	120	--	233	25	11	<25	159	--
Metsulfuron-methyl	380	4	1	<23.3	60.3	147	1	1	<23.3	41.3	0	233	3	1	<23.3	60.3	0
Prometon	689	6	1	<100	360	297	1	<1	<100	360	0	392	5	1	<100	353	0
Prometryn	380	1	<1	<3.3	4.31	147	0	0	<3.3	<3.3	0	233	1	<1	<3.3	4.31	0
Propazine	689	16	2	<25	75.1	297	0	0	<25	<25	0	392	16	4	<25	75.1	0
Propiconazole	380	26	7	<10	727	147	8	5	<10	42.4	0	233	18	8	<10	727	0
Pyroxasulfone	380	24	6	<50	302	147	4	3	<50	89.8	0	233	20	9	<50	302	2
Saflufenacil	380	131	34	<15	512	147	28	19	<15	200	0	233	103	44	<15	512	0
Sulfentrazone	380	194	51	52	2,710	147	48	33	<50	583	0	233	146	63	94.0	2,710	0
Sulfometuron-methyl	380	8	2	<8.3	51.3	147	4	3	<8.3	34.5	0	233	4	2	<8.3	51.3	0
Tebuconazole	380	13	3	<10	45.6	147	5	3	<10	18.6	0	233	8	3	<10	45.6	0
Tembotrione	380	21	6	<50	505	147	6	4	<50	224	0	233	15	6	<50	505	0
Tetraconazole	380	4	1	<10	16.8	147	0	0	<10	<10	0	233	4	2	<10	16.8	0
Thiamethoxam	380	43	11	<25	241	147	5	3	<25	38.6	0	233	38	16	<25	241	0
Triclopyr	380	23	6	<50	2,310	147	9	6	<50	2,310	0	233	14	6	<50	203	0

**Non-detections are reported as "less than MRL" (<MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*

3.3 2019 PMR analysis of surface water pesticides of concern

The Commissioner of Agriculture has designated three pesticides as a surface water pesticide of concern (POC). Designation as a POC initiated the development of chemical specific best management practices (BMPs) and increased water quality monitoring and data analysis. The criteria for such designations are presented in the Pesticide Management Plan (PMP). The herbicides acetochlor and atrazine were designated as a POC in 2002 and in 2012 for the insecticide chlorpyrifos.

This section provides a summary of the 2019 POC data at the PMR level. This analysis is based upon data from all tier monitoring locations (Figure 3-1) and provides an opportunity to review detection tendencies in each PMR across Minnesota (Table 3-4). Within this section, the concentration summary statistics are presented with the 2019 MRL for each analyte.

A total of 689 samples were collected statewide and analyzed with the GC-MS/MS analytical method for pesticides, including acetochlor, atrazine and chlorpyrifos. Forty-nine percent (336) of the total samples were collected in PMRs 8 and 9.

- Acetochlor
  - Statewide detection frequency was 50%.
    - The detection frequency ranged from 3% in PMR 5 to 84% in PMR 10 for PMRs with at least one detection.
  - No detections occurred in PMR 3.
  - The maximum concentration occurred in PMR 8 (58,000 ng/L).
  - The maximum concentrations in PMRs 6 and 8 were greater than the numeric MPCA 3,600 ng/L chronic aquatic life standard.
- Atrazine
  - Statewide detection frequency was 67%.
    - The detection frequency ranged from 25% in PMR 4 to 79% in PMR 9 for PMRs with at least one detection.
  - The maximum concentration occurred in PMR 9 (7,230 ng/L).
  - No detections occurred in PMR 3.
  - No detections were greater than the MPCA 10,000 ng/L chronic aquatic life standard.
  - Two samples collected from one location in PMR 9 had an atrazine concentration greater than the numeric 3,400 ng/L chronic human-health based standard.
- Chlorpyrifos
  - Statewide detection frequency was <1%.
    - The detection frequency ranged from <1% in PMR 8 to 2% in PMR 6 for PMRs with at least one detection.
  - The maximum concentration occurred in PMR 6 (70.2 ng/L).
  - No detections occurred in PMRs 3, 4, 5, 7, 9, 10, and at urban locations.

- The maximum concentrations in PMRs 1, 6, and 8 were greater than the numeric MPCA 41 ng/L chronic aquatic life standard and all detections were below the MPCA 83 ng/L maximum aquatic life standard.

Table 3-4. 2019 PMR analysis of acetochlor, atrazine and chlorpyrifos tier river and stream water quality data.

		Acetochlor					Atrazine					Chlorpyrifos				
PMR	Samples	Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)	Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)	Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)
1	75	11	15	<30	144	2,970	43	57	38.6	451	2,890	1	1	<40	<40	45.3
3	8	0	0	<30	<30	<30	0	0	<30	<30	<30	0	0	<40	<40	<40
4	36	6	17	<30	42.4	66.1	9	25	<30	40.1	280	0	0	<40	<40	<40
5	32	1	3	<30	<30	270	11	34	<30	75.8	113	0	0	<40	<40	<40
6	53	38	72	115	2,206	3,670	34	64	46.4	464	5,810	1	2	<40	<40	70.2
7	52	31	60	46.3	976	2,690	40	77	56.6	493	5,070	0	0	<40	<40	<40
8	212	145	68	93.7	1,232	58,000	160	75	73.2	790	3,840	1	<1	<40	<40	56.6
9	124	60	48	<30	723	3,050	98	79	62.5	783	7,230	0	0	<40	<40	<40
10	49	41	84	130	956	2,760	34	69	51.7	439	1,150	0	0	<40	<40	<40
Urban	48	12	25	<30	122	350	34	71	36.4	97.4	553	0	0	<40	<40	<40
Total	689	345	50	<30	811	58,000	463	67	48.2	528	7,230	3	<1	<40	<40	70.2

3.4 Long-term analysis of surface water pesticides of concern

This section presents a review of the MDA's long-term water quality data for each POC. Each POC will be presented independently and there will be variation in the data that are presented in each section to best display the data. The herbicide POC (acetochlor and atrazine) were detected frequently but most detections were well below the applicable reference value. Regional trends and summaries were calculated for acetochlor and atrazine. Chlorpyrifos was infrequently detected; however, most detections were above the applicable numeric reference values. As such, all chlorpyrifos detections will be presented. A description of the data included in the graphics is provided within the subsection.

Additional historic data are available in previous MDA Water Quality Monitoring Reports available at the MDA Monitoring and Assessment webpage. The MDA water quality data is also available for download through the National Water Quality Monitoring Council Portal.

3.4.1 Long term POC data summary approach

Long term herbicide POC data summary approach

In the case of acetochlor and atrazine, data collected in May and June from 2007 to 2019 at the Tier 1 and Tier 2 river and stream locations are included for evaluation in their respective sections. Historically, Tier 1 and Tier 2 monitoring was only conducted in May and June. However, in 2012 and 2013, the Tier 2 and Tier 1 monitoring seasons, respectively, were extended to include July and August to provide more comprehensive pesticide monitoring of late season insecticide and fungicide applications. In addition, many locations have transitioned from a Tier 1 to Tier 2 monitoring structure since 2012 due to elevated herbicide and insecticide detections. These two changes resulted in more samples collected later in the growing season. Tier 3, survey locations, and special study locations were excluded due to different monitoring platforms utilized for sample collection, and variation in the number of samples collected annually. To ensure a comparable dataset was available for trend analysis overtime, only data collected in May and June from Tier 1 and Tier 2 locations were included.

To account for changing MRLs overtime, all acetochlor and atrazine data were censored to the highest historical MRL. The MRL for acetochlor and atrazine was 50 ng/L from 2007 through 2012 and was reduced to 30 ng/L in 2013. All detections below 50 ng/L (including "present <MRL" detections) were censored to non-detections. Both the current and historical MRLs were low as compared to the reference values.

Basic annual summary statistics were calculated on a PMR level. Annually, the MDA collected between four and eight samples from at least four different stream and/or river locations within each agricultural PMR (PMRs 1, 4, 5, 6, 7, 8, 9, 10, and urban). There were small year-to-year variations in sample numbers per PMR based on the number of locations, monitoring intensity (*e.g.,* tier level), and environmental conditions (*e.g.,* rainfall). On a statewide level, total May and June sample counts have ranged from 175 samples in 2007 to 267 samples in 2014. In 2019,

there were 253 samples analyzed. PMR 2 does not have any monitoring locations, and PMR 3 has only one location due to low pesticide usage in these regions (statistics not calculated).

Monitoring was targeted towards storm flow conditions; however, sample collection events did occur during both base and storm flow conditions. To ensure a large enough sample population to compute statistics, this analysis does not differentiate between samples collected during base or storm flow conditions. Annual variability is expected in pesticide detections related to the timing of pesticide applications, rainfall events, and run-off events within each PMR. The MDA performed a Mann Kendall trend analysis for data collected in May and June (2007 through 2019) from Tier 1 and Tier 2 locations using a two-sided hypothesis test at a 90% confidence level (p-value of 0.10). Mann Kendall trend results can be found in Appendix 6 (available upon request). Long term analysis of acetochlor and atrazine are presented in Section 3.4.2 and Section 3.4.3, respectively.

Long term insecticide POC data summary approach

Chlorpyrifos has been monitored since 2005 and every detection (regardless of the MRL) in all surface waterbodies, and rainfall, were included because some of the MRLs were higher, or very similar to the reference values. Long term chlorpyrifos analysis can be found in Section 3.4.4.

Most chlorpyrifos data were collected through the MDA Tier network. From 2007 through 2011, samples were collected primarily in May and June. The Tier 1 and Tier 2 monitoring seasons were extended into July and August in 2013 and 2012, respectively, to include the fungicide and insecticide application period in Minnesota. Additionally, each location with a chlorpyrifos detection(s) in the previous five years received an additional monitoring round in August through the Enhanced Tier 2 monitoring level that was introduced in 2015. Most data were collected from May through August; however, limited sampling was completed from September through April.

The MDA sampled survey locations in 2010, 2011, 2012, and 2015 which received one or two samples per location. The survey locations are randomly selected locations across Minnesota and sample collection generally occurred during base flow conditions. Additionally, the MDA has had several special study locations. These special study locations were monitored to provide more in-depth pesticide water quality data in specific watersheds. The survey and special study locations are included in this analysis and are primarily responsible for the year-to-year variation in the number of monitored locations.

3.4.2 Long-term MDA acetochlor surface water quality data

Acetochlor has been analyzed and detected by the MDA in surface water since 1995, and the MDA designated acetochlor as a POC in 2002. Acetochlor is a chloroacetanilide herbicide, used primarily on corn, with water quality standards in statute (Minn. Rule Ch. 7050 chronic standard = 3,600 ng/L; Minn. Rule Ch. 7050 maximum standard = 86,000 ng/L). Information on how acetochlor data were analyzed can be found in Section 3.4.1.

3.4.2.1 MDA acetochlor water quality summary in river and streams

Long term trend results are presented for acetochlor at Tier 1 and Tier 2 locations from 2007 through 2019 in Figure 3-2 and Figure 3-3. Figure 3-2 presents the data spatially while Figure 3-3 presents the detection frequency, median concentration, and 90th percentile concentration overtime. Please note that the concentration ranges on the y-axis vary among the different PMRs. Lines on the figures represent a 4th order polynomial smooth. The polynomial smooth is a nonparametric curve fitting method which generated a line that represented the general tendency of the data over time based upon the data itself rather than being constrained by assumptions associated with fitting a specific equation to the data. The generated line can be utilized for visual assessment of the data to investigate if there are any general patterns or trends in the data that would otherwise be difficult to see (Helsel and Hirsch, 2002).

- Trend results are presented in Figure 3-2. Concentration and detection frequency graphics are presented in Figure 3-3.
- Detection frequency trends:
  - No trend was observed in PMRs 1, 4, 5, or urban.
  - A statistically significant increasing trend was observed in PMRs 6, 7, 8, 9, and 10.
- Median concentration trends:
  - Median values were below the MRL in PMRs 1, 4, 5, and urban.
  - A trend that was not statistically significant (no trend) was observed in PMR 7.
  - A statistically significant increasing trend was observed in PMRs 6, 8, 9, and 10.
- 90th percentile trends:
  - A trend that was not statistically significant (no trend) was observed in PMRs 1, 4, 5, and 9.
  - A statistically significant increasing trend was observed in PMRs 6, 7, 8, 10, and urban.

Figure 3-2. 2007 through 2019 PMR acetochlor trend analysis maps for data collected in May and June from Tier 1 and Tier 2 monitoring locations.

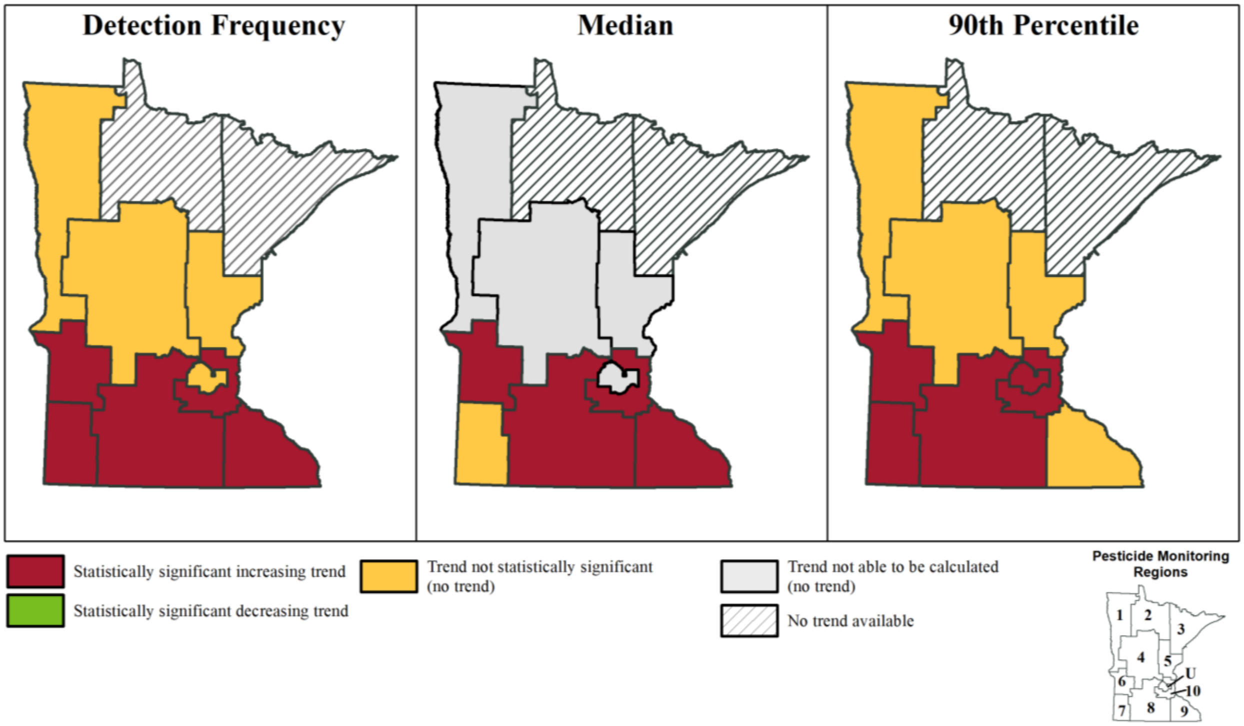
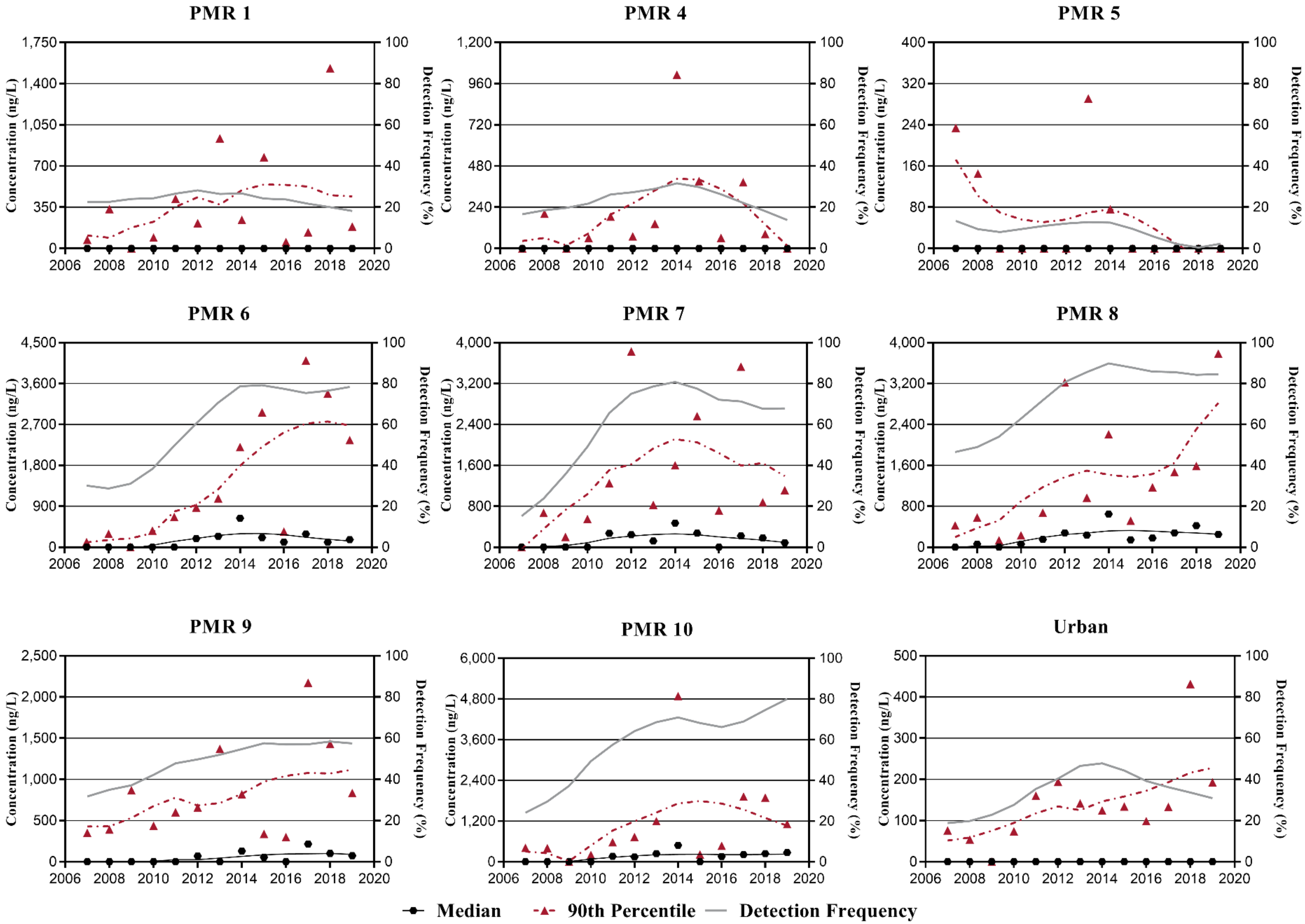


Figure 3-3. Acetochlor concentration and detection frequency by PMR, 2007 through 2019.



Minnesota Rule Ch. 7050 chronic standard = 3,600 ng/L

3.4.2.2 MDA acetochlor water quality summary in lakes and wetlands

The MDA collected 240 samples from 191 lakes from 2007 through 2019 (Table 3-5). Acetochlor was detected in six samples collected from four lakes and detections occurred in 2009, 2012, 2017 and 2018. The maximum concentration was 320 ng/L or approximately 9% of the numeric Minn. Rule Ch. 7050 chronic standard of 3,600 ng/L.

Table 3-5. MDA water quality summary of acetochlor in Minnesota lakes.

Year	Samples	Number of Detections ≥50 ng/L	Detection Frequency (%)	Maximum (ng/L)	Number of Detections ≥MN Chronic Standard (3,600 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥MN Chronic Standard (3,600 ng/L)
2007	55	0	0	<50	0	53	0
2008	17	0	0	<50	0	14	0
2009	12	1	8	70.0	0	6	0
2010	23	0	0	<50	0	21	0
2011	21	0	0	<50	0	20	0
2012	52	1	2	320	0	51	0
2013-2016	0	--	--	--	--	--	--
2017	51	1	2	89.1	0	50	0
2018	6	3	50	95.2	0	2	0
2019	3	0	0	<50	0	1	0
2007-2019	**240**	**6**	**3**	**320**	**0**	**191**	**0**

The MDA collected 43 samples from 42 wetlands from 2014 to 2016 and acetochlor was detected in nine samples. All detections occurred in 2014 and ranged from 57.2 to 275 ng/L. The maximum concentration was approximately 8% of the Minn. Rule Ch. 7050 chronic standard of 3,600 ng/L.

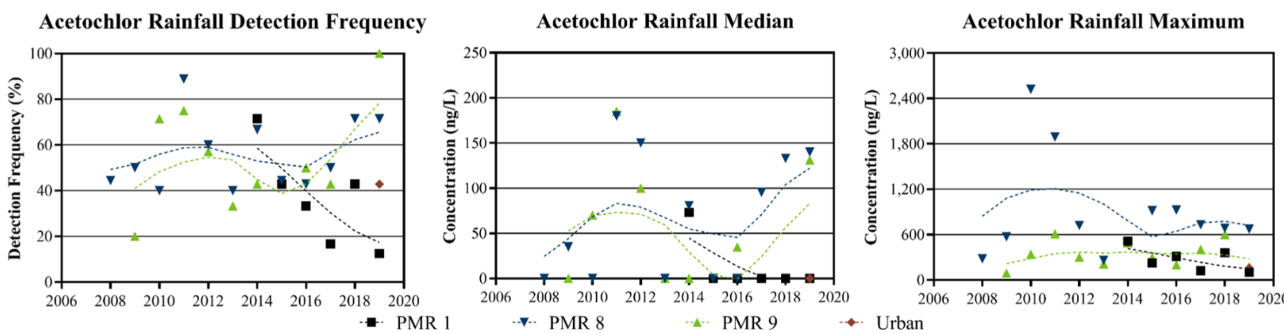
3.4.2.3 MDA acetochlor water quality summary in rainfall

The MDA operates a rainfall pesticide monitoring network (See Section 3.7 for more details). Acetochlor was detected in 49% of the 218 rainfall samples collected from 2008 through 2019 (Table 3-6). Detections have occurred at all four rainfall monitoring locations in Minnesota in each year that monitoring has occurred. Detection frequency and concentrations (median and maximum) are presented in Figure 3-4 for all rainfall monitoring locations for the time period each location was in operation.

Table 3-6. MDA water quality summary of acetochlor in Minnesota rainfall.

Year	Samples	Number of Detections ≥50 ng/L	Detection Frequency (%)	Maximum (ng/L)	Monitored Locations	PMR with Detection(s)
2008	9	4	44	280	1	8
2009	18	6	33	570	2	8,9
2010	17	9	53	2,520	2	8,9
2011	17	14	82	1,890	2	8,9
2012	12	7	58	720	2	8,9
2013	19	7	37	262	2	8,9
2014	20	12	60	514	2	8,9
2015	23	10	43	916	2	8,9
2016	19	8	42	925	3	1,8,9
2017	19	7	37	731	3	1,8,9
2018	21	11	52	685	3	1,8,9
2019	24	11	46	673	4	1,8,9,U
2008-2019	**218**	**106**	**49**	**2,520**	**4**	**1,8,9,U**

Figure 3-4. Long term MDA acetochlor rainfall monitoring results.



3.4.3 Long-term MDA atrazine surface water quality data

Atrazine has been analyzed and detected by the MDA in surface water since 1991, and the MDA designated atrazine as a POC in 2002. Atrazine is a triazine herbicide, used primarily on corn, with water quality standards in statute ((Minn. Rule Ch. 7050) the chronic standard = 10,000 ng/L and the maximum standard = 323,000 ng/L). Information on how atrazine data were analyzed can be found in Section 3.4.1.

3.4.3.1 MDA atrazine water quality summary in river and streams

Long term trend results are presented for atrazine at Tier 1 and Tier 2 locations from 2007 through 2019 in Figure 3-5 and Figure 3-6. Figure 3-5 presents the data spatially while Figure 3-6 presents the detection frequency, median concentration, and 90th percentile concentration overtime. Please note that the concentration ranges on the y-axis vary among the

different PMRs. Lines on the figures represent a 4th order polynomial smooth. The polynomial smooth is a nonparametric curve fitting method which generated a line that represented the general tendency of the data over time based upon the data itself rather than being constrained by assumptions associated with fitting a specific equation to the data. The generated line can be utilized for visual assessment of the data to investigate if there are any general patterns or trends in the data that would otherwise be difficult to see (Helsel and Hirsch, 2002).

- Atrazine
  - Detection frequency trends:
    - A trend that was not statistically significant (no trend) was observed in each PMR.
  - Median concentration trends:
    - A trend that was not statistically significant (no trend) was observed in PMRs 1, 4, 5, 6, 7, 9, 10, and urban.
    - A statistically significant increasing trend was observed in PMR 8.
  - 90th percentile trends:
    - A trend that was not statistically significant (no trend) was observed in PMRs 1, 4, 5, 6, 7, 10, and urban.
    - A statistically significant increasing trend was observed in PMRs 8 and 9.

Figure 3-5. 2007 through 2019 PMR atrazine trend analysis maps for data collected in May and June from Tier 1 and Tier 2 monitoring locations.

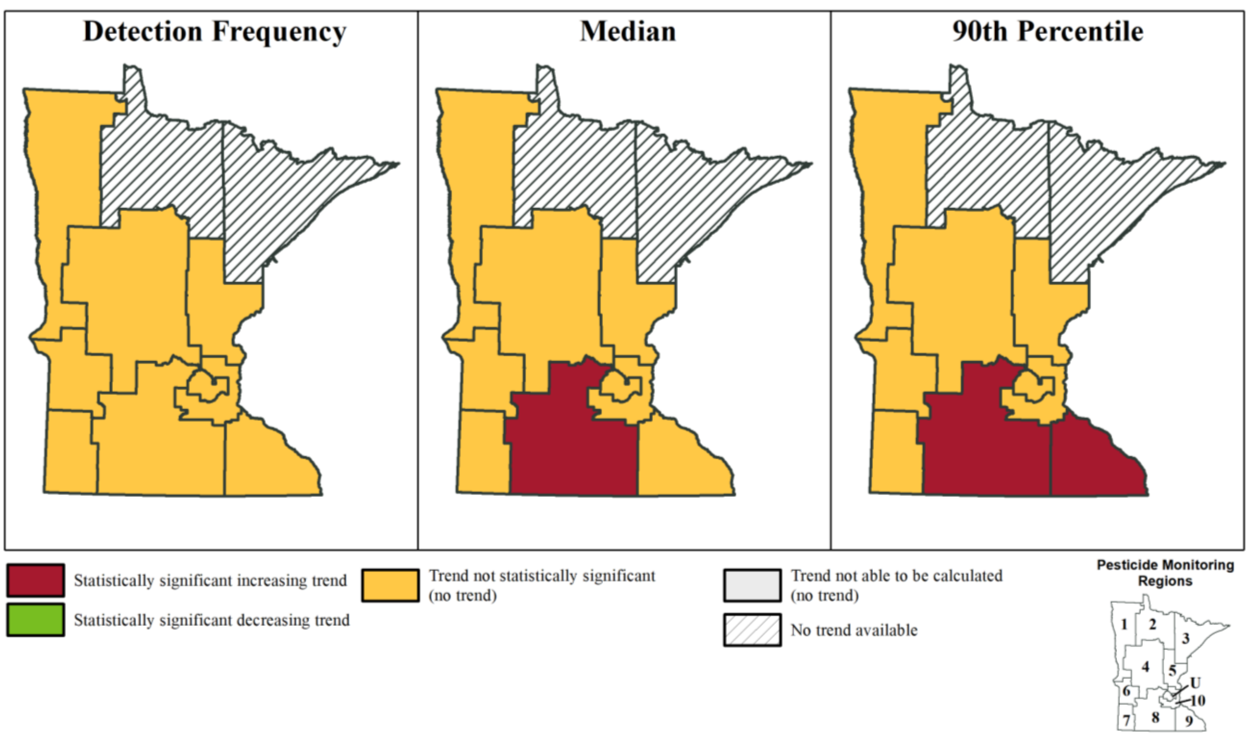
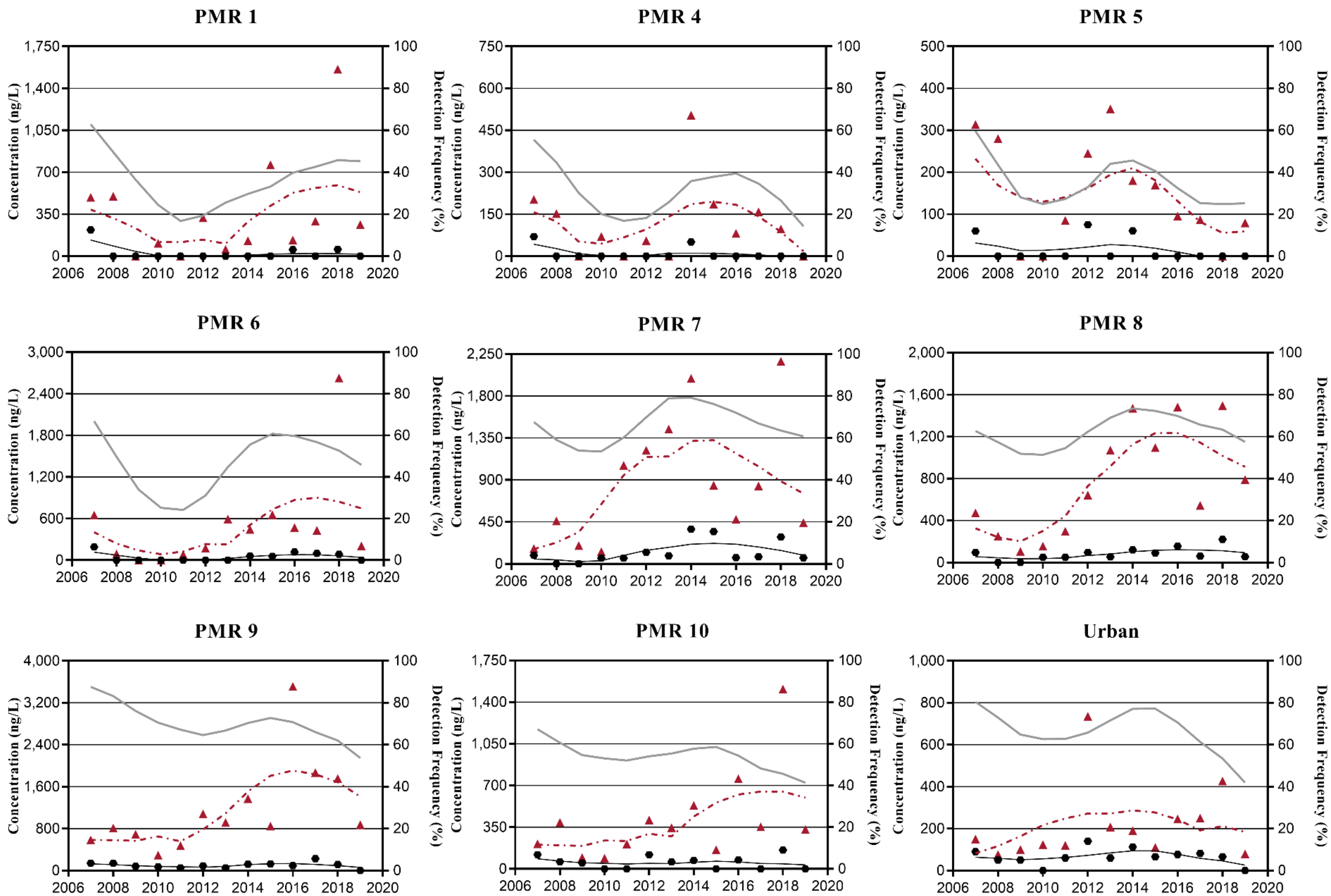


Figure 3-6. Atrazine concentration and detection frequency by PMR, 2007 through 2019.



Median 90th Percentile Detection Frequency

Minnesota Rule Ch. 7050 chronic standard = 10,000 ng/L

3.4.3.2 MDA atrazine water quality summary in lakes and wetlands

Atrazine was detected in 26% of the 240 samples collected from 191 lakes from 2007 through 2019 (Table 3-7). The maximum concentration was 680 ng/L, which is approximately 7% of the numeric Minn. Rule Ch. 7050 chronic standard of 10,000 ng/L.

Table 3-7. MDA water quality summary of atrazine in Minnesota lakes.

Year	Samples	Number of Detections ≥50 ng/L	Detection Frequency (%)	Maximum (ng/L)	Number of Detections ≥MN Chronic Standard (10,000 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥MN Chronic Standard (10,000 ng/L)
2007	55	23	42	680	0	53	0
2008	17	1	6	60.0	0	14	0
2009	12	3	25	80.0	0	6	0
2010	23	2	9	60.0	0	21	0
2011	21	4	19	140	0	20	0
2012	52	17	33	220	0	51	0
2013-2016	0	--	--	--	--	--	--
2017	51	5	10	97.3	0	50	0
2018	6	6	100	267	0	2	0
2019	3	1	33	57.7	0	1	0
2007-2019	**240**	**62**	**26**	**680**	**0**	**191**	**0**

The MDA collected 43 samples from 42 wetlands between 2014 and 2016 and atrazine was detected in 15 samples. These detections occurred in 2014 and 2016, and ranged from 50.0 to 202 ng/L. The maximum concentration was approximately 2% of the numeric Minn. Rule Ch. 7050 chronic standard of 10,000 ng/L.

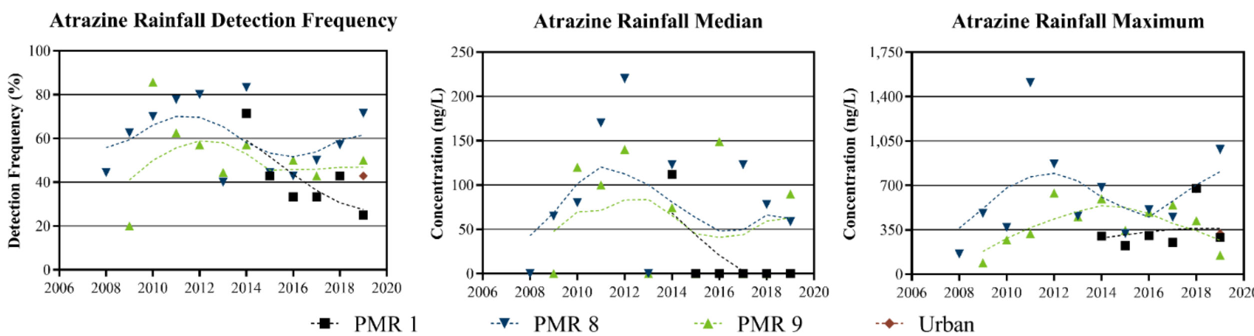
3.4.3.3 MDA atrazine water quality summary in rainfall

The MDA operates a rainfall pesticide monitoring network (See Section 3.7 for more details). Atrazine was detected in 52% of the 218 rainfall samples collected from 2008 through 2019 (Table 3-8). Detections have occurred at the four rainfall monitoring locations in Minnesota in every year that monitoring has occurred. Detection frequency and concentrations (median and maximum) are presented in Figure 3-7 for the time period each rainfall monitoring location was in operation.

Table 3-8. MDA water quality summary of atrazine in Minnesota rainfall.

Year	Samples	Number of Detections ≥50 ng/L	Detection Frequency (%)	Maximum (ng/L)	Monitored Locations	PMR with Detection(s)
2008	9	4	44	160	1	8
2009	18	7	39	480	2	8,9
2010	17	13	76	370	2	8,9
2011	17	12	71	1,510	2	8,9
2012	12	8	67	870	2	8,9
2013	19	8	42	458	2	8,9
2014	20	14	70	685	2	8,9
2015	23	10	43	347	2	8,9
2016	19	8	42	508	3	1,8,9
2017	19	8	42	545	3	1,8,9
2018	21	10	48	676	3	1,8,9
2019	24	11	46	983	4	1,8,9,U
2008-2019	**218**	**113**	**52**	**1,510**	**4**	**1,8,9,U**

Figure 3-7. Long term MDA atrazine rainfall monitoring results.



3.4.4 Long-term MDA chlorpyrifos surface water quality data

The MDA analyzed for chlorpyrifos from 1991 through 1996 and since 2000. The MDA designated chlorpyrifos as a POC in 2012. Chlorpyrifos is an organophosphate insecticide with water quality standards in statute (Minn. Rule Ch. 7050 chronic standard= 41 ng/L; Minn. Rule Ch. 7050 maximum standard= 83 ng/L).

The chlorpyrifos MRL was reduced from 100 ng/L to 40 ng/L in 2008, and the MDA Laboratory stopped reporting "present below MRL" detections for all pesticide analytes beginning in 2013. The first chlorpyrifos detection ("present below MRL") in rivers and streams occurred in 2005. All detections, regardless of the MRL, are presented in this section and are included in the calculation of detection frequency. Additional information on how chlorpyrifos data were summarized can be found in Section 3.4.1.

3.4.4.1 MDA chlorpyrifos water quality summary in river and streams

All MDA chlorpyrifos detections in rivers and streams are presented in Table 3-9, Figure 3-8 and Figure 3-9.

Key findings include:

- Chlorpyrifos was detected (including "present below MRL" detections) in 87 of 7,884 samples (1.1% detection frequency) collected from 2005 through 2019.
  - Since 2008, the annual chlorpyrifos detection frequency has ranged from 0.16% in 2013 to 2.7% in 2017.
- Chlorpyrifos was detected as "present below MRL (100 ng/L)" in six samples from 2005 through 2007, and as "present below MRL (40 ng/L)" in nine samples from 2008 through 2012.
  - Reporting of pesticide detections "present below MRL" stopped in 2013.
- Seventy-two detections of chlorpyrifos over the current MRL of 40 ng/L occurred since 2010.
  - The number of detections was variable each year, ranging from one in 2013 to 17 in 2017.
  - Sixty-five of the 72 chlorpyrifos detections have been over the numeric Minn. Rule Ch. 7050 chronic standard of 41 ng/L, including 18 chlorpyrifos detections over the Minn. Rule Ch. 7050 maximum standard of 83 ng/L.
- The MDA has monitored for chlorpyrifos at 377 different river and stream locations, and 25 of these locations had at least one detection over the chronic standard of 41 ng/L
- Thirteen watersheds in Minnesota are designated as impaired for chlorpyrifos (Section 3.1.3)
- Sixty-six of the 87 chlorpyrifos detections occurred in samples collected during August (Figure 3-8).
  - Sixty-two percent of the August detections occurred in base flow (non-runoff) periods (Figure 3-8).

Table 3-9. MDA water quality summary of chlorpyrifos in Minnesota rivers and streams since 2005.

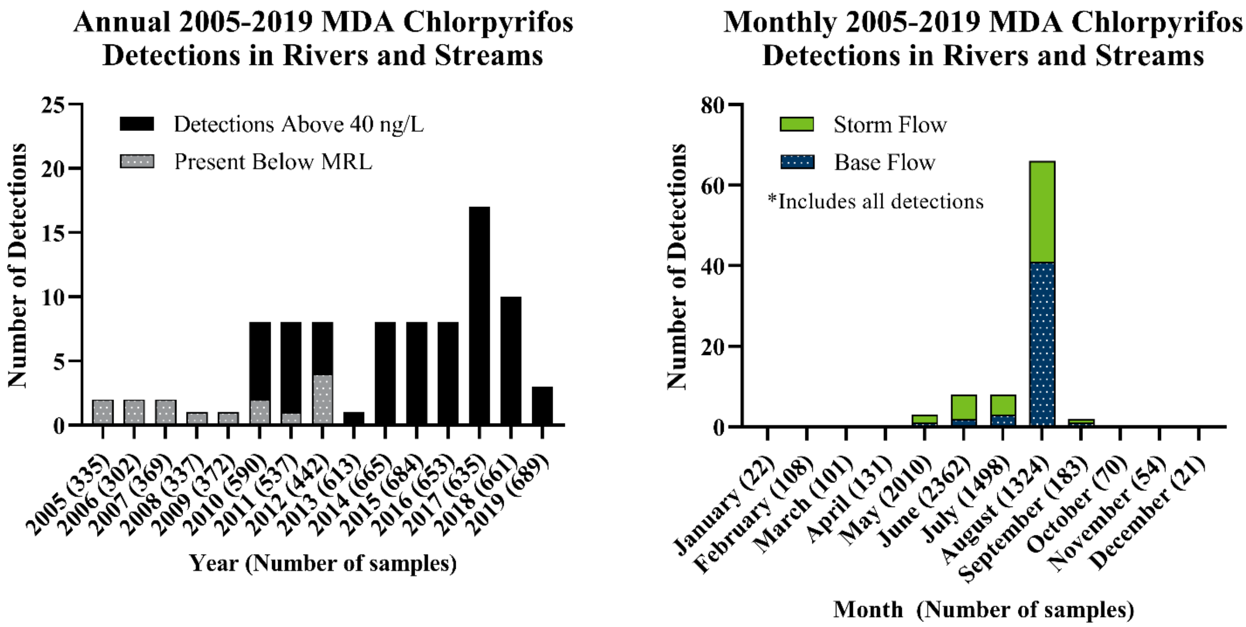
Year	Samples	Number of Detections ≥40 ng/L	Number of "Present <MRL" Detections	Detection Frequency (all detections, %)	Maximum (ng/L)	Number of Detections ≥MN Chronic Standard (41 ng/L)	Number of Detections ≥MN Maximum Standard (83 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥MN Chronic Standard (41 ng/L)
2005	335	na	2	0.6	Present <100	0	0	56	na*
2006	302	na	2	0.6	Present <100	0	0	58	na*
2007	369	na	2	0.5	Present <100	0	0	67	na*
2008**	337	0	1	0.3	Present <40	0	0	58	0
2009	372	0	1	0.3	Present <40	0	0	63	0
2010	590	6	2	1.4	240	5	2	209	5
2011	537	7	1	1.5	160	7	3	123	4
2012	442	4	4	1.8	110	4	1	82	3
2013***	613	1	na	0.2	53.4	1	0	60	1
2014	665	8	na	1.2	88.9	8	1	62	7
2015	684	8	na	1.2	196	7	5	82	7
2016	653	8	na	1.2	137	7	3	54	5
2017	635	17	na	2.7	135	14	2	56	10
2018	661	10	na	1.5	108	9	1	61	9
2019	689	3	na	0.4	70.2	3	0	55	3
2005-2019	**7,884**	**72**	**15**	**1.1**	**240**	**65**	**18**	**377**	**25**

**Unable to determine if concentrations "Present below MRL" were greater than 41 ng/L (MRL was 100 ng/L).*

***MRL was reduced from 100 ng/L to 40 ng/L prior to 2008.*

****Detections reported as "Present below MRL" stopped in 2013.*

Figure 3-8. 2005 through 2019 MDA chlorpyrifos detections in rivers and streams.



3.4.4.2 MDA chlorpyrifos water quality summary in lakes and wetlands

The MDA collected 240 chlorpyrifos samples from 191 lakes from 2007 through 2019 (Table 3-10). Chlorpyrifos was detected in three samples from two lakes: Double Lake (MN DNR Lake ID: 17-0056) in Cottonwood County in 2017 and 2018, and Cup Lake (MN DNR Lake ID: 06-0120) in Big Stone County once in 2017 (Figure 3-7). All three lake detections have been above the numeric Minn. Rule Ch. 7050 chronic standard of 41 ng/L, but below the Minn. Rule Ch. 7050 maximum standard of 83 ng/L. Double Lake (17-0056) was proposed as being designated as impaired for chlorpyrifos by the MPCA in 2020 (Section 3.1.3).

Table 3-10. MDA water quality summary of chlorpyrifos in Minnesota lakes.

Year	Samples	Number of Detections ≥40 ng/L	Number of "Present <MRL" Detections	Detection Frequency (all detections, %)	Maximum (ng/L)	Number of Detections ≥MN Chronic Standard (41 ng/L)	Number of Detections ≥MN Maximum Standard (83 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥MN Chronic Standard (41 ng/L)
2007	55	0	0	0	<100	0	0	53	0
2008*	17	0	0	0	<40	0	0	14	0
2009	12	0	0	0	<40	0	0	6	0
2010	23	0	0	0	<40	0	0	21	0
2011	21	0	0	0	<40	0	0	20	0
2012	52	0	0	0	<40	0	0	51	0
2013**-2016	0	--	--	--	--	--	--	--	--
2017	51	2	na	3.9	68.8	2	0	50	2
2018	6	1	na	16.7	47.4	1	0	2	1
2019	3	0	na	0	<40	0	0	1	0
2005-2019	**240**	**3**	**0**	**1.3**	**68.8**	**3**	**0**	**191**	**2**

**MRL was reduced from 100 ng/L to 40 ng/L prior to 2008.*

***Detections reported as "Present below MRL" stopped in 2013.*

The MDA collected 43 samples from 42 wetlands from 2014 to 2016 and chlorpyrifos was not detected in any of these wetland samples.

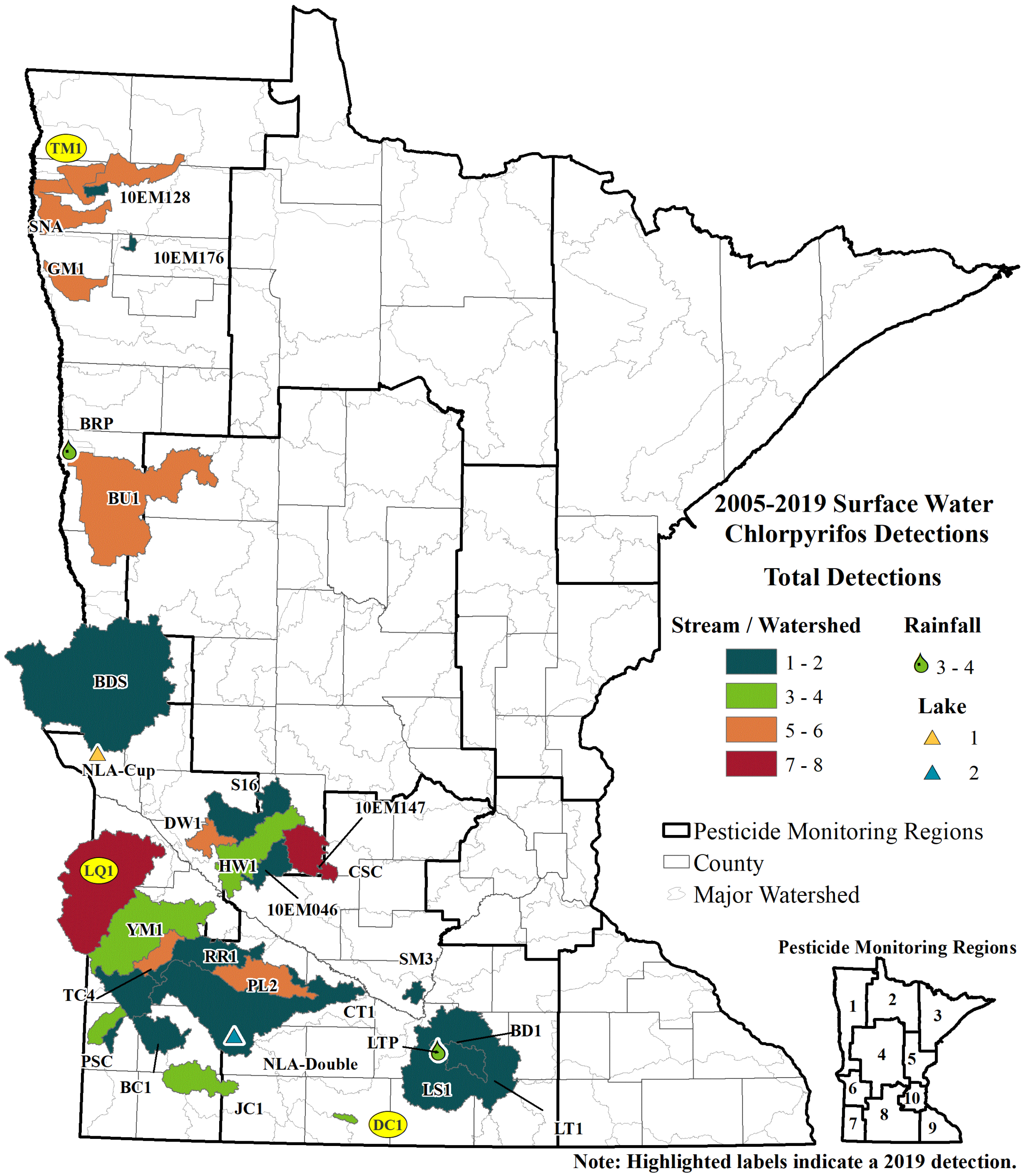
3.4.4.3 MDA chlorpyrifos water quality summary in rainfall

The MDA operates a rainfall pesticide monitoring network (See Section 3.7 for more details). Chlorpyrifos was detected in rainfall in seven of 218 rainfall samples collected since 2008. Detections have occurred in PMR 8 in 2008, 2009, 2011, and 2012; and in PMR 1 in 2014, 2017, and 2018 (Figure 3-9 and Table 3-11). All detections occurred in a sample with a collection end date in August. Chlorpyrifos has not been detected in rainfall at the PMR 9 or the urban rainfall monitoring locations.

Table 3-11. MDA water quality summary of chlorpyrifos in Minnesota rainfall.

Year	Samples	Number of Detections ≥40 ng/L	"Present <MRL" Detections (<40 ng/L)	Detection Frequency (%)	Maximum (ng/L)	Monitored Locations	PMR with Detection(s)
2008	9	1	0	11	100	1	8
2009	18	1	0	6	260	2	8
2010	17	0	0	0	<40	2	-
2011	17	1	0	6	90	2	8
2012	12	0	1	8	Present <40	2	8
2013	19	0	na	0	<40	2	-
2014	20	1	na	5	83.4	2	1
2015	23	0	na	0	<40	2	-
2016	19	0	na	0	<40	3	-
2017	19	1	na	5	612	3	1
2018	21	1	na	5	55.9	3	1
2019	24	0	na	0	<40	4	-
2008-2019	**218**	**6**	**1**	**3**	**260**	**4**	**1, 8**

Figure 3-9. Total number of MDA chlorpyrifos detections by watershed, 2005 through 2019.



3.5 Review of pesticide detections in Minnesota surface water greater than 10% of an applicable numeric reference value, 2015 through 2019

This is an overview on all pesticide compounds that were detected, at least once, at concentrations equal to or greater than 10% of their lowest applicable numeric reference value in the last five years. This section was generated to assist the members of the Pesticide Management Plan Committee (PMPC) when preparing written recommendations to the MDA Commissioner.

The PMP was developed by the MDA following the passage of the Minnesota Pesticide Control Law, which charged the MDA Commissioner to ensure pesticides are used "in a manner that will not cause unreasonable adverse effects on the environment." The PMP states the PMPC should meet to review water quality monitoring data and to provide comments related the designation of POC. Designation as a POC initiates the development of pesticide specific best management practices (BMPs) and increased water quality data collection and analysis by the MDA. The MDA uses thresholds of 10%, 50% and greater than the lowest applicable numeric reference value, to evaluate possible designation as a POC. This conservative evaluation ***does not*** include a duration assessment that is required for assessing chronic standards in the determination of impaired waters.

Using the thresholds defined in the PMP, all water quality data collected by the MDA from 2015 through 2019 (from Tier 1 through Tier 3 river and streams locations including urban locations), were evaluated for detections greater than 10% of the lowest applicable numeric aquatic life or human health (where applicable) water quality reference value. The purpose of this assessment is to provide PMPC members with information to evaluate the current "surface water pesticides of concern" and to determine if additional pesticides should be considered for a POC designation.

Table 3-12 presents detection summaries for all pesticides with at least one detection equal to or greater than 10% of the lowest applicable numeric water quality reference value from 2015 through 2019. Within Table 3-12, each detection was only assigned to one category (*i.e.*, a detection greater than the reference value was not included in either of the greater than 10% or greater than 50% categories). Figure 3-10 presents the number of detections for all pesticides with at least seven detections greater than 10% of the lowest applicable water quality reference value from 2015 through 2019. In the case of a reduced MRL, all data were evaluated without censoring to a highest historical MRL, to ensure all detections were included. In the case of an updated reference value, all data (2015-2019) were reviewed against the most current reference value.

Key findings for Table 3-12 and Figure 3-10 include:

- Thirty different pesticide compounds were detected at least once at concentrations equal to or greater than 10% of the applicable numeric reference value from 2015-2019.

