2023 Surface Water Pesticide Monitoring Program

ANNUAL REPORT

Wisconsin Department of Agriculture, Trade and Consumer Protection
Agricultural Resource Management Division
Environmental Quality Unit
Final 09/17/2024

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Introduction

In 2023, 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 11 select Wisconsin rivers and streams, and one spring, for a total of 12 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 2024a). 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 2023 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 with 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.

2023 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. Long-term repeat locations include the following. The names of the stations are identical to those listed in the Surface Water Integrated Monitoring System (SWIMS) database.

- Fourteen Mile Creek (Ditch # 7) - CTH D;
- Milwaukee River at Estabrook Park;
- Mormon Coulee Creek #6 - Bridge at CTH YY;
- South Fork Bad Axe River – Oliver Rd.; and
- Nine Springs – Syene Spring.

While new locations for 2023 included:

- Ashwaubenon Creek at Creamery Road;
- East River - Hwy ZZ;
- Leola Ditch at D and 3rd;
- South Branch Tenmile Creek - Taft Rd (Site 7);
- Root River at 60th 3m (Bi Sur);
- Sinsinawa River - Sinsinawa Rd. (Bi); and
- Sugar River upstream of Hwy 69.

A total of 11 perennial rivers and streams and one spring were selected for the 2023 sampling program. A total of 64 samples were collected between March and December for chemical analysis of pesticides and nitrate plus nitrite as nitrogen (N). However, samples were not consistently collected between March and August. The DATCP BLS can process a maximum of 20 samples per week, but much of this capacity was allocated to the concurrent 2023 DATCP statewide groundwater survey.

This is the fifth 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 and Hart 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 2024b). 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 2023.

The Ashwaubenon Creek, the East River, and Sinsinawa River were sampled by the United Stated Geological Survey (USGS) between 1990 and 2004. Concentrations of atrazine exceeding the Enforcement Standard of 3 µg/L were found at that time. Moreover, at the Ashwaubenon Creek and the Sinsinawa River, atrazine concentrations exceeded the level at which atrazine is expected to adversely affect aquatic plants. This level has been recently set at 9.7 µg/L by the U.S. Environmental Protection Agency (Environmental Protection Agency 2024). To investigate whether atrazine concentrations have changed following the implementation of Wisconsin's atrazine use restrictions (under ATCP 30), we sampled one location at each of these water bodies in 2023.

Stations at Leola Ditch, Tenmile Creek, Root River, and Sugar River have been relocated this year to positions further upstream, closer to the headwaters, compared to their previous locations.

Table 1 lists the 2023 surface water sampling program locations, and Figure 1 shows the 12 locations relative to the State of Wisconsin and county boundaries. Table 2 summarizes the watershed size and simplified land use specific to each 2023 sampling location, using data provided by the U.S. Department of Agriculture's (USDA) National Agricultural Statistics Service (United States Department of Agriculture 2023).

Table 1: 2023 Surface Water Sampling Program Rivers and Streams

River / Stream Name	SWIMS ID	County	Program Years	Number of 2023 Samples Collected	Latitude	Longitude
Fourteen Mile Creek (Ditch # 7) - CTH D	013173	Adams	7	5	44.21998	-89.71865
Leola Ditch at D and 3rd	10049592	Adams	1	5	44.21376	-89.63753
South Branch Tenmile Creek - Taft Rd (Site 7)	10009196	Portage	2	5	44.272	-89.54892
Milwaukee River at Estabrook Park	413640	Milwaukee	11	6	43.088894	-87.898343
Root River at 60th 3m (Bi Sur)	413667	Milwaukee	1	5	42.855555	-87.990722
Ashwaubenon Creek at Creamery Road	053232	Brown	1	6	44.414157	-88.127047
East River - Hwy ZZ	053674	Brown	1	6	44.371944	-88.092222
Mormon Coulee Creek #6 - Bridge at CTH YY	10008928	La Crosse	3	5	43.7641	-91.12647
South Fork of the Bad Axe River – Oliver Rd.	10022633	Vernon	3	5	43.51921	-91.10715
Sinsinawa River - Sinsinawa Rd. (Bi)	223232	Grant	1	6	42.50847	-90.48112
Sugar River upstream of Hwy 69	10009477	Dane	1	6	42.94925	-89.544423
Syene Spring	10051662	Dane	5	4	43.01785	-89.39422

Notes: SWIMS – Surface Water Integrated Monitoring System

Figure 1: 2023 Surface Water Sampling Program Rivers, Streams, and Spring Locations

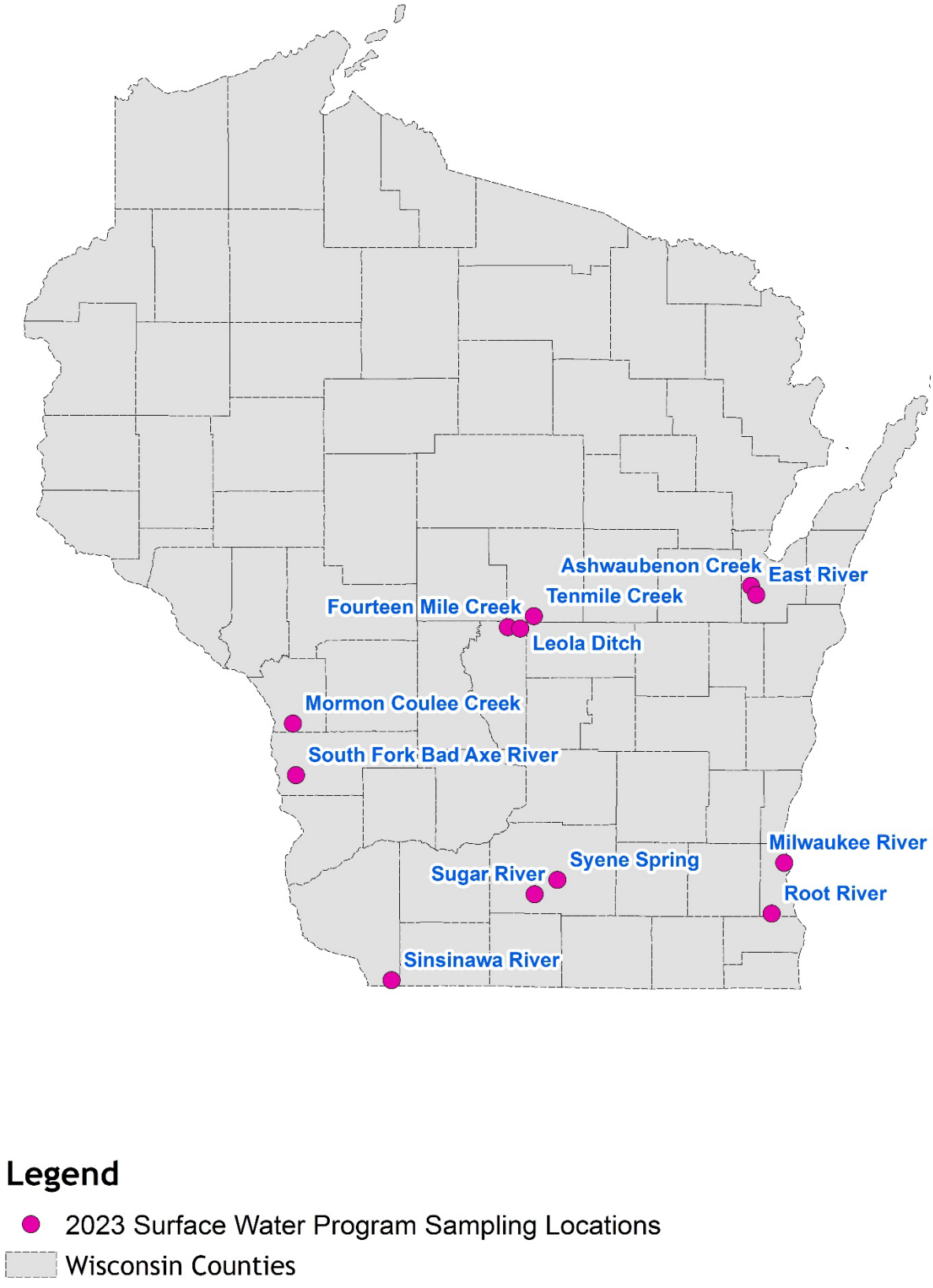


Table 2: 2023 Surface Water Sampling Program Rivers and Streams Land Use Summary and Watershed Size in Acres

