2021 Surface Water Pesticide Monitoring Program Annual Report

ANNUAL REPORT



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Introduction

In 2021, 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 effect pesticide use is having on 11 select rivers and streams and one spring in Wisconsin, for a total of 15 sampling locations. Surface water samples were collected monthly 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 2022 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, 2022a). 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 area at risk for groundwater pollution. The Surface Water Sampling Program satisfy the following statutory monitoring requirement (Wis. Stats., Ch. §160.27):

1. <u>Problem assessment monitoring</u>, 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 (January through 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 2021 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 WDNR staff conducts much of the sampling, time commitment and willingness 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.

2021 PROGRAM LOCATIONS

Since 2019, the program has generally consisted of collecting surface water samples from at least ten locations; usually, 50% are repeat locations and 50% are new locations to the program. In 2021, most samples were collected at long-term repeat locations to continue to build the database and measure annual variability. Long-term repeat locations include the following:

- Wisconsin River, near the city of Muscoda;
- Mississippi River at Lock and Dam #9;
- Milwaukee River, within Estabrook Park in Milwaukee County;
- Ten Mile Creek at Evergreen Road (Rd), within the Central Sands Region;
- Fourteen Mile Creek at County Highway (CTH) D, also within the Central Sands Region;
- Leola Ditch in the town of Aniwa, within the Central Sands Region;
- Syene Spring in Dane County.
- West Branch of the Sugar River at CTH PB in Dane County (a repeat from prior years);
- Root River at 8-Mile Rd in Racine County (a repeat from prior years); and
- Duncan Creek at 157th Avenue, just south of the City of Bloomer.

While new locations for 2021 included:

- Mormon Coulee Creek Bridge #6 at County Rd YY in La Crosse County;
- South Fork of the Bad Axe River in Vernon County;
- North Branch of Ten Mile Creek at Isherwood, within the Central Sands Region;
- Ten Mile Creek at County Rd U, within the Central Sands Region;
- North Branch of Ten Mile Creek Ditch 5 at Taft Rd, within the Central Sands Region; and
- South Branch of Ten Mile Creek at Taft Rd, within the Central Sands Region.

A total of 11 perennial rivers and streams and a spring were selected for the 2021 sampling program. A total of 82 samples were collected between March and December for chemical analysis of pesticides and nitrate plus nitrite as nitrogen (N). Ten Mile Creek at Evergreen Rd, Fourteen Mile Creek at CTH D, and Leola Ditch at Aniwa are three sites located in the Central Sands Region and are typically included as long-term repeat sample locations. These sites were included in the 2021 Surface Water Sampling Program but were only sampled in April due to the sampler's unavailability. The Ten Mile Creek was sampled at four additional sites, other than Ten Mile Creek at Evergreen Rd, in September 2021.

In February of 2021, Kirk Olson, senior fisheries biologist with DNR - Bureau of Fisheries Management, contacted DATCP regarding pesticide concentrations in trout streams within the Driftless Area (southwest Wisconsin). The DNR was getting feedback and inquiries from fishing organizations and fishery people regarding concerns about declining biota hatches within these areas. In correspondence between the DNR

and DATCP, it was mentioned that declines in macroinvertebrates had been observed and sampling for pesticides, with an emphasis on neonicotinoids, would be valuable to understand if pesticide contamination is affecting the aquatic ecosystem. In response, DATCP added Mormon Coulee Creek and the Bad Axe River to the 2021 Surface Water Monitoring Program, both located within the Driftless Area. Mormon Coulee Creek is located in La Crosse County and the South Fork of the Bad Axe River is located in Vernon County. These streams are subjects of streambank preservation and restoration as class II and class I trout streams, respectively. A significant groundwater discharge into the streams maintains a constant low stream temperature suited to trout populations. Table 1 lists the 2021 surface water sampling program locations, and Figure 1 shows the 16 locations relative to the State of Wisconsin and county boundaries. Table 2 summarizes the watershed size and land use specific to each 2021 sampling location, with the exception of locations included in large watersheds (Mississippi and Wisconsin Rivers), using data provided by the U.S. Department of Agriculture's (USDA) Agricultural Statistics Service (United States Department of Agriculture, 2021).