    - Seventeen were herbicides, nine were insecticides and four were fungicides.
    - Twenty pesticide compounds were detected at concentrations greater than 10% of the applicable numeric reference value less than 10 times.
    - Five pesticide compounds were detected at concentrations greater than 10% of the applicable numeric reference value 140 or more times.
- Nine pesticide compounds (five herbicides and four insecticides) had more than 18 detections greater than 10% of the applicable reference value from 2015 through 2019.
    - Herbicides:
        - Acetochlor, atrazine, metolachlor, dimethenamid and pyroxasulfone were detected in 44, 68, 71, 32, and 3% of samples, respectively.
        - Acetochlor, atrazine, metolachlor and dimethenamid had 39, 6, 3, and 0 detections, respectively, equal to or greater than the applicable numeric reference value in 3,293 samples.
        - Pyroxasulfone was not detected greater than the applicable numeric reference value in 1,279 samples.
    - Insecticides:
        - Clothianidin, imidacloprid, chlorpyrifos and thiamethoxam were detected in 20, 11, 1, and 9% of samples, respectively
        - Clothianidin, imidacloprid and thiamethoxam had 119, 95, and 0 detections, respectively, equal to or greater than the applicable numeric reference value in 1,279 samples.
        - Chlorpyrifos had 39 detections equal to or greater than the applicable numeric reference value in 3,293 samples.

Table 3-12. Summary of pesticide surface water detections greater than 10% of the applicable reference value, 2015 through 2019.

Pesticide	Samples	Number of Detections	Detection Frequency (%)	Number of Detections ≥10% and <50% Reference Value**	Number of Detections ≥50% and < Reference Value**	Number of Detections ≥Reference Value**	Number of Detections ≥10% Reference Value***
Acetochlor*	3,293	1,461	44	336	68	39	443
Clothianidin	1,279	256	20	0	137	119	256
Atrazine*	3,293	2,248	68	167	15	6	188
Metolachlor	3,293	2,340	71	137	6	3	146
Imidacloprid	1,279	140	11	0	45	95	140
Chlorpyrifos*	3,293	45	1	0	6	39	45
Dimethenamid	3,293	1048	32	41	1	0	42
Pyroxasulfone	1,279	37	3	34	3	0	37
Thiamethoxam	1,279	117	9	19	0	0	19
Flumetsulam	1,279	254	20	12	0	0	12
Metribuzin	3,293	201	6	9	0	0	9
Triclopyr	1,279	96	8	6	1	0	7
Metsulfuron-methyl	1,279	7	1	5	0	0	5
Sulfometuron-methyl	1,279	33	3	4	0	0	4
2,4-D	1,279	1,024	80	3	0	0	3
Carbendazim	1,279	46	4	3	0	0	3
Diuron	1,279	20	2	2	0	1	3
Bifenthrin	3,293	1	<1	0	0	2	2
Carbaryl	1,279	4	<1	2	0	0	2
Dicamba	1,279	191	15	2	0	0	2
Dichlorvos	3,293	2	<1	0	0	2	2
Tembotrione	1,279	42	3	1	1	0	2
Benzovindiflupyr	1,071	1	<1	1	0	0	1
Bromoxynil	1,279	8	1	1	0	0	1
Chlorothalonil	3,293	1	<1	1	0	0	1
Diazinon	3,293	1	<1	0	0	1	1
Dimethoate	2,169	1	<1	1	0	0	1
Halosulfuron-methyl	1,279	1	<1	0	1	0	1
Imazethapyr	1,279	495	39	1	0	0	1
Pyraclostrobin	1,262	5	<1	1	0	0	1

**MDA Pesticide of Concern.*

***Detection only assigned to one category (i.e., a detection greater than the reference value is not included in greater than 10% or greater than 50% categories).*

****The values in this column are a summation of all detections greater than 10% of a reference value.*

Figure 3-10. Number of pesticide detections above 10% of a reference value in Minnesota surface water, 2015-2019.

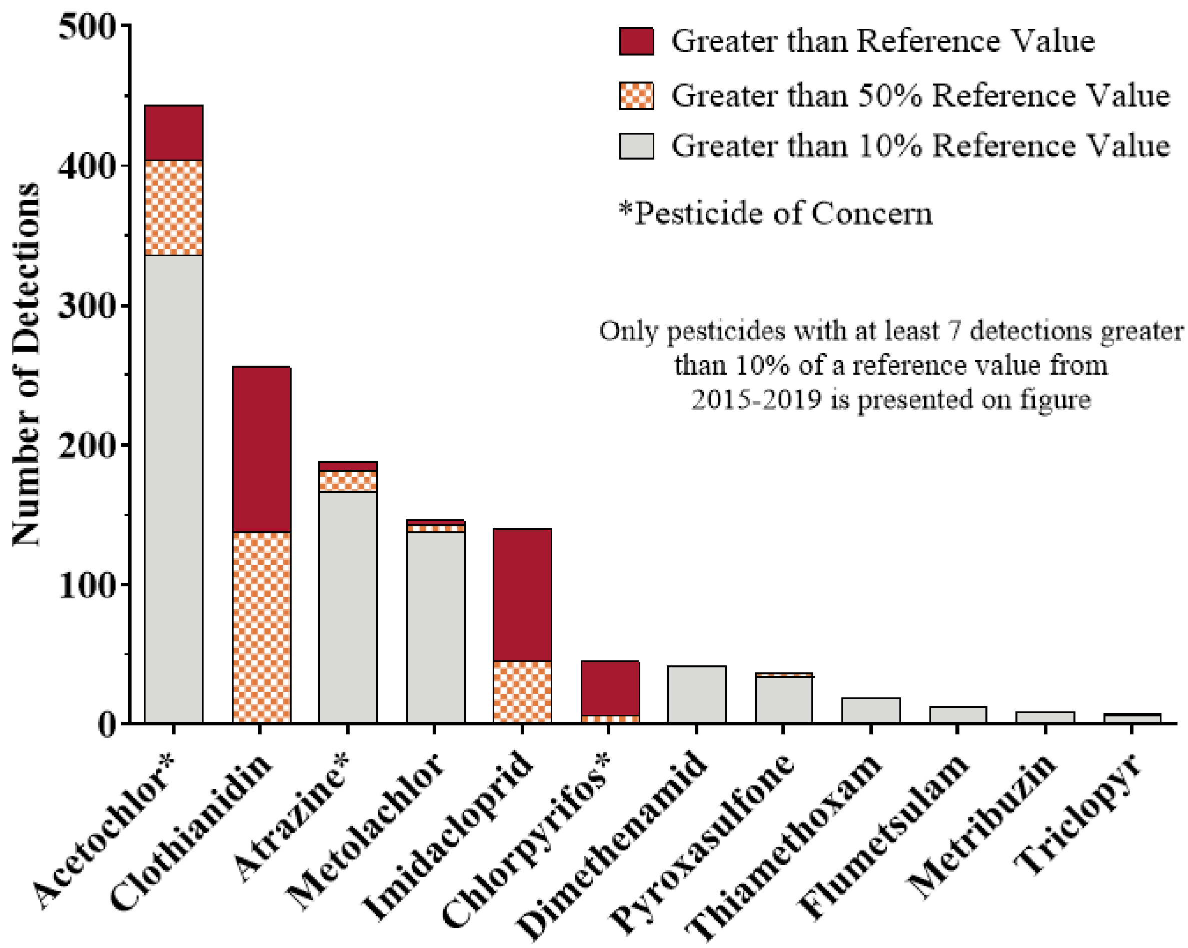


Table 3-13 presents the total number of annual pesticide detections greater than 10% of the lowest applicable water quality reference value from 2015 through 2019.

Key findings of Table 3-13 include:

- A total of 1,389 pesticide detections greater than 10% of the applicable numeric reference value have occurred from 2015 through 2019.
  - The total number of detections greater than 10% of the applicable numeric reference value for all pesticides ranged from 127 in 2015 to 496 in 2019.
- The most detections greater than 10% of the applicable numeric reference value for acetochlor and metolachlor occurred in 2019, and for atrazine in 2018.
- Acetochlor had the most detections greater than 10% of the applicable numeric reference value every year from 2015 through 2019.
- Clothianidin and imidacloprid had more detections above their applicable numeric reference values in 2019 compared to the previous four years. The MDA analyzed more

samples for these compounds in 2019 and the imidacloprid MRL was reduced from 10 to 5 ng/L.

- Annual detections are inconsistent across the years for pesticides with five or fewer detections greater than 10% of the applicable numeric reference value occurring from 2015 through 2019.

Table 3-13. 2015 through 2019 pesticide surface water detections greater than 10% of the applicable reference value, by year.

Pesticide	2015	2016	2017	2018	2019	Total 2015-2019
Acetochlor*	53	47	96	120	127	443
Clothianidin	19	33	25	65	114	256
Atrazine*	20	27	33	66	42	188
Metolachlor	8	24	24	38	52	146
Imidacloprid**	1	2	3	31	103	140
Chlorpyrifos*	7	8	17	10	3	45
Dimethenamid	7	3	12	11	9	42
Pyroxasulfone	2	0	3	8	24	37
Thiamethoxam	0	4	3	9	3	19
Flumetsulam	1	1	4	2	4	12
Metribuzin	0	2	2	4	1	9
Triclopyr	3	2	2	0	0	7
Metsulfuron-methyl	1	1	0	0	3	5
Sulfometuron-methyl	0	0	3	0	1	4
2,4-D	0	1	0	1	1	3
Carbendazim	1	1	0	0	1	3
Diuron	2	1	0	0	0	3
Bifenthrin	0	0	1	1	0	2
Carbaryl	0	2	0	0	0	2
Dicamba	0	0	1	0	1	2
Dichlorvos	0	0	1	0	1	2
Tembotrione	0	1	0	1	0	2
Benzovindiflupyr	na	0	0	0	1	1
Bromoxynil	1	0	0	0	0	1
Chlorothalonil	0	1	0	0	0	1
Diazinon	0	0	0	1	0	1
Dimethoate	1	0	0	0	0	1
Halosulfuron-methyl	0	1	0	0	0	1
Imazethapyr	0	0	0	1	0	1
Pyraclostrobin	0	0	1	0	0	1
Grand Total	127	162	231	373	496	1,389

** Current pesticide of concern.*
***MRL was reduced from 20 ng/L to 10 ng/L in 2018 and from 10 ng/L to 5 ng/L in 2019.*
na = not analyzed

3.6 Neonicotinoid insecticide monitoring in surface water

Neonicotinoids are currently one of the most widely used classes of insecticides in the world. They are effective at very low concentrations, have low toxicity to mammals, and are not cross-resistant to other classes of insecticides. However, recent research has suggested potential toxicity concerns for neonicotinoids to various life stages of pollinating insects, as well as to aquatic invertebrates that play a critical role in ecosystem services and food chains.

Neonicotinoids were first analyzed by the MDA Laboratory in water samples in 2010. In 2019, the MDA Laboratory analyzed water samples for six neonicotinoid parent pesticides and two degradates: acetamiprid, imidacloprid, thiamethoxam (analysis began in 2010), clothianidin (analysis began in mid-2011), dinotefuran (analysis began in 2012), thiacloprid (analysis began in 2014), and the degradates imidacloprid-urea and imidacloprid-olefin (analysis began in 2017). All neonicotinoid compounds were analyzed with the LC/MS-MS method and have MRLs ranging from 5 to 50 ng/L.

3.6.1 2019 MDA neonicotinoid monitoring

The MDA collected 380 LC-MS/MS pesticide samples from 30 different river and stream locations that were analyzed for neonicotinoid insecticides in 2019. Acetamiprid, dinotefuran, thiacloprid, and two degradates of imidacloprid, imidacloprid-olefin, and imidacloprid-urea were not detected in 2019. Clothianidin, imidacloprid, and thiamethoxam were detected in 2019.

Key findings from Table 3-14 include:

- Clothianidin
    - Statewide detection frequency was 30%.
        - The detection frequency ranged from 13% in PMR 1 to 57% in PMR 9 for PMRs with at least one detection.
        - Clothianidin was detected, at least once, at 22 of the 30 locations.
            - Clothianidin was not detected at the four urban locations.
    - The maximum concentration occurred in PMR 8 (201 ng/L).
    - No detections occurred in PMRs 3, 4, 5, and urban locations.
    - The maximum concentrations in PMRs 6, 7, 8, 9, and 10 were greater than the numeric USEPA OPP 50 ng/L benchmark value.
- Imidacloprid
    - Statewide detection frequency was 27%.
        - The detection frequency ranged from 12% in PMR 7 to 36% in PMR 10 for regions with at least one detection.
        - Imidacloprid was detected, at least once, at 25 of the 30 locations.
    - The maximum concentration occurred in PMRs 8 and 9 (32.0 ng/L).
    - No detections occurred in PMRs 3, 4, and 5.

    - The maximum concentrations in PMRs 1, 6, 7, 8, 9, 10, and at urban locations were greater than the numeric USEPA OPP 10 ng/L benchmark value.
- Thiamethoxam
    - Statewide detection frequency was 11%.
        - The detection frequency ranged from 6% in PMR 1 to 25% in PMR 9 for PMRs with at least one detection.
        - Thiamethoxam was detected, at least once, at 16 of the 30 locations.
    - The maximum concentration occurred in PMR 9 (241 ng/L).
    - No detections occurred in PMRs 3, 4, 5, 7, and at urban locations.
    - No detections were greater than the numeric USEPA OPP 740 ng/L benchmark value.

Table 3-14. 2019 PMR analysis of clothianidin, imidacloprid, and thiamethoxam tier river and stream water quality data.

		Clothianidin					Imidacloprid					Thiamethoxam				
PMR	Samples	Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)	Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)	Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)
1	32	4	13	<25	31.0	37.6	7	22	<5	8.70	27.8	2	6	<25	<25	35.7
3	8	0	0	<25	<25	<25	0	0	<5	<5	<5	0	0	<25	<25	<25
4	12	0	0	<25	<25	<25	0	0	<5	<5	<5	0	0	<25	<25	<25
5	8	0	0	<25	<25	<25	0	0	<5	<5	<5	0	0	<25	<25	<25
6	27	9	33	<25	77.3	88.4	9	33	<5	17.8	28.4	2	7	<25	<25	44.0
7	26	5	19	<25	39.3	58.0	3	12	<5	<5	22.2	0	0	<25	<25	<25
8	93	36	39	<25	64.3	201	28	30	<5	14.5	32.0	13	14	<25	27.1	149
9	87	50	57	36.5	97.9	145	26	30	<5	11.6	32.0	22	25	<25	47.4	241
10	39	10	26	<25	39.0	55.4	14	36	<5	14.8	29.1	4	10	<25	<25	115
Urban	48	0	0	<25	<25	<25	16	33	<5	12.8	21.5	0	0	<25	<25	<25
Total	380	114	30	<25	65.8	201	108	27	<5	12.3	32	43	11	<25	26.1	241

3.6.2 2010 through 2019 MDA neonicotinoid monitoring

The MDA has not detected acetamiprid in 2,351 river or stream, 156 lake, and 43 wetland samples (2010-2019). The MDA has not detected imidacloprid-olefin or imidacloprid-urea in 858 river or stream and 60 lake samples (2017-2019). The MDA has not detected thiacloprid in 1,524 river or stream, 60 lake, and 43 wetland samples (2014-2019). The MDA has not detected dinotefuran in 111 lake and 43 wetland samples (2012-2019). The MDA has detected dinotefuran in two of 1,838 river and stream samples. The dinotefuran detections occurred in 2013 (30.9 ng/L) and 2016 (548 ng/L) at non-urban locations.

Clothianidin, imidacloprid and thiamethoxam are the most frequently detected neonicotinoid insecticides in surface water. A summary of the MDA monitoring data for each of these neonicotinoids is provided below.

Long term clothianidin, imidacloprid and thiamethoxam data summary approach

Every detection (regardless of the MRL) in all surface waterbodies and rainfall were included because some of the MRLs were higher or very similar to the reference values.

Most data were collected through the MDA Tier network. From 2010 through 2011, samples were collected primarily in May and June. The Tier 2 and Tier 1 monitoring seasons were extended into July and August in 2012 and 2013, respectively to include the fungicide and insecticide application period in Minnesota. Most data were collected from May through August; however, limited sampling was completed from September through April. The MDA has been increasing the number of LC-MS/MS samples analyzed from the tier network, which include the neonicotinoids, since 2018.

The MDA sampled survey locations in 2010, 2011, 2012, and 2015 which received one or two samples per location. The survey locations are randomly selected locations across Minnesota and sample collection generally occurred during base flow conditions. Additionally, the MDA has had several special study locations. These special study locations were monitored to provide more in-depth pesticide water quality data in specific watersheds. The survey and special study locations are included in this analysis and are primarily responsible for the year-to-year variation in the number of monitored locations.

3.6.3 Long-term MDA clothianidin surface water quality data

The MDA has analyzed and detected clothianidin since 2011. Clothianidin is a neonicotinoid insecticide with a numeric USEPA OPP chronic aquatic life benchmark of 50 ng/L, and a numeric USEPA OPP acute aquatic life benchmark of 11,000 ng/L. The clothianidin MRL has been 25 ng/L since analysis began in 2011. Clothianidin has been detected in rivers and streams each year since 2011 and all reported detections were above the MRL. Additional information on how clothianidin data were summarized can be found in Section 3.6.2.

3.6.3.1 MDA clothianidin water quality summary in river and streams

All MDA clothianidin detections in rivers and streams are presented in Table 3-15 and Figures 3-11 and 3-12. Key findings include:

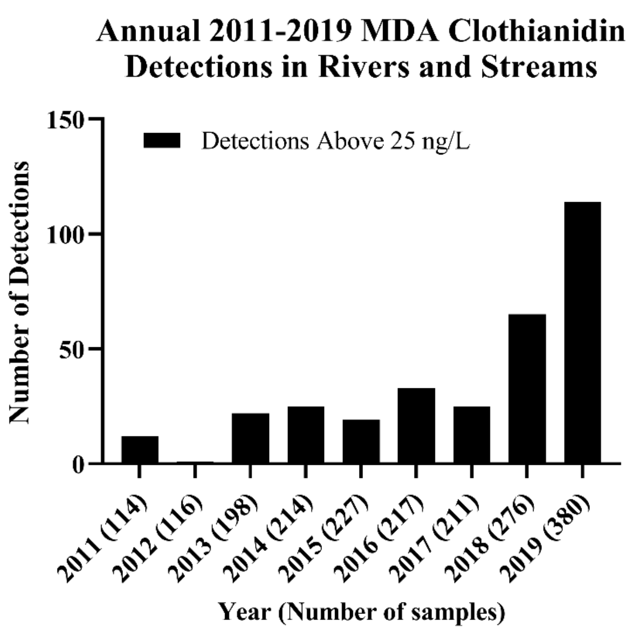
- The MDA monitored for clothianidin at 139 different river and stream locations.
- Annual clothianidin detections ranged from 1 in 2012 to 114 in 2019.
    - The MDA increased the number of samples collected in agricultural watersheds in the MDA Tier network starting in 2018, leading to more detections.
        - The detection frequencies in 2016 and 2017 were 15% and 12%, respectively, compared to 24% and 30% in 2018 and 2019, respectively.
- One-hundred forty-three clothianidin detections over the numeric USEPA OPP chronic aquatic life benchmark of 50 ng/L occurred at 17 different locations from 2011-2019.

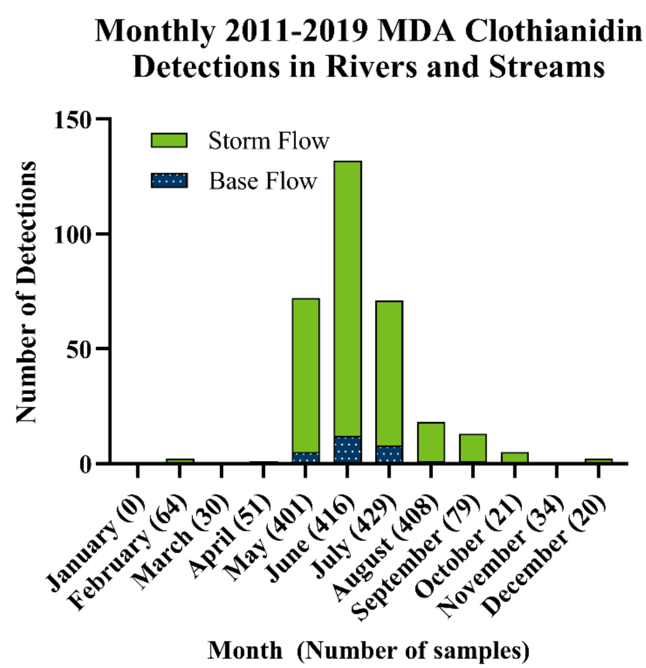
- Clothianidin has not been detected over the numeric USEPA OPP acute aquatic life benchmark of 11,000 ng/L.
- The majority of clothianidin detections occurred from May through July (Figure 3-11).
    - Detections have occurred in every month except January (no samples collected), March (30 samples collected), and November (34 samples collected).
- Overall, 92% percent of clothianidin detections occurred in storm flow conditions (Figure 3-11).

Table 3-15. MDA water quality summary of clothianidin in Minnesota rivers and streams.

Year	Samples	Number of Detections ≥25 ng/L	Maximum (ng/L)	Number of Detections ≥USEPA OPP Chronic Benchmark (50 ng/L)	Number of Detections ≥USEPA OPP Acute Benchmark (11,000 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥USEPA OPP Chronic Benchmark (50 ng/L)
2011	114	12	141	5	0	69	1
2012	116	1	36	0	0	32	0
2013	198	22	150	6	0	20	5
2014	214	25	260	13	0	21	7
2015	227	19	167	5	0	45	3
2016	217	33	162	14	0	21	7
2017	211	25	246	9	0	21	6
2018	276	65	237	29	0	35	15
2019	380	114	201	62	0	30	15
2011-2019	**1,953**	**316**	**260**	**143**	**0**	**139**	**17**

Figure 3-11. 2011 through 2019 MDA clothianidin detections in rivers and streams.





3.6.3.2 MDA clothianidin water quality summary in lakes and wetlands

The MDA collected 132 samples from 120 lakes (2011 through 2019) and 43 samples from 42 wetlands (2014 through 2016). Clothianidin was not detected in any lake or wetland samples.

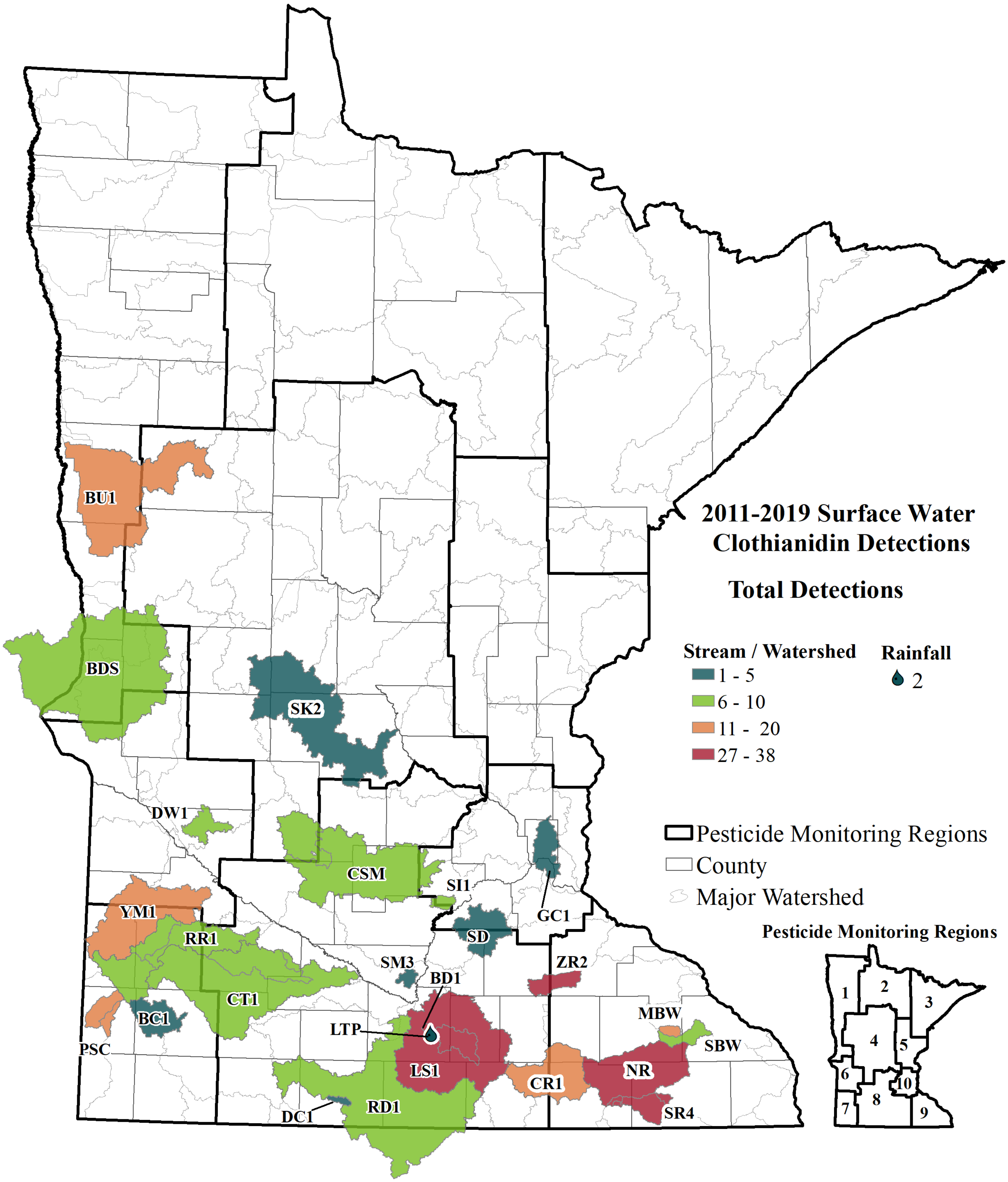
3.6.3.3 MDA clothianidin water quality summary in rainfall

The MDA operates a rainfall pesticide monitoring network (See Section 3.7 for more details). Clothianidin was detected in two of 72 rainfall samples collected since 2011. Both detections occurred in PMR 8 in May in 2016 and 2017 (Figure 3-12 and Table 3-16).

Table 3-16. MDA water quality summary of clothianidin in Minnesota rainfall.

Year	Samples	Number of Detections ≥25 ng/L	Detection Frequency (%)	Maximum (ng/L)	Monitored Locations	PMR with Detection(s)
2011	2	0	0	<25	2	-
2012	3	0	0	<25	2	-
2013	7	0	0	<25	2	-
2014	11	0	0	<25	2	-
2015	9	0	0	<25	2	-
2016	10	1	10	25.8	3	8
2017	9	1	11	32.4	3	8
2018	9	0	0	<25	3	-
2019	12	0	0	<25	4	-
2011-2019	**72**	**2**	**3**	**32.4**	**4**	**8**

Figure 3-12. Total number of MDA clothianidin detections by watershed, 2011 through 2019.



3.6.4 Long-term MDA imidacloprid surface water quality data

The MDA has analyzed and detected imidacloprid since 2010. Imidacloprid is a neonicotinoid insecticide with a numeric USEPA OPP chronic aquatic life benchmark of 10 ng/L, and a numeric USEPA OPP acute aquatic life benchmark of 385 ng/L. The imidacloprid MRL was 20 ng/L between 2010 and 2017, 10 ng/L in 2018 and 5 ng/L in 2019. Imidacloprid has been detected in rivers and streams each year since 2010 and all reported detections were above the MRL. All detections, regardless of MRL, are presented in this section. Additional information on how imidacloprid data were summarized can be found in Section 3.6.2.

3.6.4.1 MDA imidacloprid water quality summary in river and streams

All MDA imidacloprid detections in rivers and streams are presented in Table 3-17 and Figures 3-13 and 3-14. Key findings include:

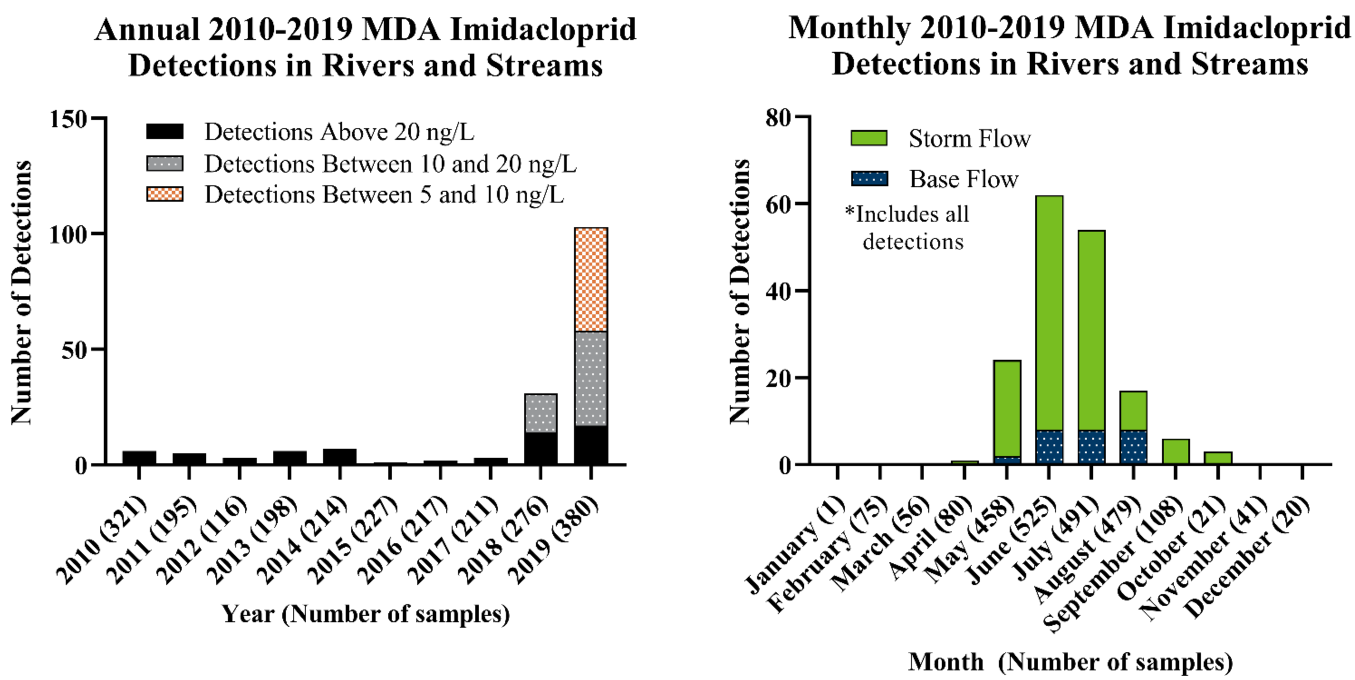
- The MDA monitored for imidacloprid at 266 different river and stream locations since 2010.
- One-hundred twenty-two detections of imidacloprid over the numeric USEPA OPP chronic aquatic life benchmark of 10 ng/L occurred at 28 different locations from 2010-2019.
- Two detections of imidacloprid over the numeric USEPA OPP acute aquatic life benchmark of 385 ng/L occurred at two different urban locations in 2012 and 2014.
- The majority of imidacloprid detections occurred in June and July (Figure 3-13).
    - Detections occurred in each month from April through October.
    - No detections occurred in January (one samples collected), February (75 samples collected), March (56 samples collected), November (41 samples collected), and December (20 samples collected).
- Overall, 84% of imidacloprid detections have occurred in storm flow conditions when rivers and streams had elevated water levels due to runoff or snowmelt (Figure 3-13).
- Annual imidacloprid detections above 20 ng/L ranged from one in 2015 to 17 in 2019.
    - The MDA increased the number of samples collected in agricultural watersheds in the MDA Tier network starting in 2018, leading to more detections.

Table 3-17. MDA water quality summary of imidacloprid in Minnesota rivers and streams.

Year	Samples	Number of Detections ≥20 ng/L	Number of Detections ≥10 ng/L and <20 ng/L*	Number of Detections ≥5 ng/L and <10 ng/L*	Maximum (ng/L)	Number of Detections ≥USEPA OPP Chronic Benchmark (10 ng/L)	Number of Detections ≥USEPA OPP Acute Benchmark (385 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥USEPA OPP Chronic Benchmark (10 ng/L)
2010	321	6	na	na	95.7	6	0	157	4
2011	195	5	na	na	131	5	0	69	4
2012	116	3	na	na	618	3	1	32	2
2013	198	6	na	na	32.2	6	0	20	6
2014	214	7	na	na	467	7	1	21	5
2015	227	1	na	na	23.1	1	0	45	1
2016	217	2	na	na	26.6	2	0	21	2
2017	211	3	na	na	27.6	3	0	21	3
2018	276	14	17	na	114	31	0	35	19
2019	380	17	41	45	32	58	0	30	23
2010-2019	**2,355**	**167**	**58**	**45**	**618**	**122**	**2**	**266**	**28**

**Detections in these columns are presented independently due to lowered MRL.*

Figure 3-13. 2010 through 2019 MDA imidacloprid detections in rivers and streams.



3.6.4.2 MDA imidacloprid water quality summary in lakes and wetlands

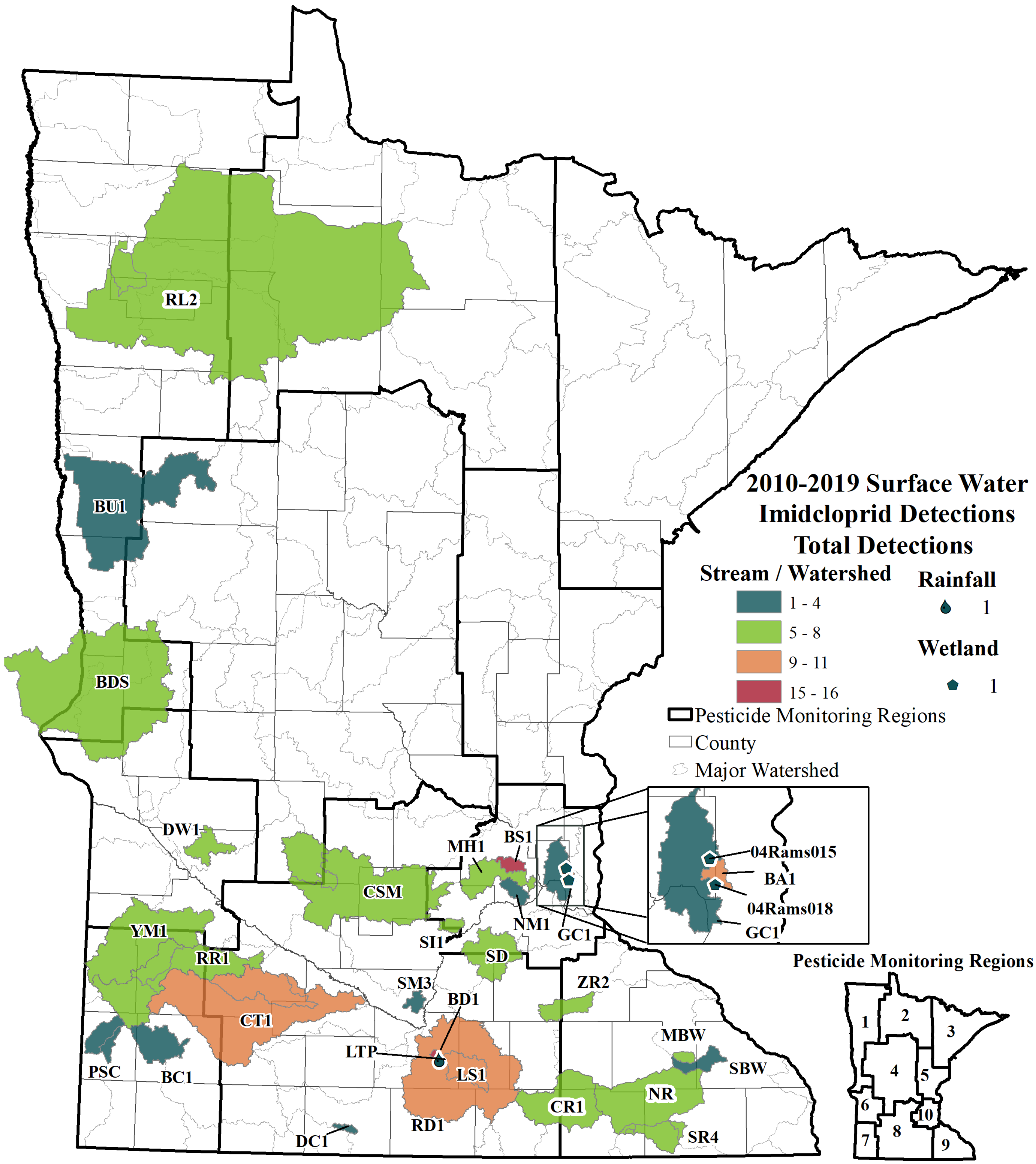
The MDA collected 156 samples from 133 lakes (2010 through 2019), and imidacloprid was not detected.

The MDA collected 43 samples from 42 wetlands from 2014 to 2016 and imidacloprid was detected in two wetlands in Ramsey County in June 2014 (25.2 ng/L and 76.8 ng/L). Both wetlands are in mixed land-use development within proximity to golf courses and residential dwellings.

3.6.4.3 MDA imidacloprid water quality summary in rainfall

The MDA operates a rainfall pesticide monitoring network (See Section 3.6 for more details). Imidacloprid was detected once in 77 rainfall samples collected since 2010 (Figure 3-14). The detection (10.1 ng/L) occurred in PMR 8 in May 2018.

Figure 3-14. Total number of MDA imidacloprid detections by location, 2010 through 2019.



3.6.5 Long-term MDA thiamethoxam surface water quality data

The MDA has analyzed and detected thiamethoxam since 2010. Thiamethoxam is a neonicotinoid insecticide with a numeric USEPA OPP chronic aquatic life benchmark of 740 ng/L, and a numeric USEPA OPP acute aquatic life benchmark of 17,500 ng/L. The thiamethoxam MRL was 25 ng/L since 2010. Thiamethoxam is an active ingredient that also degrades into clothianidin. Additional information on how thiamethoxam data were summarized can be found in Section 3.6.2.

3.6.5.1 MDA thiamethoxam water quality summary in river and streams

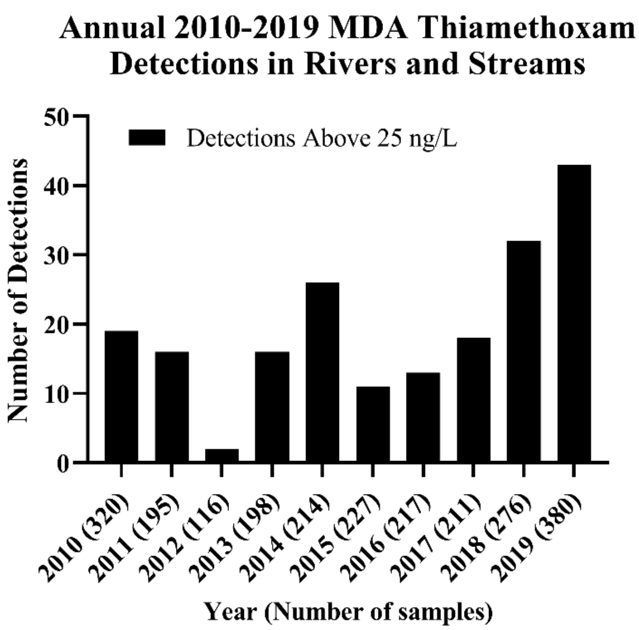
All MDA thiamethoxam detections in surface water (rivers and streams) are presented in Table 3-18 and Figures 3-15 and 3-16. Key findings include:

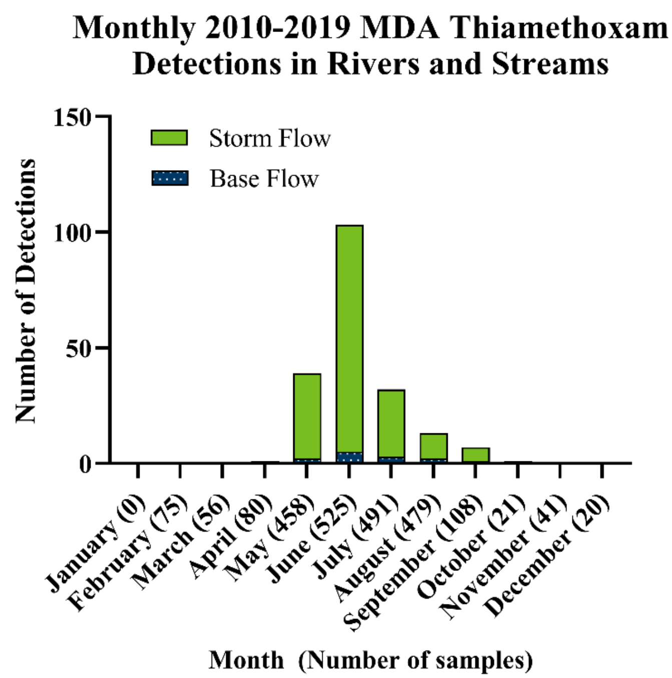
- The MDA monitored for thiamethoxam at 266 different river and stream locations.
- Thiamethoxam has not been detected over the numeric USEPA OPP chronic aquatic life benchmark of 740 ng/L. However, thiamethoxam does degrade to clothianidin, which has been detected over the numeric USEPA OPP aquatic life benchmark of 50 ng/L (Section 3.4.4).
- Thiamethoxam has not been detected over the numeric USEPA OPP acute aquatic life benchmark of 17,500 ng/L.
- The majority of thiamethoxam detections occurred from May through July (Figure 3-15).
    - Detections occurred in each month from April through October.
    - No detections occurred in January (one sample collected), February (75 samples collected), March (56 samples collected), November (41 samples collected), and December (20 samples).
- Overall, 93% of thiamethoxam detections occurred in storm flow conditions when rivers and streams had elevated water levels due to runoff.

Table 3-18. MDA water quality summary of thiamethoxam in Minnesota rivers and streams.

Year	Samples	Number of Detections ≥25 ng/L	Maximum (ng/L)	Number of Detections ≥USEPA OPP Chronic Benchmark (740 ng/L)	Number of Detections ≥USEPA OPP Acute Benchmark (17,500 ng/L)	Monitored Locations	Number of Locations with at Least One Detection(s) ≥USEPA OPP Chronic Benchmark (740 ng/L)
2010	320	19	130	0	0	157	0
2011	195	16	214	0	0	69	0
2012	116	2	39.5	0	0	32	0
2013	198	16	84	0	0	20	0
2014	214	26	223	0	0	21	0
2015	227	11	71.9	0	0	45	0
2016	217	13	118	0	0	21	0
2017	211	18	120	0	0	21	0
2018	276	32	277	0	0	35	0
2019	380	43	241	0	0	30	0
2010-2019	**2,354**	**196**	**277**	**0**	**0**	**266**	**0**

Figure 3-15. 2010 through 2019 MDA thiamethoxam detections in rivers and streams.





3.6.5.2 MDA thiamethoxam water quality summary in lakes and wetlands

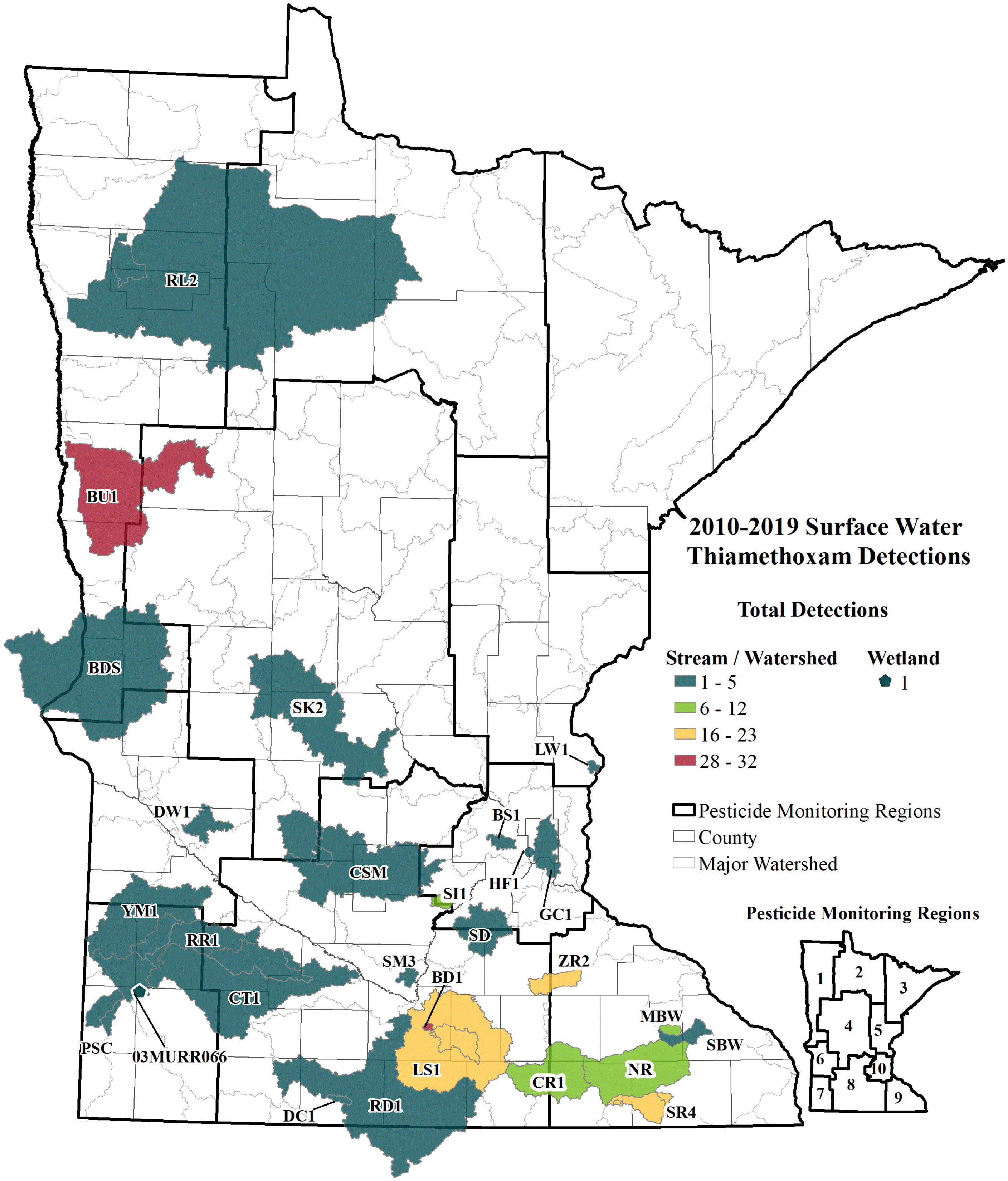
The MDA collected 156 samples from 133 lakes (2010 through 2019), and thiamethoxam was not detected in any lake samples.

The MDA collected 43 samples from 42 wetlands from 2014 to 2016, and thiamethoxam was detected (39.1 ng/L) in one wetland in Murray County in June 2014. The wetland is in an agricultural area with row crop fields in proximity.

3.6.5.3 MDA thiamethoxam water quality summary in rainfall

The MDA operates a rainfall pesticide monitoring network (See Section 3.6 for more details). Thiamethoxam was not detected in 77 rainfall samples collected since 2010.

Figure 3-16. Total number of MDA thiamethoxam detections by location, 2010 through 2019.

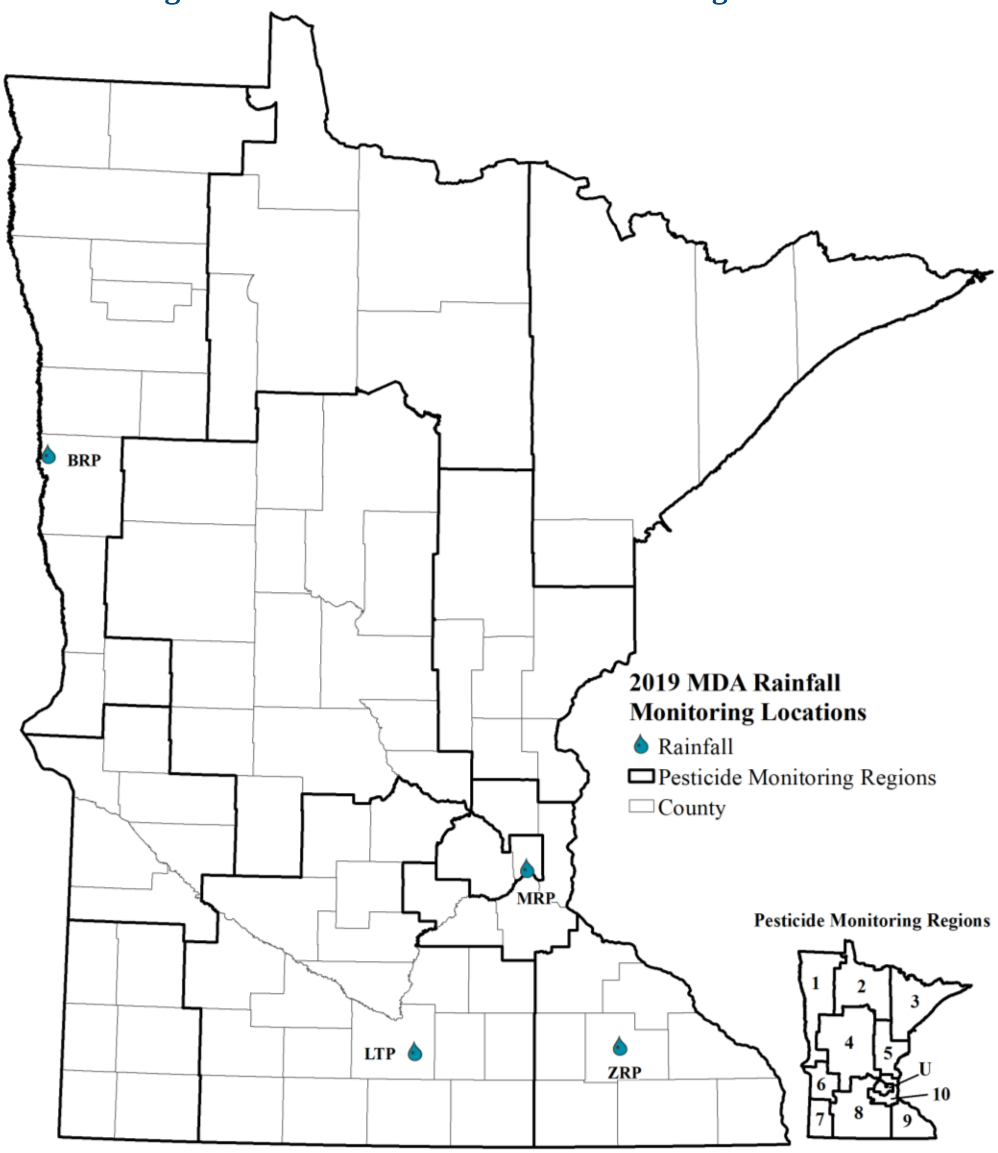


3.7 Rainfall pesticide monitoring

The current rainfall monitoring network for pesticides and nutrients began in PMR 8 in 2008, PMR 9 in 2009, PMR 1 in 2014 and at an urban location (St. Paul) in 2019 (Figure 3-16). Rainfall monitoring allows the MDA to assess atmospheric deposition of pesticide compounds and nutrients in rainfall in Minnesota.

Rainfall from April through October was collected in rainfall samplers. These samplers automatically opened a collection vessel at the onset of a rainfall event and closed immediately after the event. The sampler collected composite rainfall samples throughout the rainfall event or over a series of rainfall events. Samples were transferred to an on-site refrigerator at the time of collection for temporary storage until sufficient volume was collected for pesticide analysis. Nutrient samples were collected when sufficient volume was available after the volume necessary for pesticide analysis was attained (See Section 6 for nutrient results).

Figure 3-17. MDA 2019 rainfall monitoring locations.



3.7.1 2019 Rainfall pesticide monitoring results

A total of 24 GC-MS/MS, 12 LC-MS/MS, and seven glyphosate LC-MS/MS samples were collected at the four locations in 2019 (Table 3-19).

Key data findings include:

- Twenty of the 166 pesticide analytes were detected at least once.
  - Detected pesticide types included: herbicide (13), herbicide degradates (4), and fungicide (3).
- Pesticides detection frequencies included: 2,4-D (100%), deisopropylatrazine (67%), metolachlor (67%), and didealkylatrazine (58%).
  - 2,4-D and metolachlor are herbicides.
  - Deisopropylatrazine and didealkylatrazine are degradates of atrazine.
- 2,4-D, acetochlor, atrazine, deisopropylatrazine, didealkylatrazine, and metolachlor were detected at every rainfall monitoring location.
- Four analytes were detected for the first time in MDA's rainfall monitoring:
  - Clomazone (15.1 ng/L), EPTC (13.3 ng/L), and sulfentrazone (56.5 ng/L) were detected in PMR 1.
  - Clopyralid (44.9 ng/L) was detected in PMR 8.
- Neither glyphosate nor AMPA were detected in the seven samples they were analyzed in.

Table 3-19. 2019 rainfall pesticide results for detected analytes.