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	5,241 9.4%	6,729 12.1%	16,146 29.1%	3,641 6.6%	7,892 14.2%	3,573 6.4%	4,857 8.8%	55,472
Tenmile Creek	5,291 5.4%	6,902 7.0%	23,227 23.7%	15,908 16.2%	14,973 15.3%	12,724 13.0%	8,895 9.1%	97,975
Milwaukee River	55,907 52.6%	12,632 11.9%	8,122 7.6%	5,968 5.6%	15,300 14.4%	3,827 3.6%	0 0%	106,259
Root River	40,743 48.2%	6,461 7.6%	8,961 10.6%	6,806 8.1%	8,538 10.1%	8,016 9.5%	0 0%	84,458
Ashwaubenon Creek	39,002 36.7%	6,147 5.8%	5,791 5.5%	20,178 19.0%	22,698 21.4%	8,248 7.8%	2 0.002%	106,224
East River	21,462 22.7%	7,599 8.1%	5,455 5.8%	21,150 22.4%	27,565 29.2%	5,361 5.7%	2 0.002%	94,364
Mormon Coulee Creek	3,979 6.0%	4,834 7.3%	2,333 3.5%	3,903 5.9%	10,622 16.0%	2,512 3.8%	0 0%	66,412
South Fork of Bad Axe River	7,771 6.5%	1,367 1.1%	1,620 1.3%	18,037 15.0%	32,064 26.6%	11,907 9.9%	0 0%	120,345
Sinsinawa River	1,956 4.8%	400 1.0%	2,383 5.8%	12,123 29.6%	16,202 39.6%	5,710 13.9%	8 0.02%	40,961
Sugar River	14,111 32.9%	1,265 3.0%	10,026 23.4%	14,496 33.8%	16,666 38.9%	8,266 19.3%	6 0.01%	42,848
Syene Spring	Size of the capture zone is unknown							

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 reduce bias to collect surface water samples 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 2023 program. A summary of the analytical data for the 2023 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 106 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 compounds tested and the respective laboratory reporting limits. We are unable to determine if the water samples contain other compounds not listed in Appendix B.

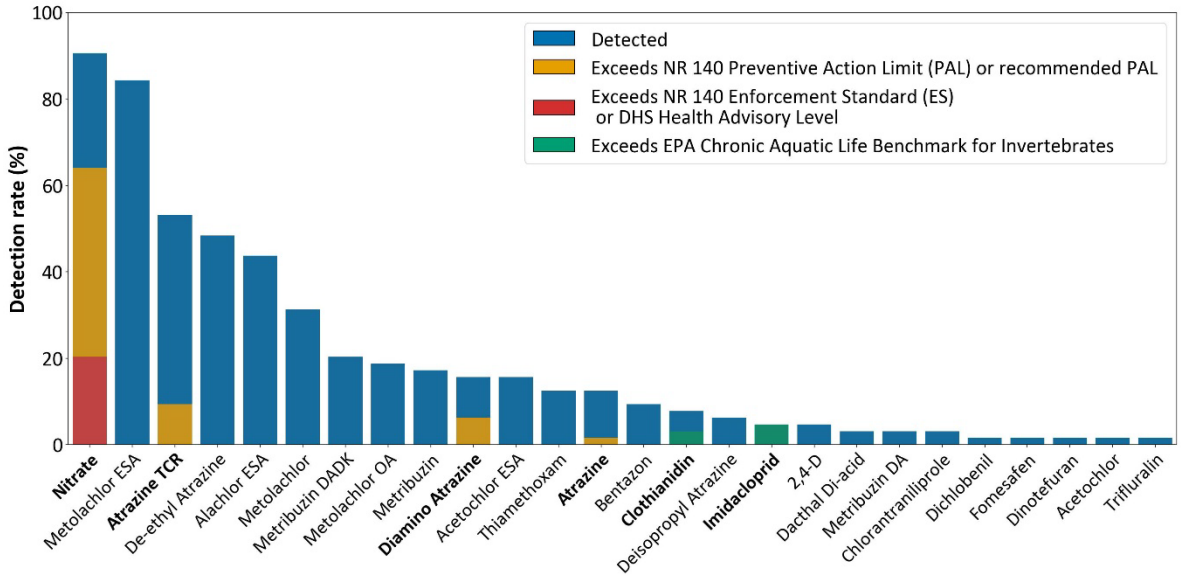
Results

A total of 64 surface water samples were collected and submitted for chemical analysis as a part of the DATCP's 2023 Surface Water Sampling Program. The table in Appendix B summarizes the 2023 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 U.S. Environmental Protection Agency (EPA) Office of Pesticide Programs - Aquatic Life Benchmarks for Registered Pesticides.

Summary

Figure 2 and the following bulleted items represent a summary of the sampling results. A detailed narrative for the 2023 data follows.

Figure 2: 2023 Detections and Exceedances of Surface and Groundwater Standards



[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.

Detections

- Of the 106 pesticides included in the laboratory testing methods, 24 compounds were detected in 2023 surface water samples. Detections include nine herbicides, 10 herbicide metabolites, and five insecticides.
- At least one pesticide compound was detected at every surface water location for every monthly sampling event.
- The maximum number of pesticides detected in a single sample was 12 individual pesticide compounds (from the Tenmile South Branch station).
- Nitrate plus nitrite as Nitrogen (N) was the most detected compound. It was detected in 91% of samples collected.
- Metolachlor ethane sulfonic acid (ESA) was the most detected pesticide compound. It was detected in 84% of samples collected.
- De-ethyl atrazine was the second most frequently detected pesticide, found in 48% of the samples, while alachlor ESA was the third most frequently detected pesticide, with a detection rate of 44%.
- 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.
- In 2023 neonicotinoid compounds were detected at the stations within the Central Sands Region (Fourteen Mile Creek, Leola Ditch, and Tenmile Creek), and at the Sugar River Upstream of Hwy 69 station.
- The detection of pesticides during months outside the application season suggests that most of these pesticides in surface water likely originate from steady baseline groundwater discharge rather than from overland flow.
- Due to lab capacity limitations in 2023, we were unable to conduct monthly sampling consistently. As a result, we could not determine which month had the highest detection of pesticides.

Exceedance of Aquatic Life Benchmarks

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

- Imidacloprid was detected in three samples collected in 2023 at South Branch Tenmile Creek (March, June, and September), at concentrations ranging from 0.0113 to 0.0172 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 two samples collected at South Branch Tenmile Creek (March and June), at concentrations of 0.0638 and 0.0672 µg/L. These concentrations exceed the Chronic Exposure value of 0.05 µg/L for Invertebrates.

Exceedance of Groundwater Standards

- Nitrate plus nitrite as Nitrogen (N) was detected at concentrations exceeding the Wis. Admin. Code Ch. NR 140 Enforcement Standard (ES) of 10 mg/L in 13 samples collected from Leola Ditch at D and 3rd, Syene Spring, and Tenmile South Branch. Concentrations ranged from 10.2 mg/L to 16 mg/L.
- The Wis. Admin. Code Ch. NR 140 Preventive Action Limit (PAL) of 0.3 µg/L for atrazine TCR was exceeded in six samples. These samples were collected at Milwaukee River, Syene Spring, and Sugar River upstream of Hwy 69. Concentrations ranged from 0.371 µg/L to 1.4833 µg/L.
- Diamino atrazine was detected in exceedance of the 0.3 µg/L Wis. Admin. Code Ch. NR 140 PAL in four samples collected at Syene Springs, with a concentrations ranging from of 0.384 µg/L to 0.519 µg/L.
- Atrazine was detected in exceedance of the 0.3 µg/L Wis. Admin. Code Ch. NR 140 PAL in one sample collected at the Milwaukee River, with a concentration of 1.43 µg/L.

2023 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 2023, the state of Wisconsin as a whole experienced below-average precipitation levels (30.13 inches) (NOAA National Centers for Environmental information 2024a). The annual average precipitation for 2023 was lower than 2022 (32.28 inches).

Figure 3 shows the statewide monthly precipitation departures from the historic normal (NOAA National Centers for Environmental information 2024a). From January to April and in October, precipitation levels were higher than the 1991-2020 baseline period, with increases ranging from 0.51 to 1.27 inches above the average. Conversely, lower-than-average precipitation occurred during the typical pesticide application and growing seasons. From May to December 2023, with the exception of October, precipitation levels were lower compared to the average for the 1991-2020 period. The decrease ranged from 0.05 to 2.81 inches below normal.