River / Stream Name	SWIMS ID	County	Program Years
Duncan Creek at 157 th Avenue	093072	Chippewa	2
Root River at 8-Mile Rd	10039425	Racine	4
Fourteen Mile Creek at CTH D	013173	Adams	5
Leola Ditch at Aniwa	10009165	Adams	5
Milwaukee River within Estabrook Park	413640	Milwaukee	4
Mississippi River at L&D #9	123016	Crawford	9
Mormon Coulee Creek - Bridge #6 at County Rd YY	10008928	La Crosse	1
Syene Spring	10051662	Dane	3
South Fork of the Bad Axe River	10022633	Vernon	1
Ten Mile Creek at Evergreen Rd	10016427	Portage	7
North Branch of Ten Mile Creek at Isherwood	10042017	Portage	1
Ten Mile Creek at County Rd U	10009128	Portage	1
North Branch of Ten Mile Creek - Ditch 5 at Taft Rd	10009200	Portage	1
South Branch of Ten Mile Creek at Taft Rd	10009196	Portage	1
Wisconsin River near Muscoda	223282	Grant	9
West Branch of the Sugar River at CTH PB	10017221	Dane	4

Table 1: 2021 Surface Water Sampling Program Rivers and Streams

Notes: SWIMS - Surface Water Integrated Monitoring System

Figure 1: 2021 Surface Water Sampling Program Rivers, Streams, and Spring Locations



Table 2: 2021 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 Size (Acres)
Poot Piver	40,649	6,615	9,223	6,519	10,299	10,651	0	84 450
Root River	(48.1%)	(7.8%)	(10.9%)	(7.7%)	(12.2%)	(12.6%)	(0%)	04,430
Milwaukee	55,827	13,886	7,692	5,579	16,730	5,136	0	106 163
River	(52.6%)	(13.1%)	(7.2%)	(5.3%)	(15.8%)	(4.8%)	(0%)	100,105
Duncan Creek	7,058	3,673	14,533	19,718	17,669	13,972	3	76 783
Duncan creek	(9.2%)	(4.8%)	(18.9%)	(25.7%)	(23%)	(18.2%)	(0%)	70,705
Bad Ave River	7,727	1,598	47,969	18,910	32,201	11,765	0	120 275
Dad Axe River	(6.4%)	(1.3%)	(39.9%)	(15.7%)	(26.8%)	(9.8%)	(0%)	120,275
Mormon Creek	3,996	4,892	25,147	4,521	10,026	2,820	0	66 350
Mormon creek	(6%)	(7.4%)	(37.9%)	(6.8%)	(15.1%)	(4.3%)	(0%)	00,330
Mississippi River		Too lar	ge of a wat	ershed to r	nake a mea	ningful cal	culation	
Ten Mile Creek	5,407	6,566	23,552	17,408	17,542	14,832	11,817	97 908
	(5.5%)	(6.7%)	(24.1%)	(17.8%)	(17.9%)	(15.1%)	(12.1%)	77,700
Fourteen Mile	5,231	6,443	16,701	6,804	8,553	4,866	5,279	EE 424
Ditch)	(9.4%)	(11.6%)	(30.1%)	(12.3%)	(15.4%)	(8.8%)	(9.5%)	JJ,420
Wisconsin River		Too lar	ge of a wat	ershed to r	nake a mea	ningful cal	culation	
Syene Spring			Size of	the captur	e zone is ur	ıknown		
West Branch	2,996	709	9,481	9,564	15,007	5,051	1	12 811
Sugar River	(7%)	(1.7%)	(22.1%)	(22.3%)	(35.1%)	(11.8%)	(0%)	42,014

This is the third 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, 2019). Analytical results of water samples collected from 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, 2022b). Because atrazine cannot be used in this area, no atrazine detections would be expected in the area's surface or spring water. DATCP wanted to further confirm the atrazine detection and identify potential trends, thus the site was included in the surface water quality monitoring program between 2019 and 2021.

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 the Syene Spring.

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 breakage with the 2021 program. A summary of the analytical data for the 2021 program is included in Appendix B. Actual analytical reports are available upon request.

