2022 Surface Water Pesticide Monitoring Program Annual Report

ANNUAL REPORT

Wisconsin Department of Agriculture, Trade and Consumer Protection
Agricultural Resource Management Division
Environmental Quality Unit
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Introduction

In 2022, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP), in cooperation with the Wisconsin Department of Natural Resources (DNR), continued the Surface Water Monitoring Program to document the effects pesticide use at nearby agricultural fields are having on water quality at 14 select Wisconsin rivers and streams, and three springs, for a total of 17 sampling locations. Surface water samples were collected between March and December and submitted to DATCP's Bureau of Laboratory Services (BLS) for chemical analysis. This document provides a narrative of the activities, summarizes the analytical data, and presents DATCP's proposed 2023 Surface Water Sampling Program plan.

A compilation of acronyms and definitions used throughout this document is provided in Appendix A – Acronyms and Definitions.

Purpose of Surface Water Sampling

It is estimated that agriculture contributes $104.8 billion annually to Wisconsin's economy (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2023a). Growers in Wisconsin use millions of pounds of pesticides and millions of tons of fertilizers annually to grow a wide variety of crops typically produced in one Wisconsin growing season. DATCP's Surface Water Sampling Program is one form of monitoring the agency performs to meet its statutory obligation to protect human health and the environment. Wisconsin's groundwater law, Chapter 160, Wis. Stats., requires state agencies to sample and monitor groundwater for substances related to facilities, activities, and practices under their jurisdiction that have a reasonable probability of entering the groundwater resources of the state, and to determine whether preventive action limits (PAL) or enforcement standards (ES) have been exceeded at points of standard application. The Legislative intent of the Chapter 160, Wis. Stats, also states that "a regulatory agency may take any actions within the context of regulatory programs established in statutes outside of this chapter, if those actions are necessary to protect public health and welfare or prevent a significant damaging effect on groundwater or surface water quality for present or future consumptive or non-consumptive uses." In light of this statement, and considering that groundwater and surface waters are highly interconnected, DATCP initiated the Surface Water Sampling Program to further evaluate the quality of the waters of the state, and to identify areas at risk for groundwater pollution. The Surface Water Sampling Program satisfies the following statutory monitoring requirement (Wis. Stats., Ch. §160.27):

1. Problem assessment monitoring, *to detect substances in the groundwater and to assess the significance of the concentrations of the detected substances*

The DATCP Surface Water Sampling Program was established in 2007 with the first monthly sampling occurring in 2008. Surface water samples are collected prior to the traditional pesticide application season (March and April), during the traditional pesticide application season (May, June, July), and after the traditional pesticide application season is over (August through December) to evaluate how the timing of pesticide application is related to surface water quality. During the 2022 sampling season, water samples were tentatively collected each month from selected rivers, streams, or springs and were dependent on ice conditions, laboratory availability, and sampler availability.

Selection Criteria and Sampling Procedures

Perennial streams and rivers selected for the annual sampling program have changed for multiple reasons in the past. Streams having a significant percentage of agricultural land in each watershed were selected for DATCP's program. Initially, streams were selected based on their inclusion in the DNR's "wadeable" stream sampling project (U.S. Environmental Protection Agency, 2016; Wisconsin Department of Natural Resources, 2015). Some years, the focus was sampling on rivers with large watersheds while others focused on streams with smaller watersheds.

Besides agricultural use, many criteria are considered when determining which flowing water body is to be included in the annual Surface Water Monitoring Program. Criteria are primarily based on local geology or environmental conditions, predominant crop types, or characteristics of the predominant pesticides used on crops in a given area. Criteria may vary from year to year. Some criteria examples used for river or stream sampling in the past have included:

- The stretch of water needs to be accessible for sampling (i.e., locations with public access);
- The watershed is within an area susceptible to groundwater contamination due to geologic conditions like sandy soils with shallow groundwater, shallow depth to bedrock, or karst features;
- Areas where prior testing by others (federal government, university, other state agencies, etc.) identified high concentrations of nitrate, pesticides, or other unusual test results;
- Areas where the same crops are grown year after year on the same fields/area (e.g., corn, cranberry, ginseng, etc.) increasing the likelihood of repetitive pesticide use in the area;
- Areas where crops are grown typically require extensive chemical or fertilizer inputs and/or irrigation;
- Areas where pesticides with known characteristics of high mobility and resistance to degradation are used; and/or
- At the request of one of the partnering agencies.

Over the years, the Surface Water Monitoring Program has evolved into a mix of 1) continuous monthly sampling of long-term repeat locations and 2) several "new" locations, added to the program each year. Program planning starts in the prior year, so sampling can start as soon as BLS completes annual maintenance and can accept samples, usually in February. Since DNR staff complete most of the sampling, time commitment and willingness to assist are necessary for the yearly program's planning and success. To this point, DATCP has not been limited in sampling selection locations based on this arrangement. Surface water program goals have been achieved through this collaborative effort.

2022 Program Locations

Since 2019, the program has generally consisted of collecting surface water samples from at least 10 locations; usually, 50% are repeat locations and 50% are new locations to the program. In 2022, most samples were collected at long-term repeat locations to continue to build the dataset and measure annual variability. Long-term repeat locations include the following:

- Fourteen Mile Creek at County Highway (CTH) D, within the Central Sands Region;
- Leola Ditch in the town of Aniwa, within the Central Sands Region
- Milwaukee River, within Estabrook Park in Milwaukee County
- Mississippi River at Lock and Dam #9
- Mormon Coulee Creek - Bridge #6 at County Rd (Road) YY in La Crosse County
- Nine Springs – Syene Spring
- Root River at 8-Mile Rd
- South Fork of the Bad Axe River
- Ten Mile Creek at Evergreen Rd, within the Central Sands Region
- West Branch of Sugar River at CTH PB
- Wisconsin River, near the city of Muscoda

While new locations for 2022 included:

- Nine Springs – Big Spring
- Nine Springs – Nursery Spring
- Pecatonica River at Martintown
- Rock River at Afton
- Wisconsin River, below Biron Dam
- Wisconsin River at Wisconsin Dells

A total of 14 perennial rivers and streams and three springs were selected for the 2022 sampling program. A total of 150 samples were collected between March and December for chemical analysis of pesticides and nitrate plus nitrite as nitrogen (N). This is the fourth consecutive year sampling the Syene Spring. In 2018, the Wisconsin Geologic and Natural History Survey (WGNHS) completed a study evaluating the water quality of Wisconsin's natural springs (Swanson, Graham, & Hart, An inventory of springs in Wisconsin , 2019).

Analytical results of water samples collected at Syene Springs indicated concerning concentrations of pesticides, specifically atrazine. This was of concern because the Syene Spring and most of its capture zone is likely located within an atrazine Prohibition Area (PA) (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2023b). Because atrazine is no longer used in this area, no atrazine detections would be expected in the area's surface or spring water. To further confirm the atrazine detection and identify potential trends, DATCP included this location in the surface water quality monitoring program between 2019 and 2022. Big Spring and Nursery Spring were also included in the 2022 Surface Water Sampling Program to better understand the detection of pesticides in the Syene Spring. Big Spring, Nursery Spring, and Syene Spring are formed by the presence of bedding-plane fractures within the Tunnel City Group (Swanson, Bahr, Bradbury, & Anderson, 2006). Big Spring and Nursery Spring are located southwest of Syene Spring. Since groundwater generally flows from SW to NE in the area (Bradbury & Parsen, 2016), then Big Spring and Nursery Spring are likely located upstream of Syene Spring.

The Pecatonica River and Rock River stations underwent sampling in 2014 and 2013, respectively. The 2022 sampling effort was intended to further evaluate trends in pesticide concentration over time.

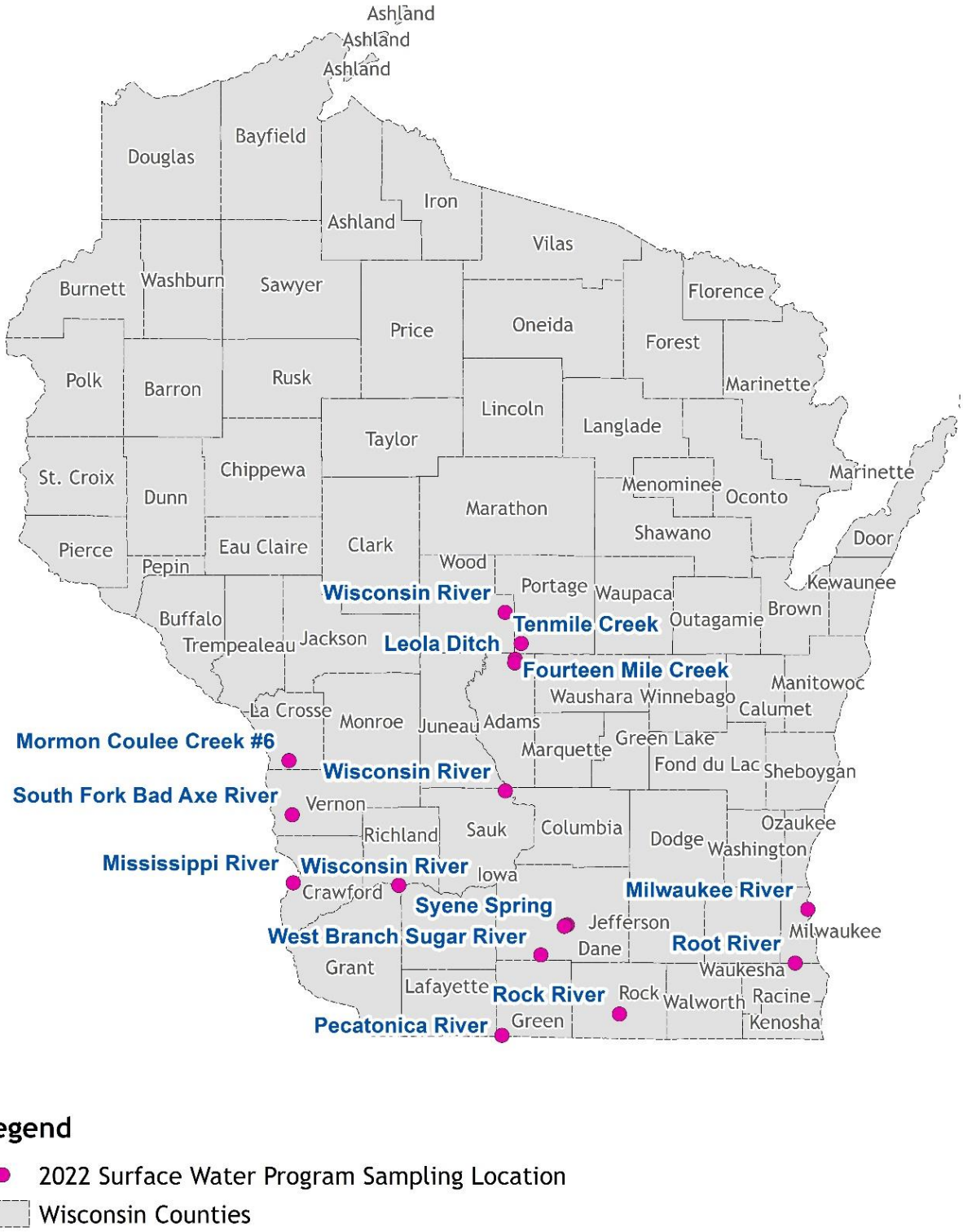
Table 1 lists the 2022 surface water sampling program locations, and Figure 1 shows the 17 locations relative to the State of Wisconsin and county boundaries. Table 2 summarizes the watershed size and simplified land use specific to each 2022 sampling location, using data provided by the U.S. Department of Agriculture's (USDA) Agricultural Statistics Service (United States Department of Agriculture, 2022).