Figure 3: 2023 Monthly Precipitation Departures from 1991-2020 Average

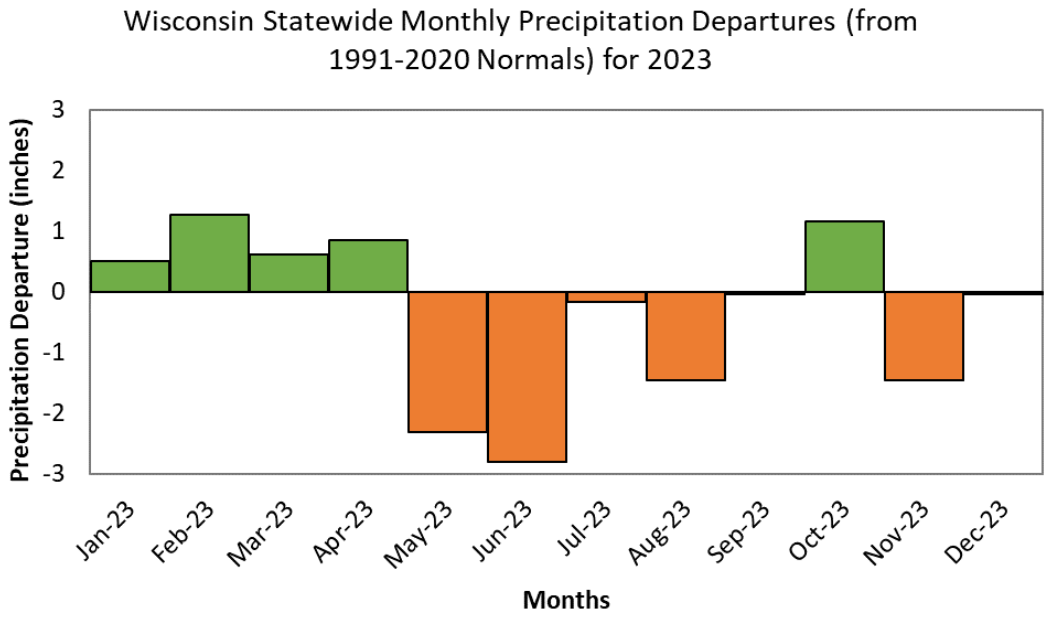


Figure 4 shows the total accumulated precipitation mapped across Wisconsin (Wisconsin State Climatology Office 2024). Accumulated precipitation in the range of 30-40 inches was experienced throughout most of the state, particularly in the northern part and the southeastern corner. Lower accumulated precipitation, in the range of 20-30 inches, was observed in the northeastern, southwestern, and some central areas of Wisconsin.

Figure 4: Accumulated Precipitation from the Wisconsin Monthly Climate Watch Archive

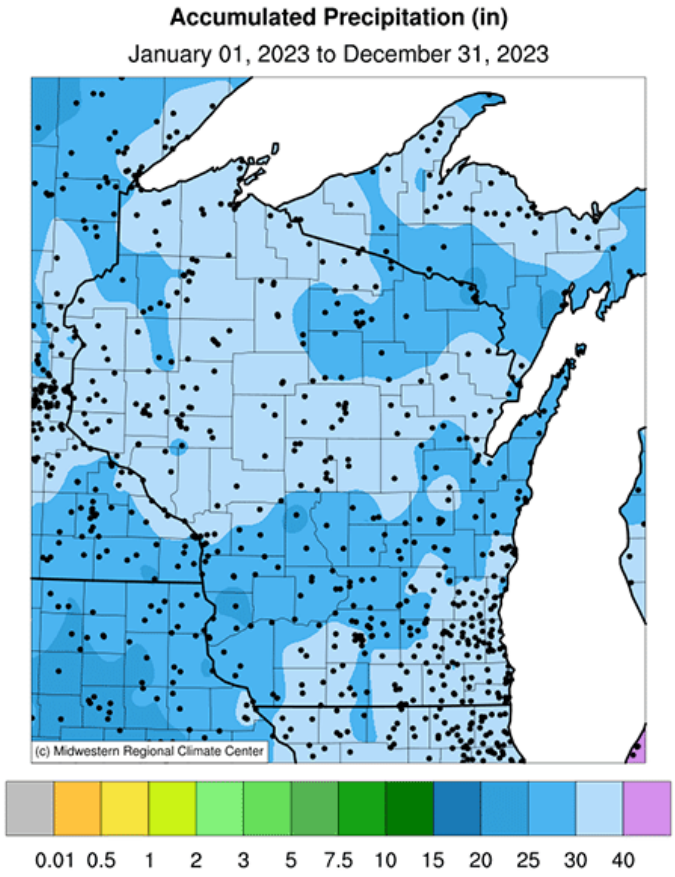
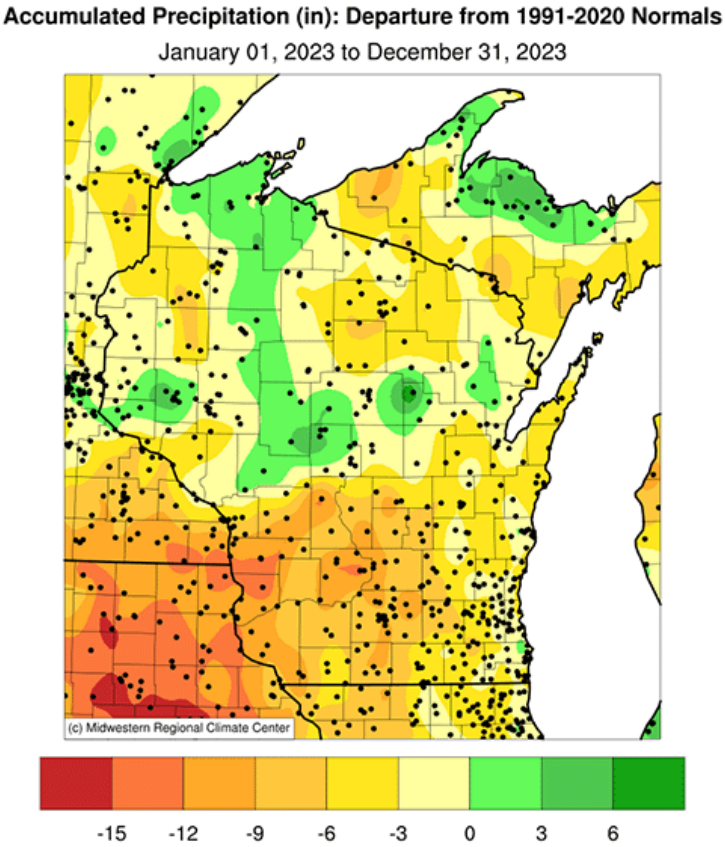


Figure 5 shows the 2023 precipitation departures, sourced from the Wisconsin State Climatology Office (Wisconsin State Climatology Office 2024). Positive deviations, shown in green, signify regions where the annual precipitation exceeded the average. Conversely, negative departures, shown in orange, highlight areas with precipitation below average. Apart from isolated regions in eastern, northern, and western Wisconsin, the state's overall precipitation either matched or were below the 1991-2020 norm. The southern half of the state, where all the DATCP Surface Water sampling locations were located, consistently experienced a below-average precipitations.

According to the NOAA Storm Events Database (NOAA National Centers for Environmental Information 2024b), the period from January to April was marked by a series of heavy snowfalls across Wisconsin. Flood and flash floods were recorded from late February to late October in the southern half of the state. Heavy rain events in October occurred on three days, primarily in the western portion of the state. Drought conditions were recorded mostly from June to December, all over the state of Wisconsin. The overall drought extent in 2023 exhibited an increase compared to 2022, with 53.5 D0% (Abnormally Dry), 37.3% D1 (Moderate Drought), 17.1% D2 (Severe Drought), 3.9% D3 (Extreme Drought), 0.2% D4 (Exceptional Drought), per the NOOA - National Oceanic and Atmospheric Administration (2024).

Figure 5: Wisconsin Accumulated Precipitation Departures from Normal



Pesticide Detection Rates

Of the 106 pesticide analytes included in DATCP's Surface Water Sampling Program testing methodology, 24 individual pesticide compounds were detected in 2023 samples from all sites (Figure 2). 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 2024). Metolachlor ESA concentrations were detected in about 84% of the samples collected. De-ethyl atrazine, a breakdown product of the active ingredient atrazine, was the second most frequently detected compound, with a detection rate of 48%. Atrazine is a widely used herbicide for controlling broadleaf and grassy weeds in crops like corn. Although atrazine TCR was calculated to be in 53% of the samples, it does not represent a single compound. Instead, it is the sum of atrazine and its three primary breakdown products (de-ethyl atrazine, de-isopropyl atrazine, and di-amino atrazine). The percentage indicates the proportion of samples that contained at least one atrazine metabolite and/or atrazine. Alachlor ESA was the third most frequently pesticide detected, with a detection rate of 44%. Alachlor was historically used as an active ingredient in herbicides for controlling grass and broadleaf weeds. However, since 2016, products containing alachlor have been cancelled, and its use is no longer permitted in the state.