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 109 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 <u>not detected</u> in the water sample. If the concentration of a certain compound is reporting limit, we consider the compound <u>detected</u> in the vater 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 82 surface water samples were collected and submitted for chemical analysis as a part of the DATCP's 2021 Surface Water Sampling Program. The table in Appendix B summarizes the 2021 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 (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 (US 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 2021 data follows.

Detections

- Of the 109 pesticide analytes included in the laboratory testing methods, 29 were detected in 2021 surface water samples. Detections include 12 herbicides, 12 herbicide metabolites, four insecticides, and one fungicide.
- At least one pesticide analyte was detected in every surface water location for every monthly sampling event.
- The maximum number of pesticides detected in a single sample was 15 individual compounds (in three locations of the Ten Mile Creek: North Branch of Ten Mile Creek at Isherwood, North Branch of Ten Mile Creek Ditch 5 at Taft Rd, and South Branch of Ten Mile Creek at Taft Rd).
- Metolachlor ethane sulfonic acid (ESA) was the most detected compound. It was identified in 96% of samples collected.
- The second most detected compound overall was de-ethyl atrazine, identified in 58% of the samples. The de-ethyl atrazine detection rate of 2021 was 8% higher than then de-ethyl atrazine detection rate of 2020.
- 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 almost 60% of the samples collected.
- Alachlor ESA was the third most detected compound, in 57% of the samples, and acetochlor ESA was the fourth most detected, in 50% of the samples.

- 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 2021, at least two neonicotinoid compounds were detected in each sample collected from the sampling sites of the Central Sands Region. These compounds were also detected in groundwater samples collected from the Central Sands Region for other DATCP programs in 2021. The regional Central Sands aquifer system is strongly connected to surface water features, with over 80 lakes and 1,000 groundwater-fed headwater streams (Kraft, Clancy, Mechenich, & Haucke, 2012). Results from DATCP 2021 (and prior) surface water and groundwater sampling programs support the hypothesis that the detection of neonicotinoids in surface waters is likely a result of groundwater discharge into surface water bodies. Neonicotinoids were also detected at Duncan Creek, Root River, and West Branch of the Sugar River. These results are similar to previous years' results.
- Analytical data associated with the surface water samples collected from the Driftless Area streams indicate that surface runoff likely contributes to the seasonal-high pesticide concentrations in the Mormon Coulee Creek. 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

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

- Atrazine was detected in the May 2021 sample collected from Mormon Coulee Creek at a concentration of 1.5 micrograms per liter (μ g/L), which exceeds the benchmark value of <1 μ g/L for non-vascular plants.
- Imidacloprid was detected in seven samples collected in 2021 from Fourteen Mile Creek (April), Root River (June), and Ten Mile Creek (April and September), at concentrations ranging from 0.0118 to 0.0886 µg/L. These concentrations exceed the Chronic Exposure value of 0.01 µg/L for Invertebrates.
- Clothianidin was detected in 15 samples collected in 2021 from Ten Mile Creek (April and September), Fourteen Mile Creek (April), Root River (June), Duncan Creek (May), and West Branch Sugar River (from March to December), at concentrations ranging from 0.0101 to 0.268 µg/L. Four samples collected at Ten Mile creek exceeded the Chronic Exposure value of 0.05 µg/L for Invertebrates.

Exceedance of Drinking Water Standards

- Each monthly sample collected from Syene Spring exceeded the Wis. Admin. Code Ch. NR 140 Enforcement Standard (ES) of 10 mg/L for nitrogen. Exceedances of the Wis. Admin. Code Ch. NR 140 Enforcement Standard (ES) for nitrogen were also recorded at the North Branch of Ten Mile Creek at Isherwood, the North Branch of Ten Mile Creek - Ditch 5 at Taft Rd, and the South Branch of Ten Mile Creek at Taft Rd in September 2021.
- The Wis. Admin. Code Ch. NR 140 Preventive Action Limit (PAL) of 0.3 µg/L for atrazine TCR was exceeded in 15 samples collected at the Syene Spring, the West Branch of the Sugar River, the Root River, and at the Mormon Coulee Creek.