Table 1: 2022 Surface Water Sampling Program Rivers and Streams

River / Stream Name	SWIMS ID	County	Program Years
Fourteen Mile Creek at CTH D	013173	Adams	6
Leola Ditch at Aniwa	10009165	Adams	6
Milwaukee River within Estabrook Park	413640	Milwaukee	10
Mississippi River at Lock & Dam #9	123016	Crawford	10
Mormon Coulee Creek - Bridge #6 at County Rd YY	10008928	La Crosse	2
Nine Springs – Syene Spring	10051662	Dane	4
Nine Springs – Big Spring	10051661	Dane	1
Nine Springs – Nursery Spring	10051660	Dane	1
Pecatonica River at Martintown	233002	Green	2
Rock River at Afton	543001	Rock	2
Root River at 8-Mile Rd	10039425	Racine	5
South Fork of the Bad Axe River	10022633	Vernon	2
Ten Mile Creek at Evergreen Rd	10016427	Portage	8
West Branch of Sugar River at CTH PB	10017221	Dane	5
Wisconsin River, near Muscoda	223282	Grant	10
Wisconsin River, below Biron Dam	10031139	Wood	1
Wisconsin River at Wisconsin Dells	573052	Sauk	1

Notes: SWIMS – Surface Water Integrated Monitoring System

Figure 1: 2022 Surface Water Sampling Program Rivers, Streams, and Spring Locations



Legend

- 2022 Surface Water Program Sampling Location
- Wisconsin Counties

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Table 2: 2022 Surface Water Sampling Program Rivers and Streams Land Use Summary and Watershed Size in Acres

River/Stream Name	Developed or Open	Wetland	Forest	Corn	Alfalfa, Grass, or Pasture	Soy or Dry Beans	Potatoes	Watershed or HUC10 Size (Acres)
Fourteen Mile Creek and Leola Ditch	5,243 9.5%	6,869 12.4%	16,589 29.9%	3,448 6.2%	8,147 14.7%	4,192 7.6%	4,988 9.0%	55,472
Milwaukee River	55,942 52.6%	13,351 12.6%	8,095 7.6%	6,786 6.4%	14,388 13.5%	4,144 3.9%	0 0.0%	106,259
Mississippi River	3,858 9.5%	4,041 9.9%	17,773 43.6%	2,551 6.3%	5,106 12.5%	1,536 3.8%	1 0.002%	40,778
Mormon Coulee Creek	3,985 6.0%	4,604 6.9%	25,282 38.1%	3,875 5.8%	9,881 14.9%	2,994 4.5%	0 0.0%	66,412
Pecatonica River	6,687 8.18%	914 1.12%	9,826 12.02%	23,327 28.54%	27,882 34.12%	11,537 14.12%	2 0.002%	81,729
Rock River	11,945 19.2%	1628 2.6%	7,092 11.4%	16,559 26.6%	7,682 12.3%	13,610 21.9%	4 0.01%	62,214
Root River	40,763 48.26%	6,608 7.82%	8,592 10.17%	7,162 8.48%	8,759 10.37%	8,377 9.92%	0 0.00%	84,458
South Fork of Bad Axe River	7,776 6.5%	871 0.7%	48,063 39.9%	17,507 14.5%	31,650 26.3%	12,222 10.2%	0 0.0%	120,345
Big Spring, Nursery Spring and Syene Spring	Size of the capture zone is unknown							
Ten Mile Creek	5,300 5.4%	6,103 6.2%	23,625 24.1%	15,960 16.3%	15,257 15.6%	13,715 14.0%	8348 8.5%	97,975
West Branch of Sugar River	3,017 7.0%	593 1.4%	9,277 21.7%	9,348 21.8%	14,437 33.7%	5,444 12.7%	1 0.002%	42,848
Wisconsin River Wisconsin Dells	15,970 9.8%	20,525 12.6%	65,139 40.0%	18,987 11.7%	21,121 13.0%	11,903 7.3%	860 0.5%	162,893
Wisconsin River Biron Dam	15,263 12.6%	30,558 25.2%	34,909 28.8%	7,278 6.0%	13,603 11.2%	4,885 4.0%	2,018 1.7%	121,278
Wisconsin River near Muscoda	6,411 5.9%	13,525 12.5%	47,504 44.0%	9,853 9.1%	19,868 18.4%	4,967 4.6%	9 0.01%	97,975

Sample Collection and Analysis

Surface water samples are collected using DNR standard protocols (Wisconsin Department of Natural Resources, 2018) and DATCP standard operating procedures (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2021), designed to collect surface water samples unbiasedly with respect to flow, weather, and other factors. Each sample was collected in free-flowing, well-mixed areas of the rivers, streams, and springs.

Surface water samples were collected by directly filling one laboratory-provided, one-liter, amber-colored glass sampling bottle at the designated sampling location. Bottles were then placed in a cooler on ice along with a properly completed sample collection form. Packages were shipped to BLS using an overnight delivery service or hand delivered to BLS. There were no reported shipping issues or bottle breakages with the 2022 program. A summary of the analytical data for the 2022 program is included in Appendix B. Raw data can be downloaded through the EPA Water Quality Portal or by scanning the QR code at the end of Appendix B.

BLS performed surface water analytical testing using GC/MS/MS and LC/MS/MS methods in accordance with ISO 17025 accreditation standards. Each sample was tested for 108 pesticides or pesticide metabolites, and nitrate plus nitrite as N. The table in Appendix B lists the parameters and corresponding laboratory reporting limits. The laboratory reporting limit is the minimum analyte concentration that can be reliably quantified and reported by the laboratory. If the concentration of a certain compound is reported to be less than the respective laboratory reporting limit, we consider the compound ***not detected*** in the water sample. If the concentration of a certain compound is reported to be greater than the respective laboratory reporting limit, we consider the compound ***detected*** in the water sample. Appendix B includes the list of the compounds we test for and the respective laboratory reporting limits. We are unable to determine if the water samples contain other compounds than the ones listed in Appendix B.

Results

A total of 150 surface water samples were collected and submitted for chemical analysis as a part of the DATCP's 2022 Surface Water Sampling Program. The table in Appendix B summarizes the 2022 Surface Water Sampling Program results and provides comparative risk values. The surface water data is compared to benchmark values to assess the potential risk to human health and the environment. The risk values are sourced from the Wisconsin Administrative Code (Wis. Admin. Code) Ch. NR 140 public health groundwater quality standards[1] (NR 140.10 – Table 1), drinking water health advisory recommendations by the Wisconsin Department of Health Services (DHS), and a listing of the US Environmental Protection Agency (EPA) Office of Pesticide Programs - Aquatic Life Benchmarks for Registered Pesticides.

Summary

The following bulleted items are a summary of the sampling results. A detailed narrative for the 2022 data follows.

Detections of Pesticides

- Of the 108 pesticide analytes included in the laboratory testing methods, 31 were detected in 2022 surface water samples. Detections include 17 herbicides, 10 herbicide metabolites, and four insecticides.
- At least one pesticide analyte was detected in every surface water location for every monthly sampling event.

[1] An essential part of Wisconsin's groundwater protection laws was the creation of water quality standards for different substances, outlined in Wis. Admin. Code Chapter NR 140. The DNR sets standards for substances of public health concern based on recommendations from DHS. The groundwater standards have two components: an enforcement standard (ES) and a preventative action limit (PAL). The ES is a concentration that, if exceeded requires intervention from the appropriate authority. The PAL is a percentage of the ES; 10% of the ES for carcinogenic, mutagenic, or teratogenic properties, and 20% of the ES for the remaining substances. The intention of the PAL is for it to act as a trigger for intervention before a pollutant becomes a serious risk to public health or the environment.

- The maximum number of pesticides detected in a single sample was 16 individual compounds (from Fourteen Mile Creek at CTH D).
- Metolachlor ethane sulfonic acid (ESA) was the most detected compound. It was identified in 99% of samples collected.
- Alachlor ESA was the second most detected compound, in 58% of the samples, and de-ethyl atrazine was the third most detected, in 49% of the samples.
- Atrazine Total Chlorinated Residue (TCR), i.e. the sum of atrazine parent material and its breakdown products (de-ethyl atrazine, de-isopropyl atrazine, and diamino atrazine), was detected in 53% of the samples collected.
- More pesticide analytes per sample were detected in June compared to any other month. June coincides with the primary pesticide application month for the growing year. These results are consistent with prior annual surface water sampling results.
- The consistent detection of pesticides throughout the calendar year suggests that most pesticides detected in surface water are likely the result of a steady baseline groundwater discharge to surface water bodies rather than overland flow.
- In 2022, neonicotinoid compounds were detected at the stations within the Central Sands Region (Fourteen Mile Creek, Leola Ditch, and Ten Mile Creek) and also at stations along for the Milwaukee River, Mississippi River, Pecatonica River, Rock River, Root River, Syene Spring, South Fork of Bad Axe River, and West Branch of the Sugar River. Neonicotinoids were detected at a higher number of stations in 2022 compared to prior years.
- Analytical data associated with the surface water samples collected at the Driftless Area streams indicate that surface runoff likely contributes to the seasonal-high pesticide concentrations at the Mormon Coulee Creek station. The consistent pesticide concentrations in surface water samples from the South Fork of the Bad Axe River likely represent the base flow of contaminants from groundwater discharge.

Exceedance of Aquatic Life Benchmarks

EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides in freshwater were exceeded for three compounds:

- Imidacloprid was detected in 13 samples collected in 2022 at the Fourteen Mile Creek (March, June, and July), Milwaukee River (July), Root River (May, June, and July), South Fork of Bad Axe River (November), and Ten Mile Creek (from March to July), at concentrations ranging from 0.0122 to 0.0641 µg/L. These concentrations exceed the Chronic Exposure value of 0.01 µg/L for Invertebrates.
- Clothianidin was detected in exceedance of the Chronic Exposure value of 0.05 µg/L for Invertebrates in four samples collected at the Fourteen Mile Creek (June and July) and Leola Ditch (April and June).
- Linuron was detected in exceedance of the Chronic Exposure value of 0.09 µg/L for Invertebrates in one sample collected at the Fourteen Mile Creek.

Exceedance of Drinking Water Standards

- Each monthly sample collected at Syene Spring exceeded the Wis. Admin. Code Ch. NR 140 Enforcement Standard (ES) of 10 mg/L for nitrogen.
- The Wis. Admin. Code Ch. NR 140 Preventive Action Limit (PAL) of 0.3 µg/L for atrazine TCR was exceeded in 28 samples. These samples were collected at the Big Spring, Nursery Spring, Syene Spring, Milwaukee River, Mississippi River, Pecatonica River, Rock River, and the West Branch of the Sugar River.

2022 Precipitation Measurements

Greater surface runoff usually correlates well with heavy precipitation events, especially when the ground surface is exposed due to a lack of vegetation and where the surficial soil is poorly drained. Variations in precipitation and surface runoff rates could result in fluctuations in pesticide concentrations found in surface

water. Surface runoff may decrease or increase the likelihood of detecting pesticides in surface water. If surface runoff occurs during the traditional pesticide application season, a peak in pesticide concentration may be expected in surface waters downward of agricultural fields. Conversely, if surface runoff occurs outside the traditional pesticide application season, it may dilute concentrations of pesticides.

Wisconsin averages 34.12 inches of precipitation annually (average period 1991-2020). In 2022, the state of Wisconsin as a whole experienced below-average precipitation levels (32.2 inches) (NOAA National Centers for Environmental information, 2023a). However, the annual average precipitation for 2022 was higher than 2021 (29.9 inches).

Figure 2 shows the statewide monthly precipitation departures from the historic normal (Wisconsin State Climatology Office, 2023). March, April, August, November, and December of 2022 showed a positive departure from the average, indicating an increase in precipitation ranging from 0.2 to 1.4 inches above normal (1991-2020 period). On the contrary, January, February, May, June, July, September, and October showed a negative departure of -0.1 to -1.8 inches below-average, indicating a decrease in precipitation. It appears that greater-than-average precipitation occurred in the spring right before the usual pesticide application season and in August during the growing season. The remainder of the year was characterized by below-average precipitation in June, July, September, and October followed by above normal precipitation in November and December.