Detected Pesticides in Rainfall	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)	Maximum (ng/L)	PMRs Detected
2,4-D	12	12	100	96.9	192	1,8,9,U
Acetochlor	24	13	54	45.4	673	1,8,9,U
Atrazine	24	12	50	<30	983	1,8,9,U
Deisopropylatrazine	12	8	67	28.0	253	1,8,9,U
Desethylatrazine	24	6	25	<50	307	1,8,U
Didealkylatrazine	12	7	58	55.9	523	1,8,9,U
Hydroxyatrazine	12	2	17	<6.7	13.5	8,9
Azoxystrobin	12	2	17	<10	62.5	8
Bentazon	12	1	8	<5	10.8	1
Bromoxynil	12	1	8	<25	107	1
Clomazone	24	1	4	<15	15.1	1
Clopyralid	12	1	8	<41.6	44.9	8
Dicamba	12	4	33	<50	82.0	1,8,U
Dimethenamid	24	2	8	<15	29.6	1,8
EPTC	24	1	4	<10	13.3	1
MCPA	12	3	25	<5	66.8	1
Metolachlor	24	16	67	71.2	958	1,8,9,U
Propiconazole	12	2	17	<10	55.4	8
Sulfentrazone	12	1	8	<50	56.5	1
Tebuconazole	12	4	33	<10	43.1	1,U

3.8 Lake pesticide monitoring

The MDA conducts statewide lake monitoring every five years as part of the National Lake Assessment (NLA), in collaboration with the MPCA. The NLA provides the MDA with an opportunity to monitor randomly selected lakes to track pesticide occurrence and magnitude overtime. The MDA analyzed pesticide samples in 2007, 2012, and 2017.

Chlorpyrifos is the only pesticide that has been detected at concentrations above a reference value. Chlorpyrifos was detected in the 2017 NLA in Cup Lake (Big Stone County; MN DNR Lake ID 06-0120) and Double Lake (Cottonwood County; MN DNR Lake ID 17-0056). The MDA resampled both lakes in 2018, and chlorpyrifos was again detected in Double Lake. As a result of the chlorpyrifos detections in 2017 and 2018, Double Lake was designated as impaired for chlorpyrifos on the 2020 USEPA Impaired Waters List. The MDA will collect annual samples from Double Lake and plans to participate in the 2022 NLA.

The MDA collected three samples during July and August from Double Lake in 2019 and detected eight pesticides (Table 3-20) at concentrations below water quality reference values. Seven pesticides were detected in every sample (2,4-D, acetochlor ESA, acetochlor OXA, atrazine, hydroxyatrazine, metolachlor ESA, and metolachlor OXA) and metolachlor was detected in 67% of the samples. All detections in 2019 were low compared to the lowest applicable reference value. Chlorpyrifos was not detected in 2019.

Table 3-20. 2019 Double Lake pesticide results for detected analytes.

Detected Pesticides	Pesticide Type	Total Samples	Detections	Detection Frequency (%)	Median (ng/L)	Maximum (ng/L)
2,4-D	Herbicide	3	3	100	29.3	32.7
Acetochlor ESA	Herbicide Degradate	3	3	100	241	246
Acetochlor OXA	Herbicide Degradate	3	3	100	245	257
Atrazine	Herbicide	3	3	100	49.7	57.7
Hydroxyatrazine	Herbicide Degradate	3	3	100	79.6	84.6
Metolachlor	Herbicide	2	3	67	29.3	41.3
Metolachlor ESA	Herbicide Degradate	3	3	100	344	363
Metolachlor OXA	Herbicide Degradate	3	3	100	132	133

Section 4: Special Monitoring Studies in 2019

2019 Water Quality Monitoring Report

Section 4: Special Monitoring Studies in 2019

4.1 Plot and field scale evaluation

The MDA Pesticide and Fertilizer Management Division (PFMD), along with project partners, conducted edge-of-field monitoring in 2019 throughout Minnesota. Each of these monitoring projects have their own unique goals but are generally focused on BMP effectiveness monitoring and/or drainage water management. PFMD staff from the MAU and the Clean Water Technical Unit (CWTU) play a critical role in these efforts. Demonstration sites include surface water run-off sites and subsurface drainage monitoring sites. The objective of these projects was to evaluate run-off characteristics as well as nutrient, total suspended solids and in some instances, pesticide losses from surface and subsurface agricultural drainage systems. Detailed information regarding agricultural inputs were collected and interpreted with water quality results to determine the impact of particular practices. The field scale monitoring sites are situated at locations throughout the state (Figure 4-0).

A brief description and website for each project can be found in Table 4-0. Additional information is also available from MAU and CWTU staff, upon request.

Figure 4-0. Current and historic MDA field scale monitoring sites.

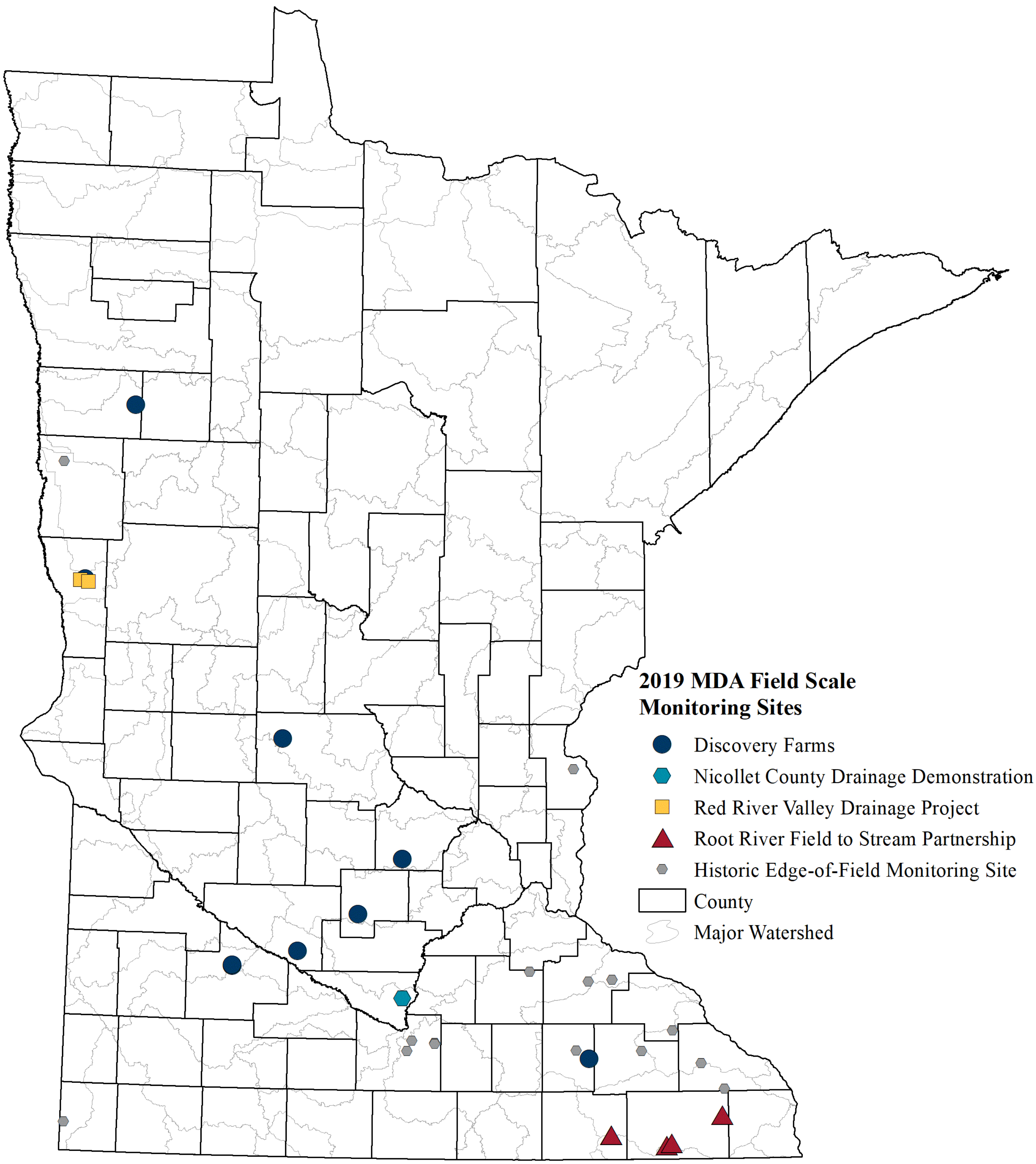


Table 4-0. 2019 plot and field scale monitoring projects.

Project	County(s)	Term/ End Date	Type	Analytes	Website
Clay County Drainage Demonstration Site	Clay	Long-term / 2019	Surface and Subsurface drainage	Nutrients and TSS	www.mda.state.mn.us/protecting/cleanwaterfund/onfarmprojects/claycounty
Discovery Farms Minnesota	Dodge, McLeod, Norman, Redwood, Renville, Rock, Stearns, Wright	Long-term	Surface and Subsurface drainage	Nutrients and TSS	www.discoveryfarmsmn.org/
Nicollet County Drainage Demonstration	Nicollet	Long-term	Subsurface drainage	Nutrients and Pesticides	none
Red River Valley Drainage Management Project	Wilkin	Long-term	Surface and Subsurface drainage	Nutrients and TSS	www.mda.state.mn.us/redrivervalleydwm
Root River Field to Stream Partnership	Mower, Fillmore	Long-term	Surface and Subsurface drainage	Nutrients and TSS	www.mda.state.mn.us/root-river-field-stream-partnership; www.rootriverfieldtostream.org

Clay County Drainage Demonstration site

The Clay County Drainage Demonstration site is located in the Red River Valley, an area where new subsurface drainage systems continue to be installed. This demonstration site was designed to evaluate the sediment and nutrient losses from both surface and subsurface drainage from agricultural fields. The site includes six subsurface drainage plots and one surface runoff plot, each ranging from 20 to 24 acres in size. The first full year of data collection was 2011 with uniform management across the seven plots. Starting in 2016, controlled drainage was implemented on two subsurface drained plots to manage tile drainage, while the other four were in conventional (free) drainage. A paired plot design was utilized to compare controlled drainage (drainage water management) and conventional drainage. Table 4-1 provides information related to the location and type of fields that were monitored in 2019. The monitoring at the Clay County Drainage site was discontinued on December 31, 2019.

Discovery Farms Minnesota

Discovery Farms Minnesota (DFM) is a producer-led effort organized by the Minnesota Agricultural Water Resource Center (MAWRC) in partnership with the MDA. The DFM activities include the edge-of-field collection of water quality and quantity data from surface runoff and/or subsurface drainage, with a focus on nutrients and sediment. Sample collection began in 2011 at four farms. In 2019, nine locations were monitored, comprising 15 different sites. Two of these locations, in McLeod and Redwood Counties, were monitored for their second full year. The Redwood County farm has two separate edge-of-field sites that provide a paired watershed design study. The three new monitoring sites monitor both surface and subsurface runoff. In the future, the program will prioritize a paired watershed design at new farms entering the program. Table 4-1 provides information related to the location and type of fields that were monitored in 2019.

Nicollet County Drainage Demonstration

Nutrient and pesticide monitoring were conducted at two adjacent edge of field sub-surface tile drainage sites from 1998 through 2009. The sub-surface drainage monitoring sites were reestablished in the spring of 2019. The sites are located near the St. Peter Drinking Water Supply Management Area (DWSMA), that is targeted for local groundwater monitoring activities under the Nitrogen Fertilizer Management Plan. In addition, the sites drain to Seven Mile Creek that has been listed as an impaired water body by nitrate by the Minnesota Pollution Control Agency. Using a paired watershed design, this project evaluates the effectiveness of nitrogen best management practices (BMPs) and alternative management tools at reducing nitrogen loss from row crop agriculture with subsurface drainage. Pesticide loss from agricultural drainage systems was also evaluated. Table 4-1 provides information related to the location and type of fields that were monitored in 2019.

Red River Valley Drainage Water Management Project

The objective of the Red River Valley Drainage Water Management project is to demonstrate controlled drainage and a saturated buffer in an effort to determine their impacts on water quality and quantity (flood mitigation). Two fields are intensively monitored to achieve these objectives. Field 1 is divided into three areas and utilizes a paired design approach to compare the areas with no subsurface drainage, conventional (free) drainage (*i.e.*, no control of the outlet elevation) and controlled drainage. Field 2 has two zones with controlled drainage and a third zone containing a saturated buffer for nitrate removal from the drainage water. The intent of the project is to be a compelling example for increasing the acceptance and adoption of drainage water management practices in the Red River Valley, with an additional benefit of showing how to minimize the environmental impact of subsurface drainage while maintaining or improving agricultural productivity. The practices were installed in the fall of 2015 and monitoring started on January 1, 2017. Table 4-1 provides information related to the location and type of fields that were monitored in 2019.

Root River Field to Stream Partnership

The primary objective of the Root River Field to Stream Partnership is to conduct intensive water quality monitoring at multiple scales and landscape settings to evaluate the effect of agricultural practices on water quality. Monitoring scales include individual agricultural fields, springsheds and small subwatersheds (HUC 14) within the Root River watershed. These data will help improve the understanding of how agricultural practices affect water quality throughout a ten- county area in southeast Minnesota. In 2017, targeted conservation practice implementation began throughout the three subwatersheds and will continue through 2020. Monitoring will continue to provide additional data on how targeted conservation practices affect nutrient and sediment loading at both the field and small watershed scales. Table 4-1 provides information related to the location and type of fields that were monitored in 2019.

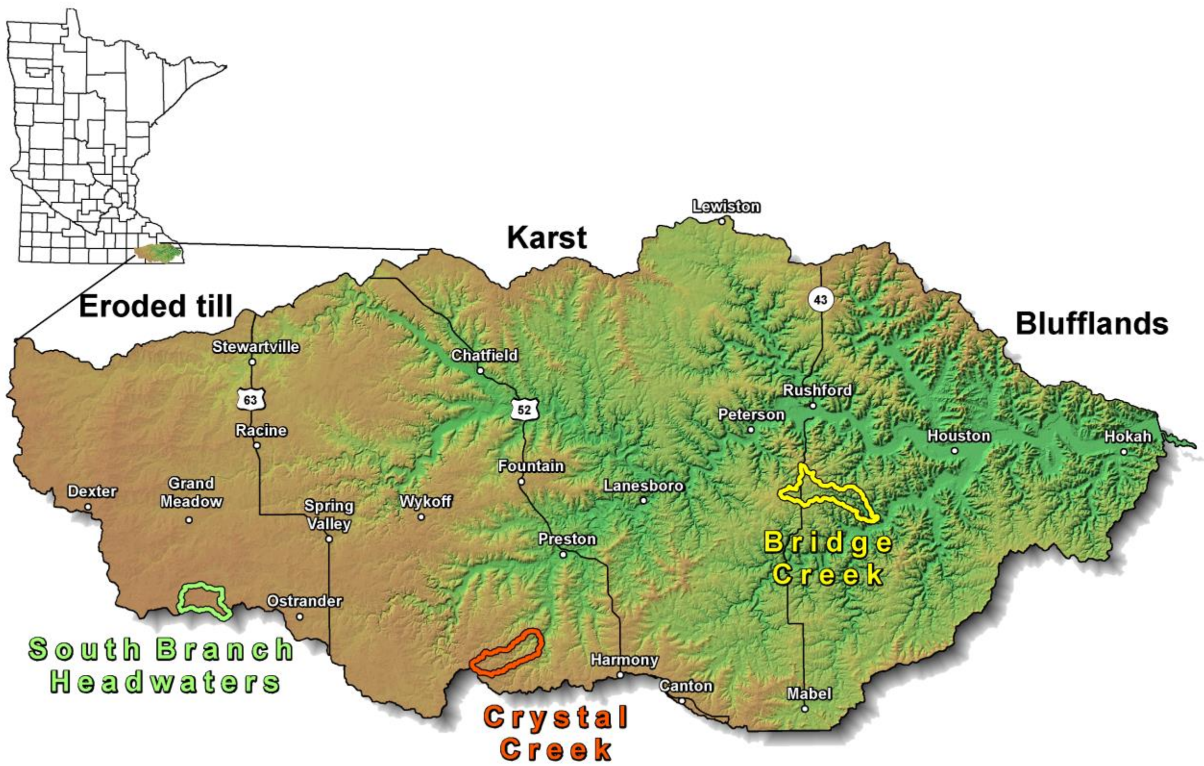
Table 4-1. 2019 MDA field scale monitoring sites.

Project	Site ID	County	Farm Type	Major Watershed	Major Basin	Drainage Area (acres) and site type	Crops Grown
Clay County Drainage Demonstration	EDS 1-3 (3 sites)	Clay	Grain	Buffalo	Red River of the North	22.7 Subsurface (each site)	Corn-Sugar Beets-Edible Bean
	WDS 4-6 (3 sites)	Clay	Grain	Buffalo	Red River of the North	20.5 Subsurface (each site)	Corn-Sugar Beets-Edible Bean
	SDS7	Clay	Grain	Buffalo	Red River of the North	24.5 Surface	Corn-Sugar Beets-Edible Bean
Discovery Farms Minnesota	DO1	Dodge	Swine	Zumbro	Lower Mississippi	13.9 Surface 13.9 Subsurface	Corn-Soybean
	MC1	McLeod	Grain	South Fork Crow River	Upper Mississippi	58.3 Surface 58.3 Subsurface	Corn-Soybean
	NO1W	Norman	Grain	Eastern Wild Rice	Red River of the North	312.5 Subsurface 258.3 Subsurface	Edible Bean-Soybean-Corn-Wheat-Sugar Beets
	RW1N	Redwood	Grain	Redwood	Minnesota	12.2 Surface 12.2 Subsurface	Corn-Soybean
	RW1S	Redwood	Grain	Redwood	Minnesota	10.2 Surface 10.2 Subsurface	Corn-Soybean
	RE1	Renville	Grain	Middle Minnesota	Minnesota	81.0 Subsurface with open inlets	Corn-Soybean-Sweet Corn-Peas
	RO1	Rock	Beef-Grain	Lower Big Sioux	Missouri	25.5 Surface	Corn-Soybean-Alfalfa
	ST1	Stearns	Dairy	Sauk	Upper Mississippi	24.8 Subsurface	Corn-Alfalfa
	WR1	Wright	Dairy	North Fork Crow	Upper Mississippi	23.9 Surface 23.9 Subsurface	Corn-Alfalfa
Nicollet County Drainage Demonstaration	RM1	Nicollet	Grain	Middle Minnesota	Minnesota	24.4 Subsurface	Corn-Soybean
	RW1	Nicollet	Grain	Miiddle Minnesota	Minnesota	57.6 Subsurface	Corn-Soybean
Red River Valley Drainage Water Management Project	CS01_16	Wilkin	Grain	Upper Red	Red River of the North	52 Subsurface	Corn-Soybean, occasional wheat
	CS02-05_16 (4 sites) (subsets of CS01_16)	Wilkin	Grain	Upper Red	Red River of the North	Approx. 13 Subsurface (each site)	Corn-Soybean, occasional wheat
	CS06_16	Wilkin	Grain	Upper Red	Red River of the North	52 Subsurface	Corn-Soybean, occasional wheat
	CS01-02_24 (2 sites)	Wilkin	Grain	Upper Red	Red River of the North	27 Subsurface (each site)	Corn-Soybean, occasional wheat
	CS03_24	Wilkin	Grain	Upper Red	Red River of the North	1 Subsurface	Corn-Soybean, occasional wheat
Root River Field to Stream Partnership	BCE	Fillmore	Dairy-Swine	Root	Lower Mississippi	21.4 Surface	Corn-Alfalfa
	CFE	Fillmore	Grain-Swine	Root	Lower Mississippi	96.0 Surface	Corn-Soybean-Alfalfa
	CFW	Fillmore	Dairy	Root	Lower Mississippi	18.4 Surface	Corn
	SRF	Mower	Grain	Root	Lower Mississippi	26.2 Surface	Corn-Soybean
	SRT	Mower	Grain	Root	Lower Mississippi	58.8 Subsurface	Corn-Soybean

4.2 Root River Pesticide Study

The MDA began monitoring for pesticides in cooperation with the Root River Field to Stream Partnership (RRFSP) in 2012. In-stream monitoring sites, featuring automated samplers for pesticide sample collection, are located at the outlet of three small (HUC 14) watersheds (South Branch of the Root River Headwaters (Headwaters), Crystal Creek, and Bridge Creek; Figure 4-1). Each small watershed monitoring site has a drainage area ranging from 2,800 – 4,700 acres. This enhanced monitoring is known as the Root River Pesticide Study. The goal is to to better characterize pesticide fate and transport in agricultural watersheds of southeastern Minnesota, in an effort to develop a better understanding of the conditions that can potentially lead to an exceedance of pesticide water quality standards.

Figure 4-1. Sub-watershed locations monitored as part of the Root River Field to Stream Partnership.



4.2.1 Root River Pesticide Study results

In 2019, 70 pesticide samples were analyzed using the MDA Laboratory’s GC-MS/MS analytical method from the three small watershed monitoring locations. Samples were collected year-round; however, most samples were collected in May through August during the typical agricultural pesticide application period. Samples were collected as a combination of equal-flow increment (EFI) composites and grab samples. Most storm flow was sampled through the use of automated samplers to collect composite samples, and base flow was sampled using grab sampling techniques. The data from the

RRFSP Pesticide Project are not included in the routine pesticide monitoring summary presented in Section 3 of this report because the objectives of this project, and subsequent sample collection methodologies are different from the MDA routine tier surface water monitoring program.

Since the RRFSP Pesticide Project began in 2012, the watersheds have experienced a wide range of climatic conditions. Conditions have ranged from very dry, to near normal precipitation, to very wet conditions. In some years runoff has occurred primarily during snowmelt. In other years, runoff occurred throughout the summer, while in other years runoff occurred primarily in the fall. This wide range of climatic conditions has provided a good opportunity to assess the water quality data based on varying climatic conditions. At this point in the study, the highest concentrations observed have coincided with precipitation-driven storm flow events during the pesticide application period in southeast Minnesota (May through August). Since 2012, over 99% of detections were herbicides or herbicide degradates. Watershed pesticide loads have been calculated each year and are available upon request.

Highlights from the 2019 Root River Pesticide Study sampling summary for 2019 (Table 4-2) include:

The GC-MS/MS analytical method included 40 analytes in 2019; seven pesticide analytes were detected at the Root River Pesticide Study locations.

The Headwaters had one sample with concentrations of acetochlor (14,100 ng/L) and atrazine (12,400 ng/L) that were above the Minn. Rules Ch. 7050 chronic standards (3,600 ng/L and 10,000 ng/L, respectively). This EFI sample represented an 84 hour period and was collected on June 16th.

The Headwaters had one EFI sample (46 hour duration) collected on May 10th with a metolachlor concentration (27,500 ng/L) greater than the Minn. Rules Ch. 7050 chronic standard (23,000 ng/L).

Metribuzin and propazine were only detected in the Headwaters watershed.

The greatest metribuzin concentration (6,100 ng/L) observed throughout the history of the MDA surface water program occurred in the Headwaters. This concentration was in the same sample that had the high metolachlor concentration collected on May 10th.

The Bridge Creek and Crystal Creek locations had almost the same number of samples collected (26 and 25 samples, respectively), while the Headwaters location had fewer samples collected (19). The difference in the number of samples collected was due to the flow at the Headwaters watershed nearly ceased for most of July and all of August due to dry conditions.

Table 4-2. 2019 summary statistics for pesticide compounds detected in the Root River Pesticide Study.

Acetochlor	Headwaters	19	8	42	<30	14,100	3,600
	Crystal Creek	25	3	12	<30	166	
	Bridge Creek	26	7	27	<30	1,930	
Atrazine	Headwaters	19	17	89	59.6	12,400	10,000
	Crystal Creek	25	10	40	<25	306	
	Bridge Creek	26	23	88	34.8	1,170	
Desethylatrazine	Headwaters	19	18	95	89.0	718	1,000,000
	Crystal Creek	25	3	12	<50	86.3	
	Bridge Creek	26	26	100	81.3	225	
Dimethenamid	Headwaters	19	15	79	61.5	3,720	8,900
	Crystal Creek	25	6	24	<15	168	
	Bridge Creek	26	2	8	<15	168	
Metolachlor	Headwaters	19	17	89	274	27,500	23,000
	Crystal Creek	25	13	52	26.2	7,380	
	Bridge Creek	26	8	31	<25	15,100	
Metribuzin	Headwaters	19	8	42	<75	6,050	8,100
	Crystal Creek	25	0	0	<75	<75	
	Bridge Creek	26	0	0	<75	<75	
Propazine	Headwaters	19	1	5	<25	146	24,800
	Crystal Creek	25	0	0	<25	<25	
	Bridge Creek	26	0	0	<25	<25	

**Non-detections are reported as "less than MRL" (< MRL). The MRL is the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.*

***Please refer to Table 3-0 of this report for the source of each reference value and for more information regarding these values.*

4.3 Private Well Pesticide Sampling Project

The Private Well Pesticide Sampling (PWPS) Project was initiated to provide information to homeowners and the general public about the presence of pesticides in private drinking water wells. The PWPS Project is a companion program to the MDA Township Testing Program (TTP). In both the TTP and PWPS Project, sample collection was targeted to townships with both vulnerable groundwater and row crop agriculture. Homeowners with a nitrate detection in their drinking water well as part of the TTP have the opportunity to have a follow-up sample collected from their well and analyzed for select pesticides and nitrate as part of the PWPS Project.

The MDA began evaluating pesticide presence and magnitude in private residential drinking water wells in 2014. From 2014 through 2019, the MDA has sampled approximately 6,100 wells in 42 counties. The MDA estimates an additional 840 wells will be sampled in an additional eight counties by the time the PWPS Project concludes on June 30, 2021 (Figure 4-2).

The MDA Laboratory was not able to accommodate the anticipated sample load for the PWPS Project due to other obligations and commitments. MDA contracted with Weck Laboratories (Weck) for sample analysis in 2019. Weck analyzes water samples for pesticides using a direct aqueous injection LC-

MS/MS method, with MRLs similar to those attainable by the MDA Laboratory. Resampling of wells, that had been previously sampled for pesticides during the 2014 and 2015 seasons, will continue to occur using the updated analytical method as time and budget allow.

4.3.1 2019 PWPS Project results

Groundwater samples collected in 2019 were analyzed for 133 pesticides and pesticide degradates with MRLs ranging from 5 to 1,000 ng/L. The MDA sampled 1,103 wells in twenty-three counties (Tables 4-3 and 4-4, Table 4-4 presents only those pesticides detected in any PWPS sample) in 2019. The results will be reported and summarized as part of the 2019 Private Well Pesticide Sampling County Summary Reports. For additional information, please visit the PWPS Project website.

A brief synopsis of the results and general findings are as follows:

2019 County Summary

- Pesticide detections and results varied by county in 2019.
  - The percentage of wells with at least one pesticide detection ranged from 16% (Meeker; 19 wells sampled) to 100% (Lincoln; one well sampled).
  - The total number of different pesticides and pesticide degradates detected in a single well ranged from one (Faribault and Lincoln) to 34 (Houston).
- Twenty-nine sampled wells had a pesticide concentration above an applicable human health reference value.
  - All were for total cyanazine (two in Chippewa, three in Houston, four in Olmsted, one in Pipestone, 17 in Scott, and two in Wright).

2019 Overall Summary

- Fifty-three pesticides and/or pesticide degradates were detected at least once.
  - Forty-six pesticides and/or pesticide degradates were detected in fewer than 10% of samples.
  - Four pesticides and/or pesticide degradates were detected in more than 20% of samples.
- At least one pesticide or pesticide degradate was detected in 72% of the wells sampled.
- Metolachlor ESA was the most frequently detected pesticide analyte.
- AMPA, a degradate of glyphosate, was detected (2,100 ng/L) in one Pipestone County well.
  - The MDA collected a confirmation sample approximately three months after the first sample, and AMPA was not detected.

- The MDA learned that the detection may have been due to contamination. Bottles of herbicide containers had been temporarily stored near where the initial sample was collected and there were well construction issues/damage noted.

- Four neonicotinoid insecticides were infrequently detected: clothianidin (3%), dinotefuran (<1%), imidacloprid (2%), and thiamethoxam (<1%).

- It was common for multiple pesticides and pesticide degradates to be detected in a single well (Figure 4-3).
  - Twenty-eight percent of the wells did not have a pesticide detection.
  - Seventeen percent of the total wells sampled had a single pesticide and/or pesticide degradate detection.
  - Forty-six percent of the total wells sampled had between two to six pesticides and/or degradates detected.
  - Nine percent of the total wells sampled had between seven and 16 pesticides and/or degradates detected.
  - The largest number of pesticides and/or pesticide degradates detected in a single well was 16.

Figure 4-2. Townships that have been sampled, or are scheduled for sampling, as part of the Private Well Pesticide Sampling Project.

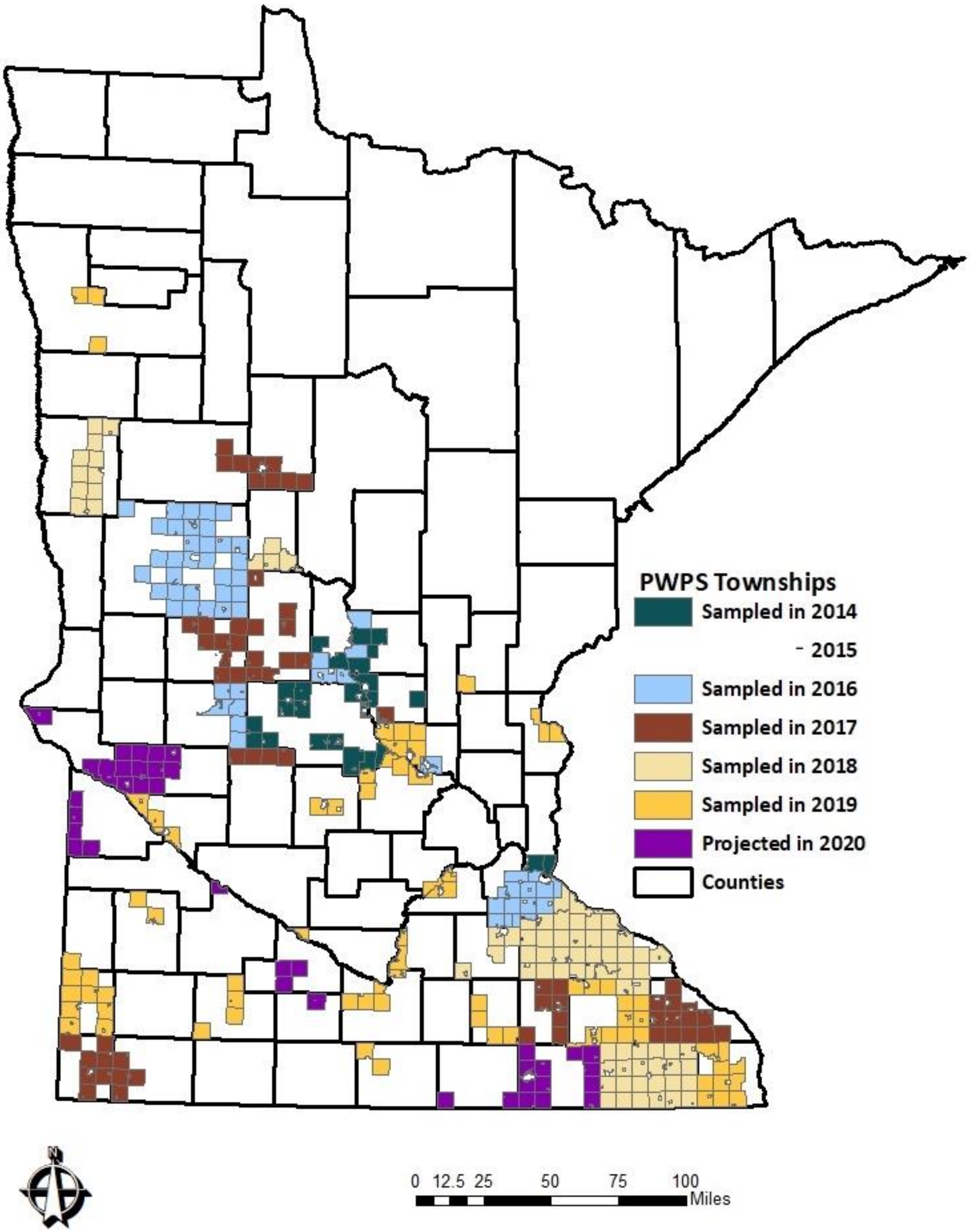


Table 4-3. PWPS Project sample numbers and pesticide detection frequencies for 2019 sampling.

County	Total Number of Pesticides & Pesticide Degradates Detected	Wells Sampled	Number of Wells with at least one Pesticide Detection	Percentage of Wells with at least one Pesticide Detected	Number of Wells with an Exceedance of a Health Reference Value
Blue Earth	13	43	20	47	0
Carver	7	27	19	70	0
Chippewa	21	46	24	52	2
Chisago	17	95	71	75	0
Cottonwood	8	5	4	80	0
Faribault	1	6	1	17	0
Houston	34	150	122	81	3
Kanabec	6	8	6	75	0
Le Sueur	11	37	22	59	0
Lincoln	1	1	1	100	0
Lyon	3	4	1	25	0
Meeker	6	19	3	16	0
Nicollet	6	4	3	75	0
Olmsted	26	123	103	84	4
Pipestone	33	35	32	91	1
Polk	4	11	3	27	0
Scott	16	91	66	73	17
Sherburne	27	189	160	85	0
Steele	16	21	8	38	0
Wright	30	177	114	64	2
2018 Carryovers*	13	11	6	55	0
Total	**53**	**1,103**	**789**	**72**	**29**

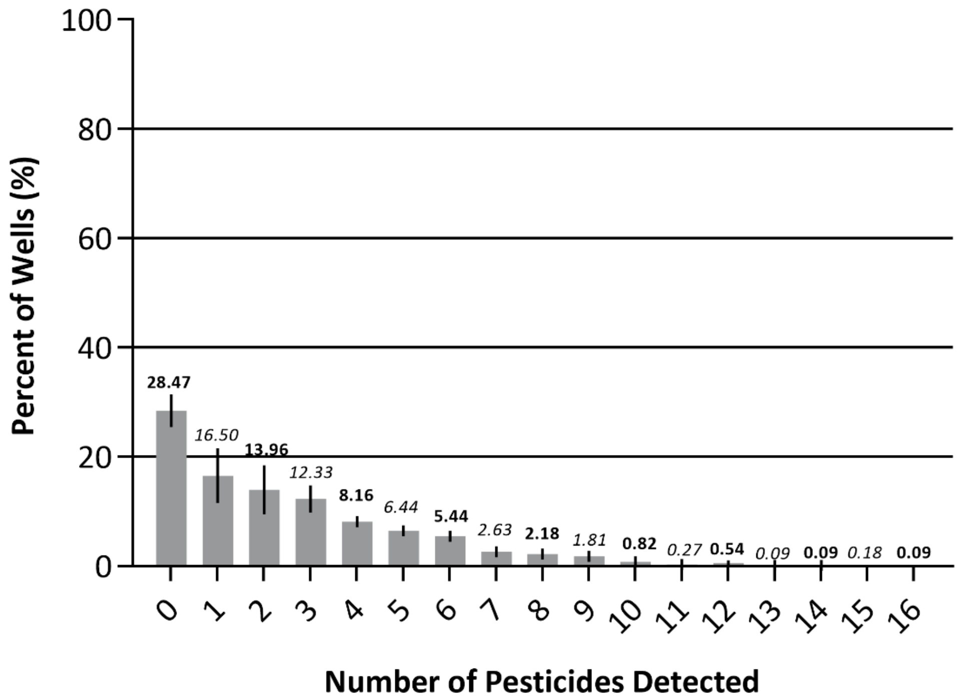
**Due to time constraints, eleven wells in Fillmore, Goodhue, and Wabasha Counties that were scheduled to be sampled in 2018 were sampled in 2019.*

Table 4-4. 2019 PWPS Project pesticide detection summary from 1,103 samples.

Pesticide	Number of Detections	Detection Frequency (%)	Median (ng/L)	90^{th} Percentile (ng/L)	Maximum (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type
2,4-D	5	<1	<10	<10	**590**	30,000	HRL_{18}
Acetochlor	2	<1	<30	<30	**100**	20,000	HRL_{18}
Acetochlor ESA	156	14	<30	**49.0**	**1,700**	300,000	HRL_{18}
Acetochlor OXA	10	1	<33	<33	**600**	90,000	HRL_{18}
Alachlor	2	<1	<30	<30	**77.0**	9,000	HRL_{18}
Alachlor ESA	446	40	<42	**340**	**5,400**	50,000	RAA_{16}
Alachlor OXA	19	2	<33	<33	**800**	50,000	RAA_{16}
Atrazine	160	15	<30	**44.0**	**630**	3,000	HRL_{MCL}
Deisopropylatrazine	77	7	<25	<25	**270**	3,000	Parent HRL_{MCL}
Desethylatrazine	167	15	<50	**87.0**	**1,500**	3,000	Parent HRL_{MCL}
Didealkylatrazine	281	25	<50	**150**	**1,100**	3,000	Parent HRL_{MCL}
Hydroxyatrazine	76	7	<6.7	<6.7	**320**	20,000	RA_{14}
Bentazon	56	5	<5	<5	**1,000**	30,000	HRL_{15}
Carbendazim	1	<1	<10	<10	**85.0**	9,000	RA_{14}
Clomazone	1	<1	<15	<15	**37.0**	70,000	RA_{14}
Clopyralid	5	<1	<50	<50	**2,000**	200,000	RA_{14}
Clothianidin	29	3	<25	<25	**370**	200,000	HRL_{18}
Cyanazine	2	<1	<25	<25	**33.0**	1,000	HRL_{18}
Cyanazine acid	25	2	<10	<10	**1,600**	1,000	Parent HRL_{18}
Cyanazine amide	38	3	<10	<10	**1,600**	1,000	Parent HRL_{18}
Deethylcyanazine acid	99	9	<25	<25	**9,000**	1,000	Parent HRL_{18}
Deethylcyanazine amide	1	<1	<25	<25	**230**	1,000	Parent HRL_{18}
Cyfluthrin	1	<1	<100	<100	**220**	6,000	RA_{14}
Dicamba	5	<1	<50	<50	**370**	700,000	RA_{14}
Dimethenamid	1	<1	<15	<15	**34.0**	300,000	HRL_{15}
Dimethenamid ESA	43	4	<6.7	<6.7	**410**	300,000	RAA_{13}
Dimethenamid OXA	12	1	<10	<10	**200**	300,000	RAA_{13}
Dinotefuran	1	<1	<25	<25	**40.0**	5,000	RA_{14}
Diuron	1	<1	<13	<13	**73.0**	2,000	RA_{14}
Flumetsulam	35	3	<50	<50	**300**	400,000	RA_{14}
Fomesafen	29	3	<50	<50	**7,000**	20,000	HBV_{20}
AMPA	1	<1	<1,000	<1,000	**2,100**	1,000,000	HBV_{17}
Hexazinone	3	<1	<10	<10	**110**	10,000	RA_{14}
Imazamox	2	<1	<13	<13	**1,600**	20,000,000	RA_{14}
Imazapyr	15	1	<8.3	<8.3	**4,100**	900,000	RA_{14}
Imazethapyr	4	<1	<10	<10	**40.0**	900,000	RA_{14}
Imidacloprid	26	2	<5	<10	**170**	3,000	HBV_{19}
MCPA	2	<1	<5	<5	**21.0**	7,000	RA_{14}
Metalaxyl	2	<1	<8.3	<8.3	**46.0**	20,000	RA_{14}
Metolachlor	14	1	<25	<25	**730**	300,000	HRL_{11}
Metolachlor ESA	661	60	**30.0**	**904**	**13,000**	800,000	HRL_{11}
Metolachlor OXA	228	21	<10	**59.0**	**2,300**	800,000	HRL_{11}
Metribuzin DA	9	1	<25	<25	**170**	10,000	RAA_{12}
Metribuzin DADK	9	1	<500	<500	**1,200**	10,000	RAA_{12}
Metsulfuron-methyl	4	<1	<23	<23	**120**	400,000	RA_{14}

Pesticide	Number of Detections	Detection Frequency (%)	Median (ng/L)	90th Percentile (ng/L)	Maximum (ng/L)	Reference Value (ng/L)	Groundwater Reference Value Type
Picloram	10	1	<42	<42	**5,200**	300,000	RA_{14}
Propiconazole	2	<1	<10	<10	**27.0**	90,000	RA_{14}
Saflufenacil	10	1	<15	<15	**100**	40,000	RA_{14}
Simazine	1	<1	<75	<75	**80.0**	4,000	HRL_{MCL}
Sulfentrazone	19	2	<50	<50	**2,900**	200,000	RA_{18}
Thiamethoxam	5	<1	<25	<25	**160**	200,000	HRL_{18}
Triclopyr	2	<1	<50	<50	**310**	80,000	RA_{14}
zeta-Cypermethrin	1	<1	<500	<500	**2,900**	50,000	RA_{14}

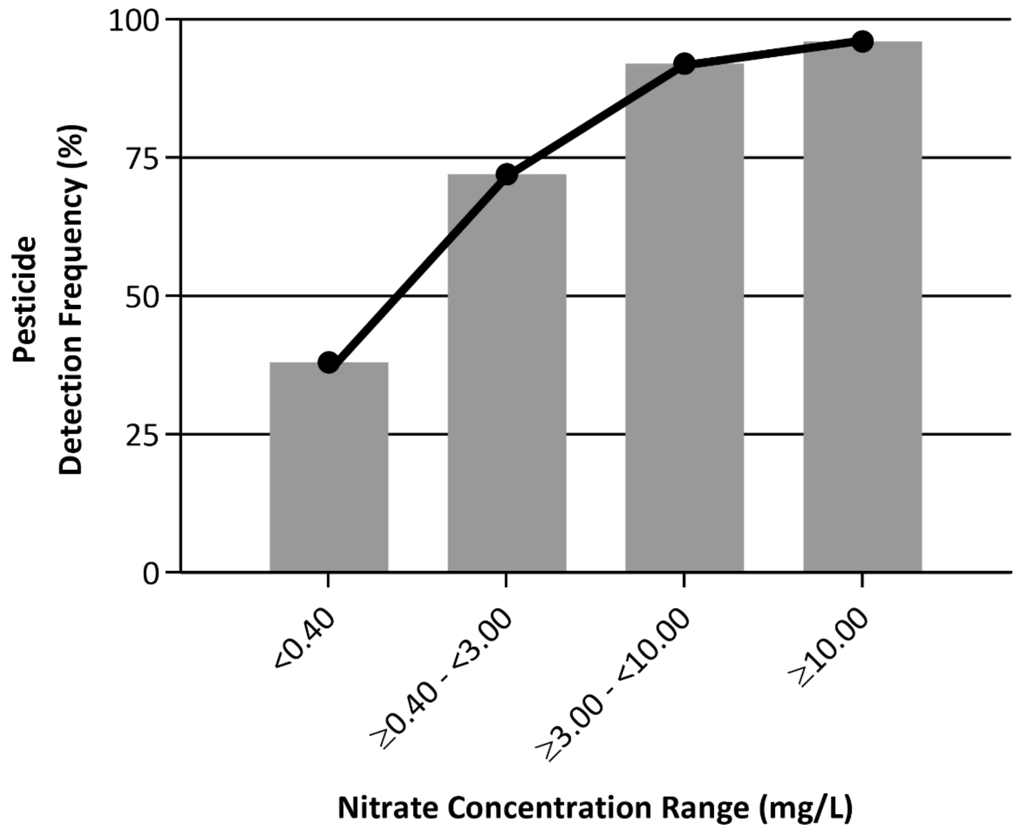
Figure 4-3. Percentage of pesticides detected in each well sampled.



4.3.2 PWPS Project nitrate and pesticide co-occurrence

A nitrate sample was collected from all of the PWPS Project wells sampled in 2019. The relationship between pesticide detection frequency and nitrate concentration range is presented in Figure 4-4. In general, as the concentration of nitrate in a well increased, the likelihood of detecting at least one pesticide compound increased. The likelihood of detecting at least one pesticide increased from 38% to 96%. These results are generally consistent with the MDA's findings from the shallow monitoring wells in agricultural areas of Minnesota when nitrate was detected (see Section 2.8). It should be noted that the MRL for nitrate analysis by Weck was 0.05 mg/L, but the data were censored to the highest historical MDA Laboratory MRL for this analysis.

Figure 4-4. Pesticide detection frequency within nitrate concentration ranges from the 2019 PWPS Project.



4.4 Bayer CropSciences isoxaflutole sampling

Isoxaflutole, an herbicide, was registered for use in a portion of Minnesota in 2015. The MDA Commissioner's Order, generated as part of the registration, stated that Bayer CropSciences (BCS) was responsible for installing and sampling 16 monitoring wells, which were to be located in areas where isoxaflutole was registered for use. Isoxaflutole was registered for use south of Interstate 94 and outside of the karst region of southeastern Minnesota. There were specific requirements, related to the soil types where the wells were to be installed and the depth to the water table, as part of the Commissioner's Order. BCS was also required to conduct agricultural subsurface tile monitoring for isoxaflutole and its degradates. All fields monitored as part of the groundwater and subsurface tile requirements had isoxaflutole applied during the study period.

Eight wells were to be installed in both 2015 and 2016. By the end of 2017, a total of seven wells had been installed in Minnesota. This was primarily due to both the difficulties in finding suitable monitoring locations where isoxaflutole could be used according to the label and that met the criteria established in the Commissioner's Order. Due to the difficulties in locating sites, BCS was granted access to an existing MDA monitoring well for sampling. BCS was also allowed to install wells in Iowa to help meet the monitoring requirement. Further, BCS was allowed to submit information from similar

monitoring that was required for registration in Wisconsin as part of the Commissioner's Order in Minnesota.

In 2019, BCS conducted four rounds of groundwater sampling (March, June, September, and December) from the monitoring wells. The samples were submitted to the BCS Laboratory for isoxaflutole and degradate analysis. In addition, one split sample was collected from each site during the June and December sampling rounds and submitted for analysis to the MDA Laboratory. There was no tile water monitoring performed in 2019.

BCS and the MDA Laboratory did not detect isoxaflutole or its degradate (isoxaflutole DKN) in any of the groundwater samples collected in Minnesota in 2019.

4.5 Fish Creek water quality monitoring summary

The MDA has monitored Fish Creek in Ramsey County since 2006. The addition of the LC-MS/MS analytical method in 2010 greatly expanded the number of pesticides that were analyzed in each sample. Soon after 2010, the MDA noted pesticide detections unique to Fish Creek when compared to the rest of the urban and non-urban monitoring networks. The MAU notified other relevant MDA programs of the unusual and elevated concentrations of bifenthrin and imidacloprid (among other pesticides) and assessments of pesticide use in the watershed are on-going.

Historically, the data from Fish Creek was included in the MDA's routine monitoring and reporting for the ambient surface water monitoring program (Section 3 of this report). Starting in this reporting year, the data has been separated and presented here, in the special monitoring studies section, because of concerns related to pesticide use in the watershed. The MDA will continue to evaluate possible sources of the unusual pesticide detections and will continue to monitor Fish Creek.

4.5.1 Fish Creek pesticide detections

From 2006 through 2019, the MDA had over 10,500 sample collection events at rivers and streams throughout Minnesota, including 138 at Fish Creek. Since sampling began in 2006, 48 pesticides were detected in Fish Creek, including six pesticides that were detected over a numeric reference value (Table 4-5). Imidacloprid and bifenthrin had the most detections over a reference value (49 and 13, respectively). The other four pesticides had two or fewer detections over a reference value. The reference value for chlorpyrifos is a Minn Rule Ch. 7050 water quality standard, whereas the others listed in Table 4-5 are USEPA aquatic life benchmarks.

Table 4-5. 2006 through 2019 Fish Creek pesticide detections over a reference value.

Pesticide	Reference Value (ng/L)	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	Total
Bifenthrin	1.3	--	--	--	--	--	--	0	0	8	0	0	3	1	1	**13**
Carbendazim	990	--	--	--	--	--	--	0	0	0	0	1	1	0	0	**2**
Chlorpyrifos	41	0	0	0	0	0	0	0	0	0	0	0	0	1	0	**1**
Clothianidin	50	--	--	--	--	--	0	0	1	1	0	0	0	0	0	**2**
Imidacloprid	10	--	--	--	--	1	4	4	9	14	2	0	0	7	8	**49**
Thiamethoxam	740	--	--	--	--	0	0	0	0	0	0	0	2	0	0	**2**

Metolachlor ESA, 2,4-D, hydroxyatrazine, and metolachlor OXA were detected in more than 80% of the samples overall (Table 4-6). Degradates of metolachlor, atrazine, and dimethenamid were also detected in 51% to 97% of samples. Fish Creek had the statewide maximum concentration for twelve pesticides including the only detections of cyantraniliprole, flupyradifurone, and oxadiazon. The statewide maximum river and stream concentrations of bosaclid, dinotefuran, bifenthrin, carbendazim, thiamethoxam, imidacloprid, fluxapyroxad, chlorantraniliprole, and pendimethalin occurred in Fish Creek. In addition, Fish Creek has had most of the statewide detections for boscalid (98%), dinotefuran (95%), bifenthrin (81%), chlorantraniliprole (67%), and pendimethalin (50%). The only detection of chlorpyrifos in an urban watershed occurred at Fish Creek.

From 2006 through 2019, Fish Creek has had 69 detections over a reference value. The MDA had four other urban monitoring locations in 2019. Basset Creek had 14 detections of imidacloprid and one detection of malathion over the reference value from 2006 through 2019. Battle Creek had two detections of dichlorvos and seven detections of imidacloprid over the reference value from 2006 through 2019. Minnehaha Creek had three detections of imidacloprid over the reference value from 2006 through 2019. The MDA has not had a detection over a reference value from the Mississippi River at Grey Cloud Island since monitoring began in 2010.

Table 4-6. 2006 through 2019 Fish Creek pesticide detection summary.

Pesticide	Samples	Detections	Detection Frequency (%)	Maximum (ng/L)	Detections >10% Reference Value*	Detections >50% Reference Value*	Detections > Reference Value*	Total Samples Greater than 10% Reference Value**
2,4-D	137	122	89	7,460	0	0	0	0
Acetochlor	138	38	28	324	0	0	0	0
Acetochlor ESA	116	3	3	400	0	0	0	0
Acetochlor OXA	116	1	1	140	0	0	0	0
Alachlor ESA	124	3	2	390	0	0	0	0
Atrazine	138	89	64	300	0	0	0	0
Azoxystrobin	114	41	36	589	0	0	0	0
Bentazon	114	1	1	1.78	0	0	0	0
Benzovindiflupyr	55	1	2	60.8	0	0	0	0
Bifenthrin	100	13	13	751^	0	0	13	13
Boscalid	136	45	33	6,800^	0	0	0	0
Bromoxynil	64	2	3	191	0	0	0	0
Carbendazim	98	53	54	2,530^	9	1	2	12
Chlorantraniliprole	101	2	2	126^	0	0	0	0
Chlorpyrifos	138	1	1	61.8	0	0	1	1
Clopyralid	114	1	1	47.9	0	0	0	0
Clothianidin	101	2	2	892	0	0	2	2
Cyantraniliprole	64	3	5	576	0	0	0	0
Deisopropyl-atrazine	138	17	12	152	0	0	0	0
Desethylatrazine	138	56	41	286	0	0	0	0
Dicamba	137	13	9	423	0	0	0	0
Didealkylatrazine	114	29	25	213	0	0	0	0
Dimethenamid	138	57	41	3,340	6	0	0	6
Dimethenamid ESA	116	59	51	308	0	0	0	0
Dimethenamid OXA	116	62	53	765	0	0	0	0
Dinotefuran	98	37	38	11,700^	0	0	0	0
Diuron	114	3	3	27.9	0	0	0	0
Flupyradifurone	55	11	20	366	1	0	0	1
Fluxapyroxad	57	14	25	1,100^	0	0	0	0
Hydroxyatrazine	114	100	88	21	0	0	0	0
Imazapic	114	5	4	28.4	0	0	0	0
Imazapyr	114	44	39	35.1	0	0	0	0
Imidacloprid	114	52	46	2,970^	0	3	49	52
MCPA	137	62	45	285	0	0	0	0
MCPP	137	57	42	576	0	0	0	0
Metalaxyl	114	3	3	80.9	0	0	0	0
Metolachlor	138	53	38	1,330	0	0	0	0
Metolachlor ESA	116	113	97	770	0	0	0	0
Metolachlor OXA	116	96	83	250	0	0	0	0
Oxadiazon	120	7	6	770	1	0	0	1
Pendimethalin	138	2	1	124^	0	0	0	0
Propiconazole	136	2	1	13.8	0	0	0	0
Pyraclostrobin	96	7	7	98.8	0	0	0	0
Siduron	114	9	8	35.6	0	0	0	0
Tebuconazole	136	14	10	34.6	0	0	0	0
Thiamethoxam	114	8	7	1,920^	2	1	2	5

Pesticide	Samples	Detections	Detection Frequency (%)	Maximum (ng/L)	Detections >10% Reference Value*	Detections >50% Reference Value*	Detections > Reference Value*	Total Samples Greater than 10% Reference Value**
Triclopyr	137	6	4	182	0	0	0	0
Trifluralin	138	1	1	60.2	0	0	0	0

**Detection only assigned to one category (i.e., a detection greater than the reference value is not included in greater than 10% or greater than 50% categories). **The values in this column are a summation of all detections greater than 10% of a reference value. ^Maximum detection of that compound.*

4.6 Surface water pesticide data compared to available drinking water reference values

This section summarizes surface water results from its routine surface water sampling program and compared the results to the lowest available chronic drinking water reference values. Surface water pesticide results have normally only been compared to aquatic life standards or benchmarks and not to drinking water reference values because the vast majority of rivers and streams are not protected as drinking water sources. This summary is to evaluate if surface water not used for drinking water had pesticide detections above available drinking water reference values. This comparison used the established chronic drinking water reference value as the reference value and not the standards established by the MPCA for surface water protected as drinking water resources.