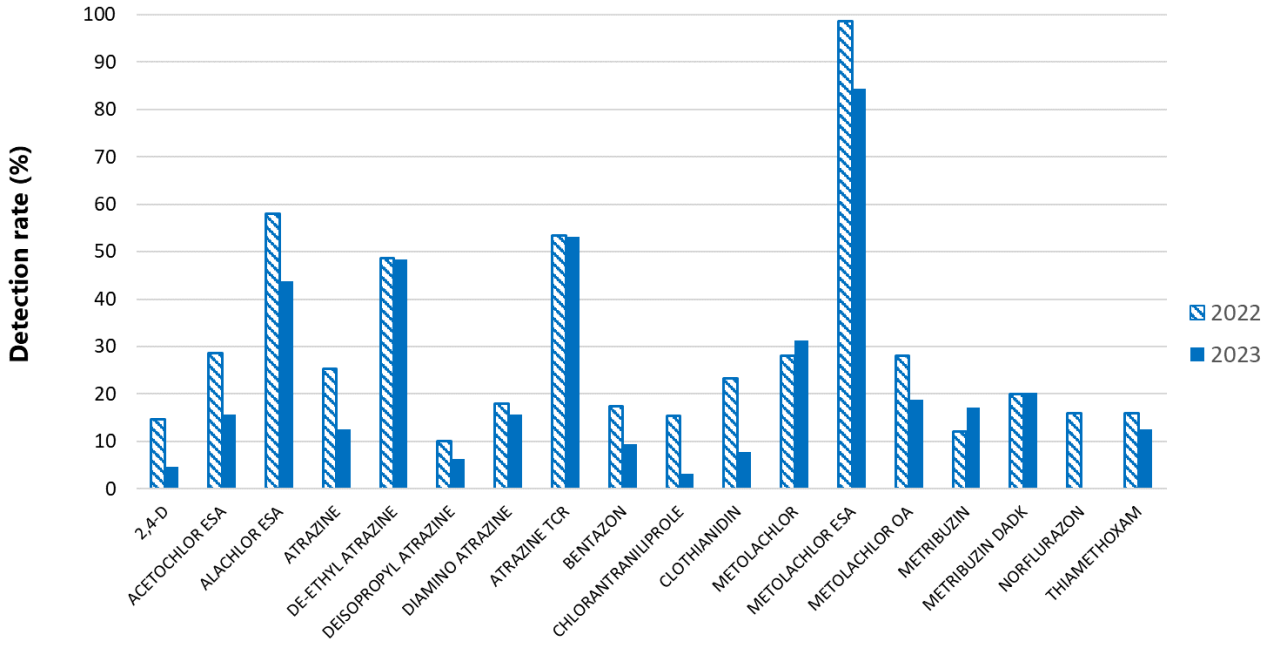
Similar compounds were also found in groundwater, as reported in the DATCP 2023 statewide survey report (Wisconsin Department of Agriculture and United States Department of Agriculture 2024d). Metolachlor ESA is historically the most widely reported pesticide detected in private potable wells, with an estimated statewide detection rate of 36.1% in 2023. According to the DATCP 2023 statewide survey report, the second most detected compound is alachlor ESA, a metabolite of alachlor, with an estimated statewide detection rate of 19.6% for 2023.

Comparison with Prior Years

In 2023, 24 individual pesticide compounds were detected, compared to 31 different pesticides detected in 2022. Dacthal-di acid, dinotefuran, and trifluralin were detected in 2023, but not in 2022, from the Tenmile Creek, Sugar River, and Fourteen Mile Creek stations, respectively. In 2023, dinotefuran, a neonicotinoid insecticide, was detected for the first time in surface water through the DATCP Surface Water Sampling Program.

Figure 6 shows the pesticide detection rates[2] in percentage for 2023 and 2022. Only pesticides detected at a rate higher than 10% in 2023 or 2022 are shown. As shown on Figure 6, the detection rates for most of the detected pesticides were lower in 2023 compared to 2022, with the exception of metolachlor. Differences in the compounds detected and their detection rates may be attributed to several factors. In 2023, samples were collected at only five out of the 11 locations sampled in 2022. Peak detections of some compounds may have been missed in 2023 because samples were not collected monthly as they were in 2022. Additionally, lower precipitation and drought events during the application and growing seasons in 2023 could have contributed to the reduced detection rates (Figure 3 and Figure 5). Less rainfall may have prevented contaminants from infiltrating groundwater and reduced surface runoff into surface water.

Figure 6: Pesticides Detection Rates in the 2023 Samples vs 2022 Samples (Includes Only the Analytes Detected in More Than 10% of the Samples in 2023 or 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. For this reason, monthly samples are usually collected, and monthly pesticide data are 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. The highest concentrations occur during the pesticide application months (May through August), followed by a decline in September and October. This decline continues over the

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

winter months, until the cycle repeats 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.

Due to restrictions on the number of samples available to be submitted to the lab, we were not able to collect monthly samples in 2023. Instead, we collected four to six samples per station throughout the year. We only collected one sample during the pesticide application months (May or June). As a result, we cannot determine the month with the highest pesticide detection rate. However, we collected three to four samples per station from September to December. The detection of compounds outside the designated application season varies not only between sites but also depending on the specific compounds being analyzed.

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 (samples collected in March, June, September, October, and December)
  - Metribuzin DADK was detected at concentrations ranging from 0.161 to 0.913 µg/L. The lowest detected concentration was recorded in June and the highest in March.
- Leola Ditch (samples collected in March, June, September, October, and December)
  - De-ethyl atrazine was detected at concentrations ranging from 0.0595 to 0.0715 µg/L. The lowest detected concentration was recorded in September and the highest in June.
  - Metribuzin was detected at concentrations ranging from 0.0916 to 0.135 µg/L. The lowest detected concentration was recorded in September and the highest in March.
  - Metribuzin DADK was detected at concentrations ranging from 0.78 to 0.858 µg/L. The lowest detected concentration was recorded in December and the highest in October.
- South Branch Tenmile Creek (samples collected in March, June, September, October, and December)
  - Alachlor ESA was detected at concentrations ranging from 0.0639 to 0.974 µg/L. The lowest detected concentration was recorded in October and the highest in March.
  - De-Ethyl atrazine was detected at concentrations ranging from 0.111 to 0.155 µg/L. The lowest detected concentration was recorded in October and the highest in March.
  - Metolachlor was detected at concentrations ranging from 0.237 to 0.452 µg/L. The lowest detected concentration was recorded in September and the highest in March.
  - Metolachlor ESA was detected at concentrations ranging from 4.37 to 6.01 µg/L. The lowest detected concentration was recorded in September and the highest in December.
  - Metribuzin was detected at concentrations ranging from 0.102 to 0.432 µg/L. The lowest detected concentration was recorded in September and the highest in March.
  - Metribuzin DADK was detected at concentrations ranging from 0.44 to 0.88 µg/L. The lowest detected concentration was recorded in September and the highest in October.
- Ashwaubenon Creek at Creamery Road (samples collected in March, June, September, October, November, and December)
  - Metolachlor ESA was detected at concentrations ranging from 0.0884 to 1.33 µg/L. The lowest detected concentration was recorded in December and the highest in March.
- East River – Hwy ZZ (samples collected in March, June, September, October, November, and December)
  - Metolachlor ESA was detected at concentrations ranging from 0.108 to 3.03 µg/L. The lowest detected concentration was recorded in October and November, and the highest in March.
- Mormon Coulee Creek (samples collected in March, May, September, October, and November)
  - De-ethyl atrazine was detected at concentrations ranging from 0.0669 to 0.0733 µg/L. The lowest detected concentration was recorded in November and the highest in September.
  - Metolachlor ESA was detected at concentrations ranging from 0.0987 to 0.131 µg/L. The lowest detected concentration was recorded in October and the highest in September.
- South Fork of Bad Axe River (samples collected in March, May, September, October, and November)

- Alachlor ESA was detected at concentrations ranging from 0.0766 to 0.0903 µg/L. The lowest detected concentration was recorded in October and the highest in March.
- De-Ethyl atrazine was detected at concentrations ranging from 0.0801 to 0.0912 mg/L. The lowest detected concentration was recorded in November and the highest in March.
- Metolachlor ESA was detected at concentrations ranging from 0.114 to 0.136 µg/L for the year. The lowest detected concentration was recorded in May and the highest in November.