Figure 2: 2022 Monthly Precipitation Departures from 1991-2020 Average

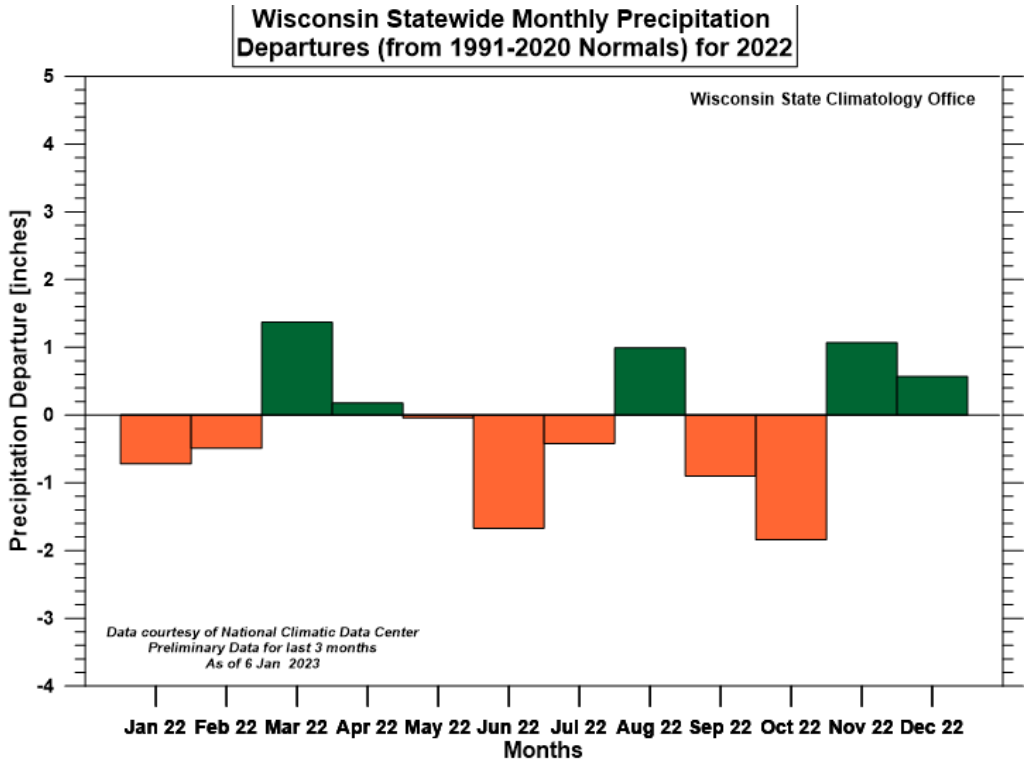


Figure 3 shows the total accumulated precipitation mapped across Wisconsin (Wisconsin State Climatology Office, 2023). As shown, there was a relatively even distribution of rainfall across the state in 2022, with precipitation ranging between 30 and 40 inches, while a few parts of the northwest and central regions of the state accumulated between 25 and 30 inches. Portions of Lafayette County and Green County in the southern region of the state accumulated the highest precipitation (above 40 inches). Southern Wisconsin generally experienced an increase in total precipitation compared to 2021. Most of the DATCP 2022 Surface Water Program sampling sites are located in the southern half of Wisconsin.

Figure 3: Accumulated Precipitation from the Wisconsin Monthly Climate Watch Archive

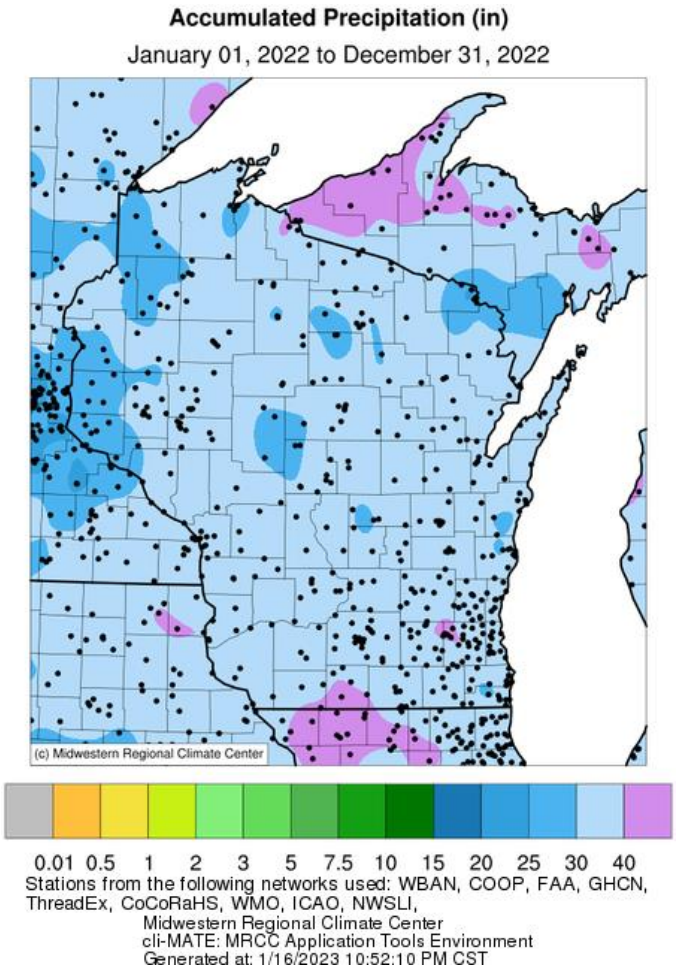


Figure 4 shows the 2022 precipitation departures, sourced from the Wisconsin State Climatology Office (Wisconsin State Climatology Office, 2023). Positive deviations, depicted in green, signify regions where the annual precipitation exceeded the average. Conversely, negative departures, depicted in yellow and orange, highlight areas with precipitation below average. Apart from isolated regions in eastern, northern, and southern Wisconsin, the state's overall precipitation either matched or exceeded the 1991-2020 norm.

According to the NOAA Storm Events Database (NOAA National Centers for Environmental Information, 2023b), the period from January to March was marked by a series of heavy snowfalls across Wisconsin. The northern regions of the state continued to experience significant snowfall even extending into April. Flood and flash floods were recorded from March to May in several regions of the state. Drought conditions were recorded mostly from January to April, in northern and southern Wisconsin. The overall drought extent in 2022 exhibited a decrease compared to 2021, with 42.79% of the state categorized as abnormally dry (D0) and 7.74% as experiencing moderate drought, as per the NOOA - National Oceanic and Atmospheric Administration (2023). A summary of the total annual and monthly precipitation in the counties where samples were collected in the 2022 program is shown on Figure 5. The various colors indicate the monthly precipitation totals at each location (NOAA National Centers for Environmental information, 2023a). It can be observed on Figure 5 that La Crosse, Adams, and Wood counties experienced lower accumulated precipitation relative to the rest of the counties across the state, with a majority of precipitation accumulated throughout the summer.

Figure 4: Wisconsin Accumulated Precipitation Departures from Normal

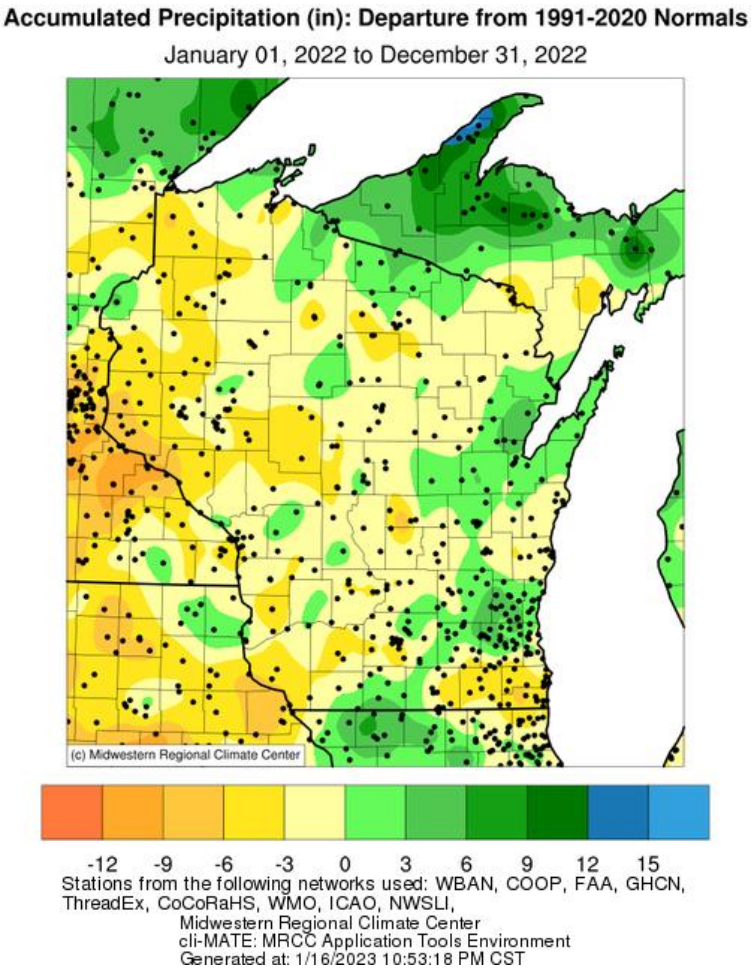
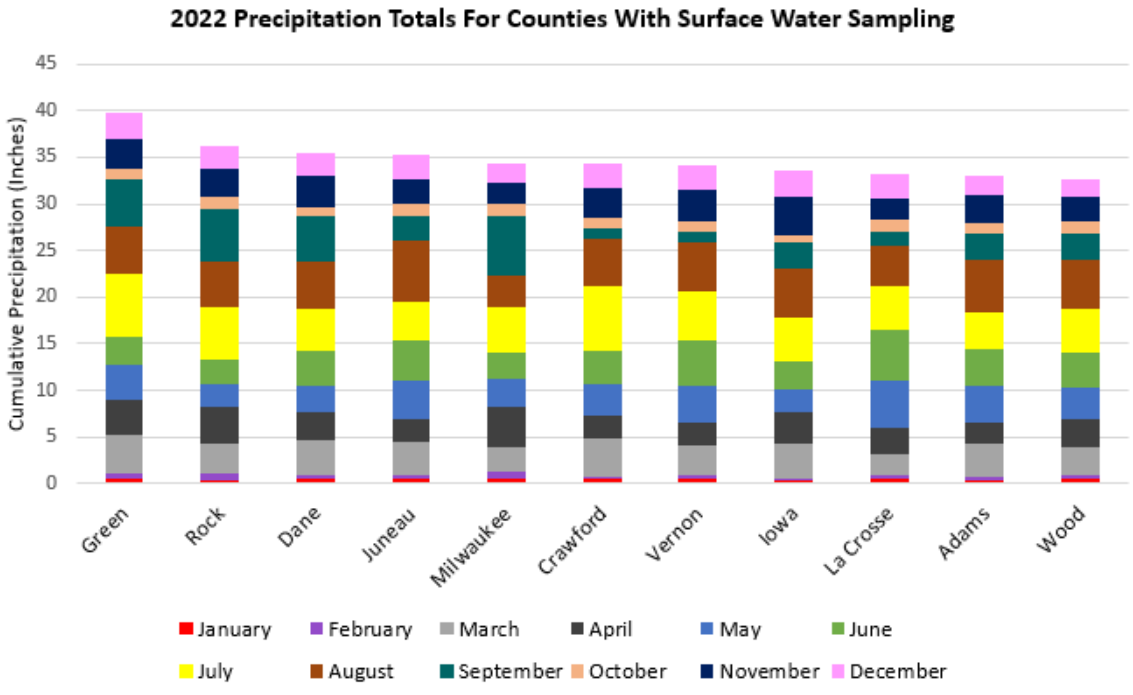


Figure 5: Accumulated Precipitation in the Counties Where Surface Water Samples Were Collected



Pesticide Detection Rates

Of the 109 analytes included in DATCP's Surface Water Sampling Program testing methodology, 31 different pesticide compounds were detected in 2022, considering all sampling sites. In 2021, 29 different pesticides were instead detected. In 2022, the herbicides bromacil, linuron, MCPA, and mesotrione were detected for the first time in the DATCP Surface Water Sampling Program. Table 3 shows the compounds detected in 2021, but not in 2022, and vice versa.

Table 3: Pesticides Detected in 2021 or in 2022 and the Sampling Sites Where the Compounds Were Detected

Pesticide Name	2021	2022	Sites Where Detected
Acifluorfen	x	--	Mormon Coulee Creek*
Dacthal Di-Acid	x	--	Ten Mile Creek (South Branch)
Trifluralin	x	--	Mormon Coulee Creek*
Alachlor OA	x	--	Ten Mile Creek (Ditch 5 and South Branch)
Metalaxyl	x	--	Ten Mile Creek (Ditch 5, North Branch at Isherwood*, and South Branch)
Acetochlor OA	--	x	Rock River
Bromacil	--	x	Wisconsin River, near Muscoda*
Clopyralid	--	x	Nursery Spring
Fomesafen	--	x	Rock River*, Wisconsin River at Wisconsin Dells
Linuron	--	x	Fourteen Mile Creek*
MCPA	--	x	Root River*, Milwaukee River*
Mesotrione	--	x	Leola Ditch*
Sulfentrazone	--	x	Root River*

Notes: *--: Indicates that the compound has not been detected for that year*
x: Indicates that the compound has been detected for that year
**: Indicates that the site has been sampled in both years, 2021 and 2022*

Figure 6 shows the pesticide detection rates[2] in percentage for 2022 and 2021 (empty bars). Only pesticides detected at a rate higher than 10% in 2022 are shown. As shown on Figure 6, the detection rates for most of the detected pesticides were higher in 2022 compared to 2021, with the exception of acetochlor ESA, de-ethyl atrazine, and atrazine TCR. By comparing the summarized land use in 2021 and 2022, it can be noticed that the difference in the percentage of each land use type for same watershed is less than 2% (Table 2 of Wisconsin Department of Agriculture, Trade and Consumer Protection, 2023c, and Table 2 of this manuscript). Assuming, therefore, that pesticide application rate and use did not change between 2022 and 2021, higher precipitation in 2022 may have influenced surface water results by increasing surface runoff and increasing pesticide infiltration, groundwater recharge, and subsequent discharge into surface water. Differences in compounds detected and detection rates may also be related to the fact that six locations sampled in 2022 were not sampled in 2021.