2021 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 about 34 inches of precipitation annually (average period 1991-2020). In 2021, the state of Wisconsin as whole experienced below-average precipitation levels (29.9 inches) (NOAA National Centers

for Environmental information, 2022). Figure 2 displays the statewide monthly precipitation departures from the historic normal (Wisconsin State Climatology Office, 2022). In 2021, July, August, and December showed a positive departure from the average, indicating an increase in precipitation ranging from 0.1 - 1.6 inches above normal. On the contrary, January, February, April through June, and September through November showed a negative departure of -0.5 to -1.5 inches below average, indicating a decrease in precipitation. It appears that greater-than-average precipitation was occurring at the end or after the usual pesticide application season.

Figure 2: Monthly Precipitation Departures from 1991-2020 Average



Figure 3 shows the total accumulated precipitation mapped across Wisconsin (Wisconsin State Climatology Office, 2022). As shown, there was an uneven distribution of rainfall across the state in 2021, with the northern half of the state accumulating between 30 and 40 inches of precipitation while the southern half accumulated 15 to 25 inches of precipitation in 2021. Most of the DATCP 2021 Surface Water Program sampling sites are located in the southern half of Wisconsin.

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

0.1 0.5 1 2 3 5 7.5 10 15 20 25 30 40 Stations from the following networks used: WBAN, COOP, FAA, GHCN, ThreadEx, CocCPaHS, WMO, ICAO, NWSU, Midwestern Regional Climate Center climate Ce

Accumulated Precipitation (in) January 01, 2021 to December 31, 2021

Shown on Figure 4 is a map of the 2021 precipitation departures, obtained from the Wisconsin State Climatology Office (Wisconsin State Climatology Office, 2022). Positive departure values, indicated in green, represent where total precipitation for the year was greater than average; negative departures, indicated by the yellow and orange colors, represent areas where total precipitation was lower than average. Notably, southern Wisconsin experienced 10 to 17 inches of total precipitation lower than normal.

Figure 4: Wisconsin Accumulated Precipitation Departures from Normal

Accumulated Precipitation (in): Departure from 1991-2020 Normals

January 01, 2021 to December 31, 2021



It was reported in the NOAA Storm Events Database (NOAA National Centers for Environmental Information, 2022), from January through late February, numerous heavy snow events in northern Wisconsin while the lower portions of the state received minimal snowfall. Although occasional storms were recorded, from April through December, it was a dry season for southern Wisconsin, where droughts were declared, and southeastern Wisconsin reported severe (D2) to extreme (D3) drought conditions indicating potentially significant crop die-off according to the National Integrated Drought Information System.

A summary of the total annual and monthly precipitation in the counties where samples were collected in the 2021 program is shown on Figure 5. The various colors indicate the monthly precipitation totals at each location (NOAA National Centers for Environmental information, 2022). It can be observed on Figure 5 that Dane, Milwaukee, and Racine County experienced lower accumulated precipitation relative to the rest of the counties across the state, with a majority of precipitation accumulated during the late summer.





2021 Precipitation Totals for Counties With Surface Water Sampling

PESTICIDE DETECTED FREQUENCY

Of the 109 analytes included in DATCP's Surface Water Sampling Program testing methodology, 29 different pesticide compounds were detected in 2021, considering all sampling sites. In 2020, 30 different pesticides were instead detected. This was the first year the herbicides Trifluralin and Dacthal Di-Acid, a metabolite of Dacthal, were detected in the DATCP Surface Water Sampling Program. Table 3 shows the compounds detected in 2021, and vice versa.