This analysis focused on pesticides that exceeded a drinking water reference value at least once and included 2,4,-D, acetochlor, atrazine, diazinon, diuron, and tembotrione. Total atrazine, which is the sum of the parent and its additive degradates (didealkylatrazine, deisopropylatrazine, and desethylatrazine), was compared to the established HRL as this is the method for analyzing atrazine against the HRL.

4.6.1 Statewide evaluation

Most of the waterbodies in the MDA's surface water monitoring program are not designated as drinking water sources. The MDA uses the Minn. Chapter 7050 stream classification designation to determine the appropriate reference value for the specific water body to compare with surface water monitoring results. Although drinking water standards generally do not apply to these waterbodies, the pesticide monitoring data does provide useful background for consideration of downstream or regional uses that may include drinking water. There are several factors to consider when evaluating the surface water data in this way. It is important to keep in mind that drinking water reference values assume a long-term exposure period. Pesticide concentrations in surface waterbodies are often dynamic. Elevated concentrations can occur during runoff periods following pesticide applications. Elevated acetochlor and atrazine concentrations in surface waters are typically not sustained long-term but decrease rapidly as the storm event recedes. Another important consideration is watershed scale. The highest pesticide concentrations often occur in smaller watersheds, as land use and pesticide use tend to be less variable. As watershed size increases, the cumulative effect of multiple land uses and the additional dilution tends to diminish pesticide concentrations even though the storm event duration is typically longer.

The MDA collects pesticide samples from agricultural and urban watersheds from May through August each year during the monitoring season. Sampling is targeted to stormflow periods when runoff was

occurring and pesticides were being used. Approximately half of the samples collected each year are collected during baseflow (low water levels) periods, and the others are collected during stormflow (high water levels) periods. Between 8 and 18 samples are typically collected during the monitoring season at most river and stream locations. Locations with a history of elevated pesticide detections receive more attention, with an increased sample collection frequency.

2,4-D was detected above the HRL (30,000 ng/L) in one of 1,685 samples (0.06%) collected by MDA statewide from 2014 through 2019 (Table 4-7). This detection occurred in June when herbicides are typically being applied and was collected over a four day period. A sample collected approximately one month later indicated a concentration of 199 ng/L. The single detection above the HRL occurred in an agriculturally dominated watershed in south-central Minnesota.

Acetochlor was detected above the HRL (20,000 ng/L) in three of 4,197 samples (0.07%) collected by the MDA statewide from 2014 through 2019 (Table 4-7). Each of these detections occurred in May during stormflow conditions. May is the month acetochlor is typically applied in Minnesota. By evaluating the concentration of the next consecutive sample, the MDA was able to confirm that the acetochlor concentration in each waterbody was below the HRL within four days for all samples. All three of these detections for acetochlor over the HRL occurred in agricultural watersheds, in either western or southern Minnesota.

Total atrazine (atrazine, didealkylatrazine, deisopropylatrazine, and desethylatrazine) was detected above the HRL (3,000 ng/L) in 53 of 4,197 samples (1.3%) collected by the MDA statewide from 2014 through 2019 (Table 4-7). These detections occurred in May (two samples), June (44 samples) and July (seven samples), and 51 of the 53 detections occurred during storm flow conditions. Atrazine is typically applied in May and June in Minnesota. Ninety-two percent (36 of 39) of the waterbodies had a total atrazine concentration below the HRL within seven days, and all waterbodies had a total atrazine concentration below the HRL within 30 days. All detections over the HRL occurred in agricultural watersheds in either western or southern Minnesota.

Diazinon was detected above the HRL (80 ng/L) in one of 4,197 samples (0.02%) collected by the MDA statewide from 2014 through 2019 (Table 4-7). This detection occurred in May during baseflow conditions. By evaluating the concentration of the next consecutive sample, the MDA was able to confirm that the diazinon concentration was below the HRL within sixteen days. This diazinon detection over the HRL occurred in an agricultural watershed in southwestern Minnesota.

Diuron was detected above the HRL (2,000 ng/L) in one of 1,685 samples (0.06%) collected by the MDA statewide from 2014 through 2019 (Table 4-7). This detection occurred in June in an agricultural watershed in central Minnesota during baseflow conditions. The next sample collected eighteen days later had a concentration below the HRL.

Tembotrione was detected above the HRL (600 ng/L) in two of 1,685 samples (0.12%) collected by the MDA statewide from 2014 through 2019 (Table 4-7). These detections occurred in June in agricultural watersheds in western and southeast Minnesota during stormflow conditions. The next samples were collected within 12 days of the first and concentrations were below the HRL.

Table 4-7. Number of detections above the HRL in Minnesota surface waters, 2014 to 2019.

Pesticide Analyte	Health Risk Limit (HRL) (ng/L)	Number of Detections Above the HRL							Total Number of Samples (2014-2019)	Percent of Samples over the HRL (%)
		2014	2015	2016	2017	2018	2019	Sum of 2014-2019		
2,4-D	30,000	1	0	0	0	0	0	1	1,685	0.06
Acetochlor	20,000	0	0	1	0	1	1	3	4,197	0.07
Atrazine (Total)	3,000	8	6	5	7	11	16	53	4,197	1.3
Diazinon	80	0	0	0	0	1	0	1	4,197	0.02
Diuron	2,000	0	0	1	0	0	0	1	1,685	0.06
Tembotrione	600	0	0	1	0	1	0	2	1,685	0.12

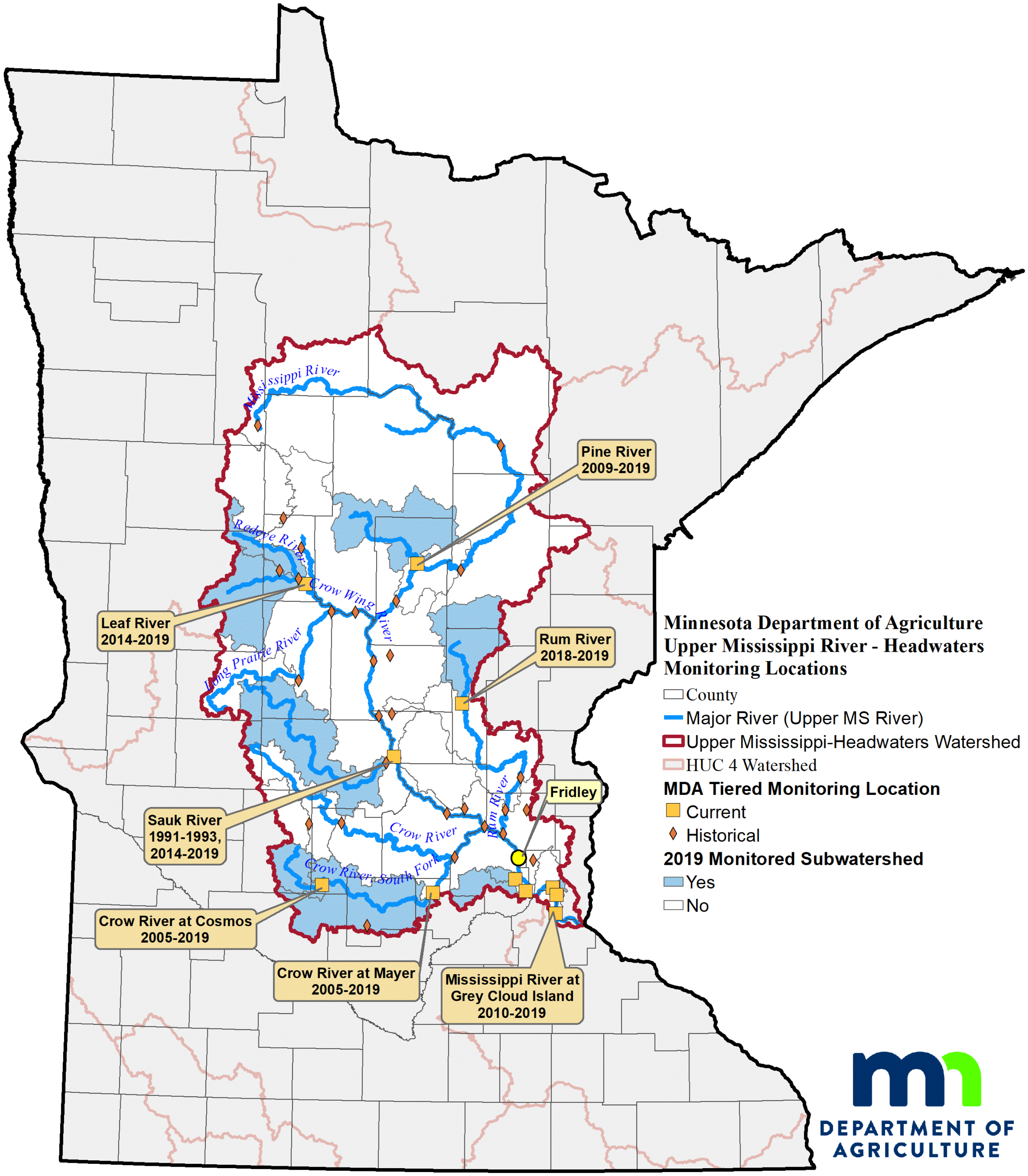
4.6.2 Evaluation relative to Twin Cities drinking water intake on the Mississippi River

The MDA monitors surface water for pesticides at several locations upstream of the Minneapolis drinking water intake, including the Crow River (2 locations), Leaf River, Pine River, Sauk River, and Rum River (Figure 4-5). The only pesticide detection above a drinking water health reference value at these locations occurred in the Sauk River. Diuron, a non-agricultural herbicide commonly used in right-of-way applications, was detected in a June 9, 2016 sample at 4,700 ng/L, which was above the 2,000 ng/L rapid assessment value for drinking water assigned by the MDH. Diuron was not detected in the next consecutive sample collected 18 days later, on June 27th. The MDA also monitors the Mississippi River at Grey Cloud Island, which is below the confluence with the Minnesota River. The MDA has not had a pesticide detection above a drinking water reference value from the Mississippi River at Grey Cloud Island since monitoring began at this location in 2010.

4.6.3 Conclusions

The MDA actively monitors surface water for an extensive list of pesticides from many locations each year in Minnesota. Although the data presented above was generally not collected from waters designated as drinking water sources, it does provide strong supporting evidence that there is low risk of pesticide concentrations exceeding established drinking water health reference values in Minnesota surface waterbodies. No sustained pesticide concentrations above the established drinking water health reference values were documented in excess of 30 days. Except for the one diuron detection, which was above a rapid assessment value in the Sauk River in 2016, pesticide concentrations in the monitored streams above the Twin Cities metropolitan area were low when compared to drinking water health reference values.

Figure 4-5. Watersheds with pesticide monitoring upstream of the Twin Cities metropolitan area.



Section 5: Cyanazine

2019 Water Quality Monitoring Report

Section 5: Introduction

5.1 Overview of cyanazine

Cyanazine is a herbicide that was mainly used on corn crops in Minnesota until 2002, after which cyanazine use was discontinued. Surveys from the National Agricultural Statistics Service indicate that cyanazine use in Minnesota steadily declined between 1990 and 2000. Some of the common trade names for cyanazine included Bladex and Fortrol. Cyanazine belongs to a group of chemicals, called triazines, that includes other herbicides that have been and are currently primarily used on corn in Minnesota, such as atrazine and simazine.

Cyanazine and its degradates have been detected in some surface water and groundwater in Minnesota, including municipal and private drinking water wells. In this report, cyanazine and its degradates may be referred to as total cyanazine. Total cyanazine is the sum of cyanazine plus its degradates. The MDA analyzes for the following degradates of cyanazine:

Cyanazine specific degradates

- Cyanazine acid
- Cyanazine amide
- Deethylcyanazine
- Deethylcyanazine acid
- Deethylcyanazine amide

Two additional cyanazine degradates are also degradates of atrazine:

- Deisopropylatrazine
- Didealkylatrazine

As based upon determination by MDH, deisopropylatrazine, and didealkylatrazine were only included in total cyanazine concentrations when cyanazine or a cyanazine specific degradate was detected in the sample.

The MDH developed long-term guidance value (an HRL) for total cyanazine, which included cyanazine and the seven cyanazine related degradates, in drinking water at 1,000 nanograms per liter (ng/L, or parts per trillion). Consuming water with a total cyanazine concentration greater than 1,000 ng/L may present a health risk. Further information from the MDH can be found in a fact sheet on their website: "Cyanazine in Drinking Water."

5.1.1 Past total cyanazine detections in groundwater

Since 2004, there have been on-going concerns related to the presence of cyanazine degradates detected in groundwater, primarily related to private drinking water wells in Dakota County. Total cyanazine had been detected at concentrations above the HRL in initial testing completed by Dakota County Environmental Resources Department (ERD). Cyanazine degradate data collected from Dakota County's ambient network of private wells in subsequent years generally indicated declining concentrations of the cyanazine degradates, which would be expected since cyanazine was no longer being used. However, in 2017 a targeted sampling effort focused on other private wells in areas with previous detections identified additional wells with concentrations over the HRL for total cyanazine. Laboratory analysis of samples collected by Dakota County ERD were completed by the United States Geological Survey (USGS) Organic Geochemistry Research Laboratory (OGRL) using the triazine and phenylurea parents and degradation products, Water Analysis Code LCEA method.

In 2005, the MDA assessed for presence of cyanazine degradates in groundwater from select groundwater monitoring sites. At that time, no commercial analytical laboratory had cyanazine degradate standards, which were necessary for laboratory analysis, nor were they available from the EPA, DuPont Chemical Company, or any commercial suppliers of standards in the United States. In response, the MDA Laboratory contracted to have analytical standards synthesized for the five cyanazine degradates. Numerous efforts were made by the MDA Laboratory in an attempt to secure standards for the cyanazine degradates. However, only three of the chemicals were successfully synthesized. Unfortunately, deethylcyanazine acid, the most prevalent cyanazine degradate found in groundwater, was not able to be synthesized. The efforts to develop an analytical method ultimately failed with the lack of standards and the analytical standards that were obtained were found to have low purity.

In 2005 and early 2006, the MDA contracted with the USGS OGRL for sample analysis to test for the presence of cyanazine and associated degradates. Eighty groundwater sites were selected based on historic pesticide detections or because they were scheduled for routine sampling during the time frame of this effort. Results indicated 12 of the 80 samples collected (15%) had at least one cyanazine degradate detected. One sample also indicated the presence of the cyanazine parent. Three of the samples had total cyanazine concentrations greater than the HRL (1,000 ng/L). The locations with the highest total cyanazine concentrations were in Pope (3,690 ng/L), Stevens (3,200 ng/L), and Kandiyohi Counties (3,110 ng/L).

The MDA continued to monitor these three wells for cyanazine but did not have the capability to analyze for cyanazine degradates until 2019. Results from 2019 did not indicate the presence of cyanazine or cyanazine degradates in the wells in Pope and Stevens Counties. The well in Kandiyohi County was not sampled in 2019, but the companion well at the site was sampled and no cyanazine or cyanazine degradates were detected.

5.1.2 Laboratory challenges and successes

As referenced above, prior to 2019, only one laboratory in the nation, USGS OGRL, was capable of analyzing for the five cyanazine degradates. In late 2018, the MDA Laboratory contracted with two different chemical manufacturers, both of which successfully synthesized five cyanazine degradates. In early 2019, using these chemicals as standards, the MDA Laboratory, and the contract laboratory utilized for the PWPS Project (Weck Laboratory (Weck)), developed analytical methods for the analysis of the cyanazine degradates in water. The MDA Laboratory utilized a solid phase extraction LC-MS/MS method, while Weck utilized a direct aqueous injection LC-MS/MS method. Both the MDA Laboratory and Weck have been conducting analysis for cyanazine degradates in water samples since March 2019.

5.1.3 Human Health Risk assessment for cyanazine

The MDA has coordinated closely with the MDH on the human health risk assessment of cyanazine degradates detected in drinking water wells, as is the protocol whenever elevated concentrations of chemicals are found. An initial MDH human health risk assessment of the cyanazine degradate data collected in Dakota County occurred in 2006. The outcome of that assessment concluded that nitrate posed the greatest concern in the wells sampled in Dakota County, but it concluded to express concern about the number of pesticides and degradates detected in the wells. The 2017 data from Dakota County was provided to the MDH for a human health risk assessment in November 2018. In late December 2018, the MDH completed a cumulative risk assessment for the Dakota County data and indicated that total cyanazine concentrations should be compared to the 1,000 ng/L HRL established for cyanazine.

5.2 Results

In 2019, the MDA included the analysis of cyanazine degradates in its ambient surface water and groundwater programs, as well as the PWPS Project, providing data from monitoring locations throughout the state. In response to the 2017 detections in Dakota County private wells, the MDA also collected samples from 84 additional private well locations that had previously indicated the presence of cyanazine-related compounds in Dakota County. The MDA also evaluated the effectiveness of existing in-home point-of-use water treatment systems (primarily reverse osmosis) at removing pesticides (including the cyanazine degradates). The following sections summarize results for each of these areas outlined above.

5.2.1 Surface water

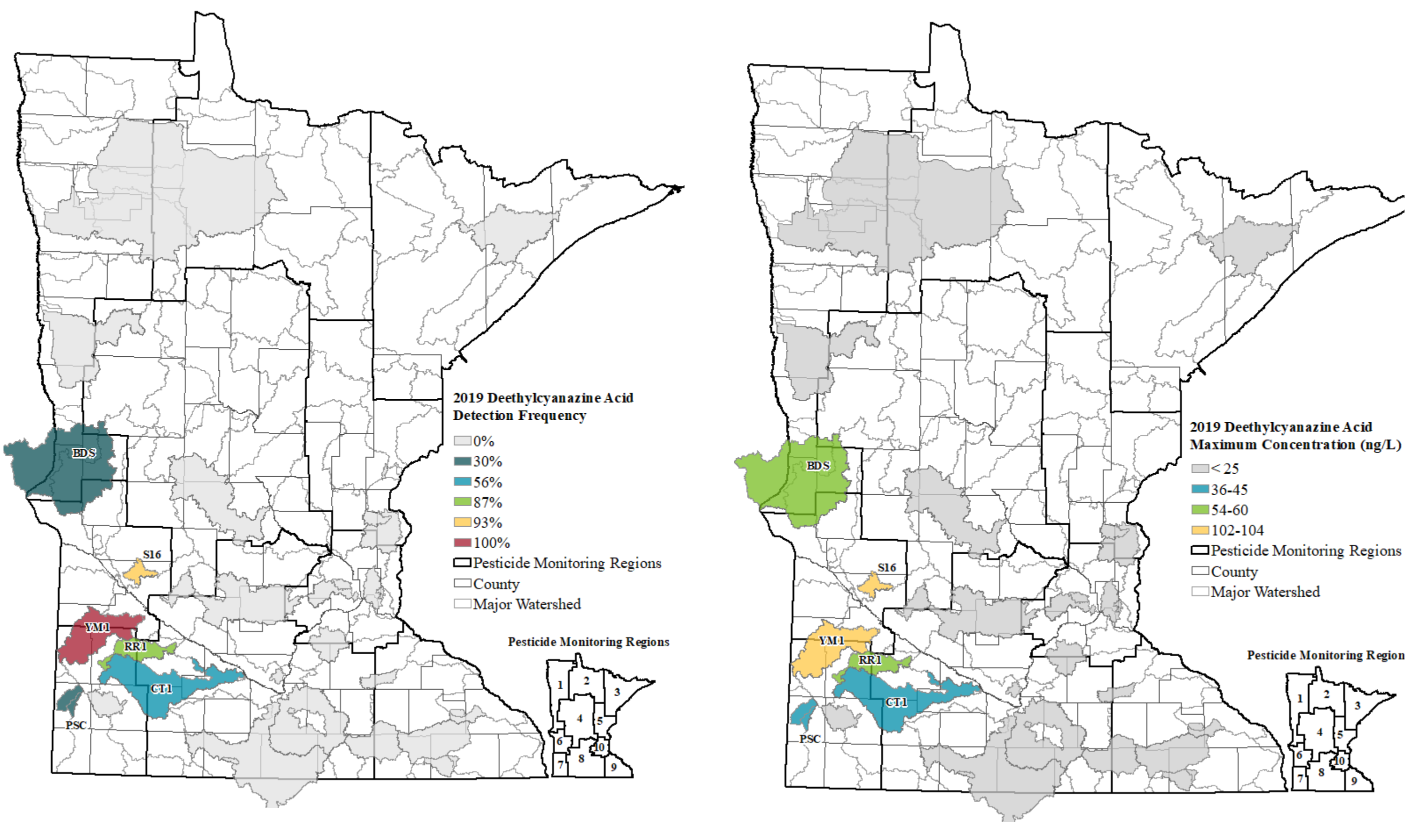
The MDA analyzed 380 samples for cyanazine and 373 samples for cyanazine degradates, which were collected at 30 river and stream locations across the state in 2019. Deethylcyanazine acid was detected in 15% of these surface water samples (Table 5.0). These detections only occurred in PMRs 1, 6, 7, and 8 (Figure 5.0), with a maximum detection of 104 ng/L. Deethylcyanazine acid does not have a surface water reference value available. No other cyanazine or cyanazine degradate analytes were detected in rivers or streams in 2019.

Table 5.0. 2019 river and stream cyanazine and cyanazine degradate results.

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng/L)	Reference Value (ng/L)	Surface Water Reference Value Type	PMRs with Detection
Cyanazine	380	0	0	<25	–	–	None
Cyanazine acid	373	0	0	<10	–	–	None
Cyanazine amide	373	0	0	<10	–	–	None
Deethylcyanazine	373	0	0	<25	–	–	None
Deethylcyanazine acid	373	55	15	104	–	–	1,6,7,8
Deethylcyanazine amide	373	0	0	<25	–	–	None

Deethylcyanazine acid detections were limited to six watersheds in western and southwestern Minnesota in 2019 (Figure 5.0). The watersheds where deethylcyanazine acid detections occurred often had detection frequencies over 50% and detections occurred in both base flow and storm flow conditions. The maximum concentration at each of these watersheds ranged from 36 to 104 ng/L.

Figure 5.0. 2019 river and stream deethylcyanazine acid detection frequency and maximum detection.



5.2.2 Ambient groundwater

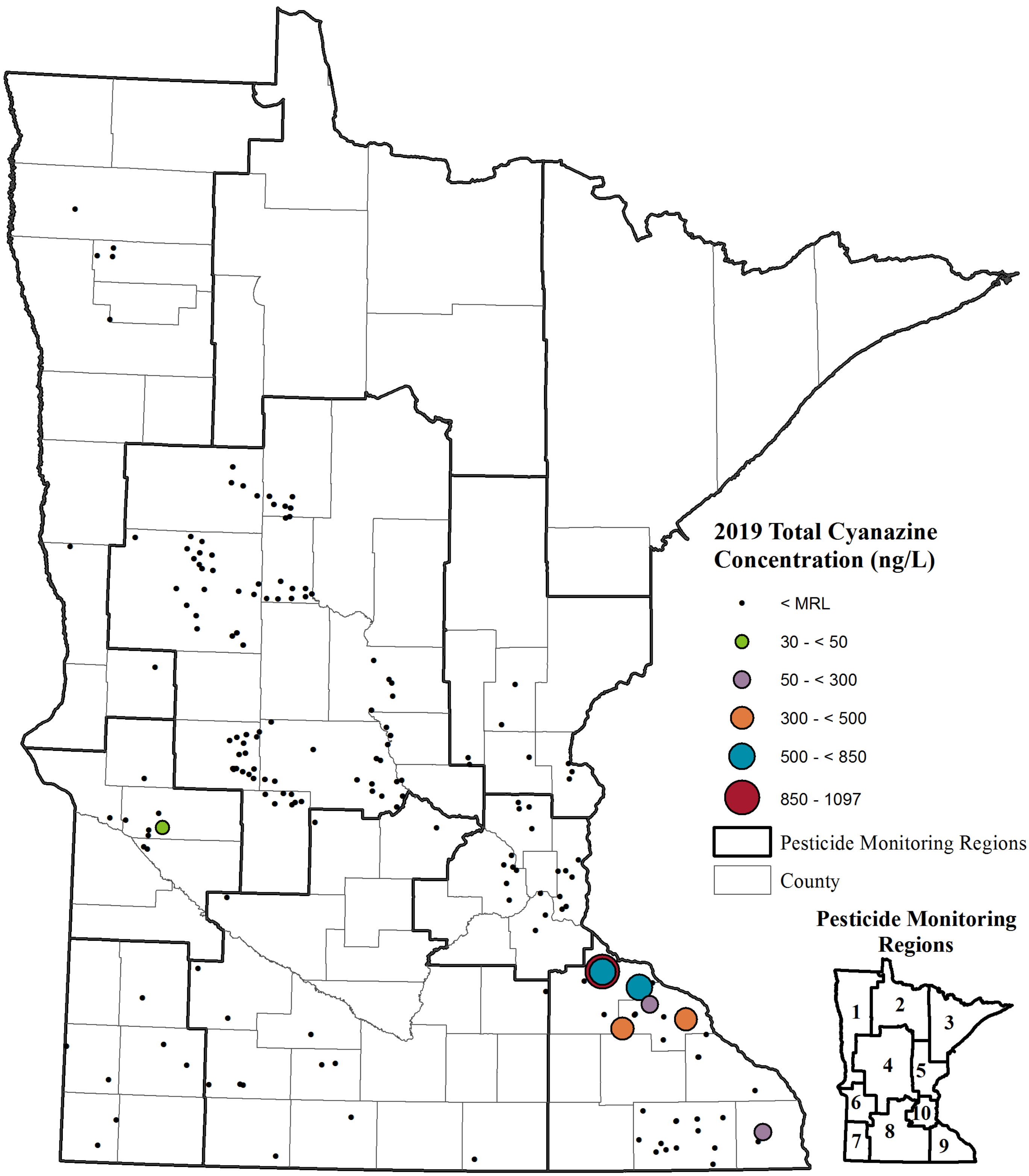
In 2019 the MDA collected approximately 220 samples from 166 monitoring wells, springs and domestic wells for analysis of cyanazine and its degradates. Cyanazine acid and cyanazine amide were detected in five samples. Deethylcyanazine acid was detected in nine samples. These detections occurred in samples collected from three springs and three domestic wells in SE Minnesota and one sample from a monitoring well in Swift County. The sites where detections of cyanazine degradates were found in 2019 are presented in Figure 5.1. Deethylcyanazine acid had the highest maximum concentration (653 ng/L) for an individual cyanazine-related compound. This sample was collected from a spring in Goodhue county in June 2019, where the total cyanazine concentration (1,035.9 ng/L) was above the 1,000 ng/L HRL. The total cyanazine concentration in a second sample from the same spring in September 2019, was 743 ng/L, which was below the HRL.

Table 5.1. 2019 ambient groundwater cyanazine and cyanazine degradate results.

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng /L)	Reference Value (ng /L)	PMRs with Detection
Cyanazine	222	0	0	<25	1,000	none
Cyanazine acid	219	**5**	**2**	**26.2**	1,000 (cumulative with parent)	9
Cyanazine amide	219	**5**	**2**	**30.6**		9
Deethylcyanazine	219	0	0	<25		none
Deethylcyanazine acid	219	**9**	**4**	**653**		6,9
Deethylcyanazine amide	219	0	0	<25		none
Deisopropylatrazine*	222	**6**	**3**	**82**		9
Didealkylatrazine*	222	**9**	**4**	**379**		9

**Deisopropylatrazine and didealkyatrazine were only included when other cyanazine degradates were present*.

Figure 5.1. 2019 ambient groundwater monitoring sites with detections of cyanazine and cyanazine degradates.



5.2.3 PWPS Project

There were 1,103 samples collected from 23 counties during the PWPS Project in 2019. Table 5.2 provides a summary of the results. It should be noted that the samples for this project were analyzed by Weck, while the samples for the ambient surface water and groundwater programs were analyzed by the MDA Laboratory. The differences in the analytical techniques described previously could factor into differences in the general findings. Deethylcyanazine was the only cyanazine degradate not detected. Deethylcyanazine acid was the most frequently detected (9%) cyanazine degradate and was found at the highest concentration (9,000 ng/L).

Twenty-nine samples from private wells indicated total cyanazine concentrations above the HRL as presented in Figure 5.2. The counties that had a detection above the human health reference value included: two in Chippewa, three in Houston, four in Olmsted, one in Pipestone, 17 in Scott, and two in Wright. Additional total cyanazine detections above the HRL from private well samples collected in Dakota County are summarized in Section 5.2.4 of this report.

Table 5.2. 2019 PWPS Project cyanazine and cyanazine degradate results (Weck analysis).

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	Maximum Detection (ng /L)	Reference Value (ng /L)
Cyanazine	1,103	**2**	**<1**	**33.0**	1,000
Cyanazine acid	1,103	**25**	**2**	**1,600**	1,000 (cumulative with parent)
Cyanazine amide	1,103	**38**	**3**	**1,600**	
Deethylcyanazine	1,103	0	0	<25	
Deethylcyanazine acid	1,103	**99**	**9**	**9,000**	
Deethylcyanazine amide	1,103	**1**	**<1**	**230**	
Deisopropylatrazine*	1,103	**43**	**4**	**270**	
Didealkylatrazine*	1,103	**89**	**8**	**1,100**	

**Deisopropylatrazine and didealkyatrazine detections were only included when other cyanazine degradates were present.*

Figure 5.2. 2019 PWPS Project locations with total cyanazine concentration above the human health reference value.

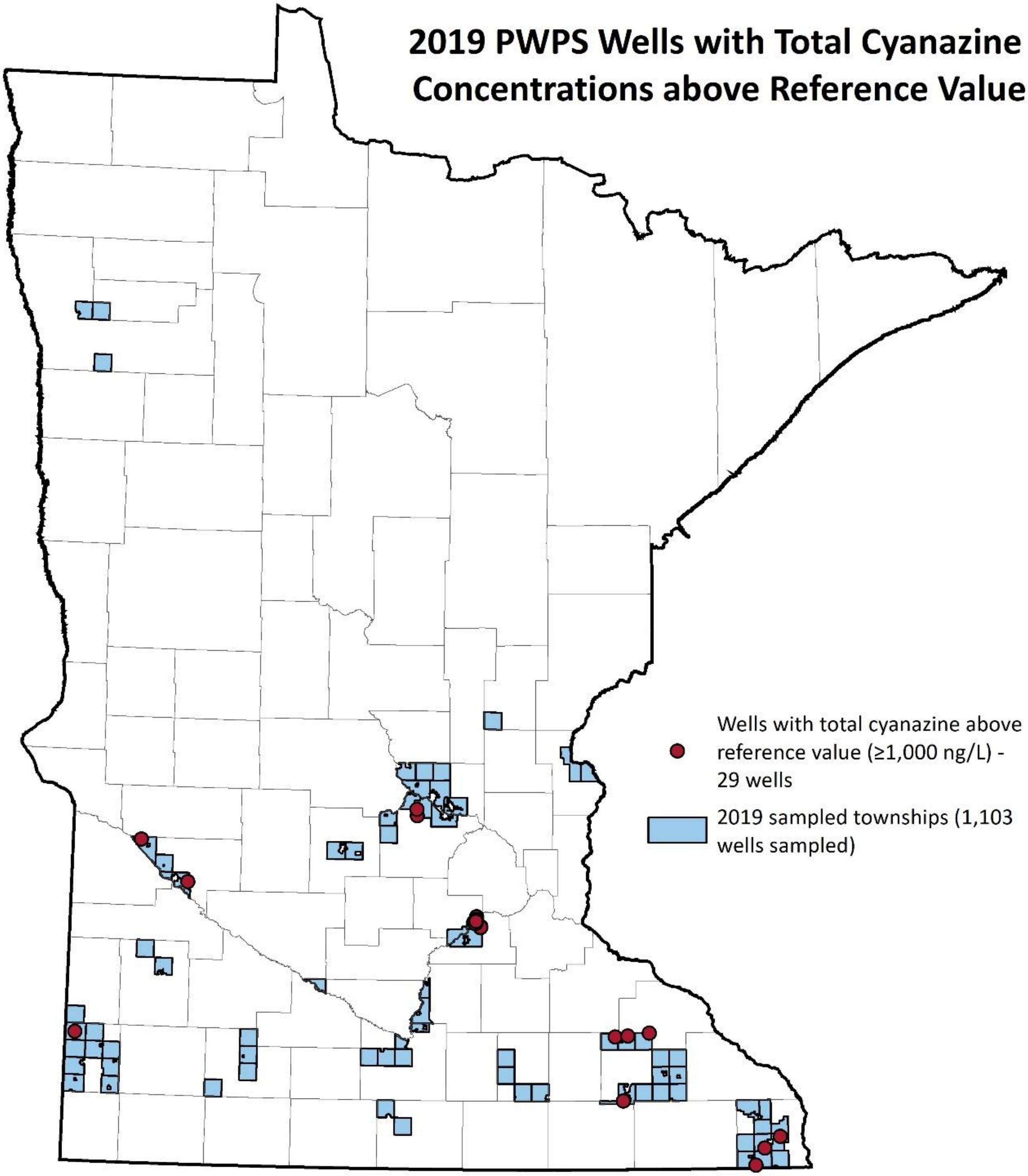
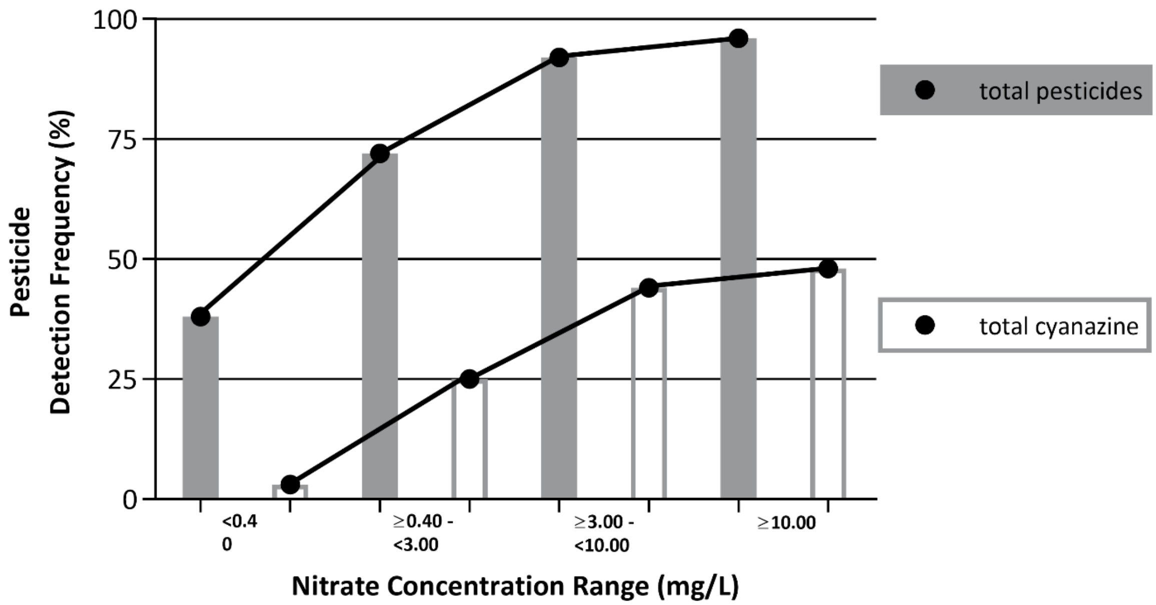


Figure 5.3 presents the detection frequency of total pesticides and total cyanazine within different nitrate concentration ranges, based on results from the PWPS Project in 2019. In general, as nitrate concentration increased, the probability of detecting at least one pesticide compound increased. Although more muted, a similar relationship between nitrate and total cyanazine was displayed.

Figure 5.3. PWPS Project 2019 total pesticide and total cyanazine detection frequencies in certain nitrate concentration ranges.



A more detailed co-occurrence evaluation was also conducted to determine possible relationships between concentrations of other pesticides when cyanazine degradates were detected. Findings from this evaluation were mixed. Although there were no clear relationships found based on an evaluation of the full data set from 2019, different relationships seemed to be present if the data was evaluated on a regional basis. The MDA will continue to evaluate co-occurrence as additional data comes in from the 2020 sampling season.

5.2.4 Dakota County Sampling Project

In response to the detections of cyanazine degradates in 2017, the MDA and Dakota County ERD sent sampling invite letters out to residents in Dakota County that previously had any detectable total cyanazine concentration in their well water. Approximately 150 letters were sent out in early June 2019, and the response rate was 56% (84 locations). MDA hydrologists collected samples from July through August 2019. In addition, 27 homeowners allowed the MDA to collect a second water sample from a home treatment system inside their house after the water had passed through it (*i.e.*, carbon filter, reverse osmosis, etc.). A summary of those results can be found in Section 5.2.5.

Three different labs were utilized for this project. At each location, a sample was collected for analysis by Weck. A second sample was then collected for either the MDA Laboratory or the USGS OGRL. At

three locations, samples for all three labs (triple split) was performed. Approximatley 10% QA/QC samples were also collected. Results from both the MDA Laboratory (46 samples) and Weck (84 samples) have been returned. Results are still pending from the USGS OGRL (41 samples).

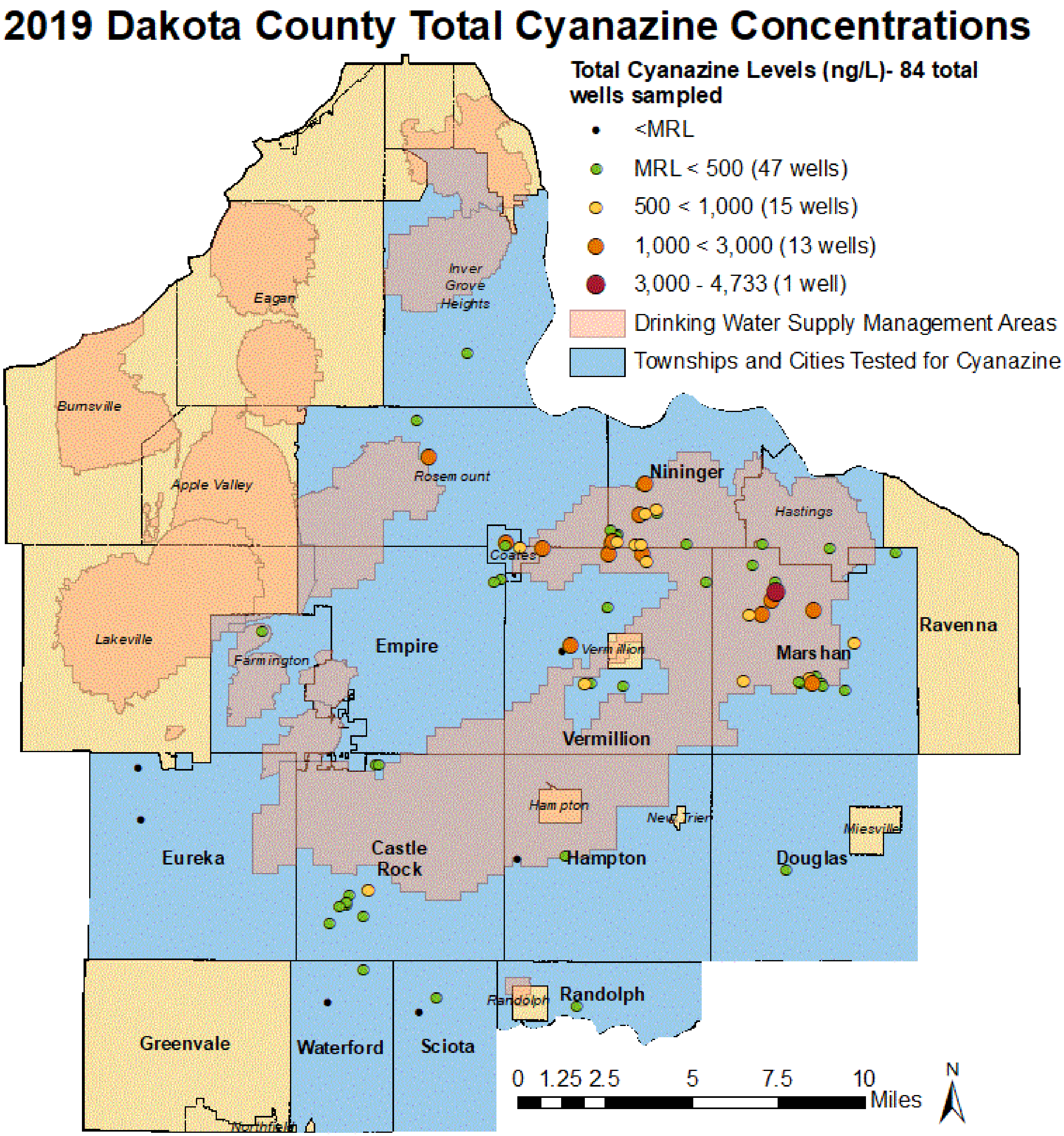
Table 5.3 presents the 2019 Dakota County sampling results from both labs. Only the parent cyanazine compound and the degradates deethylcyanazine and deethylcyanazine amide were not detected in any of the samples. Of the cyanazine related chemicals, deethylcyanazine acid was detected most frequently by both labs (87%) and at the highest concentration (5,400 ng/L MDA Laboratory and 4,600 ng/L Weck). Overall, 14 locations indicated a total cyanazine concentration greater than 1,000 ng/L. Figure 5.4 displays the results from the 84 samples analyzed by Weck.

Table 5.3. 2019 Dakota County groundwater cyanazine and cyanazine degradates results, MDA and Weck Laboratories.

Pesticide Analyte	MDA Samples	MDA Detections	MDA Detection Frequency (%)	MDA Maximum Detection (ng /L)	Weck Samples	Weck Detections	Weck Detection Frequency (%)	Weck Maximum Detection (ng /L)	Reference Value (ng /L)
Cyanazine	46	0	0	<25	84	0	0	<25	1,000
Cyanazine acid	46	**24**	**52**	**170**	84	**42**	**50**	**310**	
Cyanazine amide	46	**17**	**37**	**51.7**	84	**37**	**44**	**87**	
Deethylcyanazine	46	0	0	<25	84	0	0	<25	
Deethylcyanazine acid	46	**40**	**87**	**5,400**	84	**73**	**87**	**4,600**	1,000 (cumulative with parent)
Deethylcyanazine amide	46	0	0	<25	84	**1**	**1**	**30**	
Deisopropyl atrazine*	46	**8**	**17**	**109**	84	**13**	**15**	**130**	
Didealkylatrazine*	46	**22**	**48**	**298**	84	**50**	**59**	**430**	

**Deisopropylatrazine and didealkyatrazine were only included when other cyanazine specific degradates were present.*

Figure 5.4. 2019 Dakota County total cyanazine detections, Weck results.



5.2.5 Dakota County municipal wells

Dakota County Environmental Resources Department requested the analysis of additional samples collected from community public water supply (municipal) wells. Samples were collected from the municipal wells in Dakota County during December by an MDH District Engineer, with assistance from a MDA hydrologist, and were sent to Weck and MDA Laboratories. Water was collected before treatment (raw) and after treatment (finished), where possible. Eight total samples were collected, with five raw and three finished samples (Table 5.4 and Table 5.5). Earlier sample collection in September 2019 had laboratory analysis issues with Weck results, which led to this December collection, with split samples sent to both labs.

Table 5.4 summarizes the results from the raw and finished water analyzed by Weck. Several degradates were found in both raw and finished samples. Cyanazine acid, deethylcyanazine acid and didealkylatrazine were detected in both. One sample had a total cyanazine concentration greater than the 1,000 ng/L HRL. Table 5.5 summarizes the results from raw and finished water analyzed by the MDA Laboratory from samples collected in December 2019. As seen in the earlier Weck results, only cyanazine acid, deethylcyanazine acid and didealkylatrazine were detected in both raw and finished samples. There were no sample results that were over the 1,000 ng/L HRL for total cyanazine from the MDA Laboratory. Based upon variability between the MDA and Weck Laboratories for some of the cyanazine degradate detections, the MDA has worked with Weck to conduct additional evaluation and method development to improve cyanazine degradate recoveries and reporting accuracy.

Table 5-4. 2019 Dakota County municipal groundwater cyanazine and cyanazine degradate results for raw and finished water, Weck, December 2019.

Pesticide Analyte	Samples (Raw)	Detections (Raw)	Detection Frequency (Raw) (%)	Maximum Detection (Raw) (ng /L)	Samples (Finished)	Detections (Finished)	Detection Frequency (Finished) (%)	Maximum Detection (Finished) (ng /L)	Reference Value (ng /L)
Cyanazine	5	0	0	<25	3	0	0	<25	1,000
Cyanazine acid	5	**5**	**100**	**59**	3	**3**	**100**	**73**	1,000 (cumulative with parent)
Cyanazine amide	5	0	0	<10	3	0	0	<10	
Deethylcyanazine	5	0	0	<25	3	0	0	<25	
Deethylcyanazine acid	5	**5**	**100**	**520**	3	**3**	**100**	**1,100**	
Deethylcyanazine amide	5	0	0	<25	3	0	0	<25	
Deisopropylatrazine	5	0	0	<25	3	0	0	<25	
Didealkylatrazine	5	**4**	**80**	**140**	3	**3**	**100**	**76**	

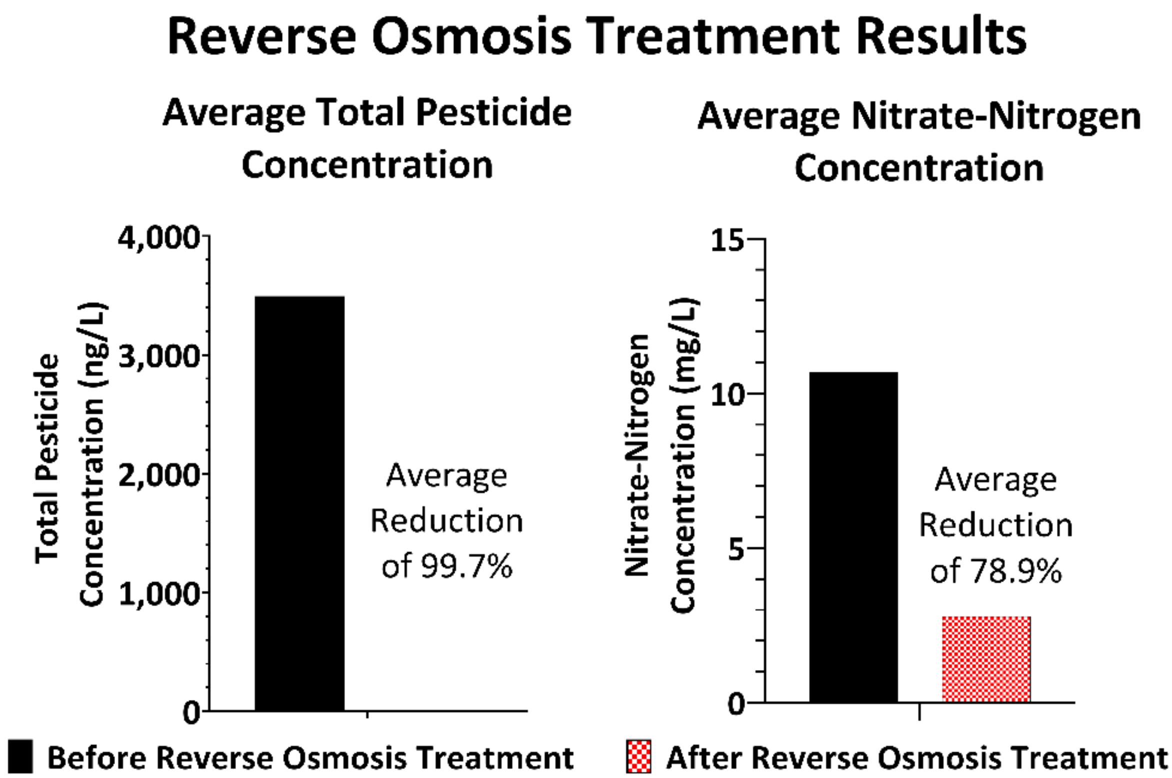
Table 5-5. 2019 Dakota County municipal groundwater cyanazine and cyanazine degradate results for raw water and finished water, MDA Laboratory, December 2019.

Pesticide Analyte	Samples (Raw)	Detections (Raw)	Detection Frequency (Raw) (%)	Maximum Detection (Raw) (ng /L)	Samples (Finished)	Detections (Finished)	Detection Frequency (Finished) (%)	Maximum Detection (Finished) (ng /L)	Reference Value (ng /L)
Cyanazine	5	0	0	<25	3	0	0	<25	1,000
Cyanazine acid	5	**5**	**100**	**66**	3	**3**	**100**	**67**	1,000 (cumulative with parent)
Cyanazine amide	5	0	0	<10	3	0	0	<10	
Deethylcyanazine	5	0	0	<25	3	0	0	<25	
Deethylcyanazine acid	5	**5**	**100**	**400**	3	**3**	**100**	**311**	
Deethylcyanazine amide	5	0	0	<25	3	0	0	<25	
Deisopropylatrazine	5	0	0	<25	3	0	0	<25	
Didealkylatrazine	5	**2**	**40**	**93**	3	**1**	**33**	**51**	

5.2.6 Before and after water treatment in private water systems

The MDA collected before (pre-treatment) and after (post-treatment) water samples from 51 home water treatment systems across Minnesota, to evaluate pesticide and nitrate-nitrogen removal efficiency, from 2017 through 2019. An evaluation of 44 reverse osmosis treatment systems out of this group showed an average total pesticide concentration reduction of 99.7% and an average nitrate-nitrogen reduction of 78.9% (Figure 5.5). The MDA evaluated an additional seven home treatment systems (other than reverse osmosis) and found that the results ranged from poor to mixed for pesticide and nitrate removal.

Figure 5.5. Before and after reverse osmosis treatment.



Section 6: Nutrient and Sediment Results

2019 Water Quality Monitoring Report

Section 6: Nutrient and Total Suspended Solids Results

In conjunction with pesticide monitoring, the MDA collected nutrient and total suspended solids samples at most locations to provide additional water quality information about the groundwater and surface water of Minnesota. The following section provides a summary of the nutrient and total suspended solids results collected in 2019 from groundwater and surface water by the MDA.

6.1 Statewide groundwater nitrate sampling

Nitrate is one of the most frequently detected chemical compounds in Minnesota's groundwater. High concentrations of nitrate pose health risks to humans, particularly to infants under six months old, and pregnant women. The MDA collected nitrate samples at all of the MDA's groundwater monitoring sites whenever pesticide samples were collected. In urban areas, the MPCA collected and analyzed nitrate samples with pesticide samples they collected for the MDA.

6.1.1 2019 MDA nitrate data

In 2019, 201 nitrate samples were collected from shallow groundwater monitoring wells, springs, or domestic wells around the state (Table 6-0). Only the domestic wells (five percent of sites in the network) are directly used as a source of drinking water. The principal findings for nitrate include:

- Nitrate was detected in 89% of samples collected statewide.
  - Detection frequencies ranged from 57% in PMR 1 to 100% in PMRs 5 and 9.
- The highest concentration (39.8 mg/L) occurred in a PMR 4 monitoring well.
- The highest median concentration (13.8 mg/L) was in PMR 4.

Table 6-0. Summary of nitrate results in groundwater samples for 2019.

PMR	Samples Analyzed	Number of Detections	Detection Frequency (%)	Median (mg/L)	90th Percentile (mg/L)	Maximum (mg/L)
1	14	8	57	0.64	8.14	22.1
4	78	76	97	13.8	26.9	39.8
5	16	16	100	8.76	30.3	39.7
6	16	10	63	0.93	19.0	32.0
7	14	9	64	2.83	12.9	13.7
8	26	22	85	1.73	13.7	24.7
9	37	37	100	8.31	13.1	14.9
All Samples	201	178	89	7.08	22.5	39.8

6.1.2 Evaluation of MDA nitrate data

The MDH convened a work group in 1998 and developed a classification system that can be used for evaluating potential human impacts to groundwater based on nitrate concentrations (MDH, 1998). The classification system was modified slightly by the MDA, due to the MDA Laboratory's analytical MRL. The four general classes are:

- Less than 0.4 mg/L – assumed to represent natural background concentration (ambient conditions without human impact).
- 0.4 to less than 3.0 mg/L – transitional concentrations that may or may not represent human influence.
- 3.0 to less than 10 mg/L – may indicate elevated concentrations resulting from human activities.
- 10 mg/L and higher – exceeds drinking water standards (*i.e.* HRL) for public and private drinking water supplies.

The 2019 MDA nitrate data are presented at the PMR-level in Table 6-1, based on the modified MDA general nitrate classification system. The nitrate data were censored to the highest historical MRL (0.4 mg/L), due to the MDA Laboratory lowering their MRL to 0.2 mg/L in 2017.

The principal findings from the nitrate data were:

- Statewide, 32% of the nitrate samples were classified as elevated, while 37% exceeded the HRL.
- PMR 4 had the highest percentage of samples (58%) that exceeded the HRL.