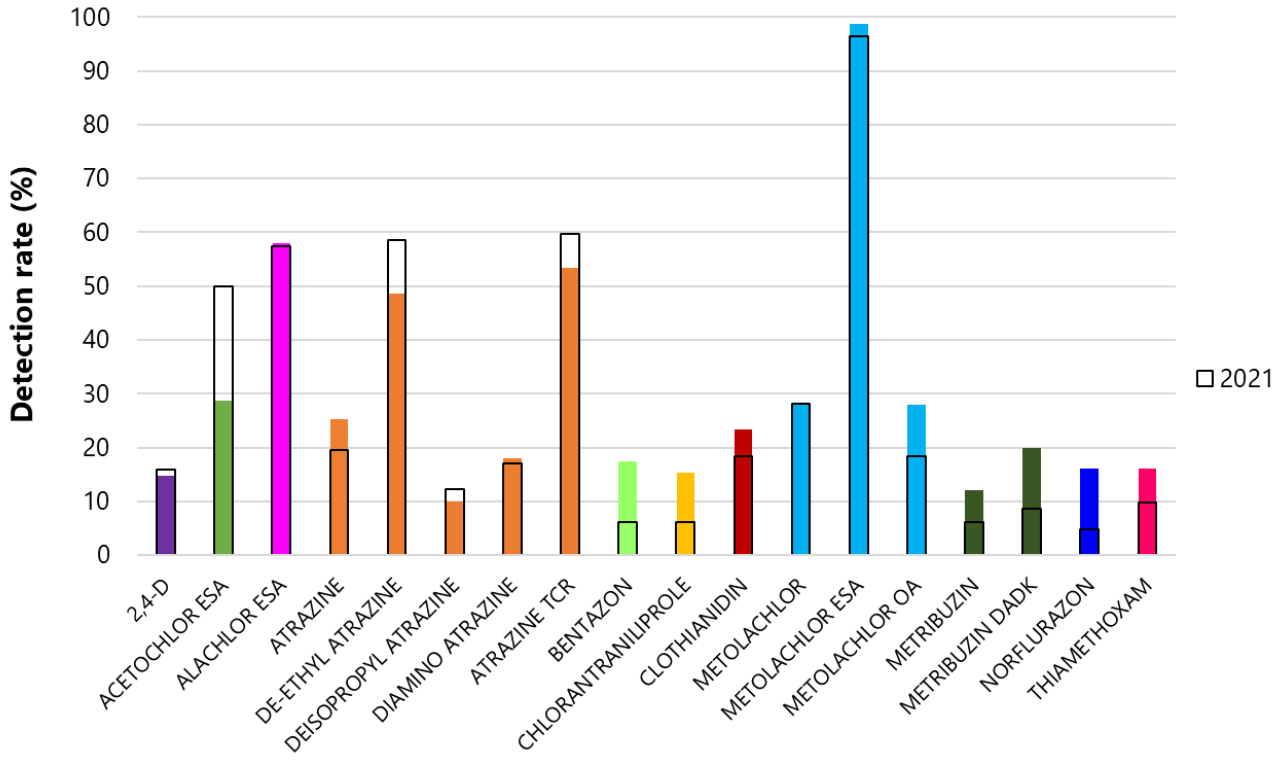
The most frequently detected pesticide analyte was metolachlor ESA. This is a breakdown product of metolachlor, an active ingredient in corn herbicides such as Dual, Halex GT, Lumax, and many others (Kelly Solutions, 2023). Metolachlor ESA concentrations were detected in about 99% of the samples collected.

[2] The detection rate (%) is calculated as follow: $\frac{number\ of\ detects}{total\ number\ of\ samples}\ x\ 100$

Alachlor ESA, was the second most frequently detected compound, with a detection rate of 58%. De-ethyl atrazine, an atrazine metabolite was the third most frequently detected compound, with a detection rate of 49%.

Similar compounds were also found in groundwater, as reported in the DATCP 2017 statewide survey report (Wisconsin Department of Agriculture & United States Department of Agriculture, 2017). Metolachlor ESA is historically the most widely reported pesticide detected in private potable wells, with a detection rate of 32%. According to the DATCP 2017 statewide survey report, the second most detected compound is alachlor ESA, a metabolite of alachlor, with a detection rate of 21.5 %.

Figure 6: Pesticides Detection Rates in the 2022 Samples vs 2021 Samples (Includes the Analytes Detected in More Than 10% of the Samples in 2022)



Notes: Atrazine TCR - Total chlorinated residues of atrazine includes the sum of atrazine plus its metabolites de-ethyl atrazine, deisopropyl atrazine, and diamino atrazine (only analytes detected in over 10% of samples are shown).

Monthly Pesticide Detections

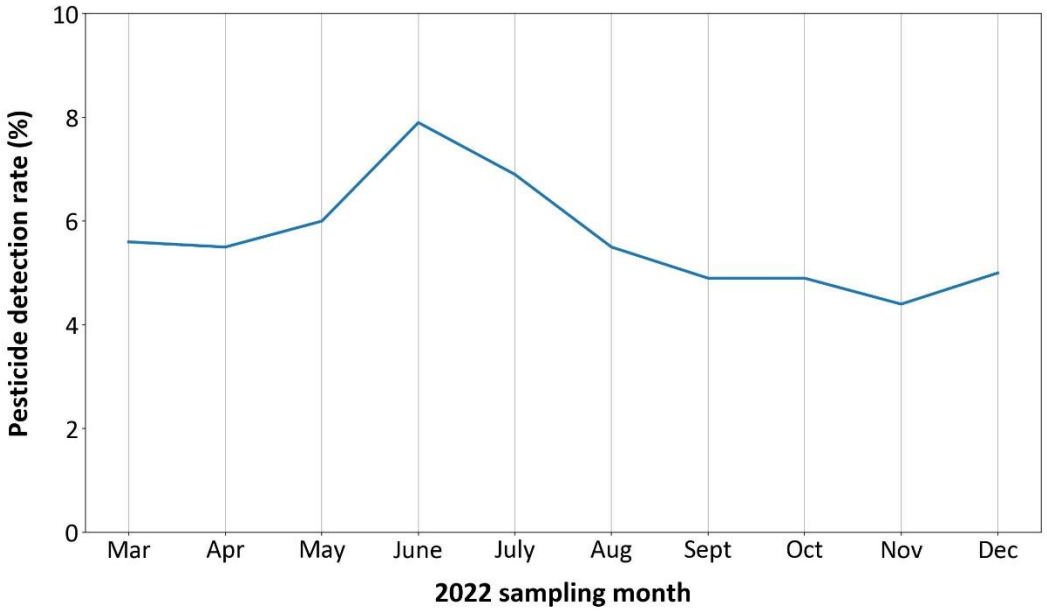
One of the program's objectives is to evaluate the relationship between pesticide application and seasonal effects on surface water quality. Monthly pesticide data were evaluated to determine if concentrations are influenced by seasonal surface water flows or groundwater/aquifer discharge (base flow). A seasonal flow would have the analyte concentrations fluctuating throughout the year, with the greatest concentrations in the surface water during the pesticide application months (May through August), followed by a decline in the following months (September through October). Then, a continued decline over the winter months until the cycle is repeated during the next application season. A baseline aquifer flow would likely exhibit a consistent number of analytes and steady concentrations throughout the year. The baseline flow would reflect pesticide concentrations within the watershed aquifer that discharges to surface water throughout the year.

Figure 7 shows that overall pesticides are detected in surface water throughout the year, even after pesticide applications are limited. This, and the fact that similar pesticides are detected in surface water and groundwater (see section above), suggests that groundwater discharge plays an important role in

pesticide detections in surface waters. The greatest rate of pesticides detected was observed in June, during peak pesticide application season, with detection rates attenuating in the following months of July and August. Natural groundwater recharge is not usually pronounced during the summer, and a higher rate of pesticide discharge into surface water may have been limited in June. The fast response in the surface water system due to pesticide application suggests that the peak in pesticides detected in June may be related to surface runoff at some of the stations. A possible reduction in pesticide applications and higher-than-average precipitation in August (Figure 2) likely contributed to the declining trend in pesticide detections in July and August.

As demonstrated in the subsequent sections, the detection of compounds outside the designated application season exhibits variability not only from one site to another but also depends on the specific compounds under consideration.

Figure 7: Average Rate of Pesticide Detections per Sample by Month



Notes: No surface water samples were collected in January or February due to the lab closing for annual maintenance.

The following is a compilation of pesticides that have been consistently detected in multiple instances and detected outside the pesticide application season. These instances likely indicate the baseline aquifer flow for the respective locations:

- Fourteen Mile Creek
  - Alachlor ESA concentrations ranged from 0.242 to 0.667 µg/L for the year;
  - Bentazon concentrations ranged from 0.0587 to 0.24 µg/L for the year;
  - Chlorantraniliprole concentrations ranged from 0.0672 to 0.432 µg/L for the year;
  - Clothianidin concentrations ranged from 0.0101 to 0.0833 µg/L for six of the 10 samples from March to August;
  - Metolachlor concentrations ranged from 0.0601 to 0.292 µg/L for six of the 10 samples from March to August;
  - Metolachlor ESA concentrations ranged from 1.57 to 3.92 µg/L for the year;
  - Metolachlor OA concentrations ranged from 0.777 to 2.28 µg/L for the year;
  - Metribuzin DADK concentrations ranged from 0.561 to 0.816 µg/L for the year;
  - Norflurazon concentrations ranged from 0.0507 to 0.385 µg/L for nine of the 10 samples collected (no detection in November);
  - Thiamethoxam concentration ranged from 0.0288 to 0.275 µg/L for six of the 10 samples from March to August.

- Leola Ditch
  - Alachlor ESA concentrations ranged from 0.176 to 1.22 µg/L for the year;
  - Bentazon concentrations ranged from 0.0592 to 0.188 µg/L for seven of the 10 samples collected (detected from May to December, except in September);
  - Chlorantraniliprole concentrations ranged from 0.0523 to 0.32 µg/L for seven of the 10 samples collected (detected from March to September);
  - Clothianidin concentrations ranged from 0.0102 to 0.0672 µg/L for seven of the 10 samples collected (detected from March to October, except in September);
  - Metolachlor ESA concentrations ranged from 1.13 to 3.46 µg/L for the year;
  - Metolachlor OA concentrations ranged from 0.58 to 1.68 µg/L for the year;
  - Metribuzin concentrations ranged from 0.0502 to 0.0795 µg/L for seven of the 10 samples collected (detected in May and then from July to December).
  - Metribuzin DADK concentrations ranged from 0.367 to 0.957 µg/L for the year;
  - Norflurazon concentration ranged from 0.0699 to 1.81 µg/L for seven of the 10 samples collected (detected from March to September); and
  - Thiamethoxam concentrations ranged from 0.0235 to 0.208 µg/L for nine of the 10 samples collected (no detections in November).
- Milwaukee River at L & D #9
  - Metolachlor ESA concentrations ranged from 0.0611 to 0.311 µg/L for nine of the 10 samples collected (no detections in March).
- Mississippi River
  - Acetochlor ESA concentrations ranged from 0.0533 to 0.177 µg/L for seven of the 10 samples collected (from April to October); and
  - Metolachlor ESA concentrations ranged from 0.161 to 0.298 µg/L for nine of the 10 samples collected (no detections in April).
- Mormon Coulee Creek
  - De-ethyl atrazine concentrations ranged from 0.0703 to 0.109 µg/L for nine of the 10 samples collected (no detections in December); and
  - Metolachlor ESA concentrations ranged from 0.106 to 0.168 µg/L for nine of the 10 samples collected (no detections in December).
- Pecatonica River
  - Clothianidin concentrations ranged from 0.0534 to 0.108 µg/L for eight of the 10 samples collected (from March to September and in December);
  - De-ethyl atrazine concentrations ranged from 0.0518 to 0.0838 µg/L for nine of the 10 samples collected (no detections in March); and
  - Metolachlor ESA concentrations ranged from 0.453 to 0.662 µg/L for the year.
- Rock River
  - Acetochlor ESA concentrations ranged from 0.0556 to 0.285 µg/L for nine of the 10 samples collected (no detections in May);
  - Acetochlor ESA concentrations ranged from 0.0504 to 0.0952 µg/L for nine of the 10 samples collected (no detections in September);
  - Metolachlor ESA concentrations ranged from 0.373 to 0.953 µg/L for the year.
- Root River
  - 2,4-D concentrations ranged from 0.0865 to 0.481 µg/L for six of the 10 samples collected (detected in April, May, July, August, September, and November); and
  - Metolachlor ESA concentrations ranged from 0.118 to 0.353 µg/L for six of the 10 samples collected (detected in April, May, June, September, November, and December).
- South Fork of Bad Axe River