Table 3: Pesticides Detected in 2020 or in 2021 and the Sampling Sites Where the Compounds Were Detected

Pesticide name	2020	2021	Sites where detected
Fomesafen	х		Root River, Mississippi River, West Branch Sugar River
Sulfentrazone	х		Root River
Prometone	х		Root River
Acetochlor OA or OXA	x		Root River
Dicamba	х		Root River
Clopyralid	х		Root River
Azoxystrobin	х		Fourteen Mile Creek
Bentazon		x	Fourteen Mile Creek, Ten Mile Creek (all sites except Ten Mile Creek at Evergreen Rd)
Trifluralin		x	Mormon Coulee Creek - Bridge #6 at County Rd YY
Dimethenamid ESA		x	Ten Mile Creek (North Branch - Ditch 5 and North Branch at Isherwood)
Metalaxyl		x	Ten Mile Creek (North Branch - Ditch 5, North Branch at Isherwood, and South Branch)
Alachlor OA		x	Ten Mile Creek (North Branch - Ditch 5 and South Branch)
Dacthal Di-Acid		x	Ten Mile Creek (South Branch)

Figure 6 shows the percentage pesticide detection rate for 2021 and 2020 (empty bars). Only pesticides detected at a rate higher than 10% in 2021 are shown. As shown on Figure 6, with the exception of de-ethyl atrazine and atrazine TCR, the most detected pesticides in 2021 were detected at a similar or lower rates compared to 2020. Assuming that pesticide application rate and use did not change between 2021 and 2020, lower precipitation in 2021 may have influenced surface water results by reducing pesticide infiltration and groundwater discharge into surface waters.



Figure 6: Pesticides Detection Rates in the 2021 Samples vs 2020 Samples (Includes the Analytes Detected in More Than 10% of the Samples in 2021)

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).

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, 2022). Metolachlor ESA concentrations were detected in 96% of the samples collected. De-ethyl atrazine, an atrazine metabolite, was the second most frequently detected compound, with a detection rate of 58%. Alachlor ESA was the third most frequently detected compound, with a detection rate of 58%. Alachlor ESA was the third most frequently detected compound, with a detection rate of 57%. 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 %.

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 the monthly detection rate of pesticide analytes (ratio between the total detects and the total measurements collected expressed in percentage). Surface water sampling was not completed in January and February because the lab was not open due to equipment upgrades and maintenance. On Figure 7, the blue line includes all of the sampling locations and the orange line excludes the Central Sands sampling sites (Leola Ditch, Fourteen Mile Creek, and the five sites along the Ten Mile Creek), which were only sampled in April and September. The distinction is made to better interpret the results and avoid biases due to the limited sampling in the Central Sands Region. For example, the peak in detection rate recorded in September, when all the sampling sites are taken into account, is due to the high pesticide detection rate found at the Central Sands sampling locations.

Regardless of the distinction, results show that 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), suggest that groundwater discharge is the primary process contributing to consistent 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. Reduced pesticide spraying and higher-than-average precipitation (Figure 2) likely contributed to the declining trend in pesticide detections in July and August.





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

The following is a list of pesticides that were detected in multiple instances within each watershed, and likely represent baseline aquifer flow:

- Duncan Creek at 157th Avenue
 - Acetochlor ESA concentrations ranged from 0.0963 to 0.187 µg/L for the year;
 - $\,$ Alachlor ESA concentrations ranged from 0.171 to 0.294 $\mu g/L$ for the year; and
 - Metolachlor ESA concentrations ranged from 0.689 to 0.995 µg/L for the year.
- Milwaukee River at Estabrook Park
 - Metolachlor ESA concentrations ranged from 0.184 to 0.265 µg/L for the year.
- Milwaukee River at L & D #9
 - Acetochlor ESA concentrations ranged from 0.0568 to 0.116 µg/L for the year;

- Alachlor ESA concentrations ranged from 0.0574 to 0.0729 µg/L for four of the nine samples collected (July, October, November, and December); and
- Metolachlor ESA concentrations ranged from 0.17 to 0.311 µg/L for the year.
- Root River at 8-Mile Rd
 - 2,4-D concentration ranged from 0.111 to 0.725 µg/L for five of the seven samples collected (June, August, September, October, and December).
- West Branch of the Sugar River
 - Acetochlor ESA concentrations ranged from 0.0525 to 0.161 µg/L for six of the eight samples collected (March, April, beginning of July, August, October, and December);
 - Clothianidin concentrations ranged from 0.0101 to 0.0216 µg/L for six of the eight samples collected (March, April, beginning and end of July, October, and December);
 - De-ethyl atrazine concentrations ranged from 0.061 to 0.0799 µg/L for the year;
 - Diamino atrazine concentrations ranged from 0.209 to 0.295 µg/L for six of eight samples collected (March, April, beginning July, August, September, and December); and
 - Metolachlor ESA concentrations ranged from 0.27 to 0.603 µg/L for the year.
- Wisconsin River near Muscoda
 - Acetochlor ESA concentrations ranged from 0.0534 to 0.108 µg/L for five of the eight samples collected (July, August, September, October, November, and December);
 - Alachlor ESA concentrations ranged from 0.0534 to 0.108 µg/L for the year; and
 - Metolachlor ESA concentrations ranged from 0.228 to 0.384 µg/L for the year.
- Syene Spring is a natural groundwater discharge and hence it's strictly a representation of the groundwater quality of the area.