Table 6-1. 2019 Detection frequency in groundwater samples compared against the general nitrate classification system.

PMR	<0.4 mg/L (%)	> =0.4 - <3.0 mg/L (%)	> = 3.0 - <10 mg/L (%)	> = 10 mg/L (%)
1	43	21	29	7
4	3	17	23	58
5	6	25	31	38
6	44	19	25	13
7	36	14	21	29
8	23	35	19	23
9	0	3	70	27
All Samples	13	17	32	37

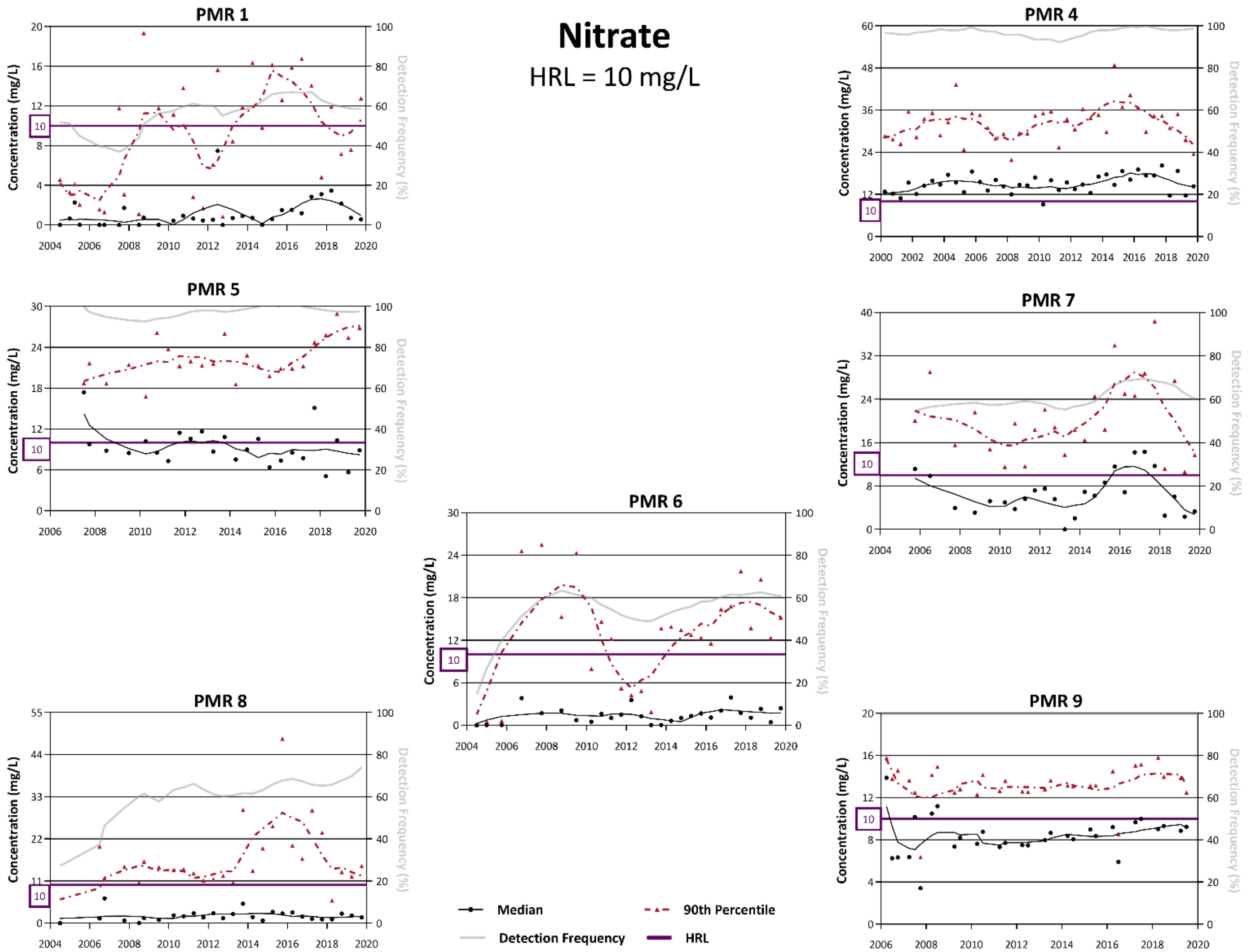
6.1.3 MDA long-term nitrate data review

Time-series graphics by PMR have been prepared using long-term data available from the groundwater monitoring network, with the earliest data results back to 2000 (from PMR 4). These graphics provide a historical perspective on nitrate concentrations and the detection frequency from the MDA's monitoring networks (Figure 6-0). The nitrate data were censored to the highest historical MRL (0.4 mg/L), due to the MDA Laboratory lowering their MRL to 0.2 mg/L in 2017.

The principal findings for the MDA's long-term nitrate data include:

- PMR 4 has consistently had the highest median nitrate concentrations.
- The median concentration best fit line has consistently been at or above 10 mg/L in PMR 4.
- The detection frequency best fit line has always been greater than 80% in PMRs 4 and 5 and 100% in PMR 9.

Figure 6-0. Long-term nitrate concentration results and detection frequencies for all monitored PMRs.



6.1.4 Review of nitrate data from the shallow and deep well nests in PMR 4

A summary of the 2019 nitrate results, from the eight well nests in PMR 4, is presented in Table 6-2. Time-trend graphics for nitrate concentration and detection frequency from the shallow and deep well wells are shown in Figure 6-1 (See Section 2.6 for further information about the shallow and deep well nests).

The principal findings for the results from the shallow and deep well nests include:

2019

- The deep wells had higher nitrate concentrations than the shallow wells, with median concentrations being 28.3 mg/L and 19.0 mg/L, respectively.
- All wells had detectable nitrate concentrations.
- The highest nitrate concentration (39.6 mg/L) was measured in a deep well, compared to the maximum concentration of 27.8 mg/L from a shallow well.
- Eighty-eight percent of the shallow and deep well samples exceeded the HRL of 10 mg/L.

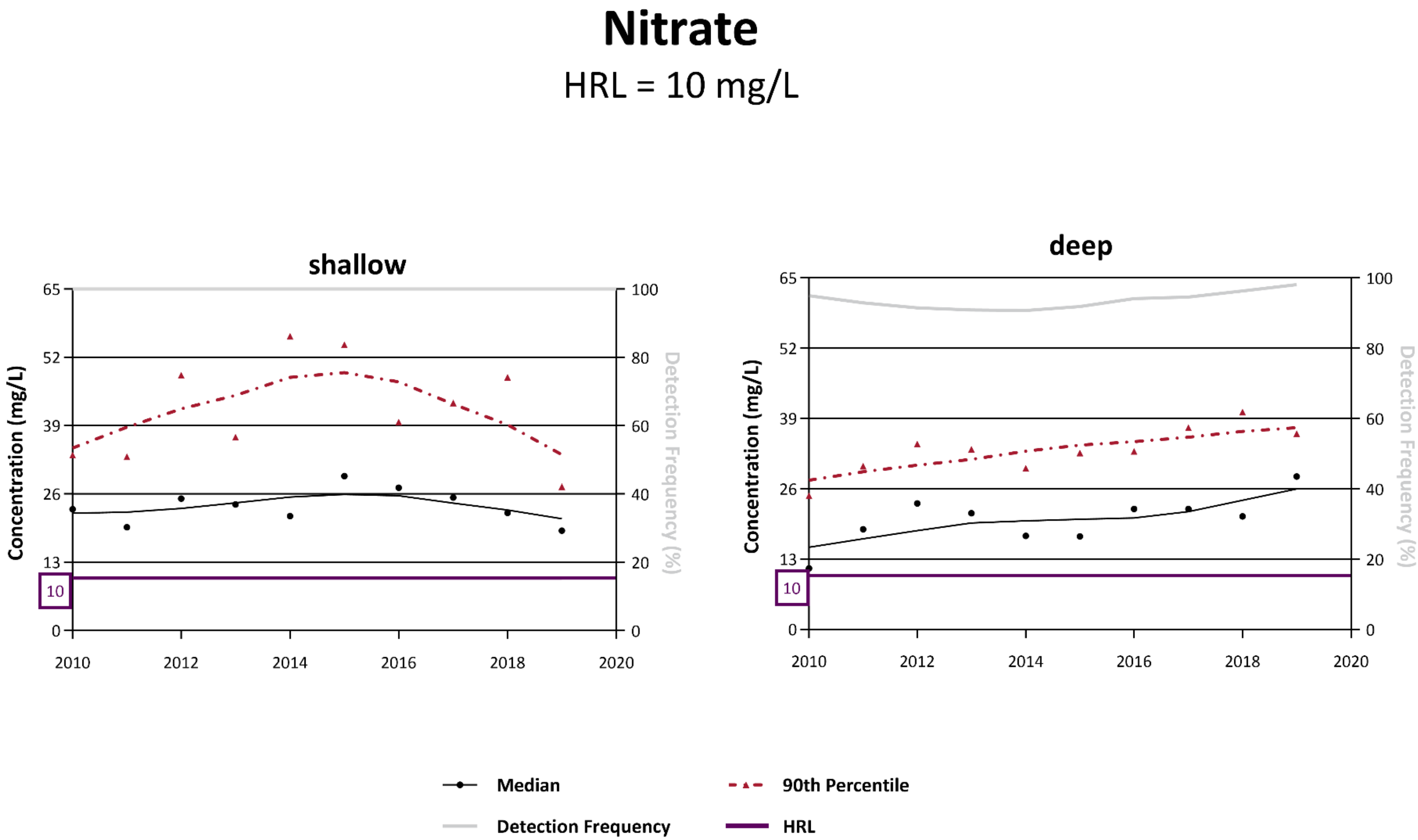
2010-2019

- The annual detection frequency in the shallow wells has been 100% every year since monitoring began in the fall of 2010, while the detection frequency in the deep wells has ranged between 80-100%.
- Median nitrate concentrations from the shallow and deep wells have been above the HRL since sampling began.

Table 6-2. Summary of nitrate results from shallow and deep well nests in PMR 4 in 2019.

Depth Type	Samples Analyzed	Number of Detections	Detection Frequency (%)	Median (mg/L)	90th Percentile (mg/L)	Maximum (mg/L)	Percent Exceeding 10 mg/L HRL
Shallow	8	8	100	19.0	27.4	27.8	88
Deep	8	8	100	28.3	36.2	39.6	88

Figure 6-1. Nitrate concentration and detection frequency over time in the shallow and deep wells in MDA PMR 4.



6.2 Nutrient and sediment monitoring in surface waters

Nitrate, DOP and TP samples were collected with most pesticide samples at each river and stream monitoring location. Total suspended solids samples were collected with select pesticide samples at limited locations.

Nitrate was analyzed in 722 samples, while DOP and TP were analyzed in 721 samples collected in 2019 (Table 6-4). Approximately 42% of the samples were collected under base flow conditions (301 samples for all three analytes) and 58% of the samples were collected under storm flow conditions (421 nitrate; 420 DOP and TP samples).

Eighty-nine TSS samples were collected (19 from base flow conditions and 70 from storm flow conditions). The TSS samples were collected at one location in PMR 1 (Buffalo River) and four locations in PMR 9 (Cedar River, Middle Branch of the Whitewater River, Nork Branch of the Root River and the South Branch of the Root River).

Key findings from the nutrient and sediment results for stream and river water samples include:

Nitrate

- With base flow and storm flow conditions combined, nitrate was detected in 98% to 100% of samples from PMRs 6, 7, 8, 9, and 10, 46-56% of the samples from PMRs 1, 4, 5, and urban locations and was not detected in PMR 3.
- Base flow conditions:
  - PMR 9 had the greatest median concentration (7.47 mg/L).
  - PMR 8 had the greatest maximum concentration (12.3 mg/L).
  - Median concentrations were less than the MRL (0.2 mg/L) in PMRs 1, 3, and 4.
- Storm flow conditions:
  - PMR 7 had the greatest median concentration (8.29 mg/L).
  - PMR 8 had the greatest maximum concentration (17.0 mg/L).
  - Median concentrations were less than the MRL (<0.2 mg/L) in PMRs 3, 5, and Urban.

Dissolved orthophosphorus

- With base flow and storm flow conditions combined, DOP was detected in at least 97% of the samples from every PMR, except PMR 3 (75% detection frequency).
- Base flow conditions:
  - Median DOP concentrations ranged from 0.007 mg/L in PMR 3 to 0.053 mg/L in PMR 10.
  - PMR 1 had the highest maximum concentration (0.450 mg/L).
- Storm flow conditions:
  - Median DOP concentrations ranged from 0.006 mg/L in PMR 3 to 0.136 mg/L in PMR 1.
  - PMR 1 also had the highest maximum concentration (0.396 mg/L).

Total phosphorus

- TP was detected in every sample collected in 2019.
- Base flow conditions:
  - Median TP concentrations ranged from 0.015 mg/L in PMR 3 to 0.195 mg/L in PMR 1.
  - PMR 9 had the highest maximum concentration (1.190 mg/L).
- Storm flow conditions:
  - Median TP concentrations ranged from 0.014 mg/L in PMR 3 to 0.354 mg/L in PMR 9.
  - PMR 9 had the highest maximum concentration (3.62 mg/L).

Total suspended solids

- TSS was detected in every sample collected in 2019.
- PMRs 1 and 9 had higher median and maximum concentrations during storm flow compared to base flow.

Table 6-4. 2019 nutrient and sediment results for stream and river water samples by PMR.

Inorganic Analyte	Monitoring Region	Base flow					Storm flow				
		Total Samples	Detections	Detection Frequency (%)	Median (mg/L)	Maximum (mg/L)	Total Samples	Detections	Detection Frequency (%)	Median (mg/L)	Maximum (mg/L)
Nitrate	PMR 1	51	16	31	<0.20	1.9	26	20	77	0.61	7.0
	PMR 3	5	0	0	<0.20	<0.20	3	0	0	<0.20	<0.20
	PMR 4	21	9	43	<0.20	0.8	15	11	73	0.46	1.0
	PMR 5	19	11	58	0.77	1.4	13	5	38	<0.20	1.0
	PMR 6	20	20	100	2.84	8.5	33	33	100	5.50	11.6
	PMR 7	18	18	100	6.53	8.7	34	33	97	8.29	9.5
	PMR 8	75	74	99	5.10	12.3	138	138	100	7.98	17.0
	PMR 9	48	48	100	7.47	11.6	98	98	100	7.76	12.5
	PMR 10	15	15	100	5.69	12.2	42	42	100	5.39	13.7
	Urban	29	15	52	0.20	4.3	19	7	37	<0.20	3.5
	Statewide	301	226	75	2.66	12.3	421	387	92	6.53	17.0
DOP	PMR 1	51	50	98	0.048	0.450	26	26	100	0.136	0.396
	PMR 3	5	4	80	0.007	0.009	3	2	67	0.006	0.010
	PMR 4	21	21	100	0.023	0.079	15	14	93	0.008	0.063
	PMR 5	19	19	100	0.021	0.113	13	13	100	0.015	0.144
	PMR 6	20	20	100	0.035	0.115	33	33	100	0.044	0.170
	PMR 7	18	18	100	0.024	0.045	34	33	97	0.031	0.177
	PMR 8	75	75	100	0.026	0.111	138	138	100	0.035	0.191
	PMR 9	48	48	100	0.013	0.195	97	97	100	0.040	0.292
	PMR 10	15	15	100	0.053	0.145	42	42	100	0.068	0.264
	Urban	29	28	97	0.023	0.090	19	19	100	0.015	0.060
	Statewide	301	298	99	0.025	0.450	420	417	99	0.037	0.396
TP	PMR 1	51	51	100	0.195	0.542	26	26	100	0.296	0.572
	PMR 3	5	5	100	0.015	0.036	3	3	100	0.014	0.016
	PMR 4	21	21	100	0.052	0.161	15	15	100	0.049	0.174
	PMR 5	19	19	100	0.052	0.153	13	13	100	0.052	0.264
	PMR 6	20	20	100	0.178	0.380	33	33	100	0.196	0.540
	PMR 7	18	18	100	0.109	0.206	34	34	100	0.179	0.882
	PMR 8	75	75	100	0.119	0.940	138	138	100	0.202	1.440
	PMR 9	48	48	100	0.060	1.190	97	97	100	0.354	3.620
	PMR 10	15	15	100	0.171	0.375	42	42	100	0.224	0.672
	Urban	29	29	100	0.064	0.190	19	19	100	0.072	0.154
	Statewide	301	301	100	0.101	1.190	420	420	100	0.207	3.620
TSS	PMR 1	5	5	100	31.2	139	5	5	100	94.1	179
	PMR 9	14	14	100	8.7	113	65	65	100	334	4,790

6.3 Nutrient monitoring in rainfall

Rainfall monitoring allows the MDA to assess atmospheric deposition of nutrients in rainfall across Minnesota. Samples for nutrient analysis are collected after pesticide sample collection, if sufficient water is available. The four locations where the MDA collects rainfall are presented in Figure 3-17.

Key findings, based on rainfall monitoring for nutrients, are summarized below and the results are presented in Table 6-5.

- Eight nitrate, DOP, and TP samples were collected in PMR 9 and in St. Paul.
    - No nutrient samples were collected in PMR 1 or PMR 8.
- Nitrate was detected in 38% of the samples, and the maximum concentration was 0.37 mg/L.
- DOP was not detected in any of the samples.
- TP was detected in 75% of the samples, and the maximum concentration was 0.011 mg/L.

Table 6-5. 2019 rainfall nutrient data.

Analyte	Samples	Detections	Detection Frequency (%)	Median (mg/L)	Maximum (mg/L)
Nitrate	8	3	38	<0.2	0.37
DOP	8	0	0	<0.005	<0.005
TP	8	6	75	0.008	0.011

Section 7: References

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Section 7: References

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Appendix 1

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2019 MDA Pesticide list by method and analyte: analyte name; Chemical Abstracts Service (CAS) registry number; and Method Reporting Limit (MRL)

Appendix 1a. 2019 MDA GC-MS/MS Pesticide Analytes, CAS Number, and Method Reporting Limit (MRL).

Pesticide Analyte	CAS Number	MRL (ng/L)
Acetochlor	34256-82-1	30
Alachlor	15972-60-8	30
Atrazine	1912-24-9	30
Benfluralin	1861-40-1	25
Bifenthrin	82657-04-3	20
Chlorothalonil	1897-45-6	50
Chlorpyrifos	2921-88-2	40
Clomazone	81777-89-1	15
Cyfluthrin	68359-37-5	100
Desethylatrazine	6190-65-4	50
Diazinon	333-41-5	30
Diazinon Oxon	962-58-3	75
Dichlobenil	1194-65-6	5
Dichlorvos	62-73-7	15
Dimethenamid	87674-68-8	15
Disulfoton	298-04-4	60
EPTC	759-94-4	10
Esfenvalerate	66230-04-4	150
Ethalfluralin	55283-68-6	50
Ethofumesate	26225-79-6	50
Fonofos	944-22-9	15
lambda Cyhalothrin	91465-08-6	75
Malathion	121-75-5	50
Methoxychlor	72-43-5	50
Metolachlor	51218-45-2	25
Metribuzin	21087-64-9	75
Oxadiazon	19666-30-9	75
Parathion-methyl	298-00-0	100
Pendimethalin	40487-42-1	75
Phorate	298-02-2	25
Prometon	1610-18-0	100
Propachlor	1918-16-7	30
Propazine	139-40-2	25
Simazine	122-34-9	75
Tebupirimfos	96182-53-5	30
Terbufos	13071-79-9	30
Tolfenpyrad	129558-76-5	100
Triallate	2303-17-5	50
Trifluralin	1582-09-8	50
zeta-Cypermethrin	52315-07-8	500

Appendix 1b. 2019 MDA Glyphosate Pesticide Analytes, CAS Number, and Method Reporting Limit (MRL).

Pesticide Analyte	CAS Number	MRL (ng/L)
Aminomethylphosphornic acid (AMPA)	1066-51-9	5,090
Glyphosate	1071-83-6	1,020

Appendix 1c. 2019 MDA LC-MS/MS Pesticide Analytes, CAS Number, and Method Reporting Limit (MRL).

Pesticide Analyte	CAS Number	MRL (ng/L)
2,4,5-T	93-76-5	50
2,4,5-TP	93-72-1	50
2,4-D	94-75-7	8.3
2,4-DB	94-82-6	20
Acetamiprid	135410-20-7	25
Acetochlor ESA	187022-11-3	30
Acetochlor OXA	194992-44-4	33.3
Aciflourfen	50594-66-6	25
Afidopyropen	915972-17-7	50
Alachlor ESA	142363-53-9	41.6
Alachlor OXA	171262-17-2	33.3
Aldicarb Sulfone	1646-88-4	15
Aldicarb Sulfoxide	1646-87-3	50
Aminopyralid	150114-71-9	25
Azoxystrobin	131860-33-8	10
Bensulfuron-methyl	83055-99-6	16.7
Bensulide	741-58-2	250
Bentazon	25057-89-0	5
Benzovindiflupyr	1072957-71-1	50
Bicyclopyrone	352010-68-5	10
Bicyclopyrone SYN503780	380355-55-5	100
Boscalid	188425-85-6	50
Bromacil	314-40-9	30
Bromoxynil	1689-84-5	25
Carbaryl	63-25-2	25
Carbendazim	10605-21-7	10
Carbofuran	1563-66-2	13.3
Chlorantraniliprole	500008-45-7	50
Chlorimuron-ethyl	90982-32-4	20
Chlorpyrifos oxon	5598-15-2	40
Clethodim Sulfone	111031-17-5	100
Clethodim Sulfoxide	111031-14-2	50
Clopyralid	1702-17-6	41.6
Clothianidin	210880-92-5	25
Cyanazine	21725-46-2	25
Cyanazine Acid	36576-43-9	10
Cyanazine Amide	36576-42-8	10
Cyantraniliprole	736994-63-1	100
Deisopropylatrazine	1007-28-9	25
Dicamba	1918-00-9	50
Dichlorprop	120-36-5	50
Dicrotophos	141-66-2	25
Didealkylatrazine	3397-62-4	50
Deethylcyanazine	21725-40-6	25
Deethylcyanazine Acid	36749-35-6	25

Pesticide Analyte	CAS Number	MRL (ng/L)
Deethylcyanazine Amide	36556-77-1	25
Difenoconazole	119446-68-3	25
Dimethenamid ESA	205939-58-8	6.7
Dimethenamid OXA	87674-68-8-OXA	10
Dimethoate	60-51-5	50
Dinotefuran	165252-70-0	25
Disulfoton Sulfone	2497-06-5	20
Diuron	330-54-1	13.3
Flufenacet OXA	201668-31-7	8.3
Flumetsulam	98967-40-9	50
Flupyradifurone	951659-40-8	10
Flutianil	958647-10-4	25
Flutianil OC 56574	958647104_56574*	50
Flutianil OC 56635	958647104_56635*	25
Flutriafol	76674-21-0	10
Fluxapyroxad	907204-31-3	10
Fomesafen	72178-02-0	50
Halauxifen Acid	943832-60-8	25
Halauxifen-methyl	943831-98-9	10
Halosulfuron-methyl	100784-20-1	30
Hexazinone	51235-04-2	10
Hydroxyatrazine	2163-68-0	6.7
Imazamethabenz Acid	81405-85-8-ACID	10
Imazamethabenz-methyl	81405-85-8	5
Imazamox	114311-32-9	13.3
Imazapic	104098-48-8	10
Imazapyr	81334-34-1	8.3
Imazaquin	81335-37-7	16.7
Imazethapyr	81335-77-5	6.7
Imidacloprid	138261-41-3	5
Imidacloprid Olefin	115086-54-9	50
Imidacloprid Urea	120868-66-8	50
Isoxaflutole	141112-29-0	40
Isoxaflutole DKN	143701-75-1	50
Linuron	330-55-2	20
Mandestrobin	173662-97-0	25
MCPA	94-74-6	5
MCPB	94-81-5	20
MCPP	93-65-2	50

Pesticide Analyte	CAS Number	MRL (ng/L)
Mesotrione	104206-82-8	50
Metalaxyl	57837-19-1	8.3
Metolachlor ESA	171118-09-5	10
Metolachlor OXA	152019-73-3	10
Metribuzin DA	35045-02-4	25
Metribuzin DADK	52236-30-3	500
Metribuzin DK	56507-37-0	500
Metsulfuron-methyl	74223-64-6	23.3
Momfluorothrin	609346-29-4	50
Myclobutanil	88671-89-0	10
Nicosulfuron	111991-09-4	26.6
Norflurazon	27314-13-2	20
Norflurazon-desmethyl	23576-24-1	50
Oxathiapiprolin	1003318-67-9	100
Oxydemeton-methyl	301-12-2	20
Parathion-methyl Oxon	950-35-6	25
Picloram	1918-02-1	41.6
Picoxystrobin	117428-22-5	50
Prometryn	7287-19-6	3.3
Propachlor ESA	947601-88-9	30
Propachlor OXA	70628-36-3	10
Propiconazole	60207-90-1	10
Pydiflumetofen	1228284-64-7	25
Pyraclostrobin	175013-18-0	25
Pyroxasulfone	447399-55-5	50
Saflufenacil	372137-35-4	15
Sedaxane	874967-67-6	75
Siduron	1982-49-6	6.7
Sulfentrazone	122836-35-5	50
Sulfometuron-methyl	74222-97-2	8.3
Tebuconazole	107534-96-3	10
Tembotrione	335104-84-2	50
Tetraconazole	112281-77-3	10
Thiacloprid	111988-49-9	50
Thiamethoxam	153719-23-4	25
Thifensulfuron-methyl	79277-27-3	16.7
Thiobencarb	28249-77-6	8.3
Tolpyralate	1101132-67-5	50
Triasulfuron	82097-50-5	23.3
Triclopyr	55335-06-3	50

* These compounds do not have a registered CAS number. These CAS numbers were created to allow for entry of the data into EQuIS

Appendix 2

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Pesticide compounds detected in Minnesota water resources by the MDA

Pesticide compounds listed in this Appendix display compounds that are currently or have historically been analyzed at least once since the inception of either the groundwater or surface water monitoring program. Compounds without an "x" in the target analyte list column indicate a historical analyte that was not included in the current monitoring season. Compounds with an "x" in the column for either groundwater or surface water indicate an analyte that has been detected.

Pesticide Compound*	2019 Target Groundwater and Surface Water Analyte***	Detection in Minnesota Groundwater (1985-2019)**	Detection in Minnesota Surface Water (1991-2019)**	Detection in Minnesota Rainfall (2008-2019)**
2,4-D	x	x	x	x
2,4-DB	x			
2,4,5-T	x			
2,4,5-TP	x			
2,6-Dichlorobenzamide			x	
3-hydroxycarbofuran				
Acetamiprid	x			
Acetochlor	x	x	x	x
Acetochlor ESA	x	x	x	
Acetochlor OXA	x	x	x	
Acifluorfen	x		x	
Afidopyropen	x			
Alachlor	x	x	x	x
Alachlor ESA	x	x	x	
Alachlor OXA	x	x	x	
Aldicarb		x		
Aldicarb Sulfone	x		x	
Aldicarb Sulfoxide	x		x	
Aminomethylphosphonic acid (AMPA)	x		x	
Aminopyralid	x	x	x	
Atrazine	x	x	x	x
Azoxystrobin	x		x	x
Benfluralin	x			
Bensulfuron-methyl	x			
Bensulide	x			
Bentazon	x	x	x	x
Benzovindiflupyr	x		x	
Bicyclopyrone	x	x	x	
Bicyclopyrone SYN503870	x			
Bifenthrin	x		x	
Boscalid	x	x	x	
Bromacil	x	x	x	
Bromoxynil	x		x	x
Butylate				
Carbaryl	x		x	
Carbendazim	x		x	x
Carbofuran	x			
Chloramben				
Chlorantraniliprole	x	x	x	
Chlorimuron-ethyl	x		x	
Chlorothalonil	x	x	x	
Chlorpyrifos	x		x	x
Chlorpyrifos Oxon	x			
Clethodim sulfone	x		x	
Clethodim sulfoxide	x		x	
Chlorsulfuron****				
Clomazone	x	x	x	x
Clopyralid	x	x	x	x
Clothianidin	x	x	x	x
Cyanazine	x	x	x	
Cyanazine acid	x	x		
Cyanazine amide	x	x		
Cyantraniliprole	x		x[†]	
Cyfluthrin	x			
Deethylcyanazine	x			
Deethylcyanazine acid	x	x	x	
Deethylcyanazine amide	x			
Deisopropylatrazine	x	x	x	x
Desethylatrazine	x	x	x	x
Diaminochlorotriazine (DACT)		x	x	
Diazinon	x		x	
Diazinon Oxon	x			
Dicamba	x	x	x	x

Pesticide Compound*	2019 Target Groundwater and Surface Water Analyte***	Detection in Minnesota Groundwater (1985-2019)**	Detection in Minnesota Surface Water (1991-2019)**	Detection in Minnesota Rainfall (2008-2019)**
Dichlobenil	x		x	
Dichlorprop	x		x	
Dichlorvos	x		x	
Dicrotophos	x			
Didealkylatrazine	x	x	x	x
Difenoconazole	x			
Dimethenamid	x	x	x	x
Dimethenamid ESA	x	x	x	
Dimethenamid OXA	x	x	x	
Dimethoate	x	x	x	
Dinotefuran	x		x	
Disulfoton	x			
Disulfoton Sulfone	x			
Diuron	x	x	x	
EPTC	x		x	x
Esfenvalerate	x			
Ethalfluralin	x			
Ethofumesate	x		x	
Fenoprop****			x*****	
Flufenacet OXA	x			
Flumetsulam	x	x	x	
Flupyradifurone	x		x†	
Flutianil	x			
Flutianil OC56574	x			
Flutianil OC56635	x			
Flutriafol	x		x	
Fluxapyroxad	x		x	
Fomesafen	x	x	x	
Fonofos	x	x		
Glyphosate	x		x	x
Halauxifen Acid	x			
Halauxifen-methyl	x			
Halosulfuron-methyl	x		x	
Hexazinone	x			
Hydroxyatrazine	x	x	x	x
Imazamethabenz Acid	x		x	
Imazamethabenz-methyl	x			
Imazamox	x	x	x	
Imazapic	x		x	
Imazapyr	x	x	x	x
Imazaquin	x			
Imazethapyr	x	x	x	
Imidacloprid	x	x	x	x
Imidacloprid Olefin	x			
Imidacloprid Urea	x			
Isoxaflutole	x			
Isoxaflutole DKN	x	x		
lambda-Cyhalothrin	x			
Linuron	x			
Malathion	x		x	
Mandestrobin	x			
MCPA	x	x	x	x
MCPB	x		x	
MCPP	x	x	x	
Mesotrione	x	x	x	
Metalaxyl	x	x	x	
Methoxychlor	x			
Metolachlor	x	x	x	x
Metolachlor ESA	x	x	x	
Metolachlor OXA	x	x	x	
Metribuzin	x	x	x	
Metribuzin DA	x	x	x	
Metribuzin DADK	x	x	x	
Metribuzin DK	x	x	x	
Metsulfuron-methyl	x	x	x	

Pesticide Compound*	2019 Target Groundwater and Surface Water Analyte***	Detection in Minnesota Groundwater (1985-2019)**	Detection in Minnesota Surface Water (1991-2019)**	Detection in Minnesota Rainfall (2008-2019)**
Momfluorothrin	x			
Myclobutanil	x			
Neburon				
Nicosulfuron	x	x	x	
Norflurazon	x		x	
Norflurazon-desmethyl	x			
Oxadiazon	x		x†	
Oxathiapiprolin	x			
Oxydemeton-methyl	x			
Parathion-methyl	x			
Parathion-methyl Oxon	x			
Pendimethalin	x		x	
Pentachlorophenol (PCP)		x	x	
Phorate	x		x*****	
Phosphamidon				
Picloram	x	x	x	
Picoxystrobin	x			
Primisulfuron methyl****			x*****	
Prometon	x	x	x	
Prometryn	x		x	x
Propachlor	x		x	
Propachlor ESA	x	x		
Propachlor OXA	x			
Propazine	x	x	x	
Propiconazole	x		x	x
Propoxur				
Prosulfuron****				
Pyraclostrobin	x		x	
Pyroxasulfone	x		x	
Rimisulfuron****				
Saflufenacil	x	x	x	
Sedaxane	x			
Siduron	x		x	
Simazine	x	x	x	
Sulfentrazone	x	x	x	x
Sulfometuron-methyl	x	x	x	
Tebuconazole	x		x	
Tebupirimfos	x		x	
Tebuthiuron****				
Tembotrione	x		x	
Terbufos	x		x	
Tetraconazole	x	x	x	x
Thiacloprid	x			
Thiamethoxam	x	x	x	
Thifensulfuron-methyl	x		x	
Thiobencarb	x			
Tolfenpyrad	x			
Tolpyralate	x			
Triallate	x			
Triasulfuron	x			
Tribenuron methyl****				
Triclopyr	x	x	x	
Trifluralin	x		x	
Triflusulfuron methyl****				
zeta-Cypermethrin	x			

* Laboratory analytes have changed during years presented. All target and detected non-target analytes (1985-2019) are presented.
** Detection is defined as compound occurring in water sample at concentration of "present" or higher.
*** Surface water sites include lakes, streams, rivers, and tile demonstration sites.
**** Analysis of pesticide compound only completed at tile demonstration sites.
***** Analyte only detected in tile demonstration site.
† Analyte only detected in surface water during a special monitoring study.

Appendix 3

2019 Water Quality Monitoring Report

January – December 2019

2019 MDA groundwater and surface water annual summaries.

MDA Groundwater Program Annual Summary

The goal of this document is to provide a snapshot of the annual MDA Groundwater Program activities. The below tables includes data from monitoring wells, private wells, domestic wells and springs. No QA/QC or special project samples are included in the summaries.

Number of Sites and Overall Pesticide Monitoring Sample Collection Events (any analytes)

Year	Total Sites	Pesticide Monitoring Sample Events	Monitoring Wells	Urban Wells	Domestic Wells	Springs
2010	174	260	128	20	14	12
2011	171	276	123	20	14	14
2012	166	270	120	20	13	13
2013	165	271	120	20	12	13
2014	167	274	122	20	12	13
2015	175	248	130	20	12	13
2016	169	249	124	20	12	13
2017	168	248	124	19	12	13
2018	171	290	126	20	12	13
2019	166	270	122	20	11	13

Number of Pesticide Analyses and Analytes by Laboratory Method

Year	Total Analyses	Total Analytes	Detected Analytes	GC-MS/MS		LC-MS/MS		Glyphosate	
				Analyses	Analytes	Analyses	Analytes	Analyses	Analytes
2010	520	110	43	260	44	260	66	0	0
2011	551	114	40	275	44	276	70	0	0
2012	540	126	41	270	50	270	76	0	0
2013	542	129	35	271	44	271	85	0	0
2014	560	135	37	274	44	274	89	12	2
2015	506	138	36	248	45	248	91	10	2
2016	659	143	39	249	45	248	96	162	2
2017	688	150	37	248	40	248	108	194	2
2018	785	155	40	290	40	290	115	205	2
2019	742	166	47	270	40	270	124	202	2

Number of Individual Pesticide Analyses

Year	Total	GC-MS/MS	LC-MS/MS	Glyphosate
2010	28,600	11,440	17,160	0
2011	31,420	12,100	19,320	0
2012	34,020	13,500	20,520	0
2013	34,959	11,924	23,035	0
2014	36,466	12,056	24,386	24
2015	33,748	11,160	22,568	20
2016	35,337	11,205	23,808	324
2017	37,620	9,920	27,280	420
2018	45,360	11,600	33,350	410
2019	44,684	10,800	33,480	404

Number of Individual Pesticide Concentrations above Reference Value

Year	Total	Total Metribuzin HRL13 (10,000 ng/L)	Fomesafen*HBV20 (20,000 ng/L)*
2010	0	0	--
2011	0	0	--
2012	0	0	--
2013	0	0	--
2014	0	0	--
2015	1	1	--
2016	0	0	--
2017	0	0	--
2018	1	0	1
2019	0	0	0

** Analysis began in 2018. In 2018, the RA from the MDH was 3,000 ng/L. In 2020, the MDH issued an HBV of 20,000 ng/L.*

MDA Surface Water Program Annual Summary

The goal of this summary is to provide a snapshot of the annual MDA surface water program activities. The below tables include program data from monitoring of rivers/streams, lakes, and wetlands. No quality control/quality assurance (QA/QC) samples or special project samples including rainfall, ELISA immunoassay pesticide analyses, investigations, or the Root River Pesticide Pilot, are included in this summary.

Number of locations and overall pesticide monitoring sample collection events.

Year	Pesticide Monitoring Sample Collection Events	Number of Locations						
		Total Locations	Tier 1	Tier 2	Tier 3	Non-Tier River/Streams	Lakes	Wetlands
2009	373	65	36	9	6	8	6	0
2010	642	227	43	10	7	146	21	0
2011	554	139	40	13	7	59	20	0
2012	485	128	35	16	7	19	51	0
2013	614	60	23	28	7	2	0	0
2014	686	81	24	31	7	0	0	19
2015	683	81	13	35	7	25	0	1
2016	677	77	11	36	7	0	0	23
2017	788	207	12	37	7	0	151	0
2018	667	57	9	39	7	0	2	0
2019	702	56	9	39	7	0	1	0

Number of pesticide analyses and analytes by laboratory method.

Year	Total Samples	Total Analytes	Detected Analytes	GC-MS/MS		LC-MS/MS		Glyphosate	
				Samples	Analytes	Samples	Analytes	Samples	Analytes
2009	488	43	22	373	29	115	6 - 14	0	0
2010	957	110	49	609	44	348	66	0	0
2011	769	114	52	553	44	216	70	0	0
2012	689	128	54	483	50	167	76	39	2
2013	865	131	57	613	44	198	85	54	2
2014	994	135	59	684	44	233	89	77	2
2015	991	138	60	682	45	228	91	81	2
2016	999	143	65	676	45	240	96	83	2
2017	1,190	150	67	686	40	262	108	242	2
2018	1,034	155	66	667	40	276	113	91	2
2019	1,167	166	69	692	40	383	124	92	2

Number of reported individual pesticide analyses and detections.

Year	Total Analyses	Total Number of Pesticide Detections
2009	11,702	851
2010	49,710	3,290
2011	38,824	2,430
2012	36,637	1,730
2013	43,875	3,033
2014	50,968	3,655
2015	51,352	3,372
2016	53,554	3,651
2017	56,157	3,689
2018	58,015	5,079
2019	75,279	6,594

Number of individual pesticide concentrations above applicable reference value (duration of concentration not considered in this table).

Year	Total	Acetochlor	Atrazine	Atrazine	Bifenthrin	Bromacil	Chlorpyrifos	Clothianidin	Diazinon	Dichlorvos	Diuron	Imidacloprid	Malathion	Metolachlor	Metsulfuron-methyl	Sulfometuron-methyl	Tebupirimfos	Terbufos
RV*	--	3,600	10,000	3,400	1.3	6,800	41	50	105	5.8	2,400	10	49	23,000	360	450	11	30
2009	2	0	0	1	--	--	0	--	0	--	--	--	0	1	--	--	0	0
2010	18	0	0	0	--	1	5	--	0	--	0	6	0	0	2	3	1	0
2011	29	2	0	0	--	5	7	5	0	--	1	5	1	0	1	2	0	0
2012	26	14	0	1	0	0	4	0	0	1	0	3	1	0	0	0	0	0
2013	19	1	0	0	0	0	1	6	0	4	0	6	0	0	0	0	0	1
2014	46	8	0	1	0	0	8	13	0	6	0	9	0	0	0	0	1	0
2015	18	5	0	0	0	0	7	5	0	0	0	1	0	0	0	0	0	0
2016	28	2	0	0	0	0	7	14	0	0	1	2	0	2	0	0	0	0
2017	45	13	2	0	1	0	16	9	0	1	0	3	0	0	0	0	0	0
2018	82	8	2	0	1	0	10	29	1	0	0	31	0	0	0	0	0	0
2019	138	11	0	2	0	0	3	62	0	1	0	58	0	1	0	0	0	0
Total	451	64	4	5	2	6	68	143	1	13	2	124	2	4	3	5	2	1

Reference Value in ng/L

Five most frequently detected pesticide analytes annually for surface water monitoring using annual MRL without censoring to a common MRL.

Year	Analyte (%)	Analyte (%)	Analyte (%)	Analyte (%)	Analyte (%)
2009	Dimethenamid ESA (100)	Metolachlor ESA (83)	2,4-D (73)	Acetochlor ESA (63)	Dicamba (61)
2010	Hydroxyatrazine (93)	Metolachlor ESA (82)	Metolachlor OXA (72)	2,4-D (65)	Acetochlor ESA (65)
2011	Hydroxyatrazine (93)	Metolachlor ESA (73)	2,4-D (65)	Metolachlor OXA (64)	Acetochlor ESA (61)
2012	Hydroxyatrazine (83)	Metolachlor ESA (65)	2,4-D (64)	Atrazine (52)	Metolachlor OXA (50)
2013	Hydroxyatrazine (91)	Metolachlor ESA (81)	2,4-D (76)	Metolachlor OXA (75)	Acetochlor ESA (70)
2014	Hydroxyatrazine (85)	Metolachlor ESA (77)	Acetochlor ESA (73)	Atrazine (72)	Metolachlor OXA (72)
2015	Hydroxyatrazine (89)	Metolachlor ESA (79)	Acetochlor ESA (75)	Metolachlor OXA (73)	2,4-D (70)
2016	Hydroxyatrazine (90)	2,4-D (78)	Metolachlor ESA (71)	Metolachlor (68)	Atrazine (67)
2017	Hydroxyatrazine (82)	2,4-D (73)	Metolachlor ESA (69)	Metolachlor OXA (66)	Acetochlor ESA (63)
2018	Hydroxyatrazine (93)	Metolachlor ESA (86)	Metolachlor OXA (82)	2,4-D (79)	Acetochlor ESA (79)
2019	Hydroxyatrazine (97)	Metolachlor ESA (90)	Metolachlor OXA (90)	2,4-D (85)	Acetochlor ESA (84)

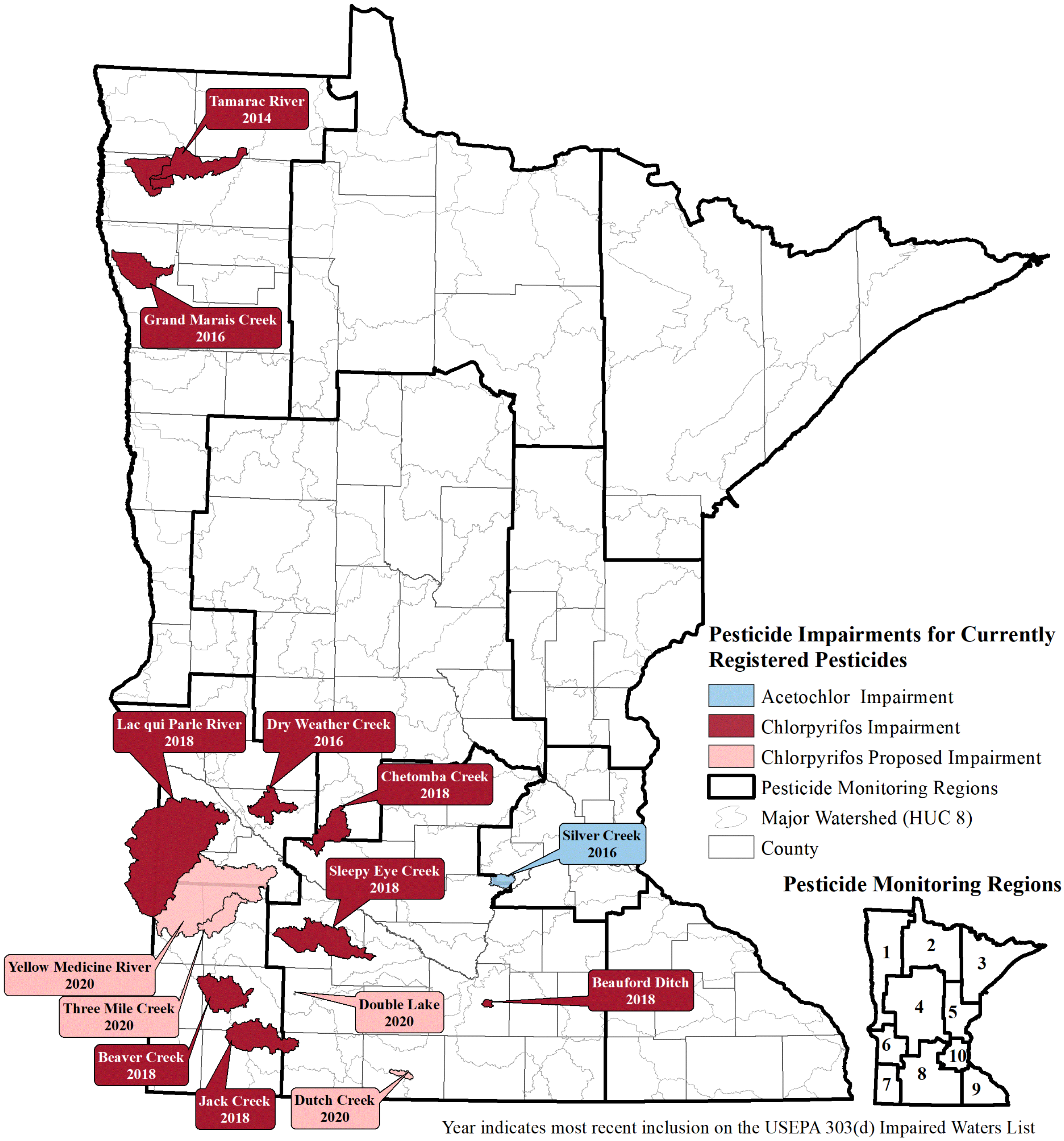
Current and proposed pesticide water quality impairments

There are 14 waterbodies in Minnesota that are either designated, or proposed to be designated, as impaired on the USEPA 303(d) Impaired Waters List for currently registered pesticides, by the MPCA, as a result of the MDA surface water pesticide monitoring (Table 3-1 and Figure 3-0). The 2017 MDA pesticide water quality data will be assessed as part of the 2020 USEPA 303(d) Impaired Waters List.

Minnesota pesticide impairments for currently registered pesticides.

Pesticide	Impaired Waters List Year	Stream	Hydrologic Unit Code (8-digit)	County	Minnesota Water Quality Standard Violation
Acetochlor	2016	Silver Creek	07020012	Carver	chronic (3,600 ng/L)
Chlorpyrifos	2018	Beauford Ditch	07020011	Blue Earth	maximum (83 ng/L)
Chlorpyrifos	2018	Beaver Creek	07100001	Murray	maximum (83 ng/L)
Chlorpyrifos	2018	Chetomba Creek	07020004	Renville	maximum (83 ng/L)
Chlorpyrifos	2020	Double Lake (North Portion)	07020008	Cottonwood	chronic (41 ng/L)
Chlorpyrifos	2016	Dry Weather Creek	07020005	Chippewa	maximum (83 ng/L)
Chlorpyrifos	2020	Dutch Creek	07020009	Martin	maximum (83 ng/L)
Chlorpyrifos	2014/2016	Grand Marais Creek	09020306	Polk	maximum (83 ng/L)
Chlorpyrifos	2018	Jack Creek	07100001	Jackson	maximum (83 ng/L)
Chlorpyrifos	2018	Lac qui Parle River	07020003	Lac qui Parle	maximum (83 ng/L)
Chlorpyrifos	2018	Sleepy Eye Creek	07020008	Redwood	maximum (83 ng/L)
Chlorpyrifos	2014	Tamarac River	09020311	Marshall	maximum (83 ng/L)
Chlorpyrifos	2020	Three Mile Creek	07020006	Lyon	maximum (83 ng/L)
Chlorpyrifos	2020	Yellow Medicine River	07020004	Yellow Medicine	maximum (83 ng/L)

Three waterbodies have been removed from the USEPA 303(d) Impaired Waters List for currently registered pesticides. The Le Sueur River and Beauford Ditch were designated as impaired for acetochlor on the 2008 and were removed from the USEPA 303(d) Impaired Waters List in 2014. Seven Mile Creek was designated as impaired on the 2012 Impaired Waters List for chlorpyrifos. Seven Mile Creek was removed from the USEPA 303(d) Impaired Waters List in 2018. Removal from the USEPA 303(d) Impaired Waters List follows several years of water quality monitoring without elevated pesticide detections.


Pesticide Impairments for Currently Registered Pesticides
Acetochlor Impairment
Chlorpyrifos Impairment
Chlorpyrifos Proposed Impairment
Pesticide Monitoring Regions
Major Watershed (HUC 8)
County
Pesticide Monitoring Regions
1
2
3
4
5
6
7
8
9
10
Tamarac River 2014
Grand Marais Creek 2016
Lac qui Parle River 2018
Dry Weather Creek 2016
Chetomba Creek 2018
Silver Creek 2016
Sleepy Eye Creek 2018
Yellow Medicine River 2020
Three Mile Creek 2020
Beaver Creek 2018
Double Lake 2020
Beauford Ditch 2018
Jack Creek 2018
Dutch Creek 2020
Year indicates most recent inclusion on the USEPA 303(d) Impaired Waters List

Appendix 4

2019 Water Quality Monitoring Report

January – December 2019

2019 MDA groundwater monitoring network sample results.

Due to the large number of samples and analytes in 2019, these tabulated results have only been made available online at the Monitoring and Assessment web page (***www.mda.state.mn.us/monitoring***).

Appendix 5a

2019 Water Quality Monitoring Report

January – December 2019

Trend analysis of pesticide concentration and detection frequency data for in Minnesota groundwater documentation.

Comments to accompany trend analysis of concentration and detection frequency data for pesticides in Minnesota groundwater.

The Minnesota Department of Agriculture utilizes nonparametric trend analysis procedures on its monitoring data. Nonparametric procedures are necessary because of the nature of the MDA data set. First, MDA water quality data is censored, meaning that concentrations below the method reporting limit are reported as not detected; second, the data contains missing values; and third, the distribution of the measured data is highly skewed, negating the validity of parametric statistical procedures.

Trend analysis procedures utilized by the MDA measure linear (straight line), monotonic (one direction) trends only. Mann-Kendall test results give a measure of the general direction of the up or down trend over time in a data set and cannot account for non-seasonal random time-series fluctuations. Inconclusive results may be due to data that is non-linear over time or contains multiple maximums and minimums. Rates of change can be over or underestimated in situations where the data does not follow a straight line.

Due to the large number of trend results, these tabulated results are available upon request.

Appendix 5b

2019 Water Quality Monitoring Report

January – December 2019

Long-term time series plots of pesticide median and 90th percentile concentration and detection frequency values for Minnesota groundwater documentation.

Comments to accompany long-term time series plots of pesticide concentration and detection frequency values for Minnesota groundwater documentation.

Within the report, time series plots were provided for the groundwater monitoring pesticide data collected from 2010 through 2019. In previous years, time series plots were provided for the entire data record. The 2010-2019 time period better represents more current agricultural practices and conditions throughout the state, while information from the long-term analysis helps to provide an overall, historical perspective from groundwater monitoring activities that have been conducted. Caution should be utilized before comparing figures from these two time periods, however, due to the underlying differences in the data sets utilized to produce these figures.

Changes to the laboratory analytical methods, which occurred starting in 2010, resulted in lower MRLs for some pesticide compounds. To ensure comparability in the analysis of results over time requires censoring (or restricting) the data set being evaluate at the highest historic MRL for each compound during the time frame of evaluation. Therefore, the statistical summaries that were performed on the two data sets, to generate concentration percentile and detection frequency values for graphics generation, are slightly different due to the different historic MRLs that were utilized for censoring. As such, the two sets of time series plots should not be directly compared.

Due to the large number of long-term groundwater time series plots, these prepared figures are available upon request.

Appendix 6

2019 Water Quality Monitoring Report

January – December 2019

Trend analysis of pesticide concentration and detection frequency in Minnesota surface water documentation.

Comments to accompany trend analysis of pesticide concentration and detection frequency in Minnesota surface water.

The Minnesota Department of Agriculture utilizes nonparametric trend analysis procedures on its monitoring data. Nonparametric procedures are necessary because of the nature of the MDA data set. First, MDA water quality data is censored, meaning that concentrations below the method reporting limit are reported as not detected; second, the data contains missing values; and third, the distribution of the measured data is highly skewed, negating the validity of parametric statistical procedures.

Trend analysis procedures utilized by the MDA measure linear (straight line), monotonic (one direction) trends only. Mann-Kendall test results give a measure of the general direction of the up or down trend over time in a data set and cannot account for non-seasonal random time-series fluctuations. Inconclusive results may be due to data that is non-linear over time or contains multiple maximums and minimums. Rates of change can be over or underestimated in situations where the data does not follow a straight line.

Due to the large number of trend results, these tabulated results are available upon request.

Appendix 7

2019 Water Quality Monitoring Report

January – December 2019

MDA Tier 1 through 3 surface water monitoring site names and characteristics of locations sampled in 2019.