  - Alachlor ESA concentrations ranged from 0.0757 to 0.099 µg/L for nine of the 10 samples collected (no detections in December);
  - De-ethyl atrazine concentrations ranged from 0.0804 to 0.1 µg/L for nine of the 10 samples collected (no detections in December); and
  - Metolachlor ESA concentrations ranged from 0.101 to 0.128 µg/L for nine of the 10 samples collected (no detections in December).
- Syene Spring is a natural groundwater discharge and hence it's strictly a representation of the groundwater quality of the area. Below are the pesticides detected in Syene Spring:
  - Acetochlor ESA concentrations ranged from 0.0857 to 0.104 µg/L for the year;
  - Alachlor ESA concentrations ranged from 0.866 to 0.976 µg/L for the year;
  - Atrazine concentrations ranged from 0.0652 to 0.081 µg/L for the year;
  - De-ethyl atrazine concentrations ranged from 0.147 to 0.174 µg/L for the year;
  - Deisopropyl atrazine concentrations ranged from 0.0753 to 0.0859 µg/L for the year;
  - Diamino atrazine concentrations ranged from 0.398 to 0.448 µg/L for the year;
  - Metolachlor concentrations ranged from 0.0567 to 0.0774 µg/L for the year;
  - Metolachlor ESA concentrations ranged from 1.96 to 2.3 µg/L for the year; and
  - Metolachlor OA concentrations ranged from 0.279 to 0.335 µg/L for the year.
- Ten Mile Creek
  - Alachlor ESA concentrations ranged from 0.252 to 0.377 µg/L for the year;
  - Bentazon concentrations ranged from 0.0503 to 0.135 µg/L for nine of the 10 samples collected (no detections in April);
  - Metolachlor ESA concentrations ranged from 1.21 to 1.86 µg/L for the year;
  - Metolachlor OA concentrations ranged from 0.686 to 1.05 µg/L for the year;
  - Metribuzin concentrations ranged from 0.112 to 0.174 µg/L for the year;
  - Metribuzin DA concentrations ranged from 0.105 to 0.14 µg/L for seven of the 10 samples collected (no detections in April, May, and November);
  - Metribuzin DADK concentrations ranged from 0.481 to 0.725 µg/L for the year;
  - Norflurazon concentration ranged from 0.0519 to 0.613 µg/L for eight of the 10 samples collected (no detections in September and November); and
  - Thiamethoxam concentrations ranged from 0.0133 to 0.112 µg/L for nine of the 10 samples collected (no detections in November).
- West Branch of Sugar River
  - Acetochlor ESA concentrations ranged from 0.0544 to 0.0876 µg/L for nine of the 10 samples collected (no detections in August);
  - Alachlor ESA concentrations ranged from 0.0516 to 0.0635 µg/L for eight of the 10 samples collected (no detections in July and August);
  - De-ethyl atrazine concentrations ranged from 0.0624 to 0.0785 µg/L for the year;
  - Diamino atrazine concentrations ranged from 0.181 to 0.26 µg/L for the year; and
  - Metolachlor ESA concentrations ranged from 4.43 to 5.88 µg/L for the year.
- Wisconsin River below Biron Dam
  - Metolachlor ESA concentrations ranged from 0.0913 to 0.177 µg/L for the year.
- Wisconsin River near Muscoda
  - Alachlor ESA concentrations ranged from 0.0577 to 0.0906 µg/L for the year for eight of the 10 samples collected (no detections in April and May); and
  - Metolachlor ESA concentrations ranged from 0.204 to 0.327 µg/L for the year.
- Wisconsin River at Wisconsin Dells
  - Alachlor ESA concentrations ranged from 0.0532 to 0.0668 µg/L for the year for four of the 10 samples collected (detected in July, September, October, and December); and

- Metolachlor ESA concentrations ranged from 0.174 to 0.275 µg/L for the year.

Comparison to Standards

Detected pesticide concentrations identified during DATCP's 2022 Surface Water Sampling Program were compared to the following three published environmental surface water/groundwater quality standards:

- EPA's Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides for freshwater;
- Wis. Admin. Code Ch. NR 140 – ES and PAL for drinking water; and
- DHS drinking water health advisories (for some pesticides, whenever ES and PAL are not established).

The table in Appendix B provides the three standards alongside the range of the detected pesticide analyte concentrations identified as part of the 2022 Surface Water Sampling Program. As labeled in the Appendix B table, several pesticides and their metabolites do not have aquatic life benchmarks (17 out of 109) or established Wis. Admin. Code NR 140 ES and PAL standards (79 out of 109). DHS currently has drinking water health advisory recommendations for an additional 15 pesticides.

EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides for freshwater were exceeded for three compounds as follows:

- Clothianidin
  - In four samples collected at the Fourteen Mile Creek and the Leola Ditch, clothianidin was detected at concentrations ranging from 0.0517 to 0.0833 µg/L, which exceeds the 0.05 µg/L value for chronic exposure on invertebrates;
- Imidacloprid
  - In 13 samples collected at the Fourteen Mile Creek, Milwaukee River, Root River, South Fork of Bad Axe River, and Ten Mile Creek, imidacloprid was detected at concentrations ranging from 0.0122 to 0.0641 µg/L, which exceeds the 0.01 µg/L value for chronic exposure on invertebrates.
- Linuron
  - In one sample collected at the Fourteen Mile Creek, linuron was detected at a concentration of 0.144 µg/L, which exceeds the 0.09 µg/L value for chronic exposure on invertebrates.

No pesticides or pesticide metabolites were detected at concentrations exceeding existing Wis. Admin. Code Ch. NR 140 ES values. The Wis. Admin. Code Ch. NR 140 PAL standard was exceeded for one compound in 28 samples as follows:

- Atrazine TCR (Wis. Admin. Code Ch. NR 140 PAL = 0.3 µg/L)
  - In June, atrazine TCR was detected at a concentration of 0.5607 µg/L at the Milwaukee River;
  - In June and July, atrazine TCR was detected at concentrations between 0.3321 and 0.4545 µg/L at the Mississippi River;
  - In September, November, and December, atrazine TCR was detected at concentrations between 0.4255 and 0.5545 µg/L at the Big Spring. This spring was only sampled in September, November, and December;
  - In September, November, and December, atrazine TCR was detected at concentrations between 0.4353 and 0.4717 µg/L at the Big Spring. This spring was only sampled in September, November, and December;
  - In June, atrazine TCR was detected at a concentration of 0.3021 µg/L at the Pecatonica River;
  - In June and July, atrazine TCR was detected at concentrations between 0.496 and 1.256 µg/L at the Rock River;
  - From March to December, atrazine TCR was detected at concentrations between 0.6904 and 0.7742 µg/L at Syene Spring;
  - In May, June, August, September, November, and December, atrazine TCR was detected at concentrations between 0.3055 and 0.3385 µg/L at the West Branch of Sugar River.

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Table 4 identifies the pesticides and the metabolite exceedances for Wis. Admin. Code Ch. NR 140 ES and PAL standards, as well as health advisory recommendations set by DHS.

Table 4: Summary of Pesticides and Metabolites Exceeding Wisconsin Admin. Code NR 140 Standards and DHS Drinking Water Health Advisory Recommendations

Compound	ES (µg/L)	PAL (µg/L)	DWHA (µg/L)	Location	Date	Detection (µg/L)
Atrazine	3	0.3	---	Rock River	6/23/2022	0.895
				Rock River	7/27/2022	0.355
				Mississippi River	6/20/2022	0.368
				Milwaukee River	6/27/2022	0.367
Diamino atrazine	3	0.3	---	Syene Spring	3/29/2022	0.434
					4/26/2022	0.41
					5/23/2022	0.429
					6/23/2022	0.427
					7/27/2022	0.398
					8/31/2022	0.398
					9/29/2022	0.4
					10/31/2022	0.417
					11/23/2022	0.448
					12/07/2022	0.426
				Big Spring	9/20/2022	0.327
					11/23/2022	0.392
					12/07/2022	0.346
Atrazine TCR	3	0.3	---	Milwaukee River	6/27/2022	0.5607
				Mississippi River	6/20/2022	0.4545
					7/6/2922	0.3321
				Big Spring	9/29/2022	0.4266
					11/23/2022	0.5545
					12/7/2022	0.5098
				Nursery Spring	9/29/2022	0.4353
					11/23/2022	0.4717
					12/7/2022	0.46
				Pecatonica River	6/23/2022	0.3021
				Rock River	6/23/2022	1.256
					7/27/2022	0.496
				Syene Spring	3/29/2022	0.7475
					4/26/2022	0.7143
					5/23/2022	0.7534
					6/23/2022	0.7674
					7/27/2022	0.7293
					8/31/2022	0.7082
					9/29/2022	0.6904
					10/31/2022	0.7298

Compound	ES (µg/L)	PAL (µg/L)	DWHA (µg/L)	Location	Date	Detection (µg/L)
Atrazine TCR	3	0.3	---	Syene Spring	11/23/2022	0.7742
					12/07/2022	0.748
				West Branch Sugar River	5/23/2022	0.3126
					6/23/2022	0.3385
					8/31/2022	0.3055
					9/28/2022	0.3091
					11/21/2022	0.3064
					12/5/2022	0.3114

Notes: *ES - Wisconsin Administrative Code, Natural Resources 140 – Enforcement Standard*
PAL - Wisconsin Administrative Code, Natural Resources 140 – Preventive Action Limits
DWHA - Wisconsin Department of Health Services (DHS) drinking water health advisory recommendations
µg/L - micrograms per liter
Atrazine TCR - Total chlorinated residues of atrazine includes the sum of atrazine plus its metabolites de-ethyl atrazine, deisopropyl atrazine, and diamino atrazine
--- Indicates value not established

Comparing a detected pesticide (including metabolites) to the regulatory standards may not fully identify the total risk to human health and the environment. The majority of the published water quality standards or benchmarks are based on concentrations for the occurrence of a single compound. This approach does not account for potential cumulative risk and may underestimate toxicity.

Other Notable Observations

Neonicotinoids

In recent years there has been interest in the neonicotinoid class of insecticides due to possible adverse effects on pollinators (Van der Sluijs, et al., 2013). They are present in insecticide products labeled for use on most crops grown in the state, including corn, soybeans, potatoes, many other vegetables, fruit crops, and most small grains.

DATCP began testing for these compounds in 2011 with thiamethoxam. BLS now analyzes six neonicotinoid compounds (acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid, and thiamethoxam). Three of these compounds (clothianidin, imidacloprid, and thiamethoxam) were detected in surface water samples collected in 2022. The remaining three neonicotinoid compounds were not detected in any surface water samples collected since the program started in 2008. The detection of clothianidin, imidacloprid, and/or thiamethoxam is not unexpected, given their high solubility in water. This characteristic increases the likelihood of their leaching into groundwater.

Thiamethoxam was first detected at the Milwaukee River and at the Neenah Slough sampling locations in 2011. Since then, DATCP recorded a total of 158 thiamethoxam detections in Wisconsin's surface waters, 150 of which were found in the Central Sands area. In 2022, thiamethoxam was detected in 24 samples collected at the Fourteen Mile Creek, Leola Ditch, and Ten Mile Creek stations. Concentrations ranged from 0.0133 to 0.275 µg/L.

Imidacloprid was first detected at the Ten Mile Creek in December 2014. Since then, DATCP recorded a total of 74 imidacloprid detections in Wisconsin's surface waters, 64 of which were found in the Central Sands area. Since 2018, imidacloprid has also been detected at the Root River station, predominantly in June samples. In 2022, imidacloprid was detected in 13 samples collected at the Fourteen Mile Creek, Milwaukee River, Root River, South Fork of Bad Axe River, and Ten Mile Creek stations. Concentrations ranged from 0.0122 to 0.0641 µg/L.