Bentazon, chlorantraniliprole, dichlobenil, dimethenamid ESA, metalaxyl, metribuzin and metabolites, and norflurazon were detected in one or more of the following locations:

- Ten Mile Creek,
- Leola Ditch, and
- Fourteen Mile Creek (Central Sands Region).

These less-common constituents were not observed at any other DATCP 2021 Surface Water Program sampling locations. Groundwater samples collected by DATCP in private potable wells since 2010 confirm that these compounds are predominantly detected in the Central Sands Region. Sixty-five percent of the detections for the above-listed compounds were found in Adams, Juneau, Portage, and Waushara County. This confirms that surface water and groundwater are highly interconnected in the Central Sands Region.

Additional interpretation of pesticide data from multiple years is needed to validate these observations. This evaluation will be performed as part of the detailed DATCP Surface Water Sampling 15-year report, anticipated to be published in 2024.

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COMPARISON TO STANDARDS

Detected pesticide concentrations identified during DATCP's 2021 Surface Water Sampling Program were compared to the following three published environmental surface water/groundwater quality standards:

- US EPA's Office of Pesticide Programs Aquatic Life Benchmarks for Pesticides for freshwater;
- Wis. Admin. Code Ch. NR 140 ES and PAL for drinking water¹, 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 2021 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). The DHS currently has drinking water health advisory recommendations for an additional 15 pesticides.

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

- Atrazine
 - A sample collected in May from the Mormon Coulee Creek reported an atrazine detection at a concentration of 1.5 µg/L, which exceeds the <1 µg/L benchmark for vascular plants;
- Clothianidin
 - Four samples collected from the Ten Mile Creek (each location, except for the Ten Mile Creek at Evergreen Rd), and the Fourteen Mile Creek detected clothianidin at concentrations ranging from 0.0547 to 0.268 µg/L, which exceeds the 0.05 µg/L value for chronic exposure on invertebrates;
- Imidacloprid
 - Seven samples collected from the Root River, the Ten Mile Creek (all five locations), and the Fourteen Mile Creek detected imidacloprid at concentrations ranging from 0.0118 to 0.0886 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 one compound in 15 samples as follows:

- Atrazine TCR (Wis. Admin. Code Ch. NR 140 PAL = 0.3 μg/L)
 - In May, atrazine and atrazine TCR were detected at concentrations of 1.5 and 1.7849 µg/L, respectively, at the Mormon Coulee Creek - Bridge #6 at County Rd YY;
- From March to December (eight samples collected in total), concentrations of atrazine TCR ranged between 0.6659 and 0.8077 μ g/L at Syene Spring;
 - In April, July, August, September, and December (in five of the eight samples collected), atrazine TCR was detected at concentrations between 0.3039 and 0.3666 µg/L at the West Branch of Sugar River;
 - In June, atrazine TCR was detected at a concentration of 0.3522 µg/L at the Root River.

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 the DHS.

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 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.