- Sinsinawa River – Sinsinawa Rd. (Bi)(samples collected in March, June, August, October, November, and December)
  - Alachlor ESA was detected at concentrations ranging from 0.0563 to 0.0849 µg/L. The lowest detected concentration was recorded in March and the highest in November.
  - Metolachlor ESA was detected at concentrations ranging from 0.0817 to 1.14 µg/L. The lowest detected concentration was recorded in October and the highest in November.
- Sugar River Upstream of Hwy 69 (samples collected in March, June, August, October, November, and December)
  - Alachlor ESA was detected at concentrations ranging from 0.0656 to 0.0883 µg/L. The lowest detected concentration was recorded in December and the highest in November.
  - De-ethyl atrazine was detected at concentrations ranging from 0.0501 to 0.0899 µg/L. The lowest detected concentration was recorded in October and the highest in June.
  - Diamino atrazine was detected at concentrations ranging from 0.168 to 0.22 µg/L. The lowest detected concentration was recorded in October and the highest in June.
  - Metolachlor ESA was detected at concentrations ranging from 0.112 to 0.44 µg/L. The lowest detected concentration was recorded in October and the highest in March.
- Syene Spring is a natural groundwater discharge and hence it's strictly a representation of the groundwater quality for the area. Below are the pesticides detected in Syene Spring. Samples at this site were collected in April, June, August, and November.
  - Acetochlor ESA was detected at concentrations ranging from 0.0706 to 0.0965 µg/L. The lowest detected concentration was recorded in June and the highest in August.
  - Alachlor ESA was detected at concentrations ranging from 0.787 to 0.871 µg/L. The lowest detected concentration was recorded in June and the highest in November.
  - Atrazine was detected at concentrations ranging from 0.0664 to 0.106 µg/L. The lowest detected concentration was recorded in April and the highest in June.
  - De-ethyl atrazine was detected at concentrations ranging from 0.146 to 0.176 µg/L. The lowest detected concentration was recorded in August and the highest in June.
  - Deisopropyl atrazine was detected at concentrations ranging from 0.0673 to 0.0939 µg/L. The lowest detected concentration was recorded in November and the highest in June.
  - Diamino atrazine was detected at concentrations ranging from 0.384 to 0.519 µg/L. The lowest detected concentration was recorded in August and the highest in June.
  - Fomesafen was detected once in June at a concentration of 0.0542 µg/L.
  - Metolachlor was detected at concentrations ranging from 0.0565 to 0.0636 µg/L. The lowest detected concentration was recorded in November and the highest in June.
  - Metolachlor ESA was detected at concentrations ranging from 1.92 to 2.21 µg/L. The lowest detected concentration was recorded in June and the highest in August.
  - Metolachlor OA was detected once in November at a concentration of 0.285 µg/L.

Comparison to Standards

Pesticide concentrations identified during DATCP's 2023 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 shows these three standards alongside the range of the detected pesticide concentrations identified as part of the 2023 Surface Water Sampling Program. As noted in the Appendix B table, several pesticides and their metabolites do not have aquatic life benchmarks (17 out of 106) or established Wis. Admin. Code NR 140 ES and PAL standards (74 out of 106). DHS currently has drinking water health advisory recommendations for 17 additional pesticide compounds

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

- Clothianidin
  - In two samples collected at the Tenmile Creek South Branch, clothianidin was detected at concentrations ranging from 0.0638 and 0.0672 µg/L, which exceeds the 0.05 µg/L value for chronic exposure on invertebrates;
- Imidacloprid
  - In three samples collected at Tenmile Creek South Branch, imidacloprid was detected at concentrations ranging from 0.0113 to 0.0172 µg/L, which exceeds the 0.01 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 two individual compounds and atrazine TCR in six samples as follows:

- Atrazine (Wis. Admin. Code Ch. NR 140 PAL = 0.3 µg/L)
  - In November, atrazine was detected at a concentration of 1.43 µg/L at the Milwaukee River.
- Diamino atrazine (Wis. Admin. Code Ch. NR 140 PAL = 0.3 µg/L)
  - In samples collected at Syene Spring (all samples - April, June, August, and November), diamino atrazine concentrations ranged between 0.384 µg/L to 0.519 µg/L.
- Atrazine TCR (Wis. Admin. Code Ch. NR 140 PAL = 0.3 µg/L)
  - In November, atrazine TCR was calculated to be 1.4833 µg/L at the Milwaukee River;
  - In all the samples collected at Syene Spring (April, June, August, and November), atrazine TCR concentrations ranged between 0.6909 µg/L to 0.8949 µg/L; and
  - In June, atrazine TCR was calculated to be 0.371 µg/L at the Sugar River.

Table 4 lists 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 3: 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	---	Milwaukee River	11/29/2023	1.43
Diamino atrazine	3	0.3	---	Syene Spring	4/6/2023	0.428
					6/1/2023	0.519
					8/30/2023	0.384
					11/7/2023	0.388
Atrazine TCR	3	0.3	---	Milwaukee River	11/29/2023	1.4833
				Sugar River Upstream of Hwy 69	6/1/2023	0.371
				Syene Spring	4/6/2023	0.7258
					6/1/2023	0.8949
					8/30/2023	0.6788
					11/7/2023	0.6909

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

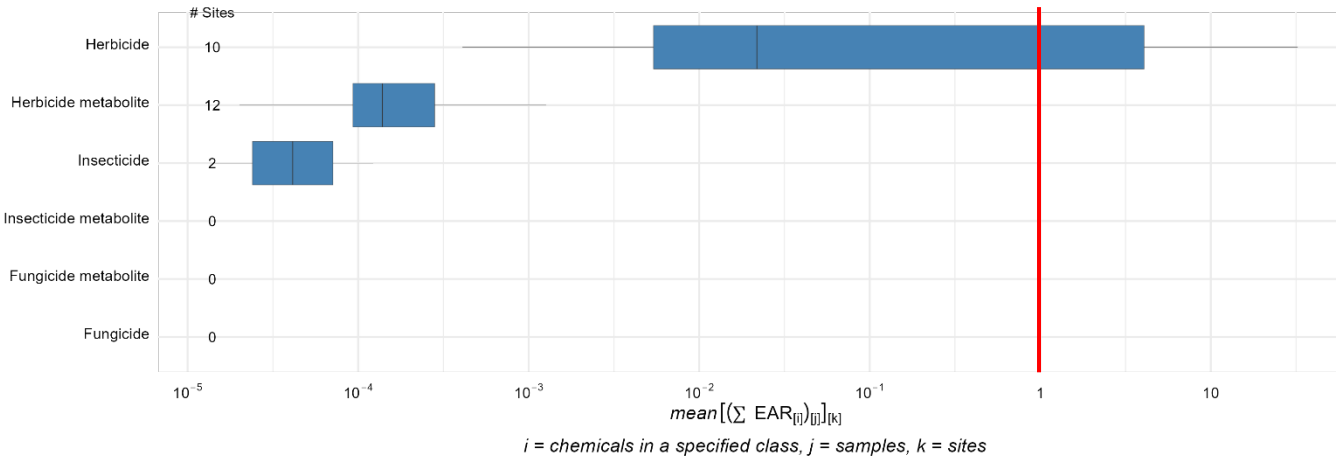
Comparing a detected pesticide (including metabolites) to the regulatory standards may not fully identify the total risk to human health and the environment. The majority of the published water quality standards or benchmarks are based on concentrations for the occurrence of a single compound. This approach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

Toxicity Evaluation

Toxicity Forecasting (ToxCast) is a research program by the U.S. Environmental Protection Agency (EPA) designed to evaluate the effects of thousands of chemicals on various biological pathways and targets (United States Environmental Protection Agency 2024). In 2018, the USGS introduced ToxEval, an R package designed to facilitate the analysis and visualization of ToxCast data (DeCicco, et al. 2024). ToxEval provides tools to assess chemical toxicity, compare chemical concentrations with ToxCast assay results, and generate summary plots and tables. One of its key features is the calculation of the Effective Activity Ratio (EAR), which determines whether the biological activity of specific chemicals in water bodies is above or below baseline levels. An EAR greater than 1 indicates that a compound exhibits activity exceeding the baseline or control level for the target being tested.