2019 Tier[a]	PMR[b]	MDA Site I.D.	MPCA Station I.D.	Site Name	County	State Water Use Classification Rule 7050[c]	Associated Major River Basin	Associated Major Watershed Name	Acres Represented[d]	MDA Sampling History		
										Tier 1	Tier 2	Tier 3
T2	**1**	BDS	S000-553	Bois de Sioux River	Wilkin	2C	Red River of the North	Bois de Sioux River	1,203,2328	2005-2008	2009-	
T3	**1**	BU1	S002-125	Buffalo River-Georgetown	Clay	2B/3C	Red River of the North	Buffalo River	708,810	2002; 2004-2006	2007-2008	2009-
ET2	**1**	GM1	S002-083	Grand Marais Creek	Polk	2B/3C	Red River of the North	Grand Marais Creek	108,941	2004-2011	2012-	
T2	**1**	RL2	S000-031	Red Lake River-Fisher	Polk	1C/2Bd/3C	Red River of the North	Red Lake River	3,579,830	2002-2003; 2011; 2016-2018	2013-2015; 2019	
T2	**1**	SH1	S002-099	Sand Hill River-Climax	Polk	2B/3C	Red River of the North	Sandhill River	294,766	2010-2013	2014-	
T1	**1**	SNA	S000-185	Snake River – Big Woods	Marshall	2B/3C	Red River of the North	Snake River	498,574	2005-2006; 2017	2007-2016; 2018-	
ET2	**1**	TM1	S005-788	Tamarac River-Stephen	Marshall	2B/3C	Red River of the North	Tamarac River	222,947	2010	2011-	
T1	**3**	KA1	S000-108	Kawishiwi River-Winton	Lake	2B/3C	Rainy River	Rainy River-Headwaters	400,000	1991-1993, 2009-		
T1	**4**	LE2	S001-931	Leaf River-CSAH29 Brg	Wadena	2B/3C	Upper Mississippi	Redeye River [Leaf River]	549,009	2014-		
T1	**4**	PEL	S000-556	Pelican River – Fergus Falls	Otter Tail	2B/3C	Red River of the North	Otter Tail River	315,588	2018-		
T1	**4**	PN1	S000-181	Pine River-Mission	Crow Wing	2B/3C	Upper Mississippi	Pine River	478,394	2009-		
T2	**4**	SK2	S000-017	Sauk River-Sauk Rapids-CR1	Stearns	2B/3C	Upper Mississippi	Sauk River	663,597	2014	2015-	
T1	**5**	LW1	S004-034	Lawrence Creek	Chisago	1B/2A/3B	St. Croix	St. Croix River-Stillwater	8,494	2007-2008; 2010-2012; 2019	2013-2018	
T1	**5**	RU3	S002-955	Rum River-Milaca	Mille Lacs	2B/3C	Upper Mississippi	Rum River	373,600	2018-		
T1	**5**	SN2	S000-198	Snake River-Pine City	Pine	2B/3C	St. Croix	Snake River	643,546	2010-		
T1	**5**	SU2	S004-032	Sunrise River-Sunrise	Chisago	2B/3C	St. Croix	St. Croix River-Stillwater	243,416	2011-		
ET2	**6**	DW1	S002-204	Dry Weather Creek	Chippewa	2C	Minnesota	Chippewa River	66,992	2009-2011	2012-	
ET2	**6**	LQ1	S003-087	Lac Qui Parle River-CH31	Lac Qui Parle	2B/3C	Minnesota	Lac qui Parle River	614,672	2014	2015-	
ET2	**6**	S16	S002-201	Shakopee Creek	Swift	2C	Minnesota	Chippewa River	194,806	2005-2013	2014-	
T2	**6**	YM1	S007-314	Yellow Medicine River-Granite Falls	Yellow Medicine	2B/3C	Minnesota	Minnesota River- Yellow Medicine River	427,387	1991-1993; 2009-2012	2013-	
ET2	**7**	BC1	S002-005	Beaver Creek	Murray	2B/3C	Des Moines River	Des Moines River - Headwaters	113,698	2007-2012	2013-	

2019 Tier[a]	PMR[b]	MDA Site I.D.	MPCA Station I.D.	Site Name	County	State Water Use Classification Rule 7050[c]	Associated Major River Basin	Associated Major Watershed Name	Acres Represented[d]	MDA Sampling History		
										Tier 1	Tier 2	Tier 3
ET2	**7**	PSC	S000-510	Pipestone Creek	Pipestone	2C/3C	Missouri	Lower Big Sioux River	77,810	2005, 2008	2006-2007; 2009-	
T2	**7**	RO1	S005-381	Rock River	Rock	2C/3C	Missouri	Rock River	268,077	1991; 2006-2012	2013-	
ET2	**7**	TC4	S002-313	Three Mile Creek-Green Valley	Lyon	2B/3C	Minnesota	Redwood River	71,534	2005- 2012	2013-	
T3	**8**	BD1	S001-210	Beauford Ditch	Blue Earth	2B/3C	Minnesota	Le Sueur River	4,500			2005-
T2	**8**	RD1	S005-379	Blue Earth River-Rapidan Dam	Blue Earth	2B/3C	Minnesota	Blue Earth River	1,549,649	2008-2012	2006-2007; 2013-	1999-2004
ET2	**8**	CT1	S001-918	Cottonwood River-New Ulm	Brown	2B/3C	Minnesota	Cottonwood River	836,793	2002; 2005-2012	2013-	
2	**8**	CSC	S002-015	Crow River-South Fork-Cosmos	Meeker	2B/3C	Upper Mississippi	South Fork Crow River	149,787	2005-2010	2011-	
T1	**8**	DC1	S003-000	Dutch Creek	Martin	2B/3C	Minnesota	Blue Earth River	11,077	2003-2005; 2010; 2017	2006-2009; 2018-	
ET2	**8**	HW1	S002-012	Hawk Creek	Renville	2B/3C	Minnesota	Middle MN River- Yellow Medicine River	32,823		2017-	
ET2	**8**	JC1	S001-590	Jack Creek	Jackson	2B/3C	Des Moines River	Des Moines River - Headwaters	130,722	2007-2009	2010-	
T3	**8**	LS1	S000-340	Le Sueur River-Hwy 66	Blue Earth	2B/3C	Minnesota	Le Sueur River	711,108			1999-
ET2	**8**	LT1	S003-574	Little Cobb River	Blue Earth	2C	Minnesota	Le Sueur River	83,561	2003-2005; 2008- 2012	2006-2007; 2013-	
T2	**8**	JB1	S001-759	Minnesota River-Judson Bridge	Nicollet	2B/3C	Minnesota	Middle MN River-Mankato	7,265,867	2005; 2008-2012	2006-2007; 2013-	1999-2004
ET2	**8**	RR1	S001-679	Redwood River-Redwood Falls	Redwood	2B/3C	Minnesota	Redwood River	399,296	2002; 2005-2012	2013-	
T3	**8**	SM3	S002-937	Seven Mile Creek #3	Nicollet	1B/2A/3B	Minnesota	Middle MN River-Mankato	23,232	2002		2003-
ET2	**8**	PL2	S001-919	Sleepy Eye Creek-CSAH 8 Bridge	Brown	2B/3C	Minnesota	Cottonwood River	173,106	2005; 2009-2011	2006-2008; 2012-	
T2	**8**	SR1	S003-557	Straight River-Faribault	Rice	2B/3C	Lower Mississippi	Cannon River	279,056	2002; 2006-2009	2010-	
T2	**8**	WA1	S000-163	Watonwan River - Garden City	Blue Earth	2B/3C	Minnesota	Watonwan River	542,220	2002;2013-		
T2	**9**	CR1	S000-001	Cedar River-Austin	Mower	2B/3C	Lower Mississippi	Cedar River	544,770	2002; 2005-2014	2015-	
T2	**9**	CN2	S004-512	Little Cannon River-Cannon Falls	Goodhue	2B/3C	Lower Mississippi	Cannon River	54,160	2009-2011	2012-	
T3	**9**	NR	S004-842	Root River-North Branch	Fillmore	2B/3C	Lower Mississippi	Root River	361,960	2003-2005		2006-
T3	**9**	SR4	S004-839	Root River-South Branch-Carimona	Fillmore	1B/2A/3B	Lower Mississippi	Root River	85,202	2002-2006		2007-

2019 Tier[a]	PMR[b]	MDA Site I.D.	MPCA Station I.D.	Site Name	County	State Water Use Classification Rule 7050[c]	Associated Major River Basin	Associated Major Watershed Name	Acres Represented[d]	MDA Sampling History		
										Tier 1	Tier 2	Tier 3
T2	**9**	SR5	S004-860	Root River-South Fork-Houston	Houston	2B/3C	Lower Mississippi	Root River	187,097	2010-2011	2012-	
T3	**9**	MBW	S001-831	Whitewater River-Middle Branch	Olmstead	1B/2A/3B	Lower Mississippi	Mississippi River-Winona	16,128			1993-
T2	**9**	SBW	S000-321	Whitewater River-South Branch	Winona	1B/2A/3B	Lower Mississippi	Mississippi River-Winona	49,919	2005; 2015	2006-2014; 2016-	1992-2000
T2	**9**	ZR2	S004-383	Zumbro River- North Fork	Goodhue	2B/3C	Lower Mississippi	Zumbro River	67,801	2010-2013	2013-	
UT2	**10**	BS1	S005-017	Basset Creek	Hennepin	2B/3C	Upper Mississippi	Mississippi River – Twin Cities	27,500	2006-2012	2013-	
UT2	**10**	BA1	S005-395	Battle Creek	Ramsey	2B/3C	Upper Mississippi	Mississippi River – Twin Cities	7,122	2006-2014	2015-	
T2	**10**	BV	S005-360	Bevens Creek	Carver	2B/3C	Minnesota	Lower MN River	83,800	2003-2005; 2008-2013	2006-2007; 2014-	1995-2001
T2	**10**	CSM	S000-165	Crow River-South Fork-Mayer	Carver	2B/3C	Upper Mississippi	South Fork Crow River	736,035	2005-2011	2012-	
UT2	**10**	FC1	S005-376	Fish Creek	Ramsey	2C	Upper Mississippi	Mississippi River – Twin Cities	2,952	2006-2012	2013-	
UT2	**10**	MH1	S003-742	Minnehaha Creek	Hennepin	2B/3C	Upper Mississippi	Mississippi River – Twin Cities	108,547	2006-2015	2016-	
UT1	**10**	GC1	S000-339	Mississippi River-Grey Cloud Island	Washington	2B/3C	Upper Mississippi	Mississippi River – Twin Cities	25,311,980	2010-		
T2	**10**	SD	S004-898	Sand Creek	Scott	2B/3C	Minnesota	Lower MN River	151,620	2003-2014	2015-	1995-2002
T2	**10**	SI1	S000-843	Silver Creek-CR41	Carver	2B/3C	Minnesota	Lower MN River	22,429	2005	2006-	

a See description of Tier Levels in appropriate Surface Water Monitoring Sections of this report.

b Pesticide Monitoring Region (PMR). In cases where the physical sampling location is in one PMR but the watershed draining to the sample point is in another PMR, the PMR that is listed represents the PMR that the watershed is located within.

c All surface waters are protected for multiple beneficial uses. A definition of Water Use Classes applicable to the above table are as follows: Classes 1B, 2A, and 3B: cold water sport fish (trout waters), also protected for drinking water. Classes 1B or 1C, 2Bd, and 3B: cool and warm water sport fish, also protected for drinking water. Classes 2B, 2C, 3B, and 3C: cool and warm water sport fish, and indigenous aquatic life. Class 3C: limited resource value waters.

d Approximate acreage of watershed area represented by surface water sampling location. One square mile = 640 acres

Appendix 8

2019 Water Quality Monitoring Report

January – December 2019

2019 MDA surface water monitoring sample results.

Due to the large number of samples and analytes in 2018, these tabulated results have only been made available online at the Monitoring and Assessment web page (***www.mda.state.mn.us/monitoring***).

Appendix 9

2019 Water Quality Monitoring Report

January – December 2019

Site code, site description, and sampling history for current and historic MDA river, stream, lake, wetland, and rain monitoring locations.

Appendix 9a. Site code, site description, and sampling history for current and historic MDA river and stream monitoring locations.

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
S004-625	ASHLEY CR AT CSAH 11, 3 MI NW OF SAUK CENTRE, MN	45.7792	-94.9815	1	7/29/2010	7/29/2010
S015-030	At downstream bridge crossing on Cty Rd 307	43.5678	-92.1093	29	6/13/2014	12/4/2019
S006-535	BANCROFT CREEK (CD-63) AT CSAH-14, 3.5 MI N OF ALBERT LEA, MN	43.7022	-93.3567	1	8/23/2011	8/23/2011
S005-017	BASSETT CK AT IRVING AVE N IN MINNEAPOLIS	44.9763	-93.2994	263	5/30/2006	8/23/2019
S004-704	BATTLE BK AT CSAH-9, 4 MI NW OF ZIMMERMAN, MN	45.5010	-93.6150	1	8/11/2011	8/11/2011
S006-710	BATTLE BK, .5 MI DWNSTR OF 136TH ST., 4 MI SW OF PRINCETON, MN	45.5272	-93.6043	1	6/16/2010	6/16/2010
S005-395	BATTLE CK, W OF US-61 AND 1 MI E OF THE MISSISSIPPI R	44.9367	-93.0327	244	5/30/2006	8/27/2019
S002-005	BEAVER CK AT MN-30 BRG, 1.75 MI W OF CURRIE	44.0729	-95.6977	129	5/31/2007	8/26/2019
S000-252	BEAVER R SOUTH OF CSAH-3 1.5 MI NW OF BEAVER BAY	47.2656	-91.3447	10	5/29/1991	7/21/1993
S002-504	BENT CK AT MN-5, 1.3 MI SW OF WACONIA, MN	44.8358	-93.8070	247	5/6/1997	11/21/2002
S005-360	BEVENS CK JUST DWNSTM OF CSAH-40, S OF EAST UNION	44.7116	-93.6820	494	6/10/1992	8/23/2019
S004-000	BIG FK R AT BIG FK AVE, 0.3 MI N OF BIG FALLS, MN	48.1958	-93.8071	28	5/13/2009	6/25/2012
S002-132	BLACK R ON CSAH-18 B/4 CONFLU W/RED LK, 6 MI W RED LK FALLS	47.8776	-96.4106	4	5/2/2012	6/19/2012
S006-664	BLACK RIVER ADJACENT TO UNN ST., 11 MI W OF THIEF RIVER FALLS, MN T153N/R45W/S3	48.1057	-96.4265	1	6/30/2010	6/30/2010
S015-034	Bloody Run Creek	43.6089	-92.1223	25	7/25/2013	12/4/2019
S006-680	BLUE EARTH R, .4 MI E OF 542ND LN, 2.5 MI NW OF GOOD THUNDER, MN (10EM051)	44.0372	-94.1009	2	8/25/2010	8/25/2010
S005-379	BLUE EARTH R, 0.25 MI N OF CSAH-9, 2 MI W OF RAPIDAN	44.0959	-94.1092	374	3/12/1999	8/27/2019
S006-644	BLUE EARTH R, 0.3 MI UPSTR OF CSAH-6, 0.5 MI SW OF BLUE EARTH, MN	43.6257	-94.1088	1	8/24/2010	8/24/2010
S005-358	BLUE EARTH R, EB N OF CR-112 & E OF CSAH-19, 2 MI W OF FROST	43.5875	-93.8861	164	4/20/1992	10/7/1997
S006-673	BLUE EARTH R, W BR, .7 MI E OF 370TH AVE, 4.25 MI NW OF ELMORE, MN (10EM028)	43.5638	-94.1139	2	7/20/2010	7/13/2015
S000-135	BLUE EARTH RIVER AT CSAH-4, 4 MI S OF BLUE EARTH	43.5728	-94.1025	9	5/22/1991	7/28/1993
S000-134	BLUE EARTH RIVER IN SIBLEY PARK AT MANKATO	44.1626	-94.0372	1	5/12/1993	5/12/1993
S008-348	BOILING SPRING CK, DOWNSTREAM OF 630TH ST (CR A1), 3 MI NE OF ECHO, MN. (15EM046)	44.6515	-95.3711	1	6/10/2015	6/10/2015
S000-553	BOIS DE SIOUX R ON CSAH-6 5.1 MI SW OF DORAN	46.1519	-96.5798	201	5/26/2005	8/29/2019
S006-648	BRIDGE CK, OUTLET AT JOHN DEERE DR, 6.7 MI SW OF HOUSTON, MN (BC0)	43.7022	-91.6738	1,020	3/10/2010	12/29/2019
S015-037	Bridge Creek Outlet	43.7024	-91.6738	12	8/7/2014	6/3/2019
S000-461	BUFFALO CK AT CSAH-25 AT BROWNTON	44.7357	-94.3509	16	5/20/2005	7/9/2007
S002-125	BUFFALO R AT CR-108, 2 MI SE OF GEORGETOWN	47.0498	-96.7537	432	6/12/2002	11/13/2019
S004-148	BUFFALO R S BR AT 28TH AVE S (CR-79), 1.5 MI SW OF GLYNDON, MN	46.8480	-96.6148	1	6/24/2010	6/24/2010
S005-608	BUFFALO R S BR, ON 130TH AVE SO (CR-60), 4 MI WSW OF BAKER	46.7031	-96.6341	1	6/24/2010	6/24/2010
S002-700	BUFFALO R UPSTRM OF CR 68 (90TH ST N), 2.5 MILES NW OF GLYNDON, MN	46.8994	-96.6099	1	6/24/2010	6/24/2010
S006-719	BURNHAM CK UPST OF 170TH AVE SW, 7.5 MI W OF CROOKSTON, MN. (10EM112)	47.7701	-96.7640	1	7/13/2010	7/13/2010
S006-317	CAMPBELL CREEK AT COUNTY STATE AID HIGHWAY 26, 4 MILES NORTH OF HOUSTON, MINNESOTA	43.8221	-91.5918	1	8/14/2010	8/14/2010
S006-672	CANNON R DNST OF MN-13, 6.7 MI SW OF MONTGOMERY, MN (10EM027)	44.3432	-93.6055	1	7/21/2010	7/21/2010
S006-661	CANNON R, 0.5 MI DWNSTR OF CSAH-7, 8 MI NE OF CANNON FALLS, MN	44.4538	-92.7276	1	8/26/2010	8/26/2010
S000-003	CANNON RIVER AT BRIDGE ON CSAH-7 AT WELCH	44.5670	-92.7376	112	6/12/2002	8/28/2015

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
S005-361	CASCADE CK AT 45TH AVE SW IN ROCHESTER	44.0170	-92.5322	76	5/10/1998	3/13/2000
S005-610	CD #10 ON 130TH AVE NO., 3.4 MI NNE OF KRAGNES, MN	47.0349	-96.7320	1	6/24/2010	6/24/2010
S006-709	CD #13A UPST OF 611TH AVE, 1.5 MI E OF GIBBON, MN. (10EM099)	44.5247	-94.4946	1	7/6/2010	7/6/2010
S005-609	CD #2 AT 90TH ST NO., 3.5 MI NW OF GLYNDON	46.9199	-96.6109	1	6/24/2010	6/24/2010
S005-605	CD #39 ON 100TH AVE, 3 MI E OF KRAGNES	46.9913	-96.6892	1	6/24/2010	6/24/2010
S007-088	CD119 AT CSAH-9, 4 MI S OF SACRED HEART, MN.	44.7243	-95.3406	2	8/14/2012	8/14/2012
S008-349	CD-23, DOWNSTREAM OF CR-22 (APPROX 0.5 MI), 2 MI W OF CLONTARF, MN. (15EM047)	45.3762	-95.7226	1	9/10/2015	9/10/2015
S008-274	CD-27, DOWNSTREAM OF CR 13, 3.5 MI NW OF KENNEDY, MN. (10EM064)	48.6662	-96.9870	1	6/17/2015	6/17/2015
S006-656	CD-38 DNST OF NATURE AVE, 5.2 MI SW OF CLEMENTS, MN. T110N / R35W / S19 (10EM007)	44.3151	-95.1069	1	8/4/2010	8/4/2010
S000-803	CEDAR RIVER - 2.3 MI SE OF BLOOMING PRAIRIE	43.8408	-93.0039	1	8/23/2011	8/23/2011
S000-001	CEDAR RIVER 1.5 MI S OF AUSTIN, MN	43.6375	-92.9747	190	6/5/2002	8/29/2019
S000-137	CEDAR RIVER AT CSAH-2, 0.5 MILES EAST OF LANSING	43.7466	-92.9581	9	5/15/1991	7/28/1993
S000-136	CEDAR RIVER AT CSAH-4, 3 MILES SOUTH OF AUSTIN	43.6052	-92.9845	8	5/15/1991	7/28/1993
S004-245	CEDAR VALLEY CK, UPSTM OF SOUTH-BOUND US-61 LANE	44.0068	-91.4961	12	5/31/2005	7/15/2006
S000-291	CENTER CK BETWEEN S34/35, 1 MILE NE OF FAIRMONT	43.6792	-94.4081	8	5/22/1991	7/28/1993
S006-659	CHAMPEPADAN CK UPST OF CSAH-9, 5.7 MI NE OF LUVERNE, MN (10EM014)	43.7097	-96.1285	2	8/17/2010	7/7/2015
S004-672	CHETOMBA CK ON CR-9 BRG CROSSING, 5.5 MI N OF SACRED HEART	44.8692	-95.3422	2	8/19/2010	8/3/2015
S002-193	CHIPPEWA R AT CSAH-22, 1 MI E OF CLONTARF	45.3853	-95.6587	66	5/14/2009	8/19/2014
S006-900	CHIPPEWA R DWNSTRM OF POPE DOUGLAS RD SW, 4 MI SW OF KENSINGTON, MN.	45.7598	-95.7531	1	9/21/2011	9/21/2011
S006-902	CHIPPEWA R E BR, UPSTRM OF CR-78, 3 MI N OF BENSON, MN.	45.3483	-95.5893	1	9/21/2011	9/21/2011
S002-203	CHIPPEWA R, AT MN-40, 5.5 MI E OF MILAN	45.1087	-95.7991	34	6/2/2004	6/30/2008
S006-911	CHIPPEWA R, E BR ADJACENT TO CSAH-26, 1 MI W OF SWIFT FALLS, MN. EMAP SITE ID MNS2009-122/FIELD NUMBER 10EM122	45.3985	-95.4366	1	9/19/2011	9/19/2011
S005-364	CHIPPEWA R, EB, AT 15TH AVE NE, 2.5 MI N OF BENSON	45.3481	-95.5927	30	5/27/2005	6/30/2008
S000-175	CHIPPEWA RIVER AT BRIDGE ON MN-7 AT MONTEVIDEO	44.9403	-95.7308	10	5/21/1991	7/29/1993
S006-704	CHUB CK UPST OF ARKANSAS AVE, 4 MI NE OF NORTHFIELD, MN. (10EM087)	44.5110	-93.1105	1	8/2/2010	8/2/2010
S006-909	CLEARWATER R, 1 MI N OF CR-24, 2.5 MI W OF AURE, MN. EMAP SITE ID MNS2009-085/FIELD NUMBER 10EM085	47.6863	-95.1720	1	9/13/2011	9/13/2011
S003-470	CO DT-3 AT KEYSTONE AVENUE, 4.2 MI NE OF N BR, MN	45.5314	-92.8985	1	9/20/2011	9/20/2011
S003-446	COBB R AT CSAH-16, 4.4 MI NE OF GOOD THUNDER, MN	44.0471	-94.0005	89	4/23/2009	8/27/2012
S004-287	COREY CK JUST OFF CSAH-17, 6.5 MI NE OF RUSHFORD	43.8638	-91.6432	2	7/28/2010	8/14/2010
S001-918	COTTONWOOD R AT COTTONWOOD ST BRG IN NEW ULM. MN	44.2892	-94.4392	193	6/4/2002	8/30/2019
S000-139	COTTONWOOD R AT MN-15, 0.5 MI SE OF NEW ULM	44.2825	-94.4353	9	5/13/1991	7/29/1993
S006-707	COTTONWOOD R DWNST OF CR-61, 2 MI E OF LAMBERTON, MN. (10EM094)	44.2321	-95.2173	1	8/16/2010	8/16/2010
S003-303	CROOKED LK DTCH AT CR-73, 4.4 M N OF OSAKIS, MINNESOTA	45.9294	-95.1388	1	7/28/2010	7/28/2010
S006-688	CROW R, SF, .3 MI DWNSTR OF CR-63, 1.5 MI SW OF LESTER PRAIRIE, MN	44.8724	-94.0650	1	9/14/2010	9/14/2010
S006-907	CROW R, W OF MAPLE ST IN ROCKFORD, MN. EMAP SITE ID MNS2009-055/FIELD NUMBER 10EM055	45.0814	-93.7570	1	9/22/2011	9/22/2011
S000-004	CROW RIVER AT BRIDGE ON CSAH-36 AT DAYTON	45.2444	-93.5225	10	5/16/1991	8/11/2010
S006-628	CROW RIVER, NF, 0.3 MI W OF 20TH ST. NW, 8 MI SE OF ANNANDALE, MN	45.1772	-94.2245	1	9/9/2010	9/9/2010

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
S006-466	CROW RIVER, NORTH FORK, AT 182ND ST NE, 3.8 MI W OF PAYNESVILLE, MN.	45.3847	-94.7938	1	8/11/2010	8/11/2010
S001-326	CROW WING R AT BR ON CR-12 AT NIMROD	46.6398	-94.8800	2	6/19/2002	6/19/2002
S000-176	CROW WING R. CSAH-1 AT PILLAGER	46.3204	-94.4746	1	6/24/2002	6/24/2002
S006-300	CRYSTAL CREEK (TRIBUTARY TO WILLOW CREEK) AT UNNAMED ROAD, 1 MILE EAST OF COUNTY STATE AID HIGHWAY 15, 5.5 MILES NORTHWEST OF HARMONY, MINNESOTA	43.5891	-92.1127	957	3/10/2010	12/29/2019
S015-032	Crystal Creek at Cty Rd 20	43.5800	-92.1386	28	8/20/2013	10/31/2019
S015-029	Crystal Creek Outlet	43.5892	-92.1127	33	11/21/2013	10/16/2019
S015-033	Crystal Spring Upstream	43.5765	-92.1461	26	7/10/2014	12/17/2019
S015-038	Daley Creek	43.7528	-91.6896	11	8/7/2014	8/1/2019
S003-151	DEER HORN CK AT CR-211, 8 MI SW OF BARNESVILLE, MN	46.5788	-96.4882	1	6/24/2010	6/24/2010
S005-936	DES MOINES R W FK AT E ASHLEY ST BRG IN JACKSON	43.6210	-94.9846	32	5/11/2013	8/28/2014
S006-915	DES MOINES R, UPSTRM OF CSAH-16, 6 MI NE OF LAKEFIELD, MN. EMAP SITE ID MNS2009-179/FIELD NUMBER 10EM179	43.7062	-95.0407	1	9/1/2011	9/1/2011
S004-359	DES MOINES R, W OF RIVER ST, 100 YDS DS OF DAM, AT JACKSON	43.6198	-94.9844	44	5/20/2003	6/24/2008
S002-204	DRY WEATHER CREEK, AT 85TH AVE NW, 4 MI NE OF WATSON	45.0498	-95.7669	179	5/14/2009	8/30/2019
S004-413	DRY WOOD CK AT 200TH AVE NW, 12 MI SE OF ALBERTA	45.4085	-95.9944	1	8/24/2010	8/24/2010
S003-000	DUTCH CREEK AT 100TH ST, 0.5 MILES W OF FAIRMONT	43.6305	-94.5038	101	5/19/2003	8/23/2019
S002-902	EAGLE CR ON BRG AT CSAH 21, 0.5 MI N OF BROWERVILLE, MN	46.0931	-94.8652	1	8/10/2012	8/10/2012
S000-141	EAST FORK DES MOINES R AT MN-263, 2 MI NE CEYLON	43.5536	-94.6144	3	5/22/1991	7/2/1991
S000-916	EDEN LAKE OUTLET ON MN-22 3.5 N OF EDEN VALLEY	45.3725	-94.5355	1	7/28/2010	7/28/2010
S005-143	EIGHTEEN MILE CK ON CSAH-7, 1.5 MI SW OF WHEATON	45.7887	-96.5313	1	8/16/2011	8/16/2011
S005-539	ELK R AT 35TH ST NE, 6.5 MI ENE OF SAUK RAPIDS, MN	45.6174	-94.0346	1	8/12/2011	8/12/2011
S003-686	ELK R AT CSAH-11, 2.5 MI SW OF BECKER, MN	45.3853	-93.8189	1	8/11/2011	8/11/2011
S006-700	ELK R UPST OF CSAH-23, 2 MI N OF BECKER, MN. (10EM084)	45.4255	-93.8782	1	6/22/2010	6/22/2010
S000-278	ELK RIVER CSAH-15, 3.9 MI E OF BIG LAKE, MN	45.3342	-93.6665	27	5/23/2005	7/6/2007
S006-631	ELK RIVER, 0.2 MI DWNSTR OF LITTLE ROCK RD NE, 5.5 MI NW OF FOLEY, MN	45.7101	-94.0065	1	6/22/2010	6/22/2010
S006-650	ELM CK. 0.5 MI UPSTR OF ELM CK RD, 2 MI NW OF OSSEO, MN	45.1569	-93.4382	1	9/13/2010	9/13/2010
S005-376	FISH CK JUST UPSTM OF US-61 IN NEWPORT	44.8977	-93.0074	249	5/30/2006	8/27/2019
S004-774	FISHHOOK R AT MN-87, 2 MI NW OF HUBBARD	46.8640	-95.0254	1	8/17/2011	8/17/2011
S000-828	GARVIN BROOK AT CSAH-23, SW OF MINNESOTA CITY	44.0712	-91.7642	21	5/23/1991	7/15/2006
S000-498	GETCHELL CR. AT CSAH-12 NEAR NEW MUNICH	45.5767	-94.7642	1	7/29/2010	7/29/2010
S001-597	GILBERT CK AT CSAH-5 BRG, 1 MI W OF LAKE CITY, MN	44.4586	-92.2927	1	7/27/2011	7/27/2011
S015-035	Girl Scout Creek	43.6911	-91.7108	14	6/12/2014	11/7/2019
S005-615	GOOSE CK (CD 10) AT CR-79, 5 MI S OF GLENVILLE, MN	43.5045	-93.2988	1	8/23/2011	8/23/2011
S000-410	GOOSE CK AT RD BTN S11/14 3 MI NE OF HARRIS	45.6150	-92.9230	1	8/22/2011	8/22/2011
S002-126	GRAND MARAIS CK AT CR-64, 9 MI N OF EAST GRAND FORKS	48.0500	-97.0624	85	5/24/2004	7/24/2013
S002-083	GRAND MARAIS CK ON CSAH-220 BRG, 3 MI N OF EAST GRAND FORKS	48.0192	-97.0204	96	7/12/2011	8/27/2019
S001-097	GROUNDHOUSE R AT CSAH-10 2M SE OF OGILVIE	45.8033	-93.3980	4	5/19/2005	7/13/2005
S003-532	GROUNDHOUSE R AT CSAH-12 (HARBOR ST), 3.6 MI W BRUNSWICK, MN	45.7896	-93.3689	4	5/19/2005	7/13/2005
S000-897	GROVE CK AT RD BTN S6/32 7 MI NE OF GROVE CITY	45.2397	-94.6074	1	8/19/2010	8/19/2010
S002-012	HAWK CK AT CR 52 BR, 6.5 MI SE OF GRANITE FALLS	44.7622	-95.4288	39	5/2/2017	8/30/2019
S002-093	HAY CK AT CR-88, 5 MI E OF NORTH BRANCH	45.5294	-92.8735	1	9/20/2011	9/20/2011
S006-718	HAY CK UPST OF 320TH ST, 6 MI SW OF RED WING, MN. (10EM111)	44.4836	-92.5727	1	6/7/2010	6/7/2010
S005-728	HAY CR AT 211TH AVE, 11.5 MI NE OF WADENA, MN	46.5072	-94.9261	1	8/10/2012	8/10/2012

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
S001-590	JACK CK AT 370TH AVE, 1 MI SW OF HERON LAKE, MN	43.7758	-95.3357	144	5/30/2007	8/26/2019
S006-697	JACK CK UPST OF LAIS AVE, 4 MI E OF WILMONT, MN. (10EM078)	43.7727	-95.7402	1	8/17/2010	8/17/2010
S008-325	JD #12, UPSTREAM OF OLIVER AVE, 4 MI SW OF FULDA, MN. (15EM023)	43.8233	-95.6596	1	6/9/2015	6/9/2015
S006-675	JD #8 DNST OF 90TH ST, 2.7 MI SE OF GLENCOE, MN. T115N / R27W / S20 (10EM035)	44.7499	-94.1036	1	8/3/2010	8/3/2010
S006-161	JD#10 (WOOD LK CK) ON 600TH ST, 6 MI N OF ECHO	44.7044	-95.4417	1	8/14/2012	8/14/2012
S001-340	JD-1 AT CSAH-3 BR, 4 MI SE OF GRAND MEADOW, MN	43.6448	-92.5236	211	3/16/2007	11/15/2010
S000-294	JEWETTS CREEK BETWEEN S13/24, 4 MI N LITCHFIELD	45.1961	-94.5205	1	8/19/2010	8/19/2010
S003-766	JOHNSON CK (AKA ST AUGUSTA CK) AT CR-7, 1 MI S OF ST AUGUSTA	45.4634	-94.1560	1	8/11/2011	8/11/2011
S000-108	KAWISHIWI RIVER BR ON MN-1 AT DAM 8 MI SE OF ELY	47.8158	-91.7842	91	5/6/1992	8/30/2019
S006-649	KETTLE R AT LOCKER PLANT RD IN KETTLE RIVER, MN (KE2)	46.4846	-92.8877	26	5/10/2010	6/14/2012
S006-552	KETTLE R AT MN-23, 2.45 WSW OF ASKOV, MN.	46.1800	-92.8328	2	6/21/2012	6/21/2012
S001-437	KETTLE R AT SANDSTONE, MN	46.1289	-92.8566	1	6/20/2002	6/20/2002
S000-121	KETTLE R BRIDGE ON MN-48, 4.5 MI E OF HINCKLEY	46.0109	-92.8398	9	5/28/1991	7/19/1993
S000-965	L CHIPPEWA R AT CR-73 3.5 MI SE OF CYRUS	45.5961	-95.6760	1	9/21/2011	9/21/2011
S003-087	LAC QUI PARLE R AT CTY HWY 31 1 MI SW OF LAC QUI PARLE, MN	44.9950	-95.9195	86	5/2/2014	8/28/2019
S006-652	LAC QUI PARLE R DNST OF MN-212, 1.5 MI NE OF DAWSON, MN (10EM003)	44.9425	-96.0235	2	8/24/2010	8/4/2015
S004-034	LAWRENCE CK AT FRANCONIA TR, IN FRANCONIA, MN	45.3715	-92.6946	175	5/31/2007	8/28/2019
S003-448	LE SUEUR R AT CSAH 28 IN SAINT CLAIR, MN	44.0830	-93.8550	88	4/23/2009	8/10/2012
S003-860	LE SUEUR R AT CSAH-8, 5.1 MI SSE OF MANKATO, MN	44.0847	-93.9887	85	4/23/2009	8/27/2012
S006-324	LE SUEUR RIVER AT 120TH STREET, 1 MILE WEST OF OTISCO, MINNESOTA.	43.9824	-93.5266	2	6/28/2010	9/3/2010
S006-330	LE SUEUR RIVER AT 220TH AVENUE, BETWEEN MINNESOTA STATE HIGHWAY 30 AND 170TH STREET, 4 MILES SOUTHEAST OF NEW RICHLAND, MINNESOTA.	43.8771	-93.4201	2	6/28/2010	9/3/2010
S001-931	LEAF R AT CSAH 29 BRG, 7 MI N OF STAPLES	46.4571	-94.8419	58	5/8/2014	8/28/2019
S001-153	LEAF RIVER AT CSAH-26, 8 MILES NE OF ALDRICH	46.4828	-94.8944	24	5/30/2005	8/10/2012
S000-340	LESUEUR R AT MN-66 1.5 MI NE OF RAPIDAN, MN	44.1175	-94.0501	923	3/12/1999	11/7/2019
S001-210	LITTLE BEAUFORD DITCH TRIB TO BIG COBB R, SH22 0.5 MI N BEAUFORD	44.0176	-93.9585	494	2/14/2005	11/7/2019
S004-512	LITTLE CANNON R AT CSAH-24, 3 MI SW OF CANNON FALLS	44.4703	-92.9339	201	5/15/2009	8/27/2019
S003-574	LITTLE COBB NEAR CSAH-16, 6.3 MI W OF PEMBERTON, MN	43.9967	-93.9083	287	5/30/2003	8/27/2019
S001-377	LITTLE COTTONWOOD RIVER 2 MI NW OF CAMBRIA, MN	44.2465	-94.3389	59	6/22/2002	6/19/2010
S006-638	LITTLE PARTRIDGE R, 0.5 MI DWNSTR OF CR-77, 5.5 MI E OF HEWITT, MN	46.3448	-94.9749	1	7/7/2010	7/7/2010
S005-384	LITTLE ROCK CK AT CR-8 (15TH AVE NW), 4 MI N OF RICE	45.8096	-94.1973	92	5/23/2005	8/29/2013
S006-722	LITTLE SWAN R E OF CR-105, 7 MI W OF FLENSBURG, MN. (10EM118)	45.9650	-94.6876	2	6/7/2010	7/8/2010
S000-282	LONG PRAIRIE R BRIDGE ON US-10, SOUTH OF MOTLEY	46.3201	-94.6482	20	5/6/1991	8/10/2012
S006-693	LONG PRAIRIE R DWNST OF HAUER LANE, 5 MI NE OF CARLOS, MN. (10EM070)	46.0059	-95.2014	1	6/30/2010	6/30/2010
S002-909	LONG PRAIRIE R ON BR AT CR 65, 2.5 MI SE OF MILTONA, MN	46.0119	-95.2698	1	8/10/2012	8/10/2012
S002-904	LONG PRAIRIE R ON BR AT RIVERSIDE DR, NW LONG PRAIRIE, MN	45.9755	-94.8662	22	5/30/2005	6/17/2008
S006-678	LONG PRAIRIE R, 450 FT S OF UNNAMED ST, 7.5 MI E OF CARLOS, MN (10EM042)	45.9751	-95.1379	2	6/30/2010	6/30/2010
S000-283	LONG PRAIRIE R. W OF LONG PRAIRIE	45.9968	-94.9597	1	8/10/2012	8/10/2012
S000-646	MAIN DITCH ON MN-23 AT PIPESTONE	44.0032	-96.3068	112	5/31/2005	8/28/2012
S006-726	MAIN DT DWNST OF CR-69, 0.5 MI E OF PIPESTONE, MN. (10EM124)	44.0017	-96.2942	1	8/17/2010	8/17/2010

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S002-427	MAPLE R AT CSAH 35 5.2 MI S OF MANKATO, MN	44.0652	-94.0260	89	4/23/2009	8/27/2012
S004-101	MAPLE R AT CSAH-18, 2 MILES NORTH OF STERLING CENTER	43.9351	-94.0709	79	4/23/2009	7/18/2012
S002-946	MAYHEW CK AT CSAH 8, 4.5 MI E OF ST. CLOUD, MN	45.5881	-94.0789	1	8/12/2011	8/12/2011
S006-696	MEDFORD CK DWNST OF CEDAR AVE N, 1 MI NE OF MEDFORD, MN. (10EM075)	44.1820	-93.2312	2	7/14/2010	8/25/2010
S004-643	MF CROW R AT CSAH 10, 7.4 MI N OF ATWATER, MN	45.2452	-94.7789	35	5/12/2010	8/28/2013
S001-831	MID FK WHTWTR R AT CR-107, 5 MI N OF ST. CHARLES	44.0371	-92.1046	1,295	3/26/1993	11/15/2019
S000-697	MIDDLE R AT CSAH-10 8.5 MI NW OF ARGYLE	48.3700	-97.0012	27	5/29/2007	6/25/2009
S004-372	MINNEHAHA CK (L HIAWATHA OUTLET) AT 28TH ST IN MINNEAPOLIS	44.9183	-93.2321	1	7/31/2018	7/31/2018
S003-742	MINNEHAHA CK AT 32ND AVE S, MINNEAPOLIS, MINNESOTA	44.9175	-93.2253	236	5/30/2006	8/23/2019
S003-733	MINNEHAHA CK AT CHICAGO AVE, MINNEAPOLIS, MINNESOTA	44.9113	-93.2625	1	7/31/2018	7/31/2018
S007-724	MINNEHAHA CK AT TRAIL BRIDGE BETWEEN LK HIAWATHA AND LK NOKOMIS, 85 FT S OF E MINNEHAHA PKWY	44.9159	-93.2422	2	7/31/2018	7/31/2018
S003-737	MINNEHAHA CK AT W 37TH ST, ST. LOUIS PARK, MINNESOTA	44.9361	-93.3897	1	7/31/2018	7/31/2018
S003-731	MINNEHAHA CK AT W 50TH ST, EDINA MINNESOTA	44.9119	-93.3422	1	7/31/2018	7/31/2018
S001-362	MINNEHAHA CK AT WALKING BR IN MPLS, MN	44.9100	-93.2975	1	7/31/2018	7/31/2018
S000-054	MINNESOTA R @ CSAH-24 BRIDGE, 1 MI S OF COURTLAND, MN	44.2542	-94.3409	9	5/13/1991	7/29/1993
S001-759	MINNESOTA R AT CSAH 42 AT JUDSON	44.2002	-94.1941	357	3/12/1999	8/27/2019
S000-310	MINNESOTA R AT MCES SITE OFF THE SE END OF RUNWAY 12L/30R	44.8698	-93.1931	9	5/14/1991	6/10/1993
S000-145	MINNESOTA R BRIDGE ON US-71 AND MN-19 AT MORTON	44.5456	-94.9951	2	6/22/2002	6/22/2002
S000-740	MINNESOTA R ON USH-59/212 0.8 MI SW OF MONTEVIDEO	44.9328	-95.7331	34	6/2/2004	6/30/2008
S006-687	MINNESOTA R, 0.4 MI N OF UNN RD (ADJACENT TO CR-59), 3 MI SW OF CORRELL, MN (10EM058)	45.2190	-96.2186	4	7/27/2010	8/4/2015
S000-039	MINNESOTA R. CSAH-9 N OF JORDAN	44.6926	-93.6423	134	3/13/1996	7/8/2004
S000-780	MINNESOTA R., CSAH-6 N. OF DELHI	44.6525	-95.2258	4	5/27/2003	7/7/2003
S000-041	MINNESOTA RIVER AT BRIDGE ON MN-22 AT ST. PETER	44.3075	-93.9603	1	6/10/2002	6/10/2002
S000-040	MINNESOTA RIVER AT MN-19 BRIDGE AT HENDERSON	44.5294	-93.9008	10	5/13/1991	7/29/1993
S003-531	MISSION CK AT CR-53, 2.5 MI W OF PINE CITY, MINNESOTA	45.8318	-93.0208	29	5/31/2007	6/29/2009
S002-010	MISSISSIPPI R @ CSAH-1 BRG @ AITKIN	46.5405	-93.7072	12	5/13/2009	6/22/2009
S000-169	MISSISSIPPI R ABOVE DAM AT BRAINERD	46.3814	-94.1789	55	5/11/2010	8/30/2013
S005-385	MISSISSIPPI R AT CSAH-115 BRG, 1 MI NO OF FORT RIPLEY	46.1805	-94.3655	1	6/22/2002	6/22/2002
S000-339	MISSISSIPPI R AT PIER AT GRAVEL QUARRY, GREY CLOUD ISLAND	44.8038	-93.0125	96	4/21/2010	8/28/2019
S000-220	MISSISSIPPI R BR ON CR-441 1 MI SW OF BLACKBERRY	47.1742	-93.4206	9	5/8/1991	7/14/1993
S000-105	MISSISSIPPI R MN-200 BR 0.5 MI W OF LAKE ITASCA	47.2534	-95.2254	10	5/7/1991	7/13/1993
S006-705	MISSISSIPPI R UPST OF 77TH ST, 4 MI NW OF CLEARWATER, MN. (10EM090)	45.4602	-94.0999	2	7/26/2010	8/30/2010
S006-630	MISSISSIPPI R, ADJACENT TO RIVER RD (DOANE TR), 0.5 MI SE OF INVER GROVE HEIGHTS, MN	44.8313	-93.0104	1	8/2/2010	8/2/2010
S006-910	MISSISSIPPI R, JUST S OF CSAH-40, 4.5 MI S OF ALIDA, MN. EMAP SITE ID MNS2009-113/FIELD NUMBER 10EM113	47.3394	-95.2101	1	8/18/2011	8/18/2011
S000-221	MISSISSIPPI RIVER AT BR ON MN-25 AT MONTICELLO	45.3087	-93.7913	12	5/16/1991	7/1/2003
S004-824	MONEY CK AT MN-76, 3 MI NW OF HOUSTON, MN	43.7947	-91.5947	1	8/14/2010	8/14/2010
S002-903	MORAN CR ON BR AT 255TH AVE, 8 MI SW OF STAPLES, MN	46.2406	-94.8334	1	8/10/2012	8/10/2012
S005-633	MUD CK AT CR-87 BRG, 7 MI NW OF SUNBERG, MN	45.3648	-95.3765	1	9/21/2011	9/21/2011
S006-727	MUD CK DWNST OF CR-D7, 3 MI NE OF PORTER, MN. (10EM126)	44.6516	-96.1027	1	8/23/2010	8/23/2010
S003-104	MUSTINKA R AT CSAH-13, 6 MI NE OF HERMAN	45.8653	-96.0480	1	8/16/2011	8/16/2011
S001-418	N BR SUNRISE R AT CR-64 0.5 MI W OF NORTH BRANCH	45.5137	-92.9962	1	9/20/2011	9/20/2011
S000-301	N BR SUNRISE R AT MN-95, 4 MI E OF NORTH BRANCH	45.5133	-92.8932	9	5/28/1991	7/22/1993
S002-026	N FK CROW R AT CSAH-22, 3 1/2 MI E OF MANANNAH	45.2527	-94.5466	53	5/13/2014	8/17/2017

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S002-024	N FK CROW R ON CSAH-19 AT KINGSTON	45.1963	-94.3131	1	8/11/2010	8/11/2010
S000-451	N FK WHITEWATER R 0.15 MI W TR-16, 2.2 MI W OF ELBA	44.0925	-92.0637	20	5/19/2005	7/16/2007
S004-383	NF ZUMBRO R AT CSAH-30, 1 MI NW OF WANAMINGO	44.3123	-92.8127	161	5/12/2010	8/27/2019
S005-377	NINEMILE CK JUST S OF W 106TH ST IN BLOOMINGTON	44.8081	-93.3012	126	5/30/2006	8/12/2014
S000-240	OKABENA CREEK AT CSAH-14, 2 MILES SE OF BREWSTER	43.6739	-95.4496	4	5/22/1991	7/2/1991
S015-031	On Crystal Creek upstream of C3S	43.5839	-92.1325	30	4/8/2013	11/19/2019
S006-706	OTTER CK, 0.5 MI DWNST OF 105TH ST, 1 MI E OF LYLE, MN. (10EM092)	43.5038	-92.9218	2	7/20/2010	7/14/2015
S006-908	OTTER TAIL R, DWNSTRM OF MAIN ST IN BRECKENRIDGE, MN. EMAP SITE ID MNS2009-060/FIELD NUMBER 10EM060	46.2673	-96.5944	1	9/12/2011	9/12/2011
S006-914	OTTER TAIL R, DWNSTRM OF WANNIGAN RD, 3 MI N OF FRAZEE, MN. EMAP SITE ID MNS2009-178/FIELD NUMBER 10EM178	46.7783	-95.6905	1	8/15/2011	8/15/2011
S000-556	PELICAN R ON MN-210 1.1 MI W OF FERGUS FALLS	46.2915	-96.1434	17	5/14/2018	8/29/2019
S005-772	PETER LUND CK AT 185TH ST., 2 MI SE OF HAYWARD	43.6225	-93.2306	1	8/23/2011	8/23/2011
S006-671	PIKE CK UPST OF 95TH AVE / CR-222I, 4.9 MI W OF LITTLE FALLS, MN (10EM026)	45.9760	-94.4644	1	6/7/2010	6/7/2010
S001-941	PINE CK 2 MI NE OF CANNON FALLS, MN	44.5323	-92.8743	25	5/20/2005	6/30/2008
S000-181	PINE RIVER CSAH-11, N. OF CROSBY	46.5717	-94.0281	128	5/13/2009	8/27/2019
S000-099	PIPESTONE CREEK BR ON N LINE OF S24 (T106N/R47W)	43.9802	-96.4358	3	5/22/1991	7/2/1991
S000-510	PIPESTONE CRK ON CSAH-13 4.5 MI W OF PIPESTONE	43.9872	-96.4283	121	5/9/2013	8/27/2019
S001-930	PLATTE R AT CR-40 BRG, 2 MI S OF ROYALTON	45.7972	-94.2918	20	5/23/2005	7/5/2007
S006-712	PLATTE R UPST OF MN-25, 3 MI SW OF HARDING, MN. (10EM102)	46.0919	-94.1016	1	6/21/2010	6/21/2010
S002-058	POMME DE TERRE R AT BRG ON UNN ROAD, 4 MI S OF BARRETT	45.8614	-95.8593	1	8/24/2010	8/24/2010
S005-650	POMME DE TERRE R AT CR-58 (310TH ST), 5 MI NO OF FAIRFIELD	45.4560	-95.9552	1	8/24/2010	8/24/2010
S004-411	POMME DE TERRE R AT MN-9, 2 MI SE OF MORRIS	45.5523	-95.8759	1	8/24/2010	8/24/2010
S004-576	POMME DE TERRE R AT US-12 BRIDGE, 3 MI NE OF HOLLOWAY	45.2828	-95.9789	1	8/24/2010	8/24/2010
S004-580	POMME DE TERRE R ON CR-51 (BEFORE MARSH LK) 2 MI S APPLETON	45.1883	-96.0719	1	8/24/2010	8/24/2010
S000-195	POMME DE TERRE R UPSTR OF MN-119 / MN-7 / US-59 AT APPLETON	45.2031	-96.0205	4	5/27/2003	7/7/2003
S006-715	POMME DE TERRE R W OF 440TH AVE, 7 MI SW OF HOFFMAN, MN. (10EM106)	45.7333	-95.8569	1	8/25/2010	8/25/2010
S001-186	PRAIRIE CR AT 310TH ST 0.2 MI UPSTM OF L BYLLESBY	44.5006	-92.9927	8	5/15/1991	7/15/1993
S015-036	Private Drive Stream Crossing off of John Deere Dr.	43.7147	-91.6960	17	7/10/2014	10/16/2019
S004-176	RABBIT R AT CR-152, 3.1 MI SE OF CAMPBELL	46.0645	-96.3840	1	7/26/2012	7/26/2012
S001-052	RABBIT R AT CSAH-2 3 MI SE OF CAMPBELL	46.0793	-96.3543	1	7/26/2012	7/26/2012
S001-029	RABBIT RIVER AT US-75, 5 MILES NW OF CAMPBELL	46.1117	-96.4931	1	7/26/2012	7/26/2012
S000-013	RED LAKE R DNST OF MN-220 BR IN EAST GRAND FORKS	47.9237	-97.0162	9	5/7/1991	7/13/1993
S000-031	RED LAKE RIVER AT BRIDGE ON CSAH-15 AT FISHER	47.8006	-96.8094	136	5/28/2003	8/27/2019
S006-912	RED LK R, 2/3 MI N OF RES HWY 43, RED LK INDIAN RESERVATION. T152N/R37W/S23. EMAP SITE ID MNS2009-149/FIELD NUMBER 10EM149	47.9676	-95.3521	1	9/21/2011	9/21/2011
S006-906	RED LK R, ADJACENT TO UNN RD, 3.5 MI NW OF RED LAKE FALLS, MN. EMAP SITE ID MNS2009-048/FIELD NUMBER 10EM048	47.8939	-96.3526	2	9/14/2011	8/11/2015
S002-080	RED LK R, SAMPSON BRG, IN CROOKSTON	47.7757	-96.6101	1	6/9/2002	6/9/2002
S006-674	RED R OF THE N, .15 MI W OF CR-102, 2.7 MI N OF HALSTAD, MN (10EM032)	47.3913	-96.8386	3	9/1/2010	8/19/2015
S000-012	RED RIVER AT BR ON CSAH-18 0.5 MI W OF BRUSHVALE	46.3694	-96.6565	9	5/6/1991	7/12/1993
S000-011	RED RIVER CITY BUILDING AT FARGO	46.8611	-96.7833	1	6/9/2002	6/9/2002