Clothianidin was first detected at the Root River in June 2018. Since then, DATCP recorded a total of 108 clothianidin detections in Wisconsin's surface waters, 69 of which were found in the Central Sands area. Of the three neonicotinoids, clothianidin is the compound detected at most locations. In addition to the Central

Sands, clothianidin has been detected at the Duncan Creek (2020 and 2021), the Milwaukee River (once in 2022), the Mississippi River (2019, 2020, and 2021), the Pecatonica River (in 2022), the River (in 2022), the Root River (since 2018 – no data collected in 2019), the Syene Spring (in 2020 and 2022), and the West Branch of Sugar River (since 2020). In 2022, clothianidin was detected in 35 samples collected at the Fourteen Mile Creek, Leola Ditch, Milwaukee River, Mississippi River, Pecatonica River, Rock River, Root River, Syene Spring, Ten Mile Creek, and West Branch Sugar River. Concentrations ranged from 0.0101 to 0.0833 µg/L.

In 2022, a total of 72 neonicotinoid detections were reported and a detection rate of 16% was calculated for clothianidin, imidacloprid, and thiamethoxam. This result is an increase in neonicotinoids' detections from 2021, when 30 neonicotinoid detections were reported and the neonicotinoids' detection rate was about 12%.

In the Central Sands Region, these neonicotinoid compounds do not fluctuate seasonally in surface water samples. Similarly, clothianidin was detected throughout the year 2022 in the majority of the samples collected at the Pecatonica River. However, samples from the Root River and the West Branch of Sugar River exhibited a seasonality in their imidacloprid detections. Imidacloprid was only detected from May to July at the Root River and from March to June at the West Branch of Sugar River, suggesting a trend in neonicotinoid detections in the Root River coinciding with the peak pesticide application period.

For more details on neonicotinoid concentrations exceeding EPA Aquatic Life Benchmarks and/or Wis. Admin. Code Ch. NR 140 ES and PAL values, please refer to the Comparison to Standards section of this document.

Atrazine

Atrazine is a restricted-use herbicide. To protect groundwater, the use of atrazine is prohibited within 101 atrazine PAs, covering approximately 1.2 million acres within the state (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2023d). It is illegal to apply any pesticide containing the active ingredient atrazine within an atrazine PA. Outside of PAs, atrazine use is restricted but not prohibited.

Because most of the PAs have been in place for over 10 years, it would be expected that atrazine and its metabolite concentrations in surface or spring water would be limited, or not present within the PAs. Excluding the Milwaukee River, Mormon Coulee Creek, and Bad Axe River, the streams sampled as part of the 2022 Surface Water Program flow through or are adjacent to a PA.

Atrazine parent material concentrations were detected in 25% (17 samples) of the 2022 collected river, stream, or spring water samples, marking an increase in the rate of atrazine detections relative to the 2021 samples (19%).

At least one atrazine metabolite (de-ethyl atrazine, deisopropyl atrazine, and diamino atrazine) was detected in 49% (73 samples) of the 2022 collected river, stream, or spring water samples, marking an increase in the rate of atrazine metabolite detections relative to the 2021 samples (58%).

Atrazine TCR (sum of atrazine and its metabolite) was detected in 53% (80 samples) of the 2022 collected river, stream, or spring water samples, marking a slight decrease in the atrazine TCR detection rate relative to the 2021 samples (59%).

The following is a summary of the atrazine findings for each river or stream where it was detected in 2022:

- The greatest concentrations of parent material atrazine and atrazine total chlorinated residues (atrazine TCR, i.e. the sum of atrazine and its metabolites) were identified in a surface water sample collected at the Rock River in June; atrazine parent material was detected at a concentration of 0.895 µg/L and atrazine TCR was detected at a concentration of 1.256 µg/L, respectively. Atrazine was detected from June to August at concentrations between 0.0775 and 0.895 µg/L. De-ethyl atrazine was the most detected atrazine metabolite (from June to September) in the Rock River at concentrations ranging from 0.0513 (September) to 0.217 (June) µg/L. Deisopropyl atrazine was detected only once in June at a concentration of 0.144 µg/L. Diamino atrazine was not detected in samples collected at this location in 2022. Atrazine and atrazine metabolites' concentrations overall increased since 2013. No atrazine metabolites were detected in 2013 or 2014 in the Rock River.
- In samples collected at the Fourteen Mile Creek between May and August, de-ethyl atrazine was detected at concentrations ranging from 0.0515 to 0.0758 µg/L. No atrazine or other metabolites were detected.

- In samples collected at the Leola Ditch in June and July, atrazine was detected at concentrations ranging from 0.0506 and 0.0512 µg/L. De-ethyl atrazine was detected in July at a concentration of 0.0573 µg/L.
- In samples collected at the Milwaukee River in June, July, and October, atrazine was detected at concentrations ranging from 0.0603 and 0.367 µg/L. De-ethyl atrazine and deisopropyl atrazine were detected only in July at concentrations of 0.123 µg/L and 0.070 µg/L, respectively. Deisopropyl atrazine was not detected in 2021. Concentrations and the number of detections increased compared to 2021.
- In samples collected at the Mississippi River between June and August, atrazine was detected at concentrations ranging from 0.125 and 0.368 µg/L. De-ethyl atrazine was also detected between June and August, at concentrations ranging from 0.0721 to 0.0865 µg/L. Atrazine TCR was calculated to be between 0.1973 and 0.4545 µg/L. Concentrations and the number of detections increased compared to 2021.
- In samples collected at the Mormon Coulee Creek, de-ethyl atrazine was detected at concentrations ranging from 0.0703 and 0.109 µg/L throughout the year. Atrazine was also detected in May and June, at concentrations ranging from 0.145 to 0.16 µg/L. Atrazine TCR was calculated to be between 0.0703 and 0.269 µg/L. Overall, concentrations of atrazine and de-ethyl atrazine decreased compared to 2021.
- In samples collected at the Pecatonica River between April and December (except March), de-ethyl atrazine was detected at concentrations ranging from 0.0518 and 0.0838 µg/L. Atrazine was also detected in May and June at concentrations between 0.061 and 0.0623 µg/L. No other atrazine metabolite was detected. No de-ethyl atrazine was detected in 2014, while atrazine was detected once in June 2014 at a concentration of 1.16 µg/L. Atrazine concentrations decreased since 2014, but de-ethyl atrazine concentrations increased since that time.
- In samples collected at the Root River in May and June, atrazine was detected at concentrations ranging from 0.0992 and 0.109 µg/L. De-ethyl atrazine was also detected in May and June at concentrations between 0.0567 and 0.0908 µg/L. In May, deisopropyl atrazine was detected at 0.0635 µg/L. These compounds were detected in June 2021 and June 2022 samples at similar concentrations.
- In samples collected at the South Fork of the Bad Axe River, de-ethyl atrazine was detected at concentrations ranging from 0.0804 and 0.1 µg/L throughout the year. Atrazine or other atrazine metabolites were not detected. Similar results were found in 2021 at this location.
- In samples collected at the West Branch of Sugar River, de-ethyl atrazine and diamino atrazine were detected throughout the year. De-ethyl atrazine concentrations ranged between 0.024 and 0.0785 µg/L, while concentrations of diamino atrazine ranged between 0.181 and 0.26 µg/L. Atrazine TCR was calculated to be between 0.2434 and 0.3385 µg/L. The Wis. Admin. Code Ch. NR 140 PAL value of 0.3 µg/L for atrazine TCR was exceeded in May, June, August, September, November, and December. The concentrations found in 2022 are similar to the concentrations found in 2021.
- Atrazine and de-ethyl atrazine were detected from June to August at the Wisconsin River near Muscoda. While atrazine concentrations ranged from 0.0525 (August) to 0.156 (June) µg/L, de-ethyl atrazine concentrations ranged from 0.0531 to 0.0624 µg/L. Atrazine TCR was calculated to be between 0.1056 (August) and 0.2184 (June) µg/L.
- Atrazine and de-ethyl atrazine were detected also at the Wisconsin River at Wisconsin Dells. While atrazine was detected from May to August between 0.0602 (August) to 0.136 (June) µg/L, de-ethyl atrazine was detected only in June and July at 0.0713 to 0.0529 µg/L, respectively. Atrazine TCR was calculated to be between 0.0602 and 0.2033 µg/L.
- At the Wisconsin River below Biron Dam, atrazine was detected in June at a concentration of 0.0803 µg/L.
- De-ethyl atrazine and diamino atrazine were detected in all three samples collected at the Big Spring (September, October, and November). De-ethyl atrazine concentrations ranged from 0.996 to 0.109 µg/L. Diamino atrazine concentrations ranged from 0.327 to 0.392 µg/L. In the samples collected in November and December, deisopropyl atrazine was also detected between 0.548 and 0.555 µg/L. Atrazine TCR ranged from 0.4266 to 0.5545 µg/L.

- Atrazine, de-ethyl atrazine, and diamino atrazine were all detected in the three samples collected at the Nursery Spring. Atrazine concentrations ranged from 0.0573 to 0.061 µg/L. De-ethyl atrazine concentrations ranged from 0.127 to 0.15 µg/L. Diamino atrazine concentrations ranged from 0.251 to 0.263 µg/L.
- Atrazine, de-ethyl atrazine, deisopropyl atrazine, and diamino atrazine were detected at Syene Spring in every monthly sample. Atrazine concentrations ranged from 0.0652 to 0.081 µg/L. Diamino atrazine was detected at concentrations ranging from 0.38 to 0.503 µg/L. De-ethyl atrazine was detected at concentrations ranging from 0.142 to 0.174 µg/L. Deisopropyl atrazine was detected at concentrations ranging from 0.0753 to 0.0859 µg/L.

Syene Spring has been included in the DATCP Surface Water Monitoring Program since 2018, when atrazine was identified in a spring water sample as part of a Wisconsin Geological and Natural History Survey (WGNHS) project; atrazine TCR was detected at a concentration of 0.78 µg/L at that time. Because this spring is located within a PA that was established in 1995, atrazine detections would not be expected. The 2022 data for this location continued to consistently detect atrazine parent material and metabolites' concentrations in excess of the 0.3 µg/L Wis. Admin. Code Ch. NR 140 PAL for atrazine TCR. Sustained concentrations of atrazine and its metabolites detected in monthly samples collected at Syene Spring since 2018 may be related to either 1) a nearby point source release of atrazine (e.g., from a spill); or 2) a slow but steady atrazine release from the aquifer matrix resulting from historic field use within the spring recharge area. Since atrazine and atrazine metabolites were also detected at the Big Spring and the Nursery Spring, and since these locations are located upstream of Syene Spring, we exclude the option of a source release of atrazine (spill) near Syene Spring.

Data collected at the Fourteen Mile Creek, the Leola Ditch, the Milwaukee River, the Mississippi River, the Rock River, the Root River, and the Wisconsin Rivers showed seasonal influence, with the summer months showing the only detections of atrazine and its metabolites. The atrazine concentrations found in the surface water samples at some locations appear to be associated with the seasonal pesticide application trends, thus intermittently influencing surface water quality.

For more details on atrazine and atrazine metabolites' concentrations exceeding EPA Aquatic Life Benchmarks and/or Wis. Admin. Code Ch. NR 140 ES and PAL values, please refer to the *Comparison to Standards* section of this document.

Nitrate

In addition to pesticides, DATCP's Surface Water Sampling Program includes analyses for nitrate plus nitrite as N to evaluate how surface water quality is affected by agriculture. Nitrogen in groundwater and surface water is regulated by the DNR. However, DATCP includes nitrogen analyses as part of this program and shares results with DNR.

Nitrogen was detected in 130 of the 150 surface water samples collected for DATCP's 2022 Surface Water Sampling Program. The greatest nitrogen concentration observed in 2022 was 11.4 mg/L detected in the sample collected at Syene Spring in June.

The following is a summary of nitrogen results for 2022 river and stream samples:

- At Syene Spring, nitrogen concentrations exceeded the Wis. Admin. Code NR 140 ES of 10 mg/L in each sample collected, ranging in concentration from 10.7 mg/L to 11.4 mg/L. This is very similar to what found in the samples collected at Syene Spring in 2021.
- Nitrate concentrations remained overall stable at Big Spring and Nursery Spring, both of which were sampled exclusively in September, November, and December. Big Spring recorded higher nitrate concentrations, ranging from 8.29 to 8.54 mg/L, in contrast to Nursery Spring, where nitrate concentrations ranged from 6.43 to 6.51 mg/L. Nitrogen concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L in each sample collected at these springs.
- Among the sites sampled in the DATCP Surface Water Sampling program through 2022, Fourteen Mile Creek exhibited the most significant variation in nitrogen values. Nitrogen concentrations ranged from 0.575 to 7.68 mg/L. Nitrogen concentrations displayed a consistent upward trend from March, reaching a peak in June, before gradually declining from August onwards. From March to August, nitrogen concentrations exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL.