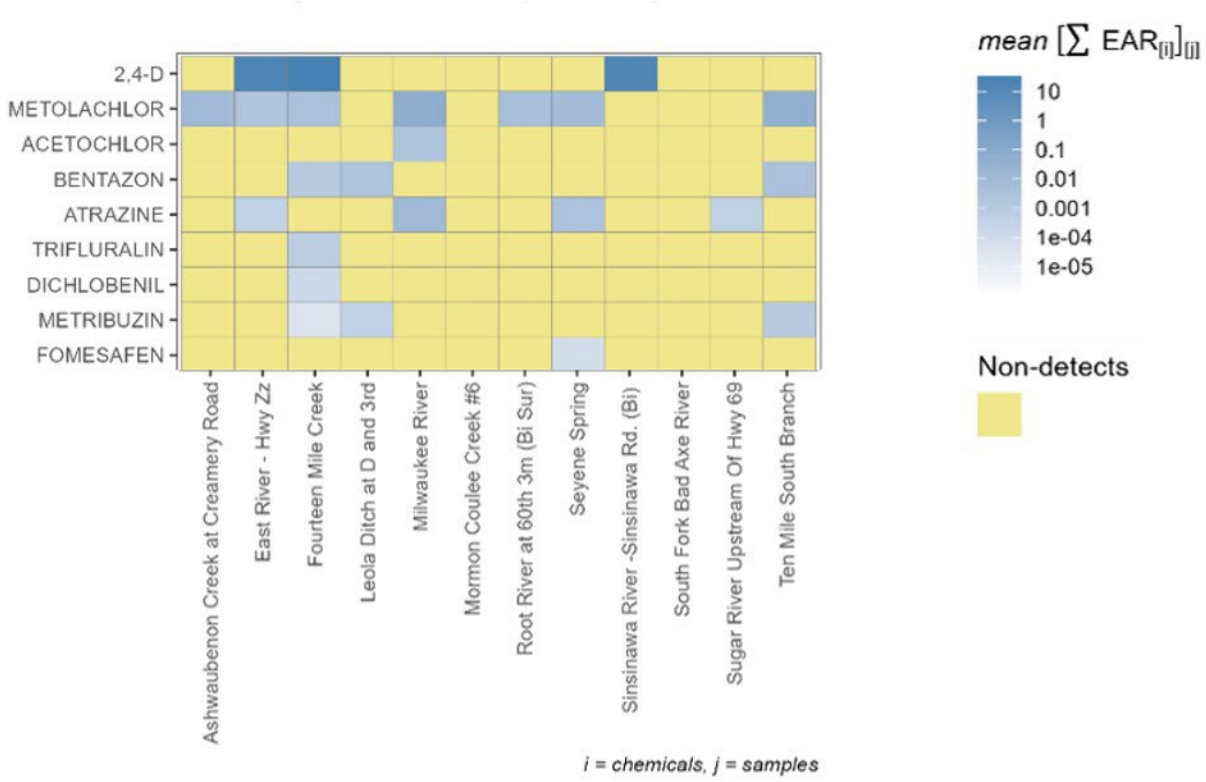
We analyzed data from the 2023 DATCP Surface Water program, focusing on the mean Effective Activity Ratio (EAR) rather than the maximum, to provide a general sense of the typical activity level of each compound. Figure 7 presents a boxplot displaying the mean EAR ranges for each pesticide group (herbicides, herbicide metabolites, insecticides, insecticide metabolites, fungicides, and fungicide metabolites) at the various sites investigated, and the total number of sites where each pesticide group was detected. The graph reveals that a mean EAR greater than 1 was only associated with the herbicide group.

Figure 7. Boxplot with Mean Effective Activity Ratio (EAR) Calculated for Each Pesticide Group at Each Site Sampled.



To further investigate which specific herbicides have a mean EAR greater than 1, we generated heat maps for each site and each detected herbicide compound. As shown in Figure 8, an EAR greater than 1 is primarily associated with the 2,4-D compound detected at the sampling stations on the East River, Fourteen Mile Creek, and Sinsinawa River. This suggests the concentrations at which 2,4-D has been detected at those stations could have a significant biological effect or toxicity and pose a potential risk to the environment or human health.

Figure 8. Heat map with Mean Effective Activity Ratio (EAR) Calculated for Each Herbicide Detected at Each Site Sampled.



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). Four of these compounds (clothianidin, dinotefuran, imidacloprid, and thiamethoxam) were detected in surface water samples collected in 2023. The remaining two neonicotinoid compounds were not detected in any surface water samples collected through the DATCP Surface Water Program. The detection of clothianidin, dinotefuran, imidacloprid, and/or thiamethoxam is not unexpected, given their high solubility in water.

Thiamethoxam was first detected at the Milwaukee River and at the Neenah Slough sampling locations in 2011. Since then, DATCP recorded a total of 166 thiamethoxam detections in Wisconsin's surface waters. Of these, 158 were found within the Central Sands area since 2014. Between 2017 and 2021, thiamethoxam was detected on several occasions, predominantly in June samples, at one of the Root River stations. In 2023, thiamethoxam was detected in eight samples collected from stations within the Central Sands region, specifically at Fourteen Mile Creek, Leola Ditch at D and 3rd, and Tenmile Creek South Branch. Concentrations ranged from 0.0141 to 0.0879 µg/L.

Imidacloprid was first detected at the Tenmile Creek in December 2014. Since then, DATCP recorded a total of 77 imidacloprid detections in Wisconsin's surface waters. Of these, 67 were found within the Central Sands area since 2014. Imidacloprid was detected once in the Milwaukee River in 2022 and on several occasions, primarily in June samples, in the Root River between 2018 and 2022. In 2023, imidacloprid was detected in three samples collected at the South Branch Tenmile Creek station. Concentrations ranged from 0.0113 to 0.0172 µg/L.

Clothianidin was first detected at the Root River in June 2018. Since then, DATCP recorded a total of 113 clothianidin detections in Wisconsin's surface waters. Of these, 74 were found within the Central Sands area since 2014. 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 2022), the Pecatonica River (in 2022), the Rock River (in 2022), the Root River (between 2018 and 2022), the Syene Spring (in 2020 and 2022), and the West Branch of Sugar River (between 2020 and 2022). In 2023, clothianidin was detected in five samples collected at the Leola Ditch at D and 3rd and Tenmile Creek South Branch. Concentrations ranged from 0.0106 to 0.0672 µg/L.

Dinotefuran was detected for the first time this year (2023) since the beginning of the DATCP Surface Water Sampling Program. Dinotefuran was detected in one sample collected at the Sugar River Upstream of Hwy 69 in October at a concentration of 0.0196 µg/L.

In 2023, one or more neonicotinoids were detected in 10 out of 64 samples, yielding a detection rate of 16%. This represents a decrease from 2022, when one or more neonicotinoids were found in 46 out of 150 samples, yielding a detection rate of 31%.

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 in Wisconsin. 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 2024c). 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. This means its application is subject to stricter regulations compared to the federal guidelines.

Because most of the PAs have been in place for almost 30 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. Syene Spring and the Sugar River Upstream of Hwy 69 stations are located within a PA.

Atrazine parent material concentrations were detected in 12% (eight samples) of the river, stream, or spring water samples collected in 2023, marking a decrease in the rate of atrazine detections relative to the 2022 samples (25%).

Atrazine TCR (sum of atrazine and its metabolite) was detected in 53% (34 samples) of the river, stream, or spring water samples collected in 2023, marking a slight decrease in the atrazine TCR detection rate relative to the 2022 samples (53%).

The following is a summary of the atrazine or atrazine TCR findings for each river or stream where it was detected in 2023:

- In samples collected at the Leola Ditch station in March, June, September, and December, de-ethyl atrazine was detected at concentrations ranging from 0.0628 and 0.0715 µg/L. No other metabolites or atrazine parent material were detected.
- In samples collected at the Tenmile station in March, June, September, October, and December, de-ethyl atrazine was detected at concentrations ranging from 0.111 and 0.155 µg/L. No other metabolites or atrazine parent material were detected.
- The greatest concentrations of atrazine and atrazine TCR were found in a surface water sample from the Milwaukee River collected in November. In this sample, atrazine was detected at 1.43 µg/L and de-ethyl atrazine was detected at 0.0533 µg/L, resulting in an atrazine TCR concentration of 0.14833 µg/L. In the subsequent sample collected in December, atrazine concentrations decreased to 0.0959 µg/L and de-ethyl atrazine was not detected. Atrazine and its metabolites were not detected in other samples collected at the Milwaukee River in 2023. Although concentrations of atrazine increased since 2022, fewer Milwaukee River samples detected atrazine in 2023 compared to 2022.
- In the June sample collected at the East River Hwy ZZ, atrazine was found at a concentration of 0.0567 µg/L.
- In samples collected at the Mormon Coulee Creek station in March, May, September, October, and November, de-ethyl atrazine was detected at concentrations ranging from 0.0669 and 0.0733 µg/L. Overall, concentrations of de-ethyl atrazine decreased compared to 2022.