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S005-729	REDEYE R AT CSAH-26, 8.7 MI NE OF VERNDALE, MN	46.4870	-94.8850	1	8/10/2012	8/10/2012
S002-461	REDEYE R AT US-71 IN SEBEKA, MN	46.6287	-95.0952	1	8/10/2012	8/10/2012
S006-669	REDEYE R N OF MN-227, 2.7 MI E OF SEBEKA, MN (10EM022)	46.6371	-95.0330	1	8/23/2010	8/23/2010
S006-916	REDEYE R, UPSTRM OF CSAH-26, 3 MI N OF CENTRAL SCHOOL, 11.5 MI NW OF STAPLES, MN. EMAP SITE ID MNS2009-198/FIELD NUMBER 10EM198	46.4879	-94.8886	1	9/15/2011	9/15/2011
S000-299	REDWOOD R AT BRIDGE ON CSAH-101 AT NORTH REDWOOD	44.5657	-95.0998	9	5/21/1991	7/29/1993
S000-696	REDWOOD R AT CSAH-15 IN RUSSELL	44.3219	-95.9534	20	5/24/2005	7/11/2007
S001-679	REDWOOD R AT CSAH-17, 3 MILES SW OF REDWOOD FALLS	44.5237	-95.1715	189	6/22/2002	8/30/2019
S003-049	RICE CK 150 METERS W OF CENTRAL AVE (HWY 65) IN FRIDLEY	45.0937	-93.2454	14	4/30/2010	8/11/2010
S002-431	RICE CK AT CR-151 0.9 MI SE OF STERLING CENTER, MN	43.8988	-94.0622	2	6/29/2010	9/3/2010
S001-523	RICE CK AT CSAH-16 BRG, 2.5 MI N OF CLEAR LAKE, MN	45.4866	-93.9795	1	8/12/2011	8/12/2011
S001-444	RICE CR 1 MI N OF DUNDAS, MN	44.4457	-93.2112	16	5/20/2005	6/30/2008
S006-365	RICE CREEK AT MINNESOTA STATE HIGHWAY 109/190TH STREET (BETWEEN COUNTY STATE AID HIGHWAY 11 AND 420TH AVENUE), 1.2 MILES SOUTHWEST OF DELVAN, MINNESOTA.	43.7605	-94.0400	2	6/29/2010	9/3/2010
S007-176	RICE R AT CSAH-87, 5 MI SW OF COOK, MN	47.8028	-92.6139	1	8/21/2012	8/21/2012
S004-813	RICE R AT US-53, 3 MI S OF COOK	47.8092	-92.6744	1	8/21/2012	8/21/2012
S005-380	RILEY CK (GRASS LK INLET) AT US-212 IN EDEN PRAIRIE	44.8179	-93.4797	83	5/30/2006	8/11/2010
S001-182	ROBERTS CK UPSTRM OF 550TH AVE, 4 MI NW OF BROWNSDALE, MN	43.7588	-92.9497	1	8/23/2011	8/23/2011
S001-138	ROBINSON CR BRIDGE AT DEAD END RD, NW HIGH FOREST	43.8482	-92.5529	8	5/15/1991	7/27/1993
S005-381	ROCK R AT CSAH-4 IN LUVERNE	43.6541	-96.2011	123	5/30/2006	8/27/2019
S000-097	ROCK RIVER BR ON STATELINE RD 10 MI S OF LUVERNE	43.5002	-96.1846	3	5/22/1991	7/2/1991
S006-698	ROOT R ADJACENT TO MN-16, 2 MI NE OF WHALAN, MN. (10EM079)	43.7479	-91.8932	1	8/24/2010	8/24/2010
S005-405	ROOT R AT UNN TRIB AT EAGLE BLUFF, 2.5 MI NW OF LANESBORO	43.7557	-91.9963	55	6/5/2002	9/28/2005
S004-842	ROOT R, MB AT CSAH-21, 3 MI S OF PILOT MOUND	43.7827	-92.0322	563	5/9/2006	11/15/2019
S006-725	ROOT R, N BR DWNST OF CSAH-2, 1 MI S OF CHATFIELD, MN. (10EM123)	43.8347	-92.1852	1	6/9/2010	6/9/2010
S004-839	ROOT R, SB AT CSAH-12 IN CARIMONA	43.6601	-92.1544	491	3/10/2008	11/15/2019
S004-123	ROOT R, SF AT CSAH-13 AT CHOICE	43.6588	-91.7809	69	6/5/2002	6/25/2009
S004-860	ROOT R, SF AT MN-16, 1.5 MI E OF HOUSTON	43.7645	-91.5358	153	5/13/2010	8/27/2019
S006-635	ROOT R, SF, 0.4 MI UPSTR OF MN-43, 9 MI N OF MABEL, MN	43.6557	-91.7941	1	6/8/2010	6/8/2010
S000-065	ROOT RIVER AT BRIDGE ON MN-26 3 MI EAST OF HOKAH	43.7768	-91.2979	8	5/23/1991	7/28/1993
S006-308	ROOT RIVER, NORTH BRANCH AT 680TH AVENUE, 10 MILES SOUTHWEST OF STEWARTVILLE, MINNESOTA	43.8250	-92.6891	1	7/28/2010	7/28/2010
S006-310	ROOT RIVER, NORTH BRANCH AT COUNTY STATE AID HIGHWAY 7, 7 MILES NORTHEAST OF BROWNSDALE, MINNESOTA	43.7689	-92.7295	1	7/28/2010	7/28/2010
S015-039	Root River-Lower South Branch drainage ditch at 750th Ave	43.6265	-92.5492	23	7/11/2017	11/19/2019
S015-040	Root River-Lower South Branch drainage ditch at Hwy 3 (190th St)	43.6308	-92.5394	23	7/11/2017	11/19/2019
S007-589	ROSEAU R BELOW SD51, JUST NO OF CSAH-4, 1/2 MI W OF CARIBOU, MN.	48.9817	-96.4631	16	5/22/2014	8/26/2014
S006-711	RUM R ADJACENT TO VINTAGE DR, 5 MI W OF EAST BETHEL, MN. (10EM100)	45.3389	-93.3620	1	8/4/2010	8/4/2010
S005-386	RUM R AT CR-22 BRG (VIKING BLVD NW), 4 MI SO OF ST. FRANCIS	45.3276	-93.3728	76	6/13/2002	8/17/2017
S006-676	RUM R, .2 MI NW OF 329TH AVE NW, 7.5 MI W OF CAMBRIDGE, MN (10EM036)	45.5669	-93.3818	1	8/5/2010	8/5/2010
S006-645	RUM R, 0.5 MI W OF RUM R BLVD., 1 MI N OF ST. FRANCIS, MN	45.4025	-93.3565	1	8/4/2010	8/4/2010
S000-016	RUM RIVER AT BRIDGE ON PLEASANT STREET IN ANOKA	45.2066	-93.3865	9	5/16/1991	7/22/1993

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S002-955	RUM RIVER AT CSAH 16, 8 MI N OF MILACA, MN	45.8659	-93.6905	17	5/14/2018	8/27/2019
S000-043	RUM RIVER BRIDGE ON CSAH-5, 0.5 MI W OF ISANTI	45.4931	-93.2657	9	5/28/1991	7/22/1993
S006-637	RUSH CK, 0.3 MI UPSTR OF CSAH-5, 2 MI E OF RUSH CITY, MN	45.6781	-92.9122	1	9/14/2010	9/14/2010
S001-263	S BR GRINDSTONE R, 1.6 MI NW OF HINCKLEY, MN	46.0247	-92.9714	32	5/31/2007	6/29/2009
S001-729	S BR MID FK ZUMBRO R, 3.3 MI E OF MANTORVILLE, MN	44.0694	-92.6890	24	5/26/2005	7/17/2007
S001-320	S BR ROOT R AT CR-118 IN FORESTVILLE ST PK	43.6422	-92.2149	63	6/4/2002	9/19/2007
S001-539	S BR ROOT R AT GRVL RD BR 1 MI W OF CSAH14 5 MI SE GR MEADOW	43.6343	-92.5292	1,066	3/16/2007	12/31/2019
S001-156	S BR YELLOW MEDICINE R AT CSAH-10, AT MINNEOTA	44.5579	-95.9981	8	5/21/1991	6/28/1993
S006-684	S CORMORANT R, 2 MI E OF CSAH-41, 1.4 MI NW OF FUNKLEY, MN (10EM053)	47.7927	-94.4601	1	6/14/2010	6/14/2010
S002-015	S FK CROW R ON MN-7, 1/2 MI E OF COSMOS	44.9357	-94.6752	240	5/20/2005	8/29/2019
S000-050	S FK CROW RIVER SH-55 AT ROCKFORD	45.0863	-93.7347	1	6/14/2002	6/14/2002
S000-165	S FK CROW RIVER SH-7 1 MI. N OF MAYER	44.9056	-93.8856	217	5/17/2005	8/29/2019
S000-321	S FK WHITEWATER R AT CR-112 2 MI W OF ALTURA	44.0706	-91.9793	457	2/6/1992	8/27/2019
S001-191	SALEM CR AT UNN CR IN S19 4 MI SW SALEM CORNERS	43.9700	-92.6603	8	5/15/1991	7/27/1993
S004-898	SAND CK AT MN-282 CROSSING IN JORDAN	44.6687	-93.6346	447	2/11/1992	8/23/2019
S002-099	SAND HILL R AT US-75 ON NORTH END OF CLIMAX	47.6121	-96.8148	122	5/11/2010	8/27/2019
S000-503	SAUK R AT CSAH-4 IN ST CLOUD, MN	45.5694	-94.2258	1	7/28/2010	7/28/2010
S004-621	SAUK R AT WAITE PK USGS STATION IN ST. CLOUD, MN	45.5597	-94.2339	49	5/18/2004	6/30/2008
S000-017	SAUK RIVER DNSTRM OF BR ON CSAH-1 AT SAUK RAPIDS	45.5915	-94.1776	97	5/6/1991	8/27/2019
S006-604	SCHWERIN CK AT 650TH AVE., .5 MI NE OF ROSE CK IN MOWER CTY	43.6705	-92.7493	1	8/23/2011	8/23/2011
S002-384	SEDAN BRK AN IRONSIDE RD, 3.5 MI NE OF BROOTEN, MN	45.5300	-95.0638	1	8/19/2010	8/19/2010
S002-937	SEVENMILE CK IN SEVENMILE CK CTY PK, 5.5 MI SW OF ST. PETER	44.2632	-94.0316	546	6/3/2002	11/7/2019
S002-201	SHAKOPEE CK, AT UNN TWNSHP RD, 1 MI W MN-29, 8 MI S BENSON	45.2040	-95.6135	181	5/27/2005	8/29/2019
S006-903	SHAKOPEE CK, UPSTRM OF 20TH AVE SW, 7.5 MI S OF BENSON, MN.	45.2026	-95.6108	1	9/21/2011	9/21/2011
S006-894	SHELL RIVER AT 390TH ST, 2.5 MI N OF MENAHGA, MN	46.9199	-95.1081	1	8/17/2011	8/17/2011
S002-962	SHELL RIVER AT CSAH 23, 4.5 MILES NE OF MENAHGA, MN	46.7871	-95.0174	28	5/22/2005	6/17/2008
S000-084	SHELL ROCK R AT BRG ON CSAH-1 1 MI W OF GORDONSVILLE, MN	43.5139	-93.2686	9	5/22/1991	8/23/2011
S001-946	SHINGLE CR AT 45TH AVE & RR TRACK, MPLS, MN	45.0366	-93.2934	10	4/26/2010	8/10/2010
S005-540	SILVER CK AT CURTIS AVE NW, 3.5 MI SW OF BECKER, MN	45.3740	-93.9477	1	8/11/2011	8/11/2011
S006-685	SILVER CK UPST OF UNN ST, 2.75 MI SE OF W UNION, MN (10EM054)	45.7838	-95.0326	1	6/8/2010	6/8/2010
S000-843	SILVER CR., CSAH-41 BY EAST UNION	44.6912	-93.7358	256	5/17/2005	8/29/2019
S005-378	SLEEPY EYE CK AT 320TH AVE, 5.5 MI SW OF SLEEPY EYE	44.2614	-94.8264	97	5/24/2005	8/30/2013
S001-919	SLEEPY EYE CR AT CSAH 8 BR, 2.2 MI N OF LEAVENWORTH, MN	44.2535	-94.8061	110	5/14/2014	8/30/2019
S004-694	SMITH CK (CD-125A) ON CSAH-15, 4 1/2 MI N REDWOOD FALLS	44.6059	-95.1197	1	8/14/2012	8/14/2012
S003-101	SNAKE R AT CSAH-34, 3 MI NE OF WARREN	48.2099	-96.7178	17	5/21/2014	8/25/2014
S001-644	SNAKE R AT CSAH-61 BRG IN PINE CITY, MN	45.8297	-92.9705	11	5/10/2010	6/28/2010
S004-142	SNAKE R AT MN-1 CROSSING IN ALVARADO	48.1950	-97.0055	5	5/20/2009	5/15/2013
S000-198	SNAKE R BELOW CROSS LAKE DAM, 2 MI NE OF PINE CITY	45.8397	-92.9384	107	5/28/1991	8/28/2019
S000-128	SNAKE R. AT MOUTH E OF PINE CITY	45.8254	-92.7659	2	5/23/2013	5/23/2013
S000-185	SNAKE RIVER AT BRIDGE ON MN-220 N OF BIG WOODS	48.4140	-97.1072	206	5/24/2005	8/27/2019
S002-587	SNAKE RIVER AT CSAH-7 3.5 MI WEST OF PINE CITY	45.8197	-93.0410	5	6/20/2002	7/13/2005
S005-382	SPLIT ROCK CK, E OF CSAH-20 AND S OF CSAH-2 IN IHLEN	43.9039	-96.3635	4	5/31/2005	7/5/2005
S006-683	SPRING CK, 1 MI DWNSTR OF CR-D3, 6 MI E OF ST. LEO, MN	44.6998	-95.9303	1	8/18/2010	8/18/2010

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S006-660	SPRING VALLEY CK AT E COURTLAND ST (UPSTR OF MN-63) IN SPRING VALLEY, MN (10EM015)	43.6877	-92.3896	2	6/8/2010	7/28/2015
S006-691	ST CROIX R ADJACENT TO NATURE RD, 8 MI NE OF RUSH CITY, MN. (10EM068)	45.7449	-92.8095	1	7/15/2010	7/15/2010
S000-119	ST LOUIS R BRIDGE AT CSAH-7, 0.5 MI S OF FORBES, MN	47.3627	-92.5988	9	5/28/1991	7/20/1993
S006-629	ST. CROIX R, UPSTR OF WI STATE HWY 243, 0.5 MI W OF OSCEOLA, WI	45.3288	-92.7040	1	8/3/2010	8/3/2010
S005-582	ST. FRANCIS R AT 173RD AVE, 9.7 MI SE OF FOLEY, MN	45.5443	-93.8051	1	8/11/2011	8/11/2011
S002-952	ST. FRANCIS R. AT CSAH 15, 5.5 MI. SW OF ZIMMERMAN, MN	45.3994	-93.6852	1	8/8/2011	8/8/2011
S006-913	STONY CK, UPSTRM OF 90TH AVE S, 2 MI SE OF SABIN, MN. EMAP SITE ID MNS2009-172/FIELD NUMBER 10EM172	46.7586	-96.6060	1	9/12/2011	9/12/2011
S000-497	STONY CREEK AT CO. RD. NEAR SPRING HILL	45.5383	-94.7881	1	7/29/2010	7/29/2010
S003-557	STRAIGHT R AT 227 ST E, 2.8 MI SE OF FARIBAULT, MN	44.2578	-93.2313	212	5/28/2002	8/29/2019
S002-960	STRAIGHT R AT US HWY 71, 3 MI S OF PARK RAPIDS, MN	46.8748	-95.0660	1	8/17/2011	8/17/2011
S006-658	STRAIGHT R DNST OF CSAH-45, 1.8 MI S OF MEDFORD, MN (10EM011)	44.1478	-93.2457	2	7/21/2010	7/21/2010
S000-047	STRAIGHT R NEAR CSAH-1 1 MI SE OF CLINTON FALLS	44.1241	-93.2291	8	5/13/1991	7/27/1993
S005-561	SUCKER CK AT 40TH ST SW, 1.2 MI NE OF COKATO, MN	45.0939	-94.1691	1	8/19/2010	8/19/2010
S004-032	SUNRISE R AT CR-88 IN SUNRISE, MN	45.5443	-92.8588	98	5/9/2011	8/28/2019
S004-033	SUNRISE R, N BR AT CR-69, 3.3 MI SW OF SUNRISE, MN	45.5068	-92.8983	29	5/31/2007	6/29/2009
S001-424	SUNRISE R, WB, JUST DWNSTR OF LYONS ST NE, 1 MI W OF STACY, MN	45.3909	-93.0187	1	9/20/2011	9/20/2011
S006-702	SWAN CK E OF CSAH-32, 4 MI NE OF STAPLES, MN. (10EM086)	46.4116	-94.7613	1	7/7/2010	7/7/2010
S006-994	TAMARAC R (TAMFP1) AT CSAH-1, 1.2 MI S OF FLORIAN, MN.	48.4263	-96.6278	50	5/21/2014	8/29/2017
S005-788	TAMARAC R AT CSAH-22, 4.7 MI NW OF STEPHEN	48.4923	-96.9550	155	5/13/2010	8/30/2019
S002-100	TAMARAC R AT CSAH-220, 11 MI W OF STEPHEN	48.4927	-97.1073	6	5/25/2010	7/27/2011
S002-079	THIEF R, 1 MI E CSAH-32, HILLYER BRG, 4 MI N THIEF R FALLS	48.1872	-96.1734	1	7/13/2010	7/13/2010
S002-313	THREE MILE CK AT CR-67, 1 MI NO OF GREEN VALLEY	44.5411	-95.7564	175	5/24/2005	8/28/2019
S005-631	TRAPPERS RUN CK AT 270TH AVE., 3.5 MI NE OF STARBUCK	45.6562	-95.4871	1	9/21/2011	9/21/2011
S001-936	TROUT BK 4 MI S OF MIESVILLE, MN	44.5434	-92.8041	15	5/20/2005	7/15/2007
S006-655	TROUT CREEK ADJACENT TO CSAH-31, 11.5 MI E OF PLAINVIEW, MN	44.1707	-91.9253	2	6/14/2010	9/8/2010
S004-432	TURTLE CK (JD24) AT 43RD ST BRG, 2 MI NW OF AUSTIN	43.6850	-93.0397	1	8/23/2011	8/23/2011
S004-197	TWELVE MILE CK AT MN-27, 5.8 MI E OF WHEATON	45.8026	-96.3617	1	8/16/2011	8/16/2011
S006-686	TWO RIVER, SB, 1 MI DWNSTR OF US-59, 0.5 MI W OF LAKE BRONSON, MN	48.7389	-96.6784	1	7/14/2010	7/14/2010
S005-387	TWO RIVERS AT MN-175 (BROADWAY ST) AT HALLOCK	48.7756	-96.9374	1	6/12/2002	6/12/2002
S000-569	TWO RIVERS N BR ON CSAH-16 7.1 MI W OF HALLOCK	48.7972	-97.1058	30	5/15/2013	8/26/2014
S006-603	UNN CK AT 660TH AVE., .5 MI W OF ADAMS, MN	43.5611	-92.7290	1	8/23/2011	8/23/2011
S005-527	UNN DITCH TO GOOSE CK AT CSAH-9, 2 MI E OF HARRIS	45.5898	-92.9370	1	9/27/2011	9/27/2011
S005-135	UNN DTCH (TRIB TO BUFFALO R) AT 170TH AVE 5 MI NNE LAKE PARK	46.9558	-96.0478	1	6/24/2010	6/24/2010
S004-463	UNN STR (BONE LK OUTLET) AT LOFTON AVE, 6 MI NE OF FOREST LK	45.2924	-92.8668	12	5/14/2009	6/18/2009
S006-703	UNN STR (CD-7) DNST OF CSAH-13, 3.9 MI NW OF KENNEDY, MN.	48.6662	-96.9869	2	7/14/2010	7/14/2010
S006-633	UNN STR (CHANARAMBIE CK, NB), 0.4 MI UPSTR OF CSAH-5, 4 MI NW OF CHANDLER, MN T106N/R43W/S29	43.9559	-96.0277	1	8/17/2010	8/17/2010
S006-666	UNN STR (COUNTY DITCH 66) JUST UPSTR OF CSAH-46, 5 MI W OF ALBERT LEA, MN	43.6562	-93.4825	1	7/13/2010	7/13/2010
S006-677	UNN STR (DITCH) DNST OF 273RD ST, 4.7 MI SE OF BELLE PLAINE, MN (10EM039)	44.5576	-93.7417	1	8/3/2010	8/3/2010
S006-665	UNN STR (DITCH) DNST OF 490TH ST, 5.5 MI N OF FAIRFAX, MN. T113N / R32W / S9 (10EM019)	44.6089	-94.6957	1	6/15/2010	6/15/2010

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S006-651	UNN STR (DITCH) UPST OF 11TH ST, 1.5 MI S OF HILLS, MN. T101N / R46W / S33 (10EM001)	43.5059	-96.3632	1	8/17/2010	8/17/2010
S006-647	UNN STR (HIDDEN FALLS) TO MISSISSIPPI R AT OTIS AVE IN ST PAUL, MN (HF1)	44.9500	-93.1994	39	4/30/2010	11/14/2011
S006-641	UNN STR (JUDICIAL DITCH 13), 0.2 MI DWNSTR OF CR-219, 5 MI SW OF BRICELYN, MN T101N/R26W/S25	43.5206	-93.8943	2	7/14/2010	7/14/2010
S008-950	UNN STR (N BRANCH OF LITTLE BEAUFORD DITCH TRIBUTARY TO BIG COBB R), 1 MI E OF SH-22 AND NEAR 586 LANE, 1.5 MI NE OF BEAUFORD, MN. (T107N/R26W/S34)	44.0225	-93.9370	2	5/27/2015	6/1/2015
S006-186	UNN STR (S BR LITTLE BEAUFORD DITCH TRIB TO BIG COBB R) 1 MI E OF SH-22 AND NEAR 586 LANE 1 1/2 MI NE BEAUFORD, MN. (T106N/R26W/S3)	44.0221	-93.9363	1	6/1/2015	6/1/2015
S006-679	UNN STR (TO TROUT BK) UPST OF CSAH-6, 2.3 MI SW OF GOODHUE, MN. T111N / R15W / S31 (10EM047)	44.3755	-92.6552	1	6/8/2010	6/8/2010
S006-901	UNN STR (TRIB TO BENSON LK) NEAR CSAH-21, 6 MI SE OF GLENWOOD, MN. T124N/R37W/S8	45.5648	-95.3557	1	9/21/2011	9/21/2011
S006-663	UNN STR (TRIB TO SAND CK) AT CR-744 / DRY RD, 7 MI NW OF MEADOWLANDS, MN (10EM018)	47.1569	-92.8112	1	6/16/2010	6/16/2010
S006-695	UNN STR (WATONWAN R, TRIB TO NORTH FORK) DWNST OF CSAH-9, 6 MI NW OF MOUNTAIN LAKE, MN. (10EM071) T106N/R35W/S1	44.0198	-94.9974	2	8/4/2010	8/5/2015
S004-121	UNN STR (WEDGE'S CK) W OF MN-13 NEAR ALBERT LEA, MN	43.6780	-93.4085	1	8/23/2011	8/23/2011
S006-728	UNN STR ADJACENT TO 320TH AVE NW, 6 MI NE OF ARGYLE, MN. (10EM128) T157N/R47W/S20-21	48.4014	-96.7364	1	6/30/2010	6/30/2010
S006-657	UNN STR ADJACENT TO 70TH ST., 11 MI NE OF MONTEVIDEO, MN T119N/R40W/S15	45.1227	-95.6714	1	7/7/2010	7/7/2010
S006-639	UNN STR ADJACENT TO JACKSON AVE., 2.5 MI NW OF LONSDALE, MN T112N/R22W/S16	44.5072	-93.4671	1	8/2/2010	8/2/2010
S004-354	UNN STR AT CSAH-15, 4 MI NE OF WENDELL, MN	46.0861	-96.0599	1	8/16/2011	8/16/2011
S006-899	UNN STR DWNSTRM OF CSAH-8, 10.5 MI SW OF BRANDON, MN. T128N/R40W/S7	45.9056	-95.7496	1	9/21/2011	9/21/2011
S006-653	UNN STR JUST DWNSTR OF CR-34, 6 MI SW OF BARRETT, MN T128N/R42W/S30	45.8633	-95.9917	1	6/8/2010	6/8/2010
S006-646	UNN STR JUST UPSTR OF 153RD ST., 2 MI E OF LITTLE FALLS, MN	45.9804	-94.3081	1	6/16/2010	6/16/2010
S006-692	UNN STR TO HAY CREEK UPSTREAM OF 140TH AVE, 1 MI S OF LAKE PARK, MN. (10EM069) T139N/R43W/S10	46.8686	-96.1051	1	6/9/2010	6/9/2010
S006-699	UNN STR TO LITTLE ROCK CK (JD #31) ADJACENT TO CSAH-5 (OLD FORT RD), 7 MI SE OF FAIRFAX, MN. (10EM083) T111N/R32W/S12	44.4279	-94.6370	2	6/15/2010	6/17/2015
S006-155	UNN STR TO LITTLE SAUK LK, 3.7 MI W OF LITTLE SAUK, MN	45.8612	-94.9943	1	7/28/2010	7/28/2010
S006-895	UNN STR TO MUSTINKA R, N OF 210TH ST AT 230TH AVE, 6.6 MI W OF BARRETT, MN. T128N / R34W / S1	45.9199	-96.0277	1	8/16/2011	8/16/2011
S005-651	UNN STR TO POMME DE TERRE R AT CSAH-7, 5 MI NO OF FAIRFIELD	45.4621	-95.9736	1	8/24/2010	8/24/2010
S006-642	UNN STR TO RED LAKE R, JUST DWNSTR OF MN-220, 5 MI SW OF FISHER, MN T150N/R49W/S27	47.7769	-96.9118	1	6/10/2010	6/10/2010
S005-094	UNN STR TO ROSE CK AT 570TH AVE, 4.5 MI SE OF AUSTIN	43.6161	-92.9085	1	8/23/2011	8/23/2011
S005-629	UNN STR TO THE CHIPPEWA R AT CSAH-9, 2.5 MI N OF WATSON	45.0493	-95.7976	1	9/21/2011	9/21/2011
S006-717	UNN STR UPST OF 120TH ST NW, 1.5 MI W OF PENNOCK, MN. (10EM110) T119N/R36W/S4	45.1433	-95.2055	1	8/19/2010	8/19/2010
S006-668	UNN STR UPST OF 285TH ST SE, 5 MI E OF FOSSTON, MN. T148N R39W S32 (10EM021)	47.5990	-95.6558	1	6/30/2010	6/30/2010
S006-721	UNN STR UPST OF CR-149, 4 MI NW OF PRINCETON, MN. (10EM116) T36N/R27W/S12	45.6290	-93.6410	1	9/13/2010	9/13/2010

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
S006-723	UNN STR UPST OF CSAH-25, 3.5 MI W OF WALTERS, MN. (10EM119) T102N/R24W/S29	43.6083	-93.7406	1	7/13/2010	7/13/2010
S006-694	UNN STR, .5 MI UPSTR OF SWAN LAKE RD, 7 MI S OF MEADOWLANDS, MN T52N/R19W/S26	46.9636	-92.7186	1	6/17/2010	6/17/2010
S006-720	UNN STR, 0.5 MI W OF GRANDVIEW RD, 6.5 MI SW OF NEW ULM, MN. (10EM115) T109N/R31W/S21	44.2301	-94.5623	1	8/4/2010	8/4/2010
S006-636	UNN STR, 0.8 MI DWNSTR OF CSAH-2, 4 MI SW OF COSMOS, MN T117N/R33W/S24	44.9241	-94.7779	2	8/5/2010	8/5/2010
S006-682	UNN STR, 1 MI N OF 320TH PL., 5 MI NW OF PALISADE, MN	46.7810	-93.5304	1	6/15/2010	6/15/2010
S006-643	UNN STR, ADJACENT TO MEADOWNBROOK RD, 5.5 MI SW OF BROWNSVILLE, MN T102N/R4W/S19	43.6290	-91.3545	1	6/8/2010	6/8/2010
S006-667	UNN STR, JUST DWNSTR OF 150TH AVE. SE, 4 MI N OF KERKHOVEN, MN	45.2562	-95.3177	1	7/7/2010	7/7/2010
S008-395	UNN STR, TRIB TO ROSEAU R, SO FK, DOWNSTREAM OF 370TH AVE, 10 MI S OF ROSEAU, MN. (15EM093)	48.7022	-95.7973	1	6/17/2015	6/17/2015
S008-312	UNN STR, TRIB TO ZUMBRO R, SO FK, DOWNSTREAM OF 80TH ST SW, 6 MI NW OF STEWARTVILLE, MN. (15EM010)	43.9126	-92.5889	1	8/27/2015	8/27/2015
S004-346	UNNAMED STR AT CR-124, 6 MI NW OF STAPLES, MN	46.4259	-94.8626	2	8/10/2012	8/10/2012
S006-681	UNNAMED STR, 1 MI UPSTR OF US-52, 3 MI N OF CHATFIELD, MN	43.8910	-92.2071	1	7/13/2010	7/13/2010
S006-443	UNNAMED STREAM (BATTLE CREEK) AT 310TH ST, 4.8 MI NNW OF LITCHFIELD, MINNESOTA.	45.1961	-94.5527	1	8/19/2010	8/19/2010
S006-690	UNNAMED STREAM ADJACENT TO CSAH-32, 3 MI SW OF LOUISBERG, MN. (10EM067) T119N/R44W/S9	45.1241	-96.1855	2	8/24/2010	6/9/2015
S006-714	UNNAMED STREAM ADJACENT TO OLD HWY 169 BLVD, 2 MI SW OF JORDAN, MN. (10EM103) T114N/R24W/S25	44.6547	-93.6646	1	7/15/2010	7/15/2010
S006-299	UNNAMED STREAM AT COUNTY STATE AID HIGHWAY 15 AT CONFLUENCE WITH UNNAMED STREAM, 6.5 MILES NORTHEAST OF HARMONY, MINNESOTA T101N/R11W/S3	43.5840	-92.1309	1	10/17/2018	10/17/2018
S006-311	UNNAMED STREAM AT COUNTY STATE AID HIGHWAY 7 (280TH STREET), 3 MILES NORTHWEST OF DEXTER, MINNESOTA. T103N/R16W/S2	43.7610	-92.7225	1	7/28/2010	7/28/2010
S000-896	VERMILLION R AT BLAINE AVE E BR, 4.75 MI NE OF FARMINGTON, MN	44.6667	-93.0552	116	5/14/1991	8/18/2014
S003-338	VERMILLION R AT CSAH 23, 2.5 MI SE OF LAKEVILLE	44.6185	-93.2179	1	7/28/2010	7/28/2010
S002-548	W CHASKA CK, 250' W OF CTY RD 10, BEHIND VFW, IN CHASKA, MN	44.7902	-93.6079	155	8/9/1999	7/14/2004
S000-156	W FK DES MOINES R AT PETERSBURG RD, S OF PETERSBURG	43.5262	-94.9192	3	5/22/1991	7/2/1991
S006-724	WATER HEN CK DWNST OF LONG LAKE RD, 14 MI SE OF EVELETH, MN. (10EM121)	47.3054	-92.3608	1	6/16/2010	6/16/2010
S000-163	WATONWAN R BR ON CSAH-13, 1 MI W OF GARDEN CITY	44.0462	-94.1947	102	5/28/2002	8/27/2019
S000-288	WHITEWATER R S FK N OF CR-115 3.5 MI NW OF UTICA	44.0132	-91.9839	9	5/23/1991	7/27/1993
S006-689	WHITEWATER R, N FK, AT CSAH-2, .7 MI S OF ELGIN, MN (10EM059)	44.1207	-92.2594	2	7/12/2010	8/17/2015
S002-102	WILD RICE R AT CR-25, 0.8 MI E OF HENDRUM	47.2669	-96.7970	39	5/24/2005	6/15/2009
S006-654	WILD RICE R, DSTR OF 140TH AVE, S OF MAHNOMEN, MN (10EM005)	47.3063	-95.9741	2	7/12/2010	7/7/2015
S006-634	WILLOW CK, 1.4 MI UPSTR OF CSAH-15, 3 MI SW OF PRESTON, MN	43.6307	-92.0965	1	7/19/2010	7/19/2010
S015-334	Willow Creek at Hwy22	43.6096	-92.0989	2	7/10/2013	10/21/2013
S015-333	Willow Creek at Morems, Jumper Rd/315	43.5899	-92.1085	1	9/6/2013	9/6/2013
S006-301	WILLOW CREEK AT UNNAMED ROAD, 1 MILE WEST OF COUNTY STATE AID HIGHWAY 17, 5.5 MILES NORTHEAST OF HARMONY, MINNESOTA	43.5920	-93.1070	1	7/28/2010	7/28/2010
S015-028	Willow Creek on Jumper Road	43.5920	-92.1070	34	8/5/2013	12/17/2019

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
S006-917	WILLOW R, APPROX 500 FT N OF CSAH-3, 3 MI W OF PALISADE, MN. EMAP SITE ID MNS2009-200/FIELD NUMBER 10EM200.	46.7113	-93.5551	1	9/14/2011	9/14/2011
S002-958	WING R AT CSAH 23, 2.5 MI N OF VERNDALE, MN	46.4334	-95.0095	1	8/10/2012	8/10/2012
S006-670	WOLF CK DNST OF CANBY AVE / CR-60, 6.8 MI SE OF LONSDALE, MN (10EM023)	44.4179	-93.3225	3	9/7/2010	7/21/2015
S002-316	YELLOW MED R, 1 1/3 MI NO CSAH-18, 5 1/4 MI NE HANLEY FALLS	44.7217	-95.5183	35	5/13/2009	6/25/2012
S007-314	YELLOW MEDICINE R AT MN TH-274, 4.5 MI N OF WOOD LAKE, MN.	44.7152	-95.5441	114	5/9/2013	8/30/2019
S006-662	YELLOW MEDICINE R, N BR, DNST OF CR-109, 5 MI SW OF PORTER, MN (10EM016)	44.5830	-96.2336	2	8/24/2010	6/8/2015
S006-701	YELLOW MEDICINE R, S BR, DNST OF 280TH ST, 7.9 MI SW OF MINNEOTA, MN	44.4646	-96.0772	2	8/18/2010	8/18/2010
S008-272	YELLOW MEDICINE R, SO BR, 0.25 MI DOWNSTREAM OF 280TH ST, 7.5 MI SW OF MINNEOTA, MN. (10EM062)	44.4646	-96.0772	1	6/9/2015	6/9/2015
S006-716	ZUMBRO R ADJACENT TO CSAH-11, 3 MI NE OF MILLVILLE, MN. (10EM107)	44.2721	-92.2381	2	8/23/2010	8/3/2015
S000-268	ZUMBRO R S FORK AT CSAH-14, 3 MI N OF ROCHESTER	44.1080	-92.4477	8	5/15/1991	7/27/1993
S006-708	ZUMBRO R, MID FK, S BR ADJACENT TO 90TH ST NW, 6 MI NW OF ROCHESTER, MN. (10EM095)	44.1265	-92.6106	3	6/10/2010	8/3/2015
S006-632	ZUMBRO R, NF, 0.3 MI UPSTR OF LARSON AVE., 3.5 MI W OF KENYON, MN	44.2647	-93.0624	1	6/7/2010	6/7/2010
S006-640	ZUMBRO R, SF, 0.7 MI UPSTR OF CR-126, 9.5 MI SW OF ROCHESTER, MN	43.9264	-92.6129	1	6/9/2010	6/9/2010
S000-819	ZUMBRO RIVER ON USH-63 0.4 MI SOUTH ZUMBRO FALLS	44.2796	-92.4240	31	5/25/2007	6/25/2009

Appendix 9b. Site code, site description, and sampling history for current and historic MDA lake monitoring locations.

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
44-0157-00-101	ALLEN	47.4653	-95.7702	1	8/7/2007	8/7/2007
69-0005-00-101	ALRUSS	48.0435	-91.8033	1	7/16/2007	7/16/2007
34-0206-00-201	ANDREW	45.3100	-95.0438	2	7/25/2017	7/25/2017
37-0026-01-201	ANDREW	44.9895	-95.9498	1	7/9/2012	7/9/2012
37-0026-01-202	ANDREW	44.9692	-95.9490	1	6/27/2017	6/27/2017
69-0154-00-100	ARTHUR	47.7425	-92.0407	1	7/17/2007	7/17/2007
06-0002-00-101	ARTICHOKE	45.3290	-96.1240	4	5/27/2009	8/4/2011
38-0691-00-101	AUGUST	47.7630	-91.6090	1	8/3/2007	8/3/2007
03-0478-00-201	BAKER	47.1005	-95.9360	2	9/6/2017	9/6/2017
16-0182-00-102	BALL CLUB	47.9154	-90.5038	1	9/5/2012	9/5/2012
16-0182-00-103	BALL CLUB	47.9112	-90.4866	1	7/25/2017	7/25/2017
03-0303-00-201	BEAR	47.0570	-95.7827	2	6/28/2012	7/18/2012
03-0303-00-202	BEAR	47.0575	-95.7826	1	8/3/2017	8/3/2017
43-0076-00-201	BEAR	44.9520	-94.3056	1	6/12/2012	6/12/2012
43-0076-00-202	BEAR	44.9518	-94.3058	1	6/28/2017	6/28/2017
77-0035-00-201	BEAUTY	46.0096	-94.6982	1	8/8/2017	8/8/2017
38-0472-00-101	BECOOSIN	47.9478	-91.3926	2	7/18/2007	6/26/2012
29-0146-00-204	BELLE TAINE	46.9353	-94.9040	1	6/18/2012	6/18/2012
06-0090-01-201	BENTSEN	45.3876	-96.3634	2	8/22/2012	8/22/2012
69-0050-00-201	BIG	47.5249	-91.8560	1	8/7/2012	8/7/2012
69-0050-00-202	BIG	47.5252	-91.8600	1	8/10/2017	8/10/2017
03-0096-00-202	BIG BASSWOOD	47.0751	-95.3353	1	7/13/2010	7/13/2010
06-0152-00-303	BIG STONE	45.3608	-96.4899	1	8/7/2012	8/7/2012
75-0034-00-201	BJORK	45.6426	-95.8141	1	6/26/2017	6/26/2017
73-0241-00-201	BLACK OAK	45.6276	-94.8131	2	8/2/2011	6/11/2012
73-0241-00-202	BLACK OAK	45.6318	-94.8104	1	6/21/2017	6/21/2017
31-0813-00-101	BOWSTRING	47.5438	-93.8953	1	7/28/2010	7/28/2010
31-0623-00-201	BOY	47.5226	-93.6656	1	8/15/2017	8/15/2017
10-0107-00-201	BRAUNWORTH	44.7881	-93.9128	1	8/24/2017	8/24/2017
46-0030-00-100	BUDD	43.6396	-94.4667	1	10/8/2008	10/8/2008
69-0044-00-201	BUTTERBALL	47.4635	-91.8662	1	6/28/2017	6/28/2017
19-0006-00-202	BYLLESBY	44.5117	-92.9422	1	7/25/2011	7/25/2011
60-0189-00-201	CAMERON	47.6659	-96.0195	1	7/25/2011	7/25/2011
03-0209-00-201	CARMAN	47.0361	-95.6304	2	9/5/2017	9/5/2017
34-0032-00-201	CARRIE	45.0827	-94.7858	4	6/2/2009	8/3/2011
04-0030-00-101	CASS	47.4246	-94.6288	1	8/6/2007	8/6/2007
38-0510-00-202	CATTYMAN	48.0127	-91.3181	1	8/1/2012	8/1/2012
38-0510-00-203	CATTYMAN	48.0131	-91.3203	1	7/19/2017	7/19/2017
27-0039-00-100	CEDAR	44.9597	-93.3211	1	7/2/2008	7/2/2008
31-0419-00-201	CHARLIE	47.5374	-93.5504	1	8/2/2012	8/2/2012
18-0095-00-201	CHRYSLER	46.3130	-93.9448	1	6/27/2017	6/27/2017
44-0140-00-201	CIRCLE	47.3385	-95.7600	1	7/31/2012	7/31/2012
44-0140-00-202	CIRCLE	47.3387	-95.7602	1	8/1/2017	8/1/2017
73-0172-00-201	CLEAR	45.5299	-94.5329	1	6/11/2012	6/11/2012
81-0014-01-202	CLEAR	44.0912	-93.4843	1	7/26/2011	7/26/2011
86-0263-00-101	COKATO	45.1160	-94.1694	1	8/20/2007	8/20/2007
86-0263-00-201	COKATO	45.1084	-94.1657	1	6/13/2012	6/13/2012
69-0249-00-201	COLBY	47.5314	-92.1339	1	7/18/2017	7/18/2017
18-0127-00-201	COLE	46.5317	-94.0183	2	7/24/2017	7/24/2017
62-0055-00-201	COMO	44.9799	-93.1411	1	7/23/2010	7/23/2010
31-0594-00-202	COTTONWOOD	47.4285	-93.6935	1	7/10/2012	7/10/2012
14-0103-00-201	CROMWELL	46.9644	-96.3156	1	9/6/2017	9/6/2017
38-0024-00-201	CROOKED (EAST BAY)	47.6060	-91.0734	1	7/30/2012	7/30/2012

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
38-0024-01-201	CROOKED (EAST BAY)	47.6049	-91.0750	1	7/18/2017	7/18/2017
21-0199-02-203	CROOKED (EAST CROOKED)	45.8600	-95.5534	1	9/5/2012	9/5/2012
18-0312-02-201	CROSS LAKE RESERVOIR (SOUTHEAST BAY)	46.6500	-94.1258	1	8/28/2012	8/28/2012
18-0155-00-203	CROW WING	46.2363	-94.3394	2	7/30/2007	7/25/2012
03-0571-00-201	CUCUMBER	47.1176	-96.0113	1	6/13/2012	6/13/2012
06-0120-00-201	CUP	45.4880	-96.4426	4	8/21/2017	8/29/2018
21-0080-00-203	DARLING	45.9129	-95.4053	1	7/19/2007	7/19/2007
21-0080-00-205	DARLING	45.9151	-95.4066	2	8/8/2012	8/8/2012
21-0080-00-206	DARLING	45.9194	-95.3968	1	8/9/2017	8/9/2017
11-1013-00-201	DIAMOND POND	46.9877	-94.4677	1	7/24/2012	7/24/2012
38-0256-00-201	DIVIDE	47.6088	-91.2540	1	8/28/2012	8/28/2012
17-0056-01-201	DOUBLE (NORTH PORTION)	44.0536	-95.3760	10	8/30/2017	8/28/2019
46-0098-00-201	DUTTON SLOUGH	43.5218	-94.6380	1	7/11/2012	7/11/2012
07-0060-01-101	EAGLE (NORTH)	44.2043	-93.8956	3	8/8/2007	8/14/2012
07-0060-01-102	EAGLE (NORTH)	44.1952	-93.9005	1	7/19/2017	7/19/2017
56-0573-00-201	EAST RED RIVER	46.3994	-95.8901	2	7/24/2012	7/24/2012
42-0070-00-202	EAST TWIN	44.2137	-96.0456	1	8/20/2012	8/20/2012
27-0029-00-201	EDINA	44.8683	-93.3465	1	8/9/2012	8/9/2012
27-0029-00-202	EDINA	44.8683	-93.3475	1	7/26/2017	7/26/2017
69-0810-00-202	ELEPHANT	48.1945	-92.7387	4	6/10/2009	8/2/2011
15-0010-00-100	ELK	47.1881	-95.2171	1	10/25/2008	10/25/2008
15-0010-00-101	ELK	47.1877	-95.2147	5	8/9/2007	8/3/2011
34-0033-00-201	ELLA	45.0797	-94.8141	1	8/9/2012	8/9/2012
34-0033-00-202	ELLA	45.0777	-94.8104	2	6/28/2017	7/24/2017
56-0356-00-101	FAIRY	46.7015	-95.7477	2	8/6/2007	7/31/2012
21-0336-00-101	FANNY	45.9930	-95.6877	1	7/11/2007	7/11/2007
40-0051-00-201	FISH	44.2295	-93.6661	1	7/26/2011	7/26/2011
70-0069-00-205	FISH	44.6499	-93.4588	1	8/6/2007	8/6/2007
56-0430-00-201	FISKE	46.2569	-95.7858	1	6/11/2012	6/11/2012
56-0430-00-202	FISKE	46.2570	-95.7911	1	8/9/2017	8/9/2017
03-0242-00-101	FLAT	46.9730	-95.6552	1	8/7/2007	8/7/2007
03-0242-00-201	FLAT	46.9697	-95.6482	1	6/12/2012	6/12/2012
03-0242-00-202	FLAT	46.9747	-95.6549	1	9/11/2017	9/11/2017
04-0251-00-201	FOX	47.8427	-95.0446	1	6/26/2012	6/26/2012
31-0513-00-201	GALE	47.6727	-93.4959	1	8/14/2017	8/14/2017
03-0414-00-201	GANDRUD	46.9288	-95.8933	1	6/11/2012	6/11/2012
03-0414-00-202	GANDRUD	46.9294	-95.8934	1	8/2/2017	8/2/2017
47-0127-00-201	GOOSE	44.9879	-94.5866	1	6/28/2017	6/28/2017
26-0204-00-201	GRAHAM	45.7942	-96.1138	1	6/22/2017	6/22/2017
47-0062-00-201	GREENLEAF	45.0112	-94.4709	1	6/28/2017	6/28/2017
58-0013-00-201	GREIGS	46.0528	-92.4722	1	8/31/2017	8/31/2017
27-0016-00-100	HARRIET	44.9220	-93.3053	1	11/6/2008	11/6/2008
27-0016-00-201	HARRIET	44.9206	-93.3060	1	7/23/2010	7/23/2010
31-0407-00-201	HAY	47.3736	-93.5289	1	7/10/2012	7/10/2012
31-0407-00-202	HAY	47.3736	-93.5288	1	8/8/2017	8/8/2017
72-0050-01-201	HIGH ISLAND (MAIN BASIN)	44.6623	-94.2097	1	6/13/2012	6/13/2012
72-0050-01-202	HIGH ISLAND (MAIN BASIN)	44.6707	-94.2170	1	6/20/2017	6/20/2017
01-0142-02-201	HILL (SOUTH ARM)	46.9826	-95.5953	4	5/29/2009	8/4/2011
26-0228-00-201	HODGSON	45.9122	-96.0512	1	7/23/2012	7/23/2012
26-0228-00-202	HODGSON	45.9130	-96.0554	1	6/22/2017	6/22/2017
56-0578-00-201	HOLBROOK	46.7070	-95.9230	1	7/31/2012	7/31/2012
56-0578-00-202	HOLBROOK	46.7049	-95.9207	1	8/2/2017	8/2/2017
54-0013-00-202	HOME	47.2036	-96.2158	1	8/2/2012	8/2/2012
47-0116-00-201	HOOSIER	45.0596	-94.5467	1	9/14/2017	9/14/2017
38-0580-00-201	HORSESHOE	47.8786	-91.4314	1	9/12/2017	9/12/2017

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
56-0492-00-201	HORSESHOE	46.4937	-95.8862	2	8/20/2012	8/20/2012
56-0492-00-202	HORSESHOE	46.4932	-95.8864	1	8/29/2017	8/29/2017
03-0029-00-101	HUNGRY MAN	47.0636	-95.1817	2	8/8/2007	7/28/2010
46-0049-00-201	IOWA	43.4992	-94.4595	1	6/19/2017	6/19/2017
51-0079-00-201	IRON	44.1610	-95.8643	2	7/17/2012	8/20/2012
11-0102-00-201	ISLAND	46.9279	-94.0385	1	8/11/2007	8/11/2007
56-0846-00-201	IVERSON	46.2232	-96.0438	1	9/11/2017	9/11/2017
42-0036-00-201	JACOBSONS MARSH	44.3199	-95.8277	1	6/27/2017	6/27/2017
09-0050-00-201	JASKARI	46.6787	-92.7005	1	7/10/2017	7/10/2017
01-0100-00-201	JENKINS	46.6497	-93.4817	1	8/6/2012	8/6/2012
01-0100-00-202	JENKINS	46.6512	-93.4855	1	7/20/2017	7/20/2017
47-0015-00-101	JENNIE	45.0026	-94.3341	1	8/21/2007	8/21/2007
47-0015-00-201	JENNIE	44.9960	-94.3264	1	6/12/2012	6/12/2012
47-0015-00-202	JENNIE	44.9967	-94.3410	1	8/23/2017	8/23/2017
03-0199-00-201	JOHNSON	46.9345	-95.5982	1	9/6/2017	9/6/2017
34-0440-00-201	JOHNSON	45.0108	-94.9573	1	8/22/2017	8/22/2017
69-0845-00-100	KABETOGAMA	48.4265	-92.9580	1	10/8/2008	10/8/2008
19-0011-00-201	KEGAN	44.7578	-93.1167	1	7/26/2017	7/26/2017
21-0060-00-202	KRUEGERS SLOUGH	45.9474	-95.3333	2	8/20/2012	8/20/2012
21-0060-00-203	KRUEGERS SLOUGH	45.9460	-95.3322	1	8/28/2017	8/28/2017
16-0236-00-201	LAC	47.9531	-90.5089	1	6/28/2017	6/28/2017
42-0020-00-201	LADY SLIPPER	44.5702	-95.6305	1	7/27/2011	7/27/2011
42-0032-00-201	LAKE OF THE HILL	44.2277	-95.7925	1	8/30/2017	8/30/2017
69-0341-00-101	LAMB	48.1638	-92.1055	1	7/19/2007	7/19/2007
07-0124-00-201	LIEBERG	44.1533	-94.3127	1	7/12/2012	7/12/2012
26-0282-00-201	LIGHTNING	46.0687	-96.0858	1	7/15/2010	7/15/2010
26-0282-00-202	LIGHTNING	46.0693	-96.0848	1	8/9/2017	8/9/2017
34-0294-00-201	LINDGREN	45.1779	-95.1454	1	8/14/2012	8/14/2012
69-0296-00-202	LITTLE CRAB	47.9547	-92.0758	1	7/31/2012	7/31/2012
71-0044-00-201	LITTLE DIAMOND	45.4781	-93.6213	1	8/7/2012	8/7/2012
27-0179-01-201	LITTLE LONG (N BAY)	44.9482	-93.7078	1	8/9/2012	8/9/2012
11-0487-00-201	LITTLE TWIN	47.3002	-94.5600	1	7/11/2017	7/11/2017
11-0136-00-201	LOMISH	47.0755	-94.1310	1	7/12/2017	7/12/2017
11-0480-00-101	LONG	47.0741	-94.6020	1	7/10/2007	7/10/2007
11-0480-00-201	LONG	47.0725	-94.6011	3	6/19/2012	8/27/2012
11-0480-00-202	LONG	47.0737	-94.6020	1	7/12/2017	7/12/2017
17-0048-02-201	LONG	43.9584	-95.3731	1	8/29/2017	8/29/2017
30-0072-00-208	LONG	45.4702	-93.3473	1	6/21/2012	6/21/2012
30-0072-00-209	LONG	45.4743	-93.3452	1	7/10/2017	7/10/2017
31-0266-01-101	LONG	47.5971	-93.4017	1	8/15/2007	8/15/2007
69-0653-00-202	LONG	47.4033	-92.5430	1	7/24/2012	7/24/2012
86-0069-00-101	LONG	45.2934	-93.8459	1	6/26/2007	6/26/2007
31-0266-01-203	LONG (MAIN BAY)	47.5866	-93.3794	2	7/11/2012	7/11/2012
31-0266-01-204	LONG (MAIN BAY)	47.5864	-93.3791	1	8/1/2017	8/1/2017
18-0123-00-201	LOOKOUT	46.4368	-93.9596	1	8/7/2012	8/7/2012
18-0123-00-202	LOOKOUT	46.4368	-93.9578	2	7/24/2017	7/24/2017
18-0123-00-101	LOOKOUT (CROCKER)	46.4365	-93.9535	1	8/13/2007	8/13/2007
29-0303-00-201	LOST	47.2436	-95.1291	1	9/5/2012	9/5/2012
69-0581-00-201	LOST	47.8217	-92.4058	1	8/2/2011	8/2/2011
69-0611-00-101	LOST (HORSESHOE)	47.4644	-92.4401	1	7/20/2007	7/20/2007
31-0893-00-201	LOWER PIGEON	47.5631	-94.1650	1	7/10/2012	7/10/2012
31-0893-00-202	LOWER PIGEON	47.5644	-94.1615	1	8/7/2017	8/7/2017
56-0476-00-101	MAINE (ROUND)	46.4192	-95.8388	2	7/25/2007	8/8/2012
56-0476-00-102	MAINE (ROUND)	46.4194	-95.8400	1	8/8/2017	8/8/2017
18-0408-00-100	MAYO	46.5673	-94.3251	1	7/9/2007	7/9/2007