- Variations in nitrogen levels were also observed at the Leola Ditch, where nitrogen concentrations ranged from 3.22 to 9.43 mg/L. The highest concentration was recorded during the months of October, November, and December. Nitrogen concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L in each sample collected.
- Nitrogen concentrations in samples from Ten Mile Creek exhibited minimal variation, ranging from 5.18 to 7.88 mg/L. The highest readings were observed in October, November, and December, consistently exceeding the Wisconsin Administrative Code NR 140 PAL limit of 2 mg/L.
- Similarly, nitrogen concentration found at the Pecatonica River, South Fork of Bad Axe River, and West Branch of Sugar River consistently exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL. The highest nitrogen concentrations at Pecatonica River were recorded in September, November, and December, while the South Fork of Bad Axe River saw its peak concentrations in October and November (with no samples collected in December). At the West Branch of Sugar River, the highest nitrogen concentrations were observed in November and December.
- At the Milwaukee River, nitrogen concentration exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL only in November and December. No nitrogen was detected in August.
- At the Root River, nitrogen concentrations exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL April, May, and June. No nitrogen was detected in July and August.
- At the Rock River, nitrogen concentrations exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL only in March and November, while lower concentrations were detected in May, June, and July.
- Nitrogen concentrations in Mormon Coulee Creek exceeded the 2 mg/L PAL in June, November, and March, with overall stable concentrations.
- The Mississippi River and the three stations along the Wisconsin River consistently showed nitrogen concentrations below the Wisconsin Administrative Code NR 140 PAL limit of 2.0 mg/L.

Table 5 includes a summary of the DATCP's 2022 Surface Water Sampling Program detections for nitrate plus nitrite as N.

Table 5: 2022 Surface Water Sampling Program Nitrogen (Nitrate and Nitrite) Analytical Results

Sample Location	Nitrogen (Nitrate + Nitrite) Concentration Range (mg/L)
Fourteen Mile Creek	0.575-7.68
Leola Ditch	3.22-9.43
Milwaukee River	ND-2.24
Mississippi River	0.781-1.96
Mormon Coulee Creek	1.63-2.07
Big Spring	8.29-8.54
Nursery Spring	6.43-6.51
Syene Spring	10.7-11.4
Pecatonica River	4.53-5.83
Rock River	0.583-2.13
Root River	ND-5.03
South Fork Bad Axe River	2.15-2.95
Ten Mile Creek	5.18-7.88
West Branch Sugar River	4.43-5.88
Wisconsin River, near Muscoda	ND-1.42
Wisconsin River at Wisconsin Dells	ND-1.14
Wisconsin River, below Biron Dam	ND-1.04

Notes: mg/L - milligrams per liter

ND - Non Detect, i.e., concentration not in excess of laboratory reporting limits

2023 Program Goals and Objectives

DATCP's Surface Water Sampling Program will continue in 2023. It is expected that the following tasks will be completed.

- Collection of monthly surface water samples at 12 stream or river locations for the calendar year to include:
  - Collect monthly samples from five locations sampled in 2022, and
  - Collect monthly samples from seven new locations.
- Prepare a 2023 Data Summary Report to be completed by the third quarter of 2023; and
- Share report(s) with the DNR Bureau of Water Quality, surface water sampling team, and other appropriate stakeholders, and have the report(s) available to the public via the DATCP website.

The 2023 surface water results will provide additional information for the following previously sampled locations:

- Fourteen Mile Creek at County Rd D;
- Milwaukee River at Estabrook Park;
- Mormon Coulee Creek - Bridge #6 at County Rd YY;
- South Fork of the Bad Axe River; and
- Syene Spring in Dane County.

The intent is to evaluate water quality data over time and identify if and how agricultural land use affects water quality. In addition to groundwater data, surface water data will aid in evaluating the effectiveness of the atrazine PAs over the long term. Historic surface water data will be compared to groundwater data from within each watershed to identify potential relationships between surface water and groundwater quality. Monthly results will be used to evaluate seasonal trends and groundwater discharge for the regional watersheds. In 2023, we will extend our sampling efforts, including both stations located further upstream from those sampled in 2022 and entirely new additions to our program. The following stations have been selected for sampling:

- Root River at 60th;
- South Branch Ten Mile Creek Taft Rd;
- Leola Ditch at D and 3rd;
- Ashwaubenon Creek at Creamery Road;
- East River - Hwy Zz
- Sugar River, Upstream of Hwy 69; and
- Sinisinawa River - Sinsinawa Rd.

We anticipate limitations in our ability to conduct surface water monthly sampling from March to September. This constraint arises from the laboratory's extensive commitment to the 2023 DATCP Statewide Groundwater Survey, which is expected to use its resources for several months.

Acknowledgments

DATCP's Bureau of Agrichemical Management's (ACM) financial information includes the state fiscal year (FY) 2022 from July 1, 2021 through June 30, 2022. Federal grants operated from October 1, 2021, through September 30, 2022. The primary sources of revenue for ACM are industry fees for licenses, permits, registrations, and tonnage under the feed, fertilizer, soil and plant additive, lime, and pesticide programs. In addition, a federal grant provides some funding to cover annual pesticide program expenses. ACM recognizes these important partnerships with the industry and the federal government and works hard to maximize the use of this funding for the benefit of the industry, consumers, and the environment.

The raw data required to reproduce the above findings are available upon request. For any questions and clarifications, please do not hesitate to reach out to us at DATCPGW@wisconsin.gov or at (608) 224-4502.

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Appendix A – Acronyms and Definitions

The acronyms and terminology included on this list are generic definitions intended to help understand the Surface Water Pesticide Sampling Program. Some of these terms are more specifically defined in various regulations.

Acronyms

µg/L _____ Micrograms per liter (a liquid equivalent of ppb)
ACM _____ Bureau of Agrichemical Management
BLS _____ DATCP Bureau of Laboratory Services
DATCP _____ Department of Agriculture, Trade and Consumer Protection
DHS _____ Wisconsin Department of Health Services
DNR _____ Wisconsin Department of Natural Resources
EPA _____ United States - Environmental Protection Agency
ES _____ Enforcement Standard
ESA _____ Ethane Sulfonic Acid
GC _____ Gas Chromatography
ISO _____ International Organization for Standardization
LC _____ Liquid Chromatography
mg/L _____ Milligrams per liter
MS _____ Mass Spectroscopy
N _____ Nitrogen
ND _____ No Detect – concentrations are less than laboratory reporting limits
NOAA _____ National Oceanic and Atmospheric Administration
OA_____ Oxanilic Acid
PA _____ Prohibition Area
PAL _____ Preventive Action Limit
SWIMS _____ Surface Water Integrated Monitoring System
TCR _____ Total chlorinated resides of atrazine
USDA _____ United States Department of Agriculture
WGNHS _____ Wisconsin Geological and Natural History Survey
Wis. Admin. Code __ Wisconsin Administrative Code

Definitions

Analyte - A chemical substance that has a defined Chemical Abstract Service (CAS) number.

Aquatic Life Benchmarks - EPA-developed pesticide toxicity values for freshwater species. They are estimates of the concentrations below which pesticides are not expected to present a risk of concern for freshwater organisms.

Atrazine Prohibition Area - An area where atrazine use is currently prohibited under Administrative Code ATCP 30.

Chronic Exposure value - The highest concentration of a chemical to which the organism can be exposed without causing chronic toxicity to the organism in question.

Compound - A substance formed by the chemical union of two or more ingredients.

Detection - When an analyte has a concentration that can be quantified (i.e., a concentration greater than the Laboratory Reporting Limit).

Enforcement Standard (ES) - The Enforcement Standard (ES) is set to ensure that the concentration of a compound in groundwater does not exceed a specific level that could harm human health or the environment. If the ES for a certain compound in groundwater is exceeded, intervention from the appropriate authority is required.

Herbicide - A pesticide used to kill or inhibit the growth of plants, weeds, or grasses.

Insecticide - A pesticide used to kill or inhibit the growth of insects.

Metabolite or Residual compound or Breakdown product - A chemical substance left behind by a parent compound that has degraded through natural chemical breakdown and/or been metabolized by bacteria.

Neonicotinoids - Insecticides that target the neurological systems of insects. The neonicotinoid family includes acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, nithiazine, thiacloprid, and thiamethoxam.

NR140 - Wisconsin administrative code which establishes groundwater quality standards and required responses when the standards are exceeded.

Pesticide - Substance used to kill, repel, or control certain forms of plant or animal life that are considered to be pests. The pesticide category includes herbicides, insecticides, rodenticides, fungicides, and bactericides.

Preventive Action Limit (PAL) - The Preventive Action Limit (PAL) is a percentage of the Enforcement Standard (ES); 10% of the ES for carcinogenic, mutagenic, or teratogenic properties, and 20% of the ES for the remaining substances. The intention of the PAL is for it to act as a trigger for intervention before a pollutant becomes a serious risk to public health or the environment.

Reporting limit - The minimum analyte concentration that can be reliably quantified and reported by the laboratory.

Total chlorinated residues (TCR) of atrazine - Sum of atrazine and atrazine metabolites (de-ethyl atrazine, de-isopropyl atrazine, and diamino atrazine).

Watershed – A land area that channels rainfall and snowmelt water into a specific waterbody (e.g., a creek, a stream, a river, etc.)

Wadeable - Refers to streams and rivers recognized as natural habitats that support a diversity of both aquatic and terrestrial species.

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Appendix B

2022 Surface Water Sampling Program Analytical Results, Summary

2022 Surface Water Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides (µg/L)					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Enforcement Standard (ES) (µg/L)	Preventive Action Limit (PAL) (µg/L)	Drinking Water Health Advisory Recommendations (µg/L)	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Non-vascular Plants	Vascular Plants
2,4-D	Herbicide	22	0.05	0.0514-0.481	7	70	--	--	--	12500	--	--	299.2
2,4-DB	Herbicide	ND	1.5	--	--	--	--	7150	1660	12500	1500	932	83
2,4-DP	Herbicide	ND	0.05	--	--	--	--	>45750	--	279000	100000	77	32000
2,4,5-T	Herbicide	ND	0.05	--	--	--	--	--	--	--	--	--	--
2,4,5-TP	Herbicide	ND	0.05	--	5	50	--	--	--	--	--	--	--
Acetamiprid	Insecticide	ND	0.01	--	--	--	--	>50000	19200	10.5	2.1	>1000	>1000
Acetochlor	Herbicide	5	0.05	0.0525-0.32	0.7	7	--	190	130	4100	22.1	1.43	3.4
Acetochlor ESA	Metabolite	43	0.05	0.053-0.285	46	230	--	>90000	--	>62500	--	9900	--
Acetochlor OA or OXA	Metabolite	1	0.3	0.301	46	230	--	--	--	--	--	--	--
Acetochlor Metabolites	Sum of Acetochlor ESA and Acetochlor OA	43	--	0.0533-0.586	46	230	--	--	--	--	--	--	--
Acifluorfen	Herbicide	ND	0.05	--	--	--	--	--	--	--	--	--	--
Alachlor	Herbicide	ND	0.05	--	0.2	2	--	900	187	1250	110	1.64	2.3
Alachlor ESA	Metabolite	47	0.053	0.0534-1.1	4	20	--	>52000	--	>52000	--	3600	>120000
Alachlor OA	Metabolite	ND	0.25	--	--	--	--	>50000	--	>47500	--	--	--
Aldicarb Sulfone	Insecticide	ND	0.05	--	--	--	--	21000	--	140	--	--	--
Aldicarb Sulfoxide	Insecticide	ND	0.071	--	--	--	--	3570	--	21.5	--	--	--
Aminopyralid	Herbicide	ND	0.15	--	--	--	--	>50000	1360	7500	102000	18000	>88000
Atrazine	Herbicide	38	0.05	0.0506-0.895	0.3	3	--	2650	5	360	60	<1	4.6
De-ethyl atrazine	Metabolite	73	0.05	0.0513 - 0.217	0.3	3	--	--	--	--	--	--	--
De-isopropyl atrazine	Metabolite	15	0.05	0.0548 - 0.144	0.3	3	--	--	--	--	--	--	--
Di-amino atrazine	Metabolite	27	0.2	0.156 - 0.448	0.3	3	--	--	--	--	--	--	--
Atrazine TCR	Sum of Atrazine and atrazine metabolites	80		0.0506-1.256	0.3	3	--	--	--	--	--	--	--
Azoxystrobin	Fungicide	ND	0.05	--	--	--	--	235	147	130	44	49	3400
Benfluralin	Herbicide	ND	0.05	--	--	--	--	34.85	1.9	1090	15.5	>100	--
Bentazon	Herbicide	26	0.05	0.0503-0.24	60	300	--	95000	9830	31150	101200	4500	5350
Bicyclopyrone	Herbicide	ND	0.05	--	--	--	--	>46700	10000	>46650	103700	2000	13