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		Mormon Coulee Creek - Bridge #6 at County Rd YY	5/27/2021	1.5
					3/30/2021	0.434
					4/27/2021	0.472
					7/1/2021	0.503
Diamino	2	0.2		Suono Spring	7/29/2021	0.385
atrazine	5	0.5		Syene Spring	8/18/2021	0.444
					9/21/2021	0.423
					10/27/2021	0.38
					12/1/2021	0.451
				Mormon Coulee Creek - Bridge #6 at County Rd YY	5/27/2021	1.7849
				Root River	6/29/2021	0.3522
					3/30/2021	0.7622
					4/27/2021	0.791
					7/1/2021	0.8077
				Svene Spring	7/29/2021	0.7201
				Syene Spring	8/18/2021	0.7535
Atrazine TCR	3	0.3			9/21/2021	0.762
					10/27/2021	0.6659
					12/1/2021	0.7505
					4/27/2021	0.3209
					7/1/2021	0.331
				West Branch Sugar River	8/18/2021	0.3666
					9/21/2021	0.3039
					12/1/2021	0.3518

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. Published water quality standards or benchmarks are based on concentrations for the occurrence of a single compound. Currently, there are no calculations to predict the total potential comprehensive risk when multiple compounds are present, with the exception of atrazine and its metabolites (atrazine TCR). This current 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 2021. The remaining three neonicotinoid compounds were not detected in any surface water samples. The detection of clothianidin, imidacloprid, and/or thiamethoxam is not unexpected, as these compounds are known to leach into sandy soils readily.

Thiamethoxam was first detected at the Milwaukee River and the Neenah Slough sampling locations in 2011. Since then, DATCP recorded a total of 135 thiamethoxam detections in Wisconsin's surface waters, 126 of which were found in the Central Sands area. Since 2017, thiamethoxam has also been detected in the Root River, predominantly in June samples. In 2021, thiamethoxam was detected in eight samples collected from Ten Mile Creek (at all five locations), Fourteen Mile Creek, Leola Ditch, and Root River. Concentrations ranged from 0.0232 to 0.443 μ g/L.

Imidacloprid was first detected at the Ten Mile Creek in December 2014. Since then, DATCP recorded a total of 61 imidacloprid detections in Wisconsin's surface waters, 56 of which were found in the Central Sands area. Since 2018, imidacloprid has also been detected in the Root River, predominantly in June samples. In 2021, imidacloprid was detected in seven samples collected from Ten Mile Creek (at all five locations), Fourteen Mile Creek, and Root River. Concentrations ranged from 0.0118 to 0.0886 µg/L.

Clothianidin was first detected at the Root River in June 2018. Since then, DATCP recorded a total of 73 clothianidin detections in Wisconsin's surface waters, 51 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 Root River (since 2018), the Mississippi River (2019 and 2020), the West Branch Sugar River (2020 and 2021), the Syene Spring (once in July 2020) and the Duncan Creek (2020 and 2021). In 2021, clothianidin was detected in 15 samples collected from the Ten Mile Creek (all five locations), the Fourteen Mile Creek, the West Branch Sugar River, the Duncan Creek at 157th Ave, and the Root River. Concentrations ranged from 0.0104 to 0.268 µg/L.

In 2021, a total of 30 neonicotinoid detections were reported and a detection rate of 12% was calculated for clothianidin, imidacloprid, and thiamethoxam. This result is a decrease in neonicotinoids from 2020, when 82 neonicotinoid detections were reported and neonicotinoids detection rate was about 42%. However, this trend may be affected by a decrease in sampling from the Central Sands Region, an area where neonicotinoids are usually detected, due to logistical issues unique to the 2021 program.

While sampling in the Central Sands Region was limited in this year's study, historically, these neonicotinoid compounds do not fluctuate seasonally in surface water samples collected from this region. Similarly, clothianidin was detected throughout each year of sampling at the West Branch Sugar River regardless of the month. However, samples from the Root River exhibited a seasonality in their neonicotinoid detections from June to August, suggesting a trend in neonicotinoid detected at the Mississippi River and the Duncan Creek sampling locations only during the peak pesticide application period (from May to August).

For more details on neonicotinoid concentrations exceeding US 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 (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2022c). 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, 2022b). 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 ten 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 2021 Surface Water Program flow through or are adjacent to a PA.

Atrazine parent material concentrations were detected in 19% (16 samples) of the 2021 collected river, stream, or spring water samples, marking a decrease in the rate of atrazine detections relative to the 2020 samples (27%).

At least one atrazine metabolite (de-ethyl atrazine, deisopropyl atrazine, and diamino atrazine) was detected in 58% (48 samples) of the 2021 collected river, stream, or spring water samples, marking an increase in the rate of atrazine metabolite detections relative to the 2020 samples (50%).