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
36-0012-00-201	MILLER	47.9590	-94.0773	1	7/27/2017	7/27/2017
15-0107-00-201	MISKOGINEU	48.0074	-95.4395	1	6/26/2012	6/26/2012
15-0107-00-202	MISKOGINEU	48.0074	-95.4404	1	7/27/2017	7/27/2017
31-0200-00-201	MISSISSIPPI	47.1721	-93.4003	1	9/7/2017	9/7/2017
87-0032-00-201	MUD	44.6739	-95.5421	2	6/27/2017	6/27/2017
11-0047-00-201	MULE	46.8456	-93.9955	1	7/19/2017	7/19/2017
16-0104-00-101	MUSQUASH	47.9137	-90.3414	1	8/1/2007	8/1/2007
38-0492-00-201	NEGLIGE	48.0497	-91.3030	1	8/22/2017	8/22/2017
34-0154-00-205	NEST	45.2593	-94.9619	1	8/22/2007	8/22/2007
69-0757-00-101	NET	48.3941	-92.6582	1	6/21/2012	6/21/2012
69-0757-00-102	NET	48.3955	-92.6581	1	8/15/2017	8/15/2017
69-0208-00-201	NIBIN	48.1783	-91.9847	1	8/24/2017	8/24/2017
27-0019-00-202	NOKOMIS	44.9094	-93.2411	1	6/27/2007	6/27/2007
27-0019-00-203	NOKOMIS	44.9075	-93.2405	1	7/12/2012	7/12/2012
41-0055-00-101	NORTH ASH	44.4308	-96.2903	1	7/10/2007	7/10/2007
41-0055-00-202	NORTH ASH	44.4306	-96.2883	1	7/17/2012	7/17/2012
27-0179-01-202	NORTH LITTLE LONG	44.9502	-93.7090	1	6/28/2017	6/28/2017
16-0089-00-100	NORTHERN LIGHT	47.9055	-90.2438	1	10/17/2008	10/17/2008
34-0251-02-204	NORWAY (SOUTHERN)	45.3085	-95.0973	1	8/22/2007	8/22/2007
34-0251-02-207	NORWAY (SOUTHERN)	45.3066	-95.0979	2	8/6/2012	8/6/2012
53-0024-00-201	OCHEDA	43.5745	-95.5966	1	6/20/2017	6/20/2017
53-0024-02-201	OCHEDA (MIDDLE BAY)	43.5756	-95.5945	1	8/15/2012	8/15/2012
46-0051-00-102	OKAMANPEEDAN	43.5213	-94.5681	1	8/7/2007	8/7/2007
06-0050-00-201	OTREY	45.3572	-96.3356	2	6/21/2017	6/21/2017
62-0056-00-100	OWASSO	45.0378	-93.1243	1	6/24/2008	6/24/2008
26-0111-00-201	PATCHEN	45.7732	-95.9055	1	6/26/2017	6/26/2017
32-0033-00-201	PEARL	43.5273	-95.1157	1	6/19/2017	6/19/2017
56-0829-00-101	PEBBLE	46.2522	-96.0363	2	7/25/2007	8/22/2007
18-0308-00-101	PELICAN	46.5498	-94.1833	1	7/11/2007	7/11/2007
61-0111-00-201	PELICAN	45.6480	-95.4510	2	6/21/2017	6/21/2017
27-0004-00-201	PENN	44.8454	-93.3057	2	6/28/2017	6/28/2017
18-0439-00-201	PENNINGTON MINE	46.4839	-93.9866	1	6/18/2012	6/18/2012
18-0439-00-202	PENNINGTON MINE	46.4845	-93.9800	1	8/7/2017	8/7/2017
41-0067-00-201	PERCH	44.5146	-96.2888	1	7/21/2010	7/21/2010
56-0171-02-201	PETERSON	46.2664	-95.6186	1	9/12/2017	9/12/2017
03-0287-00-202	PICKEREL	46.8706	-95.7290	1	7/31/2007	7/31/2007
19-0079-00-201	PICKEREL	44.9177	-93.1188	1	7/23/2010	7/23/2010
11-0411-00-101	PINE MOUNTAIN	46.8199	-94.5329	1	7/11/2007	7/11/2007
11-0110-00-201	PISTOL	46.8142	-94.0857	1	7/23/2012	7/23/2012
62-0046-00-204	PLEASANT	45.0950	-93.1067	1	8/25/2010	8/25/2010
41-0044-00-201	POPOWSKI	44.5214	-96.2041	2	7/16/2012	7/16/2012
04-0014-00-202	POPPLE	47.5172	-94.4611	1	8/8/2012	8/8/2012
04-0014-00-203	POPPLE	47.5182	-94.4710	1	7/31/2017	7/31/2017
21-0291-00-101	RED ROCK	45.8606	-95.7181	1	7/25/2007	7/25/2007
18-0386-00-100	RED SAND	46.3658	-94.2891	2	10/8/2008	11/15/2008
16-0643-00-101	RICHEY	47.6674	-90.9898	2	8/2/2007	6/25/2012
16-0643-00-102	RICHEY	47.6678	-90.9889	1	8/15/2017	8/15/2017
46-0116-00-201	ROUND	43.7019	-94.6850	1	8/29/2017	8/29/2017
56-0490-00-201	ROUND	46.5110	-95.8951	1	8/29/2017	8/29/2017
40-0107-00-201	SAVIDGE	44.3261	-93.8687	1	7/12/2012	7/12/2012
40-0107-00-202	SAVIDGE	44.3260	-93.8697	1	6/20/2017	6/20/2017
30-0060-00-201	SECTION	45.6798	-93.1545	1	8/7/2012	8/7/2012
30-0060-00-202	SECTION	45.6806	-93.1533	1	7/20/2017	7/20/2017
42-0066-00-201	SECTION THIRTY-THREE	44.1988	-96.0331	1	6/27/2017	6/27/2017
29-0043-00-100	SHINGOBEE	47.0043	-94.6885	1	10/24/2008	10/24/2008

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
14-0100-00-101	SILVER	46.8309	-96.3343	1	8/3/2011	8/3/2011
75-0164-00-201	SILVER	45.7599	-95.9292	1	8/21/2012	8/21/2012
41-0022-00-201	SLOUGH	44.3686	-96.1100	1	8/30/2017	8/30/2017
51-0027-00-201	SMITH	44.0944	-95.6871	1	6/20/2017	6/20/2017
62-0073-00-201	SNAIL	45.0693	-93.1227	2	7/18/2007	6/7/2012
62-0073-00-202	SNAIL	45.0757	-93.1297	1	7/10/2017	7/10/2017
86-0230-00-201	SOMERS	45.2638	-94.0267	1	7/19/2017	7/19/2017
43-0014-00-101	SOUTH	44.9472	-94.0349	2	7/23/2007	8/21/2007
43-0014-00-102	SOUTH	44.9432	-94.0334	1	6/7/2012	6/7/2012
43-0014-00-103	SOUTH	44.9455	-94.0351	2	9/14/2017	9/14/2017
76-0149-00-101	SOUTH DRYWOOD	45.3920	-96.0937	1	7/12/2007	7/12/2007
56-0629-00-201	SOUTH STANG (GLORVIGAN)	46.2521	-95.9376	1	7/25/2012	7/25/2012
22-0022-00-201	SOUTH WALNUT	43.6681	-93.7918	1	8/15/2012	8/15/2012
22-0022-00-202	SOUTH WALNUT	43.6669	-93.7890	1	6/19/2017	6/19/2017
38-0623-00-201	SPREE	48.0233	-91.4391	1	6/27/2012	6/27/2012
38-0623-00-202	SPREE	48.0222	-91.4390	1	8/16/2017	8/16/2017
11-0022-00-101	SPRING	47.1227	-93.8806	1	8/10/2007	8/10/2007
33-0027-00-101	SPRING	45.8883	-93.2756	1	6/27/2007	6/27/2007
69-0129-00-202	SPRING	47.0690	-92.0021	2	6/28/2007	6/19/2012
69-0129-00-203	SPRING	47.0693	-92.0010	1	7/17/2017	7/17/2017
83-0043-00-201	ST. JAMES	43.9762	-94.6477	1	6/20/2017	6/20/2017
81-0003-00-201	ST. OLAF	43.9034	-93.4131	4	6/10/2009	8/12/2011
81-0003-00-202	ST. OLAF	43.9031	-93.4168	1	8/15/2017	8/15/2017
41-0034-00-201	STAY	44.3878	-96.1700	1	7/27/2011	7/27/2011
38-0744-00-100	STEWART	47.1866	-91.7529	1	10/16/2008	10/16/2008
03-0010-00-201	STRAIGHT	46.9548	-95.2803	1	7/31/2007	7/31/2007
17-0024-00-201	STRING	43.8781	-95.2034	1	7/11/2012	7/11/2012
17-0024-00-202	STRING	43.8756	-95.2022	1	6/20/2017	6/20/2017
69-0920-00-201	STUART	47.5589	-93.0327	1	9/6/2012	9/6/2012
69-0920-00-202	STUART	47.5597	-93.0326	1	9/6/2017	9/6/2017
86-0119-00-100	SULLIVAN	45.2221	-93.9439	2	10/8/2008	11/15/2008
86-0119-00-201	SULLIVAN	45.2209	-93.9440	4	8/23/2010	8/23/2010
32-0040-00-201	SUMMER MARSH	43.6354	-95.1885	1	8/29/2017	8/29/2017
17-0073-00-201	SUMMIT	43.8565	-95.0691	1	8/20/2012	8/20/2012
51-0068-00-201	SUMMIT	43.9971	-95.8583	1	8/20/2012	8/20/2012
29-0144-00-201	SUNDAY	46.8935	-94.9083	1	8/8/2012	8/8/2012
29-0144-00-202	SUNDAY	46.8943	-94.9085	1	6/27/2017	6/27/2017
16-0001-00-100	SUPERIOR	47.4153	-90.8034	1	10/16/2008	10/16/2008
34-0321-00-201	SWENSON	45.2673	-95.1380	1	8/6/2012	8/6/2012
34-0321-00-202	SWENSON	45.2670	-95.1387	1	6/29/2017	6/29/2017
17-0060-00-201	TALCOT	43.8787	-95.4491	1	8/15/2012	8/15/2012
11-0150-00-201	TAMARACK	46.8455	-94.2713	1	7/23/2012	7/23/2012
11-0150-00-202	TAMARACK	46.8461	-94.2706	1	6/26/2017	6/26/2017
11-0241-00-201	TAMARACK	46.8610	-94.3145	2	8/6/2012	8/6/2012
11-0241-00-202	TAMARACK	46.8614	-94.3148	1	6/26/2017	6/26/2017
16-0613-00-201	TENOR	48.1964	-90.8758	1	6/28/2012	6/28/2012
82-0031-00-451	TERRAPIN	45.1823	-92.8193	1	6/6/2012	6/6/2012
82-0031-00-452	TERRAPIN	45.1821	-92.8178	1	9/11/2017	9/11/2017
45-0001-00-201	THIEF	48.4863	-95.8720	1	7/26/2011	7/26/2011
06-0102-00-201	THIELKE	45.3978	-96.4016	1	8/21/2012	8/21/2012
31-0158-00-201	THISTLEDEW	47.7884	-93.2464	1	7/25/2011	7/25/2011
77-0066-00-201	THUNDER	46.1176	-94.7463	2	7/28/2011	8/8/2011
78-0025-00-103	TRAVERSE	45.7316	-96.6780	1	7/13/2010	7/13/2010
62-0061-00-100	TURTLE	45.0996	-93.1382	1	11/6/2008	11/6/2008
38-0671-00-201	TWO DEER	47.6870	-91.5736	1	7/23/2012	7/23/2012

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03-0077-00-201	UNNAMED	47.0129	-95.4041	1	8/2/2017	8/2/2017
03-0236-00-201	UNNAMED	47.0846	-95.5771	1	6/12/2012	6/12/2012
03-0236-00-202	UNNAMED	47.0850	-95.5783	1	9/6/2017	9/6/2017
03-0393-00-201	UNNAMED	46.8624	-95.9144	2	6/11/2012	6/27/2012
03-0393-00-202	UNNAMED	46.8620	-95.9138	1	9/6/2017	9/6/2017
03-0627-00-201	UNNAMED	46.8432	-96.1620	1	8/1/2012	8/1/2012
03-0627-00-202	UNNAMED	46.8435	-96.1617	1	8/2/2017	8/2/2017
03-0751-00-201	UNNAMED	46.7323	-96.0765	2	8/1/2012	8/1/2012
03-0751-00-202	UNNAMED	46.7324	-96.0760	1	9/7/2017	9/7/2017
06-0005-00-201	UNNAMED	45.3107	-96.2310	1	6/22/2017	6/22/2017
06-0188-00-201	UNNAMED	45.5128	-96.5414	1	6/21/2017	6/21/2017
06-0206-00-201	UNNAMED	45.4422	-96.3856	1	8/22/2012	8/22/2012
06-0266-00-201	UNNAMED	45.4020	-96.2901	2	8/20/2012	8/20/2012
06-0266-00-202	UNNAMED	45.4028	-96.2911	1	6/22/2017	6/22/2017
06-0349-00-201	UNNAMED	45.5080	-96.5131	1	8/28/2012	8/28/2012
11-0440-00-201	UNNAMED	46.6420	-94.6382	2	8/27/2012	8/27/2012
13-0061-00-201	UNNAMED	45.4041	-92.9902	1	8/7/2012	8/7/2012
13-0061-00-202	UNNAMED	45.4039	-92.9906	1	7/20/2017	7/20/2017
14-0081-00-201	UNNAMED	47.0499	-96.2508	2	8/1/2012	8/1/2012
14-0081-00-202	UNNAMED	47.0496	-96.2502	1	8/1/2017	8/1/2017
14-0088-00-201	UNNAMED	46.9818	-96.2085	1	9/6/2017	9/6/2017
14-0389-00-201	UNNAMED	46.6464	-96.3394	1	7/30/2012	7/30/2012
15-0279-00-201	UNNAMED	47.2473	-95.4662	1	6/27/2012	6/27/2012
15-0279-00-202	UNNAMED	47.2474	-95.4662	1	8/2/2017	8/2/2017
15-0491-00-201	UNNAMED	47.2039	-95.2641	1	6/27/2012	6/27/2012
16-0399-00-201	UNNAMED	47.9533	-90.6723	1	6/27/2017	6/27/2017
18-0146-00-201	UNNAMED	46.4289	-94.1235	1	7/25/2017	7/25/2017
18-0430-00-201	UNNAMED	46.4353	-93.9334	2	8/9/2017	8/9/2017
18-0527-00-201	UNNAMED	46.4060	-94.1377	1	8/7/2012	8/7/2012
21-0729-00-201	UNNAMED	45.8664	-95.2956	1	8/21/2012	8/21/2012
21-0729-00-202	UNNAMED	45.8663	-95.2958	1	8/30/2017	8/30/2017
24-0067-00-201	UNNAMED	43.7316	-93.1052	1	6/19/2017	6/19/2017
26-0071-00-201	UNNAMED	46.1015	-95.8197	1	9/13/2017	9/13/2017
26-0205-00-201	UNNAMED	45.7868	-96.1162	2	7/23/2012	7/23/2012
26-0205-00-202	UNNAMED	45.7868	-96.1147	1	6/22/2017	6/22/2017
26-0217-00-201	UNNAMED	45.7647	-96.0802	1	8/21/2012	8/21/2012
29-0296-00-201	UNNAMED	47.1600	-95.0545	1	7/31/2017	7/31/2017
31-0142-00-201	UNNAMED	47.4838	-93.2664	1	7/31/2017	7/31/2017
31-0211-00-201	UNNAMED	47.2112	-93.4255	2	8/9/2012	8/9/2012
31-1366-00-201	UNNAMED	47.6711	-93.8066	1	8/9/2012	8/9/2012
31-1367-00-201	UNNAMED	47.8192	-94.3130	1	8/9/2012	8/9/2012
34-0194-00-201	UNNAMED	45.1904	-95.0987	1	9/14/2017	9/14/2017
34-0247-00-201	UNNAMED	45.1680	-95.1234	1	6/29/2017	6/29/2017
37-0100-00-201	UNNAMED	44.8934	-96.1804	1	7/9/2012	7/9/2012
37-0100-00-202	UNNAMED	44.8932	-96.1808	1	8/31/2017	8/31/2017
40-0098-00-201	UNNAMED	44.2658	-93.8299	2	7/12/2012	8/9/2012
40-0098-00-202	UNNAMED	44.2619	-93.8246	1	7/18/2017	7/18/2017
44-0155-00-201	UNNAMED	47.4808	-95.6850	1	8/1/2017	8/1/2017
44-0228-00-201	UNNAMED	47.3535	-95.8896	1	7/19/2012	7/19/2012
44-0244-00-201	UNNAMED	47.4740	-95.8140	1	8/2/2012	8/2/2012
48-0019-00-201	UNNAMED	46.1351	-93.8102	1	7/23/2012	7/23/2012
49-0139-00-201	UNNAMED	46.1972	-94.5748	1	8/10/2012	8/10/2012
49-0139-00-202	UNNAMED	46.1967	-94.5742	1	8/7/2017	8/7/2017
56-0113-00-201	UNNAMED	46.3574	-95.4778	1	7/23/2012	7/23/2012
56-0113-00-202	UNNAMED	46.3577	-95.4750	1	8/28/2017	8/28/2017

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
56-0134-00-201	UNNAMED	46.1490	-95.5220	1	8/28/2017	8/28/2017
56-0147-00-201	UNNAMED	46.1796	-95.6213	1	7/23/2012	7/23/2012
56-0147-00-202	UNNAMED	46.1798	-95.6210	1	8/28/2017	8/28/2017
56-0630-00-201	UNNAMED	46.2522	-95.9053	2	8/29/2017	8/29/2017
56-0810-00-201	UNNAMED	46.1284	-96.1333	1	8/21/2012	8/21/2012
56-0810-00-202	UNNAMED	46.1274	-96.1332	1	8/29/2017	8/29/2017
56-0853-00-201	UNNAMED	46.2098	-96.0511	1	7/25/2012	7/25/2012
56-0853-00-202	UNNAMED	46.2085	-96.0519	1	8/30/2017	8/30/2017
56-0985-00-201	UNNAMED	46.4279	-96.2253	1	7/30/2012	7/30/2012
56-1002-00-201	UNNAMED	46.3821	-96.2388	2	8/29/2017	8/29/2017
56-1582-00-201	UNNAMED	46.4872	-96.1381	1	8/20/2012	8/20/2012
57-0027-01-201	UNNAMED	48.0989	-96.1921	2	7/12/2012	7/12/2012
58-0205-00-201	UNNAMED	46.2547	-92.5168	1	8/14/2017	8/14/2017
60-0078-00-201	UNNAMED	47.5711	-95.7246	1	8/2/2012	8/2/2012
60-0078-00-202	UNNAMED	47.5707	-95.7248	1	8/1/2017	8/1/2017
60-0099-00-201	UNNAMED	47.6649	-95.7811	1	8/22/2012	8/22/2012
60-0129-00-201	UNNAMED	47.7184	-95.7507	1	8/21/2012	8/21/2012
60-0211-00-201	UNNAMED	47.5875	-95.9665	1	7/30/2012	7/30/2012
60-0244-00-201	UNNAMED	47.5849	-96.1125	1	8/1/2017	8/1/2017
60-0275-00-202	UNNAMED	47.6222	-96.0832	1	8/2/2012	8/2/2012
60-0281-00-201	UNNAMED	47.6102	-96.1700	2	7/30/2012	7/30/2012
60-0307-00-101	UNNAMED	47.5790	-96.2353	1	8/8/2007	8/8/2007
60-0319-00-201	UNNAMED	47.6434	-96.2423	1	7/31/2012	7/31/2012
61-0091-00-202	UNNAMED	45.4235	-95.4747	1	8/14/2012	8/14/2012
61-0189-00-201	UNNAMED	45.5257	-95.7208	1	8/13/2012	8/13/2012
61-0189-00-202	UNNAMED	45.5261	-95.7205	1	8/21/2017	8/21/2017
64-0096-00-201	UNNAMED	44.3684	-95.3717	1	7/11/2012	7/11/2012
73-0317-00-201	UNNAMED	45.4738	-94.3120	1	8/7/2012	8/7/2012
73-0317-00-202	UNNAMED	45.4743	-94.3114	1	6/21/2017	6/21/2017
73-0425-00-201	UNNAMED	45.2935	-94.3013	1	8/7/2017	8/7/2017
75-0205-00-201	UNNAMED	45.5083	-96.0665	1	8/20/2012	8/20/2012
75-0205-00-202	UNNAMED	45.5091	-96.0666	1	6/26/2017	6/26/2017
76-0166-00-201	UNNAMED	45.3400	-96.1156	1	6/22/2017	6/22/2017
77-0258-00-201	UNNAMED	45.8419	-94.9134	1	8/20/2012	8/20/2012
86-0065-00-201	UNNAMED	45.3191	-93.8827	1	8/27/2012	8/27/2012
86-0065-00-202	UNNAMED	45.3182	-93.8822	2	6/21/2017	6/21/2017
14-0029-00-101	UNNAMED (NORTH MAYFIELD)	46.7634	-96.2152	1	8/9/2007	8/9/2007
26-0043-02-201	UNNAMED (WEST PORTION)	45.8616	-95.8431	1	7/23/2012	7/23/2012
06-0460-00-201	UNNAMED POOL	45.2657	-96.3693	1	7/10/2012	7/10/2012
37-0134-02-201	UNNAMED-SOUTHWEST PORTION	45.0495	-96.2253	1	7/9/2012	7/9/2012
11-0218-00-201	UPPER GULL	46.5288	-94.3402	1	7/28/2010	7/28/2010
31-0770-00-201	UPPER HATCH	47.6729	-93.7596	1	8/14/2007	8/14/2007
56-0957-00-101	UPPER LIGHTNING	46.1243	-96.1561	1	7/12/2010	7/12/2010
40-0002-00-101	UPPER SAKATAH	44.2236	-93.5488	1	8/8/2007	8/8/2007
62-0038-01-201	VADNAIS (E VADNAIS)	45.0537	-93.0931	2	7/26/2010	8/1/2011
16-0414-00-101	VESPER	47.9745	-90.7463	1	7/31/2007	7/31/2007
21-0054-00-203	VICTORIA	45.8695	-95.3457	1	7/24/2007	7/24/2007
31-0298-00-201	WALTERS	47.6668	-93.3705	1	8/6/2012	8/6/2012
31-0298-00-202	WALTERS	47.6700	-93.3732	1	7/31/2017	7/31/2017
56-0114-00-202	WEST LEAF	46.4102	-95.4827	1	8/1/2007	8/1/2007
18-0379-00-100	WHITE SAND	46.3536	-94.2871	2	10/8/2008	11/15/2008
60-0015-00-201	WHITEFISH	47.5859	-95.6527	1	8/7/2017	8/7/2017
58-0045-00-201	WILBUR	46.0202	-92.5887	1	7/10/2012	7/10/2012
85-0011-01-102	WINONA (SOUTH BAY)	44.0399	-91.6443	2	7/20/2010	7/29/2011
34-0141-00-202	WOODCOCK	45.2424	-94.9488	1	8/15/2012	8/15/2012
34-0141-00-101	WOODCOCK (W WOODCOCK)	45.2387	-94.9529	1	7/24/2007	7/24/2007

Appendix 9c. Site code, site description, and sampling history for current and historic MDA wetland monitoring locations.

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
WT00096	WETLAND (16STEA259) LOCATED APPROX 0.2 MI N OF KREIGLE LAKE RD, APPROX 2.7 MI SW OF AVON, MN. T124/R30/S5	45.5752	-94.4784	2	6/30/2016	6/30/2016
WT00056	WETLAND (03Lyon099) LOCATED E OF 120TH AVE AND S OF CR-4 APPROX 7.3 MI NW OF RUSSELL, MN. T111N/R43W/S32	44.3860	-96.0534	2	6/10/2014	8/21/2014
WT00058	WETLAND (03Lyon146) LOCATED N OF CR-66 APPROX 10.8 MI NW OF RUSSELL, MN. T110N/R43W/S8	44.3523	-96.0494	4	6/9/2014	8/21/2014
WT00057	WETLAND (03Murr028) LOCATED N OF CR-18 APPROX 6.3 MI E/SE OF RUTHTON, MN. T108N/R43W/S16	44.1546	-96.0103	3	6/9/2014	8/21/2014
WT00055	WETLAND (03MURR066) LOCATED W OF 10TH AVE APPROX 4 MI E OF RUTHTON, MN. T108/R43W/S7	44.1752	-96.0443	2	6/9/2014	8/21/2014
WT00065	WETLAND (04Aitk001) LOCATED W OF CR-76 AND 330TH ST INTERSECTION AND 1 MI W OF US-169, 3 MI S OF AITKIN, MN. T46N/R27W/S2	46.4900	-93.7229	2	6/4/2014	8/24/2014
WT00060	WETLAND (04Rams015) LOCATED E OF LAKEWOOD DR AND S OF ARLINGTON AVE E IN ST. PAUL, MN. T29N/R22W/S24	44.9831	-93.0035	4	6/2/2014	5/28/2015
WT00051	WETLAND (04Rams018) LOCATED W OF INTERSECTION OF CENTURY AVE S AND POULIOT PARKWAY ON THE PONDS OF BATTLE CREEK GOLF COURSE, WOODBURY, MN. T28/R22/S12	44.9238	-92.9856	2	6/2/2014	8/20/2014
WT00061	WETLAND (04Rams064) LOCATED W OF S WINTHROP ST AND S OF BATTLE CREEK COMMUNITY RECREATION CENTER PARKING LOT IN ST. PAUL, MN. T28N/R22W/S2	44.9380	-93.0117	2	6/2/2014	8/20/2014
WT00063	WETLAND (04Rams085) LOCATED 200 FT S OF HOLLOWAY AVE AND 0.2 MI W OF MN-120 IN NO ST PAUL, MN. T29N/R22W/S13	44.9988	-92.9894	2	6/2/2014	8/20/2014
WT00054	WETLAND (05Lyon002) LOCATED 0.3 MI S OF CR-19 AND 0.6 MI E OF LYON LINCOLN COUNTY RD, 13 MI W OF MARSHALL, MN. T111/R43/S7	44.4403	-96.0675	2	6/10/2014	8/21/2014
WT00052	WETLAND (07Dako149) LOCATED E OF 35E AND S OF HWY 110 AND NW OF MENDAKOTA COUNTRY CLUB CLUBHOUSE IN MENDOTA HEIGHTS, MN. SMALLER WETLAND LOCATED NE OF BIG WETLAND. T28/R23/S26	44.8813	-93.1364	1	6/2/2014	6/2/2014
WT00066	WETLAND (09Aitk190) LOCATED JUST SO OF 250TH ST, 1.1 MI W OF US-169, 7.2 MI N/NE OF GARRISON, MN. T45N/R27W/S20	46.3734	-93.7744	2	6/4/2014	8/24/2014
WT00075	WETLAND (11BECK204) LOCATED JUST W OF 130TH AVE, 3.4 MI WSW OF CORMORANT, MN. T138/R43/S32	46.7213	-96.1360	1	6/29/2016	6/29/2016
WT00076	WETLAND (11CHIS057) LOCATED APPROX 0.3 MI S OF CR-36, APPROX 2.0 MI SE OF STACY, MN. T33/R21/S4	45.3717	-92.9713	1	9/14/2016	9/14/2016
WT00077	WETLAND (11DOUG140) LOCATED ON CTY HWY 8, APPROX 6.3 MI NW OF HOLMES CITY, MN. T128/R40/S23-24	45.8766	-95.6549	2	6/21/2016	6/21/2016
WT00078	WETLAND (11DOUG192) LOCATED N OF DEAD END OF WHISPER LN NW, APPROX 3.8 MI NW OF EVANSVILLE, MN. T130/R40/S31	46.0301	-95.7519	1	6/21/2016	6/21/2016
WT00079	WETLAND (11KAND180) LOCATED JUST N OF 273RD AVE NW, APPROX 6.1 MI NW OF SUNDBURG, MN. T122/R35/S7	45.3898	-95.1284	1	6/15/2016	6/15/2016
WT00080	WETLAND (11KITT068) LOCATED 1.6 MI E OF 330 AVE, APPROX 7.3 MI NW OF LANCASTER, MN T163/R47/S14	48.9363	-96.6975	2	8/10/2016	8/10/2016
WT00081	WETLAND (11KOOC127) LOCATED 1.5 MI E OF CR-198, APPROX 2.0 SW OF ERICSBURG, MN. T69/R24/S13	48.4637	-93.3548	1	9/1/2016	9/1/2016
WT00082	WETLAND (11LAKE085) LOCATED 1.2 MI S OF NF-122, APPROX 4.0 MI NW OF BRIMSON, MN T56/R11/S31	47.2987	-91.7880	3	9/8/2016	9/8/2016
WT00083	WETLAND (11LAKE149) LOCATED 1.0 MI S OF INTERSECTION OF NF-15 AND MN-1, APPROX 5.5 MILES SW OF HAPPY WANTERER, MN. T60/R10/S34	47.6455	-91.5962	2	8/9/2016	8/9/2016
WT00084	WETLAND (11MCLE087) LOCATED 0.2 MI N OF 125TH ST, APPROX 2.2 MI SE OF BISCAY, MN. T115/R28/S6	44.8003	-94.2503	1	8/10/2016	8/10/2016
WT00085	WETLAND (11SCOT137) LOCATED E OF EDENVALE TRAIL, APPROX 5 MI NW OF ELKO/NEW MARKET, MN. T113/R22/S11	44.6035	-93.4224	2	7/18/2016	7/18/2016

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
WT00086	WETLAND (11STEA093) LOCATED E OF THE CORNER OF 388TH AVE AND 275TH ST, APPROX 3.8 MI W OF SPRING HILL, MN T124/R34/S25-26	45.5186	-94.9064	1	6/15/2016	6/15/2016
WT00087	WETLAND (16CARV263) LOCATED JUST S OF MN-7, APPROX 2.1 MI NNW OF VICTORIA MN. T116/R24/S2	44.8862	-93.6774	1	6/20/2016	6/20/2016
WT00088	WETLAND (16GRAN314) LOCATED 0.4 MI W OF CR-38, APPROX 2.5 MI SE OF BARRETT, MN. T128/R41/S19	45.8766	-95.8709	2	8/1/2016	8/1/2016
WT00089	WETLAND (16JACK258) LOCATED 0.3 MI N OF CR-4, APPROX 3.9 MI ENE OF ROUND LAKE, MN T101/R38/S15	43.5477	-95.3904	1	8/2/2016	8/2/2016
WT00090	WETLAND (16LACQ238) LOCATED 0.2 MI E OF US-75, APPROX 3.4 MI SW OF ODESSA, MN. T120/R45/S10	45.2223	-96.2846	1	6/22/2016	6/22/2016
WT00091	WETLAND (16MARS277) LOCATED 1.0 MI E OF WESTGATE RD, APPROX 9.8 MI ENE OF HOLT, MN. T156/R42/S13	48.3377	-95.9921	1	8/16/2016	8/16/2016
WT00092	WETLAND (16MARS293) LOCATED JUST N OF 270TH ST NE, APPROX 8.6 MI NNW OF MAVIE, MN. T155/R41/S6	48.2679	-95.9707	1	7/19/2016	7/19/2016
WT00093	WETLAND (16MURR274) LOCATED 0.6 MI W OF CR-34, APPROX 2.8 MI SW OF SLAYTON, MN. T106/R41/S25	43.9603	-95.7148	1	8/2/2016	8/2/2016
WT00094	WETLAND (16OTTE246) LOCATED 0.3 MI E OF 325TH AVE, APPROX 1.2 MI N OF VERGAS, MN. T137/R41/S13	46.6734	-95.8099	1	6/29/2016	6/29/2016
WT00095	WETLAND (16SHER315) LOCATED JUST WEST OF RAWLINS ST NW, APPROX 2.5 MI NE OF BAILEY, MN T33/R26/S19	45.3373	-93.6228	1	9/13/2016	9/13/2016
WT00097	WETLAND (16TODD279) LOCATED JUST W OF CR-102, APPROX 0.8 MI N OF GREY EAGLE, MN. T127/R32/S6	45.8361	-94.7489	3	6/21/2016	6/21/2016
WT00050	WETLAND (Breen) LOCATED JUST W OF CR-15 APPROX 5.3 MI S OF CLEVELAND, MN. T109/R25/S10	44.2621	-93.8115	2	6/9/2014	8/20/2014
WT00059	WETLAND (Franco) LOCATED N OF MN-23 APPROX 2.5 MI SW OF CLARA CITY, MN. T117N/R38W/S15	44.9378	-95.4118	2	6/10/2014	8/22/2014
WT00064	WETLAND (Glacial) LOCATED 0.7 MI N OF 270TH ST AND 1.2 M E OF 295TH AVE, 7 MI S/SE OF STARBUCK, MN. T124N/R39W/S25	45.5220	-95.5026	2	6/5/2014	8/22/2014
WT00053	WETLAND (Kerk) LOCATED 500 FT S OF CR-87 AND 0.3 MI W OF 130TH AVE NE, 13 MI E/NE OF BENSON, MN. T122/R37/S19	45.3608	-95.3735	2	6/4/2014	8/22/2014
WT00062	WETLAND (Kipling) LOCATED BETWEEN LYNN AVE AND KIPLING AVE N OF W 42ND ST IN LINDEN HILLS, MN. T28N/R24W/S7	44.9282	-93.3360	2	6/2/2014	8/20/2014
WT00067	WETLAND (New Prairie) LOCATED S OF CR-24 AND E OF T-237 APPROX 5 MI NE OF CYRUS, MN. T125N/R40W/S12	45.6543	-95.6541	2	6/5/2014	8/22/2014
WT00068	WETLAND (Tyler) LOCATED JUST N OF US-14 APPROX 0.4 MI W OF TYLER, MN. T109N/R44W/S4	44.2698	-96.1483	3	6/9/2014	8/21/2014

Appendix 9d. Site code, site description, and sampling history for current and historic MDA rainfall monitoring locations.

Site Code	Site Description	Latitude	Longitude	Sample Count	First Sample	Last Sample
LD00263	MNDA WET PRECIPITATION MONITORING - CLAY - BRP, BUFFALO R WET PRECIPITATION SITE AT CR-108, 2 MI SE OF GEORGETOWN, MN. T141N/R48W/S4	47.0498	-96.7541	45	4/17/2014	9/24/2019
LD00230	MNDA WET PRECIPITATION MONITORING - CRYSTAL SPRINGS HATCHERY, JUST N OF CR-112, 2 MI E/SE OF ELBA, MN. T107N/R10W/S14	44.0753	-91.9857	116	5/28/1998	10/5/2005
LD00232	MNDA WET PRECIPITATION MONITORING - LITTLE COBB - LTP, JUST E OF CSAH-16 AND NEAR MONITORING LOCATION S003-574, 6.3 MI W OF PEMBERTON, MN. T106N/R26W/S12	43.9967	-93.9083	95	5/29/2008	8/27/2019
LD00231	MNDA WET PRECIPITATION MONITORING - ROCHESTER - ZRP, .3 MI W OF CSAH-22, 1 MI N OF US-14 IN ROCHESTER, MN. T107N/R13W/S31	44.0266	-92.4251	82	4/24/2009	5/20/2019
LD00357	MNDA WET PRECIPITATION MONITORING - ST PAUL - MRP, MISSISSIPPI R WET PRECIPITATION SITE ON ROOF OF 625 ROBERT ST N ST PAUL, MN	44.9541	-93.0984	7	4/23/2019	8/27/2019

Appendix 10

2019 Water Quality Monitoring Report

January – December 2019

2019 summary of river and stream maximum detections and applicable pesticide water quality reference values.

Appendix 10. 2019 summary of river and stream maximum detections and applicable pesticide water quality reference values.

MDA 2019 Maximum Detections		Surface Water Reference Values as of January 2020 (ng/L)[1]					
		Minnesota Administrative Rule, Chapter 7050 Standards				USEPA/OPP Benchmark[3]	
Pesticide Analyte	Maximum Detection (ng/L)	Chronic Standards[2]			Maximum Standard[7]	Acute Value	Chronic Value
		Class 2A[4]	Class 2Bd[5]	Class 2B,C,D[6]			
2,4,5-T	<50	—	—	—	—	—	—
2,4,5-TP	<50	50,000 H	50,000 H	—	—	—	—
2,4-D	10,900	70,000 H	70,000 H	—	—	130,000 (f)	79,200 (f)
2,4-DB	<20	—	—	—	—	1,000,000 (f)	1,100,000 (n)
Acetamiprid	<25	—	—	—	—	10,500 (i)	2,100 (i)
Acetochlor	58,000	3,600 T	3,600 T	3,600 T	86,000	190,000 (f)	1,430 (n)
Acetochlor ESA	3,440	—	—	—	—	>62,500,000 (i)	9,900,000 (n)
Acetochlor OXA	4,300	—	—	—	—	—	—
Acifluorfen	226	—	—	—	—	8,500,000 (f)	>355,000 (n)
Afidopyropen[10]	<50	—	—	—	—	4,445,000 (i)	123 (i)
Alachlor	<30	3,800 H; 59,000 T	4,200 H; 59,000 T	59,000 T	800,000	900,000 (f)	1,640 (n)
Alachlor ESA	589	—	—	—	—	>52,000,000 (f)(i)	3,600,000 (n)
Alachlor OXA	39.1	—	—	—	—	>47,500,000 (i)	—
Aldicarb Sulfone	<15	2,000 H	2,000 H	—	—	140,000 (i)	—
Aldicarb Sulfoxide	<50	4,000 H	4,000 H	—	—	21,500 (i)	—
Aminopyralid	151	—	—	—	—	7,500,000 (i)	1,360,000 (f)
Atrazine	7,230	3,400 H; 10,000 T	3,400 H; 10,000 T	10,000 T	323,000	360,000 (i)	<1,000 (n)
Deisopropylatrazine	158	—	—	—	—	8,500,000 (f)	2,500,000 (n)
Desethylatrazine	518	—	—	—	—	—	1,000,000 (n)
Didealkylatrazine	262	—	—	—	—	>50,000,000 (f)(i)	—
Hydroxyatrazine	220	—	—	—	—	>1,500,000 (f)	>10,000,000 (n)
Azoxystrobin	1,910	—	—	—	—	130,000 (i)	44,000 (i)
Benfluralin	<25	—	—	—	—	34,850 (f)	1,900 (f)
Bensulfuron-methyl	<16.7	—	—	—	—	>31,500,000 (f)	7,800 (n)
Bensulide	<250	—	—	—	—	290,000 (i)	11,000 (i)
Bentazon	3,120	—	—	—	—	31,150,000 (i)	4,500,000 (n)
Benzovindiflupyr	158	—	—	—	—	1,750 (f)	950 (f)
Bicyclopyrone	56.9	—	—	—	—	46,650,000 (i)	13,000 (v)
Bicyclopyrone SYN503870	<100	—	—	—	—	—	—
Bifenthrin	<20	—	—	—	—	75 (f)	1.3 (i)
Boscalid	<50	—	—	—	—	>1,350,000 (f)	116,000 (f)
Bromacil	60.4	—	—	—	—	18,000,000 (f)	6,800 (n)
Bromoxynil	31.3	—	—	—	—	5,500 (i)	2,500 (i)
Carbaryl	<25	—	—	—	—	850 (i)	500 (i)
Carbendazim	205	—	—	—	—	5,000 (f)	990 (f)
Carbofuran	<13.3	40,000 H	40,000 H	—	—	1,115 (i)	750 (i)
Chlorantraniliprole	55.2	—	—	—	—	5,800 (i)	4,470 (i)
Chlorimuron-ethyl	<20	—	—	—	—	>5,000,000 (f)(i)	270 (v)
Chlorothalonil	<50	—	—	—	—	1,800 (i)	600 (i)
Chlorpyrifos	70.2	41 T	41 T	41 T	83	50 (i)	40 (i)
Chlorpyrifos Oxon	<40	—	—	—	—	—	—
Clethodim sulfone	190	—	—	—	—	10,100,000 (i)[8]	2,000 (f)[8]

MDA 2019 Maximum Detections		Surface Water Reference Values as of January 2020 (ng/L)[1]					
		Minnesota Administrative Rule, Chapter 7050 Standards				USEPA/OPP Benchmark[3]	
Pesticide Analyte	Maximum Detection (ng/L)	Chronic Standards[2]			Maximum Standard[7]	Acute Value	Chronic Value
		Class 2A[4]	Class 2Bd[5]	Class 2B,C,D[6]			
Clethodim sulfoxide	336	–	–	–	–	10,100,000 (i)[8]	2,000 (f)[8]
Clomazone	<15	–	–	–	–	1,450,000 (f)	167,000 (n)
Clopyralid	4,590	–	–	–	–	51,750,000 (f)	6,900,000 (n)
Clothianidin	201	–	–	–	–	11,000 (i)	50 (i)
Cyanazine	<25	–	–	–	–	–	–
Cyanazine Acid	<10	–	–	–	–	–	–
Cyanazine Amide	<10	–	–	–	–	–	–
Deethylcyanazine	<25	–	–	–	–	–	–
Deethylcyanazine Acid	104	–	–	–	–	–	–
Deethylcyanazine Amide	<25	–	–	–	–	–	–
Cyantraniliprole	<100	–	–	–	–	10,200 (i)	6,560 (i)
Cyfluthrin	<100	–	–	–	–	12.5 (i)	7.4 (i)
Diazinon	<30	–	–	–	–	105 (i)	170 (i)
Diazinon Oxon	<75	–	–	–	–	–	–
Dicamba	9,580	–	–	–	–	14,000,000 (f)	61,000 (n)
Dichlobenil	584	–	–	–	–	2,465,000 (f)	30,000 (v)
Dichlorprop	<50	–	–	–	–	>45,750,000	77,000 (n)
Dichlorvos	116	–	–	–	–	35 (i)	5.8 (i)
Dicrotophos	<25	–	–	–	–	6,300 (i)	1,700 (i)
Difenoconazole	<25	–	–	–	–	385,000 (i)	860 (f)
Dimethenamid	3,100	–	–	–	–	3,150,000 (f)	8,900 (v)[9]
Dimethenamid ESA	988	–	–	–	–	–	–
Dimethenamid OXA	710	–	–	–	–	–	–
Dimethoate	<50	–	–	–	–	21,500 (i)	500 (i)
Dinotefuran	<20	–	–	–	–	>49,550,000 (f)	6,360,000 (f)
Disulfoton	<60	–	–	–	–	1,950 (i)	10 (i)
Disulfoton Sulfone	<20	–	–	–	–	17,500 (i)	140 (i)
Diuron	26.2	–	–	–	–	80,000 (i)	2,400 (n)
EPTC	123	–	–	–	–	3,250,000 (i)	40,000 (f)
Esfenvalerate	<150	–	–	–	–	25 (i)	17 (i)
Ethalfluralin	<50	–	–	–	–	16,000 (f)	400 (f)
Ethofumesate	3,510	–	–	–	–	5,760,000 (f)	300,000 (i)
Flufenacet OXA	<8.3	–	–	–	–	–	–
Flumetsulam	1,240	–	–	–	–	127,000,000 (i)	3,100 (v)
Flupyradifurone[10]	<10	–	–	–	–	31,950 (i)	3,300 (i)
Flutianil[10]	<25	–	–	–	–	>395,000 (f)	2,240 (f)
Flutianil OC 56574	<50	–	–	–	–	–	–
Flutianil OC 56635[10]	<25	–	–	–	–	>48,400,000 (i)	100,000,000 (i)
Flutriafol	31.7	–	–	–	–	16,500,000 (f)	310,000 (i)
Fluxapyroxad[10]	27.1	–	–	–	–	145,000 (f)	22,000 (f)
Fomesafen	2,130	–	–	–	–	63,000,000 (f)	92,000 (n)
Fonofos	<15	–	–	–	–	–	–
Glyphosate	5,880	–	–	–	–	21,500,000 (f)	11,900,000 (v)
AMPA	<5,100	–	–	–	–	249,500,000 (f)	–

MDA 2019 Maximum Detections		Surface Water Reference Values as of January 2020 (ng/L)[1]						
		Minnesota Administrative Rule, Chapter 7050 Standards				USEPA/OPP Benchmark[3]		
Pesticide Analyte	Maximum Detection (ng/L)	Chronic Standards[2]			Maximum Standard[7]	Acute Value	Chronic Value
		Class 2A[4]	Class 2Bd[5]	Class 2B,C,D[6]			
Halauxifen-methyl	<10	—	—	—	—	1,005,000 (f)	135 (v)
Halauxifen acid	<25	—	—	—	—	>53,000,000 (i)	580 (v)
Halosulfuron-methyl[10]	<30	—	—	—	—	>53,500,000 (i)	42 (v)
Hexazinone	<10	—	—	—	—	75,800,000 (i)	7,000 (n)
Imazamethabenz-methyl	<5	—	—	—	—	—	—
Imazamethabenz Acid	<10	—	—	—	—	—	—
Imazamox	91.3	—	—	—	—	>59,500,000 (f)	8,000 (v)
Imazapic	20.5	—	—	—	—	>50,000,000 (f)(i)	6,220 (v)
Imazapyr	118	—	—	—	—	>50,000,000 (f)(i)	18,000 (v)
Imazaquin	<16.7	—	—	—	—	140,000,000 (f)(i)	—
Imazethapyr	240	—	—	—	—	120,000,000 (f)	8,100 (v)
Imidacloprid	32	—	—	—	—	385 (i)	10 (i)
Imidacloprid-olefin	<50	—	—	—	—	—	—
Imidacloprid-urea	<50	—	—	—	—	>47,400,000	—
Isoxaflutole	<40	—	—	—	—	>750,000 (i)	4,900 (v)
Isoxaflutole DKN	<50	—	—	—	—	>15,300,000 (f)	75,000 (v)
Lambda-Cyhalothrin	<75	—	—	—	—	3.5 (i)	2 (i)
Linuron	<20	—	—	—	—	60,000 (i)	90 (i)
Malathion	<50	—	—	—	—	49 (i)	60 (i)
Mandestrobin[10]	<25	—	—	—	—	465,000 (f)	60,000 (n)
MCPA	701	—	—	—	—	90,000 (i)	20,000 (v)
MCPB	<20	—	—	—	—	1,950,000 (f)	210,000 (v)
MCPP	222	—	—	—	—	45,500,000 (i)	14,000 (n)
Mesotrione	468	—	—	—	—	>60,000,000 (f)	17,700 (v)
Metalaxyl	14.9	—	—	—	—	14,000,000 (i)	100,000 (i)
Methoxychlor	<50	—	—	—	—	700 (i)	—
Metolachlor	23,100	23,000 T	23,000 T	23,000 T	271,000	550,000 (i)	1,000 (i)
Metolachlor ESA	7,930	—	—	—	—	24,000,000 (f)	43,000,000 (v)
Metolachlor OXA	1,680	—	—	—	—	7,700,000 (i)	57,100,000 (n)
Metribuzin	810	—	—	—	—	2,100,000 (i)	8,100 (n)
Metribuzin DA	159	—	—	—	—	—	—
Metribuzin DADK	<500	—	—	—	—	—	—
Metribuzin DK	<500	—	—	—	—	—	—
Metsulfuron-methyl	60.3	—	—	—	—	>75,000,000 (f)(i)	360 (v)
Momfluorothrin	<50	—	—	—	—	600 (f)	3,100 (i
Myclobutanil	<10	—	—	—	—	1,200,000 (f)	830,000 (n)
Nicosulfuron	<26.6	—	—	—	—	>500,000,000 (f)(i)	43,000,000 (i)
Norflurazon	<20	—	—	—	—	4,050,000 (f)	9,700 (n)
Norflurazon-desmethyl	<50	—	—	—	—	—	—
Oxadiazon	<75	—	—	—	—	600,000 (f)	5,200 (n)
Oxathiapiprolin	<100	—	—	—	—	>280,000 (f)	>140,000 (n)
Oxydemeton-methyl	<20	—	—	—	—	95,000 (i)	5,000 (f)
Parathion-methyl	<100	—	—	—	—	485 (i)	250 (i)
Parathion-methyl Oxon	<25	—	—	—	—	—	—

MDA 2019 Maximum Detections		Surface Water Reference Values as of January 2020 (ng/L)[1]					
		Minnesota Administrative Rule, Chapter 7050 Standards				USEPA/OPP Benchmark[3]	
Pesticide Analyte	Maximum Detection (ng/L)	Chronic Standards[2]			Maximum Standard[7]	Acute Value	Chronic Value
		Class 2A[4]	Class 2Bd[5]	Class 2B,C,D[6]			
Pendimethalin	<75	–	–	–	–	69,000 (f)	5,200 (n)
Phorate	<25	–	–	–	–	300 (i)	210 (i)
Picloram	<41.6	500,000 H	500,000 H	–	–	2,750,000 (f)	550,000 (f)
Picoxystrobin	<50	–	–	–	–	12,000 (i)	1,000 (i)
Prometon	360	–	–	–	–	6,000,000 (f)	98,000 (n)
Prometryn	4.31	–	–	–	–	1,455,000 (f)	1,040 (n)
Propachlor	<30	–	–	–	–	85,000 (f)	13,500 (n)
Propachlor ESA	<30	–	–	–	–	–	–
Propachlor OXA	<10	–	–	–	–	–	–
Propazine	75.1	–	–	–	–	>2,190,000 (f)	24,800 (n)
Propiconazole	727	–	–	–	–	425,000 (f)	21,000 (n)
Pydiflumetofen[10]	<25	–	–	–	–	93,000 (f)	42,000 (i)
Pyraclostrobin	<25	–	–	–	–	3,100 (f)	1,500 (n)
Pyroxasulfone[10]	302	–	–	–	–	>1,100,000 (f)	380 (n)
Saflufenacil	512	–	–	–	–	4,250,000 (i)	42,000 (n)
Sedaxane[10]	<75	–	–	–	–	310,000 (f)	110,000 (f)
Siduron	<6.7	–	–	–	–	4,050,000 (f)	6,000 (i)
Simazine	<75	4,000 H	4,000 H	–	–	500,000 (i)	6,000 (n)
Sulfentrazone	2,710	–	–	–	–	30,200,000 (i)	28,800 (v)
Sulfometuron-methyl	51.3	–	–	–	–	>74,000,000 (f)	450 (v)
Tebuconazole	45.6	–	–	–	–	1,135,000 (f)	11,000 (f)
Tebupirimfos	<30	–	–	–	–	39 (i)	11 (i)
Tembotrione	505	–	–	–	–	24,450,000 (i)	5,200 (v)
Terbufos	<30	–	–	–	–	85 (i)	30 (i)
Tetraconazole	16.8	–	–	–	–	1,315,000 (i)	190,000 (i)
Thiacloprid	<50	–	–	–	–	18,900 (i)	970 (i)
Thiamethoxam	241	–	–	–	–	17,500 (i)	740 (i)
Thifensulfuron-methyl	<16.7	–	–	–	–	>50,000,000 (f)(i)	1,590 (v)
Thiobencarb	<8.3	–	–	–	–	50,000 (i)	1,000 (i)
Tolfenpyrad	<100	–	–	–	–	81.5 (f)	188 (f)
Tolpyralate	<50	–	–	–	–	>9,500,000 (f)	6,670 (v)
Triallate	<50	–	–	–	–	45,500 (i)	14,000 (i)
Triasulfuron	<23.3	–	–	–	–	>50,000,000 (f)(i)	190,000 (v)
Triclopyr	2,310	–	–	–	–	180,000 (f)	26,000 (f)
Trifluralin	<50	–	–	–	–	9,250 (f)	1,900 (f)
zeta-Cypermethrin	<500	–	–	–	–	1.8 (i)	0.59 (i)

Key to value types and symbols in surface water reference values in Appendix 10.

In general, Minnesota Rule Chap. 7050 water quality standards supersede other reference values because they have been reviewed and promulgated for their applicability to Minnesota's water resources, and because of their potential use in making water body impairment decisions under the federal Clean Water Act.

— – For some analytes, reference values have not been developed, identified or evaluated.

(f) – USEPA/OPP benchmark value for fish.

(i) – USEPA/OPP benchmark value for invertebrates.

(n) – USEPA/OPP benchmark value for nonvascular plants.

(v) – USEPA/OPP benchmark value for vascular plants.

H – "H" Chronic Standard values are human health-based and protective for an exposure duration of 30 days.

T – "T" Chronic Standard values are toxicity-based for aquatic organisms and protective for an exposure duration of 4 days.

[1] **Reference Values** are given for all target pesticide analytes when available. Some analytes do not have an established reference value from the sources listed below.

[2] **Chronic Standard** as defined in Minn. Rule Chap. 7050.

[3] **Aquatic Life Benchmarks** based on toxicity values derived from data available to the USEPA's OPP supporting registration of the pesticide are provided only when an Minnesota Rule Chap. 7050 value is not available. Current values posted by the USEPA's OPP may differ from those of previous MDA reports. See USEPA's website for more detailed information and definitions.

[4] **State Water Classification for aquatic life (cold water streams) & all recreation.** Protected as drinking water sources.

[5] **State Water Classification for aquatic life (cold and warm water streams) & all recreation.** Protected as drinking water sources.

[6] **State Water Classification for aquatic life** (2B – sport and commercial; 2C – non-commercial; 2D – wetlands) & recreation (2B – all types; 2C, D – limited types). Not protected as drinking water sources.

[7] **Maximum Standard Value for Aquatic Life & Recreation** as defined on MPCA's website and Minn. Rule Chap. 7050. Values are the same for all classes of surface waters.

[8] **Value for Parent of Degradate,** in the absence of an applicable reference value(s) for a pesticide degradate, the parent pesticide reference value is used as directed by the USEPA/OPP.

[9] **For the Dimethenamid Chronic Value,** the MPCA has calculated a non-promulgated criterion for aquatic plants using two point estimates of toxicity to the vascular plant duckweed.

[10] **Value calculated by the MDA,** in the absence of an applicable USEPA/OPP reference value(s) for a pesticide compound, the MDA calculated the value from USEPA/OPP toxicity data.