2022 Surface Water Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides (µg/L)					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Wisconsin Admin. Code Chapter NR 140	Enforcement Standard (ES) (µg/L)	Drinking Water Health Advisory Recommendations (µg/L)	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Non-vascular Plants	Vascular Plants
Bifenthrin	Insecticide	ND	0.005	--	--	--	--	0.075	0.04	0.0002465	0.00005	>290	>330
Bromacil	Herbicide	1	0.05	0.066	--	--	--	18000	3000	60500	8200	6.8	45
Carbaryl	Insecticide	ND	0.05	--	4	40	--	110	6.8	0.85	0.5	340	1550
Carbofuran	Insecticide	ND	0.05	--	8	40	--	44	5.7	1.115	0.75	--	--
Chloramben	Herbicide	ND	0.32	--	30	150	--	--	--	--	--	--	--
Chlorantraniliprole	Insecticide	23	0.05	0.0523-0.432	--	--	16000	>6900	110	8.3	3.02	>1780	>2000
Chlorothalonil	Fungicide	ND	0.1	--	--	--	--	9	0.77	27	0.6	12	640
Chlorpyrifos	Insecticide	ND	0.05	--	0.4	2	--	0.85	<0.251	0.0069	<0.005	140	
Chlorpyrifos Oxon	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Clomazone	Herbicide	ND	0.05	--	--	--	--	1450	350	2700	2200	167	30200
Clopyralid	Herbicide	3	0.05	0.0589 - 0.0663	--	--	--	51500	10000	116500	4700	6900	90300
Clothianidin	Insecticide	35	0.01	0.0101 - 0.0833	--	--	1000	>50750	9700	11	0.05	64000	>280000
Cyantraniliprole	Insecticide	ND	0.05	--	--	--	--	>5000	10700	10.2	6.56	>10000	>12100
Cyclaniliprole	Insecticide	ND	0.2	--	--	--	--	>68.5	200	40.4	9.6	>99	>187
Cyfluthrin	Insecticide	ND	0.05	--	--	--	--	0.034	0.0042	0.0125	0.00012	>2	--
lambda- Cyhalothrin	Insecticide	ND	0.02	--	--	--	--	0.0145	0.031	0.00004	0.00022	>310	>0.508
Cypermethrin	Insecticide	ND	0.1	--	--	--	--	0.195	0.051	0.00028	<0.00005	25000	>1.62
Cyprosulfamide	Safener	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dacthal	Herbicide	ND	0.05	--	14	70	--	15000	--	13500	--	>11000	>11000
Dacthal Di-acid	Metabolite	ND	0.5	--	--	--	70	--	--	--	--	--	--
Dacthal Mono-acid	Metabolite	ND	0.5	--	--	--	70	--	--	--	--	--	--
Dacthal Total	Sum of Dacthal , Dacthal Di-acid, and Dacthal Mono-acid	ND	0.5	--	--	--	70	--	--	--	--	--	--
Diazinon	Insecticide	ND	0.05	--	--	--	--	45	<0.55	0.105	0.17	3700	--
Diazinon Oxon	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dicamba	Herbicide	ND	0.3	--	60	300	--	14000	>9900	>50000	> 42000	61	1290
Dichlobenil	Herbicide	8	0.05	0.0543 - 0.318	--	--	--	2465	<330	3100	560	1500	30
Dimethenamid	Herbicide	ND	0.05	--	5	50	--	3150	120	6000	1360	14	8.9
Dimethenamid ESA	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--

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2022 Surface Water Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides (µg/L)					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Wisconsin Admin. Code Chapter NR 140	Enforcement Standard (ES) (µg/L)	Drinking Water Health Advisory Recommendations (µg/L)	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Non-vascular Plants	Vascular Plants
Dimethenamid OA	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dimethoate	Insecticide	ND	0.05	--	0.4	2	--	3100	430	21.5	0.5	20000	>92600
Dinotefuran	Insecticide	ND	0.01	--	--	--	--	>49550	6360	>484150	>95300	>97600	>110000
Diuron	Herbicide	ND	0.05	--	--	--	--	660	26.4	87.5	0.83	3.08	0.13
EPTC	Herbicide	ND	0.05	--	50	250	--	7000	40	3250	800	1400	5600
Esfenvalerate	Insecticide	ND	0.025	--	--	--	--	0.071	0.017	0.000424	0.0000309	>5.6	>8.6
Ethalfluralin	Herbicide	ND	0.05	--	--	--	--	16	0.4	30	24	25	7.3
Ethofumesate	Herbicide	ND	0.05	--	--	--	--	5760	<306	17150	300	>2760	39000
Flumetsulam	Herbicide	ND	0.05	--	--	--	10000	>146500	197000	127000	111000	3.21	3.1
Flupyradifurone	Insecticide	ND	0.05	--	--	--	--	--	--	--	--	--	--
Fluroxypyr	Insecticide	ND	0.07	--	--	--	--	7150	--	>50000	--	>100000	--
Fomesafen	Herbicide	2	0.05	0.0535 - 0.114	--	--	25	63000	9400	188000	50000	92	210
Glyphosate	Herbicide	ND	0.5	--	--	--	10000	21500	25700	26600	49900	12100	11900
Glufosinate Ammonium	Metabolite	ND	0.5	--	--	--	--	>156000	50000	325500	31000	72	1470
AMPA	Metabolite	ND	0.5	--	--	--	10000	249500	--	341500	--	--	--
Halosulfuron methyl	Herbicide	ND	0.05	--	--	--	--	--	--	--	--	4.1	0.042
Hexazinone	Herbicide	ND	0.05	--	--	--	400	137000	17000	75800	20000	7	37.4
Imazapyr	Herbicide	ND	0.05	--	--	--	--	>50000	43100	>50000	97100	12200	24
Imazethapyr	Herbicide	ND	0.05	--	--	--	--	120000	97000	>500000	103000	4770	8.1
Imidacloprid	Insecticide	13	0.01	0.0122 - 0.0641	--	--	0.2	114500	9000	0.385	0.01	--	--
Isoxaflutole	Herbicide	ND	0.05	--	--	--	3	>850	80	>750	350	110	4.9
Isoxaflutole DKN	Metabolite	ND	0.05	--	--	--	3	>15300	--	>29800	--	5000	75
Isoxaflutole Total	Sum of Isoxaflutole and Isoxaflutole DKN	ND	0.05	--	--	--	3	--	--	--	--	--	--
Linuron	Herbicide	1	0.05	0.144	--	--	--	1500	5.58	60	0.09	13.7	2.5
Malathion	Insecticide	ND	0.05	--	--	--	--	2.05	8.6	0.049	0.06	2040	24000
MCPA	Herbicide	3	0.05	0.0639 - 0.0837	--	--	--	>34000	--	>92000	--	--	--
MCPB	Herbicide	ND	0.1	--	--	--	--	1960	<530	25100	2510	1370	200
MCPP	Herbicide	4	0.05	0.0519 - 0.138	--	--	--	>46500	--	>45500	50800	14	1300

2022 Surface Water Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides (µg/L)					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Wisconsin Admin. Code Chapter NR 140	Enforcement Standard (ES) (µg/L)	Drinking Water Health Advisory Recommendations (µg/L)	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Non-vascular Plants	Vascular Plants
Mesotrione	Herbicide	1	0.1	0.122	--	--	--	>60000	11000	67000	3055	>820	4.8
Metalaxyl	Fungicide	ND	0.05	--	--	--	800	65000	9100	14000	1200	--	85000
Methyl Parathion	Insecticide	ND	0.05	--	--	--	--	925	<10	0.485	0.25	15000	18000
Metolachlor	Herbicide	42	0.05	0.0503 - 0.806	10	100	--	1600	30	11750	3200	8	14
Metolachlor ESA	Metabolite	148	0.05	0.0611 - 3.92	260	1300	--	24000	--	>54000	--	>99450	43000
Metolachlor OA or OXA	Metabolite	42	0.27	0.279 - 2.28	260	1300	--	>46550	--	7700	--	57100	>95400
Metolachlor Metabolites	Sum of Metolachlor ESA and Metolachlor OA	148	--	0.0611-6.2	260	1300	--	--	--	--	--	--	--
Metribuzin	Herbicide	18	0.05	0.0502 - 0.174	14	70	--	21000	<3000	2100	1290	8.1	130
Metribuzin DA	Metabolite	12	0.1	0.105 - 0.155	--	--	--	--	--	--	--	--	--
Metribuzin DADK	Metabolite	30	0.12	0.367 - 0.957	--	--	--	--	--	--	--	--	--
Metsulfuron methyl	Herbicide	ND	0.05	--	--	--	--	>75000	4500	>75000	--	31	0.36
Nicosulfuron	Herbicide	ND	0.05	--	--	--	--	>500000		>500000	43000	--	--
Norflurazon	Herbicide	24	0.05	0.0507 - 1.81	--	--	--	4050	770	>7500	1000	6.03	59
Oxadiazon	Herbicide	ND	0.05	--	--	--	--	600	0.88	>1200	30	5.2	41
Pendimethalin	Herbicide	ND	0.05	--	--	--	--	69	6.3	140	14.5	5.2	12.5
Permethrin	Insecticide	ND	0.03	--	--	--	--	0.395	0.052	0.0033	0.0042	>4.4	>3.2
Picloram	Herbicide	ND	0.05	--	100	500	--	2750	550	17200	11800	950	2610
Prometon	Herbicide	ND	0.05	--	20	100	--	9800	6530	12850	3450	98	160
Prometryn	Herbicide	ND	0.05	--	--	--	--	1455	620	4850	1000	1.04	11.9
Propiconazole	Fungicide	ND	0.05	--	--	--	--	425	15	2400	180	21	3500
Desthio Prothioconazole	Metabolite	ND	0.05	--	--	--	--	--	148	--	103	4.8	35
Saflufenacil	Herbicide	ND	0.05	--	--	--	460	>54000	997	4250	1330	42	87
Simazine	Herbicide	ND	0.05	--	0.4	4	--	3200	60	500	40	6	67
Sulfentrazone	Herbicide	1	0.05	0.0678	--	--	1000	46900	2950	30200	200	31	28.8
Sulfometuron methyl	Herbicide	ND	0.05	--	--	--	--	>74000	--	>75000	97000	4.3	0.45
Tebupirimphos	Insecticide	ND	0.05	--	--	--	--	44.5	130	0.039	0.011	630	8800
Tembotrione	Herbicide	ND	0.1	--	--	--	--	>50000	604	24450	5100	310	5.2
Thiacloprid	Insecticide	ND	0.01	--	--	--	--	12600	918	18.9	0.97	45000	>95400

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2022 Surface Water Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides (µg/L)					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Wisconsin Admin. Code Chapter NR 140	Enforcement Standard (ES) (µg/L)	Drinking Water Health Advisory Recommendations (µg/L)	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Non-vascular Plants	Vascular Plants
Thiamethoxam	Insecticide	24	0.01	0.0133 - 0.275	--	--	120	>57000	20000	17.5	0.74	>99000	>90200
Thiencarbazone methyl	Herbicide	ND	0.05	--	--	--	10000	>52000	4800	>49300	3540	298	0.8
Triclopyr	Herbicide	6	0.05	0.0621 - 0.499	--	--	--	58500	--	66450	--	32500	--
Trifluralin	Herbicide	ND	0.05	--	0.75	7.5	--	9.25	1.9	125.5	2.4	21.9	49.7

Notes:

--- In column Concentration Range indicates that the concentration was found below Reporting Limits.
In columns Wisconsin Admin. Code Chapter NR 140 or Wisconsin Department of Health Services indicates that no standards or health advisory is established for that compound.
In column Aquatic Life Benchmarks for Pesticides indicates that no benchmark is established for that compound.

µg/L Micrograms per liter or parts per billion

TCR Total Chlorinated Residue for Atrazine. Sum of concentrations of atrazine and its three metabolites (de-ethyl, de-isopropyl and di-amino atrazine).

Indicates no detects in excess of laboratory reporting limits.

Indicates detects in excess of laboratory reporting limits, but not in excess of any Wisc. Admin. code Ch. NR 140 PAL and ES, Health Advisory levels or benchmark values.

Indicates detects in excess of Wisc. Admin. code Ch. NR 140 PAL, and/or in excess of any Aquatic Life benchmark values.

Indicates detects in excess of Wisc. Admin. code Ch. NR 140 ES, or Health Advisory levels

Website Used for EPA Aquatic Benchmarks for Registered Pesticides (Accessed 9/14/2023)
https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

2022 Surface Water Sampling Program Analytical Results - QR code