- In samples collected at the South Fork of the Bad Axe River station in March, May, September, October, and November, de-ethyl atrazine and atrazine TCR was detected at concentrations ranging from 0.0801 and 0.0912 µg/L. Atrazine or other atrazine metabolites were not detected. Similar results were found in 2022 at this location.
- In samples collected at the Sinsinawa River in June and August, de-ethyl atrazine was found at concentrations ranging from 0.0522 and 0.0592 µg/L. Diamino atrazine was detected a concentration of 0.158 µg/L in the month of November.
- Atrazine, de-ethyl atrazine, and diamino atrazine were all detected in the June sample collected at the Sugar River Upstream of Hwy 69. Atrazine TCR in June was calculated to be 0.371 µg/L. Atrazine was not detected in any other samples collected in 2023 at this station. De-ethyl atrazine was detected throughout the year (except for March) at concentrations ranging between 0.0501 and 0.0899 µg/L. Diamino atrazine was detected throughout the year (except for March) at concentrations ranging between 0.168 and 0.199 µg/L. Atrazine TCR was calculated to be between 0.2181 and 0.371 µg/L. The Wis. Admin. Code Ch. NR 140 PAL value of 0.3 µg/L for atrazine TCR was exceeded in June.
- Atrazine, de-ethyl atrazine, deisopropyl atrazine, and diamino atrazine were detected in each sample collected at Syene Spring. Atrazine concentrations ranged from 0.0664 to 0.106 µg/L. De-ethyl atrazine was detected at concentrations ranging from 0.146 to 0.176 µg/L. Deisopropyl atrazine was detected at concentrations ranging from 0.0673 to 0.0939 µg/L. Diamino atrazine was detected at concentrations ranging from 0.384 to 0.519 µg/L. Atrazine TCR was detected at concentrations ranging from 0.6788 to 0.8949 µg/L. The Wis. Admin. Code Ch. NR 140 PAL value of 0.3 µg/L for atrazine TCR was exceeded in each sample collected in 2023 at Syene Spring. The concentrations of atrazine and its metabolites were generally similar to those in 2022, except for June, when higher concentrations were recorded compared to the previous year.

Syene Spring has been included in the DATCP Surface Water Monitoring Program since 2019, 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 2023 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 pesticide concentrations appear to remain stable throughout the year, we plan to continue sampling in the spring but with reduced frequency, pursuing two to three samples per year.

The Ashwaubenon Creek, the East River, and Sinsinawa River were sampled by USGS between 1990 and 2004. Concentrations of atrazine exceeding the Enforcement Standard of 3 µg/L were found at that time. Moreover, at the Ashwaubenon Creek and the Sinsinawa River, historic atrazine concentrations exceeded the level at which atrazine is expected to adversely affect aquatic plants. This level has been recently set at 9.7 µg/L by the U.S. Environmental Protection Agency (Environmental Protection Agency 2024). According to the data collected at the three stations along the Ashwaubenon Creek, the East River, and Sinsinawa River through the DATCP 2023 Surface Water Program, atrazine concentrations were found well below both thresholds of 3 µg/L and 9.7 µg/L.

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 58 of the 64 surface water samples collected between March and December for DATCP's 2023 Surface Water Sampling Program. The greatest nitrogen concentration observed in 2023 was 16 mg/L detected in the December sample collected at Tenmile Creek South Branch.

The following is a summary of nitrogen results for 2023 river, stream, and spring samples:

- At the Fourteen Mile Creek station, nitrogen concentrations ranged from non-detected to 5.84 mg/L. Nitrogen concentrations peaked in March before declining in June. In March and June, nitrogen concentrations exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL. No nitrogen was detected in September and October.
- At the Leola Ditch at D and 3rd, nitrogen concentrations ranged from 11.5 to 14 mg/L. The greatest concentration was observed in March. Each sample collected at this station exceeded the Wisconsin Administrative Code NR 140 ES limit of 10 mg/L.
- At the Tenmile Creek, nitrogen concentrations ranged from 12.1 to 16 mg/L. The greatest concentration was observed in December. Each sample collected at this station exceeded the Wisconsin Administrative Code NR 140 ES limit of 10 mg/L.
- At the Milwaukee River, nitrogen concentrations ranged from 0.627 to 1.66 mg/L. The greatest concentration was observed in December.
- At the Root River, nitrogen concentrations ranged from non-detected to 4.89 mg/L. The greatest concentration was observed in December. Concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L in March, October, and December. No nitrogen was detected in September.
- At the Ashwaubenon Creek, nitrogen concentrations ranged from non-detected to 3.53 mg/L. The greatest concentration was observed in November. Concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L in March and November. No nitrogen was detected in October.
- Among the sites sampled in the DATCP Surface Water Sampling program through 2023, the East River - Hwy ZZ exhibited the most significant variation in nitrogen values with concentrations ranging from non-detected to 6.42 mg/L. The greatest concentration was recorded in March. In this only instance, the concentration exceeded the 2 mg/L Wis. Admin. Code NR PAL.
- At the Mormon Coulee Creek #6, nitrogen concentrations ranged from 1.64 to 2.2 mg/L. The greatest concentration was observed in November. Concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L in October, and November.
- At the South Fork of Bad Axe River, nitrogen concentrations ranged from 2.42 to 3.06 mg/L. The greatest concentration was observed in November. In each sample, concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L.
- At the Sinsinawa River, nitrogen concentrations ranged from 4.93 to 7.52 mg/L. The greatest concentration was observed in March. In each sample, concentrations exceeded the Wis. Admin. Code NR 140 PAL of 2 mg/L.
- At the Sugar River Upstream of Hwy 69, nitrogen concentrations ranged from 4.24 to 7.47 mg/L. The greatest concentration was observed in August. In each sample, concentrations exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL.
- At Syene Spring, nitrogen concentrations ranged from 9.45 mg/L to 10.8 mg/L. With the exception of the sample collected in June, the remaining samples had concentrations exceeding the Wis. Admin. Code NR 140 ES of 10 mg/L. This is very similar to what was found in the samples collected at Syene Spring in 2022.

Table 5 includes a summary of the DATCP's 2023 Surface Water Sampling Program detections for nitrate plus nitrite as N.

Table 4: 2023 Surface Water Sampling Program Nitrogen (Nitrate and Nitrite) Analytical Results

Sample Location	Nitrate + Nitrite as Nitrogen Concentration Range (mg/L)
Fourteen Mile Creek (Ditch # 7) - CTH D	ND-5.84
Leola Ditch at D and 3rd	11.5-14
Tenmile Creek South Branch – Taft Rd.	12.1-16
Milwaukee River at Eastbrook Park	0.627-1.66
Root River at 60th 3m	ND-4.89
Mormon Coulee Creek #6 - Bridge at CTH YY	1.64-2.2
South Fork Bad Axe River – Oliver Rd	2.42-3.06
Ashwaubenon Creek at Creamery Rd	ND-3.53
East River - Hwy ZZ	ND-6.42
Sinsinawa River	4.93-7.52
Sugar River upstream of Hwy 69	4.24-7.47
Syene Spring	9.45-10.8

Notes: mg/L - milligrams per liter
ND – Non Detect, i.e., concentration not in excess of laboratory reporting limits

2024 Program Goals and Objectives

DATCP's Surface Water Sampling Program will continue in 2024. It is expected that the following tasks will be completed:

- Collection of monthly surface water samples at 23 stream, river, or spring locations for the calendar year to include:
  - Collect monthly samples from nine locations sampled in 2023, and
  - Collect monthly samples from 14 new locations.
- Prepare a 2024 Data Summary Report to be completed by the third quarter of 2024; 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 2024 surface water results will provide additional information for the following previously sampled locations:

- Fourteen Mile Creek (Ditch # 7) - CTH D;
- Leola Ditch at D and 3rd;
- South Branch Tenmile Creek - Taft Rd (Site 7) Milwaukee River at Estabrook Park;
- Root River at 60th 3m (Bi Sur);
- Mormon Coulee Creek #6 - Bridge at CTH YY;
- South Fork Bad Axe River – Oliver Rd;
- Sugar River Upstream of Hwy 69; 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 2024, we will extend our sampling efforts, including both stations located further upstream from those sampled in 2023 and entirely new additions to our program. The following stations have been selected for sampling:

- Vermont Creek At Michaelis Road (Station ID 10012507) in Dane County;
- Wendt Creek - Hwy 78 (Station ID 10012609) in Dane County;
- Halfway Prairie Creek at Farm Near Mazomanie WI (Station ID 133413) in Dane County;
- Mill Creek at CTH C (Station ID 10030075) in Iowa County;
- Spring Brook - Before Eau Claire River at Nolan Rd. (Station ID 373384) in Marathon County;
- Eau Claire River Cty Y Upstream (Station ID 10052249) in Langlade County;
- East Branch Eau Claire River (Station ID 10020426) in Langlade County;
- Oldens Creek (Station ID 10054699) in Langlade County;
- Tomorrow River at Clementson Rd near Nelsonville (Station ID 503169) in Portage County;
- Honey Creek - Near Confluence with Menominee River (Station ID 413006) in Milwaukee County;
- Hay River at N Bridge St (Station ID 173209) in Dunn County;
- Red Cedar River 130ft N of CTH W Bridge (Station ID 10037357) in Dunn County;
- Red Cedar River Cth A & I Bridge - Downstream of Confluence w/ Chetek River (Station ID 10029519) in Barron County; and
- Red Cedar River at Cth OO (Station ID 033237) in Barron County.

Acknowledgments

DATCP's Bureau of Agrichemical Management's (ACM) financial information includes the state fiscal year (FY) 2023 from July 1, 2022 through June 30, 2023. Federal grants operated from October 1, 2022 through September 30, 2023. 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.

Raw data can be downloaded through the EPA Water Quality Portal or by scanning the QR code at the end of Appendix B. For any questions and clarifications, please do not hesitate to reach out to us at DATCPGW@wisconsin.gov or at (608) 224-4503.

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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
CTH _____ County Highway
CTY _____ County Highway
DATCP _____ Wisconsin 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
Rd _____ Road
Hwy _____ State Highway
SWIMS _____ Surface Water Integrated Monitoring System
TCR _____ Total chlorinated resides of atrazine
USDA _____ United States Department of Agriculture
USGS _____ United States Geological Survey
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

2023 Surface Water Sampling Program Analytical Results, Summary

2023 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	3	0.05	0.189 - 0.327	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	1	0.05	0.0779	0.7	7	--	190	130	4100	22.1	1.43	3.4
Acetochlor ESA	Herbicide Metabolite	10	0.05	0.0583 - 0.332	46	230	--	>90000	--	>62500	--	9900	--
Acetochlor OA or OXA	Herbicide Metabolite	ND	0.3	--	46	230	--	--	--	--	--	--	--
Acetochlor Metabolites	Sum of Acetochlor ESA and Acetochlor OA	10	--	0.0583 - 0.332	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	Herbicide Metabolite	28	0.053	0.0563 - 1.72	4	20	--	>52000	--	>52000	--	3600	>120000
Alachlor OA	Herbicide 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	8	0.05	0.0567 - 1.43	0.3	3	--	2650	5	360	60	<1	4.6
De-ethyl atrazine	Herbicide Metabolite	31	0.05	0.0501 - 0.176	0.3	3	--	--	--	--	--	--	--
De-isopropyl atrazine	Herbicide Metabolite	4	0.05	0.0673 - 0.0939	0.3	3	--	--	--	--	--	--	--
Di-amino atrazine	Herbicide Metabolite	10	0.2	0.158 - 0.519	0.3	3	--	--	--	--	--	--	--
Atrazine TCR	Sum of Atrazine and atrazine metabolites	34	--	0.0522 - 1.4833	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	6	0.05	0.0566 - 0.262	60	300	--	95000	9830	31150	101200	4500	5350
Bicyclopyrone	Herbicide	ND	0.05	--	--	--	--	>46700	10000	>46650	103700	2000	13

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2023 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	ND	0.05	--	--	--	--	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	2	0.05	0.0583 - 0.0637	--	--	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	Insecticide Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Clomazone	Herbicide	ND	0.05	--	--	--	--	1450	350	2700	2200	167	30200
Clopyralid	Herbicide	ND	0.05	--	--	--	--	51500	10000	116500	4700	6900	90300
Clothianidin	Insecticide	5	0.01	0.0106 - 0.0672	--	--	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	Herbicide Metabolite	2	0.5	0.607 - 0.93	--	--	70	--	--	--	--	--	--
Dacthal Mono-acid	Herbicide Metabolite	ND	0.5	--	--	--	70	--	--	--	--	--	--
Dacthal Total	Sum of Dacthal , Dacthal Di-acid, and Dacthal Mono-acid	2	--	0.607 - 0.93	--	--	70	--	--	--	--	--	--
Diazinon	Insecticide	ND	0.05	--	--	--	--	45	<0.55	0.105	0.17	3700	--
Diazinon Oxon	Insecticide Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dicamba	Herbicide	ND	0.3	--	60	300	--	14000	>9900	>50000	> 42000	61	1290
Dichlobenil	Herbicide	1	0.05	0.0514	--	--	--	2465	<330	3100	560	1500	30
Dimethenamid	Herbicide	ND	0.05	--	5	50	--	3150	120	6000	1360	14	8.9
Dimethenamid ESA	Herbicide Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--

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2023 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	Herbicide Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dimethoate	Insecticide	ND	0.05	--	0.4	2	--	3100	430	21.5	0.5	20000	>92600
Dinotefuran	Insecticide	1	0.01	0.0196	--	--	--	>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	1	0.05	0.0542	--	--	25	63000	9400	188000	50000	92	210
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	3	0.01	0.0113 - 0.0172	--	--	0.2	114500	9000	0.385	0.01	--	--
Isoxaflutole	Herbicide	ND	0.05	--	--	--	3	>850	80	>750	350	110	4.9
Isoxaflutole DKN	Herbicide Metabolite	ND	0.05	--	--	--	3	>15300	--	>29800	--	5000	75
Isoxaflutole Total	Sum of Isoxaflutole and Isoxaflutole DKN	ND	0.05	--	--	--	3	--	--	--	--	--	--
Linuron	Herbicide	ND	0.05	--	--	--	--	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	ND	0.05	--	--	--	--	>34000	--	>92000	--	--	--
MCPB	Herbicide	ND	0.1	--	--	--	--	1960	<530	25100	2510	1370	200
MCPP	Herbicide	ND	0.05	--	--	--	--	>46500	--	>45500	50800	14	1300
Mesotrione	Herbicide	ND	0.1	--	--	--	--	>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

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2023 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
Metolachlor	Herbicide	20	0.05	0.053 - 2.92	10	100	--	1600	30	11750	3200	8	14
Metolachlor ESA	Herbicide Metabolite	54	0.05	0.0817 - 6.01	260	1300	--	24000	--	>54000	--	>99450	43000
Metolachlor OA or OXA	Herbicide Metabolite	12	0.27	0.275 - 3.92	260	1300	--	>46550	--	7700	--	57100	>95400
Metolachlor Metabolites	Sum of Metolachlor ESA and Metolachlor OA	54	--	0.0817 - 9.44	260	1300	--	--	--	--	--	--	--
Metribuzin	Herbicide	11	0.05	0.0518 - 0.432	14	70	--	21000	<3000	2100	1290	8.1	130
Metribuzin DA	Herbicide Metabolite	2	0.1	0.115 - 0.125	--	--	--	--	--	--	--	--	--
Metribuzin DADK	Herbicide Metabolite	13	0.12	0.161 - 0.913	--	--	--	--	--	--	--	--	--
Metsulfuron methyl	Herbicide	ND	0.05	--	--	--	--	>75000	4500	>75000	--	31	0.36
Nicosulfuron	Herbicide	ND	0.05	--	--	--	--	>500000		>500000	43000	--	--
Norflurazon	Herbicide	ND	0.05	--	--	--	--	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	Fungicide 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	ND	0.05	--	--	--	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
Thiamethoxam	Insecticide	8	0.01	0.0141 - 0.0879	--	--	120	>57000	20000	17.5	0.74	>99000	>90200
Thiencarbazone methyl	Herbicide	ND	0.05	--	--	--	10000	>52000	4800	>49300	3540	298	0.8

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2023 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
Triclopyr	Herbicide	ND	0.05	--	--	--	--	58500	--	66450	--	32500	--
Trifluralin	Herbicide	1	0.05	0.115	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 7/22/2024)
https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

2023 Surface Water Sampling Program Analytical Results - QR code