Atrazine TCR (sum of atrazine and its metabolite) was detected in 59% (49 samples) of the 2021 collected river, stream, or spring water samples, marking a slight increase in the atrazine TCR detection rate relative to the 2020 samples (56%).

The following is a summary of the atrazine findings for each river or stream where it was detected in 2021:

- The greatest concentrations of parent material atrazine and atrazine total chlorinated residues
 ([atrazine TCR] the combined sum of the parent material atrazine and its metabolites) were identified
 in a surface water sample collected from the Mormon Coulee Creek in May; atrazine parent material
 was detected at a concentrations of 1.5 µg/L and atrazine TCR was detected at a concentration of
 1.785 µg/L, respectively. While only a single sample from Mormon Coulee Creek had detectable
 concentrations of atrazine parent material, atrazine TCR was consistently detected in every sample
 collected from the Mormon Coulee Creek throughout the year, ranging from 0.0714 to 1.7849 µg/L.
 De-ethyl atrazine was the most detected atrazine metabolite in the Mormon Coulee Creek at
 concentrations ranging from 0.0714 to 0.234 µg/L.
 Deisopropyl atrazine was detected only once in
 May at a concentration of 0.0509 µg/L.
 Diamino atrazine was not detected in samples collected at
 this location in 2021.
- In samples collected from the West Branch of the Sugar River, atrazine TCR was detected at concentrations ranging from 0.061 to 0.3666 µg/L throughout the year. However, there were no detections of the atrazine parent material. De-ethyl atrazine was detected in each sample collected at this location at concentrations ranging from 0.061 to 0.0799 µg/L. Diamino atrazine was also detected in several samples, with the exception of the samples collected in July and October, at concentrations ranging from 0.209 to 0.295 µg/L. Deisopropyl atrazine was not detected in samples collected at this location in 2021.
- Samples from Syene Springs consistently detected both atrazine and its metabolites in every monthly sample. Atrazine concentrations ranged from 0.06 to 0.0758 μ g/L, and atrazine TCR concentrations ranged from 0.6659 to 0.8077 μ g/L. Diamino atrazine, de-ethyl atrazine, and deisopropyl atrazine were all detected in each sample collected at this location. Diamino atrazine was detected at concentrations ranging from 0.38 to 0.503 μ g/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 0.0776 to 0.0929 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 μ g/L at that time. Because this spring is located within a PA that was established in 1995, atrazine detections would not be expected. The 2021 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. Further investigations are needed to confirm one or the other hypothesis.
- A departure from years past where atrazine was commonly detected, no concentrations of atrazine or its metabolites were observed in Leola Ditch or Fourteen Mile Creek. De-ethyl atrazine was the only atrazine compound detected in the Ten Mile Creek (all locations, except for the Ten Mile Creek at Evergreen Rd) during the sampling event of September, at concentrations ranging from 0.0595 to 0.156 µg/L.

- Atrazine, de-ethyl atrazine, and deisopropyl atrazine were detected at the Root River in June, at a concentration of 0.147, 0.13, and 0.0752 μ g/L, respectively.
- De-ethyl atrazine was detected at Duncan Creek at 157th Avenue in May, June, July, and October at concentrations ranging from 0.0535 to 0.0623 μg/L.
- Atrazine and de-ethyl atrazine were detected in June at the Milwaukee River at concentrations of 0.108 and 0.0778 µg/L, respectively.
- Atrazine was detected in June and July at the Mississippi River at concentrations of 0.108 and 0.0864 µg/L, respectively. In July, de-ethyl atrazine was also detected at a concentration of 0.0591 µg/L.
- Atrazine and de-ethyl atrazine were both detected at the Wisconsin River location, in July and August. Atrazine concentrations ranged from 0.0789 to 0.118 μ g/L, while de-ethyl atrazine concentrations ranged from 0.0553 to 0.0648 μ g/L.
- The Root, Milwaukee, Mississippi, and 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 US 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 70 of the 82 surface water samples collected for DATCP's 2021 Surface Water Sampling Program. The greatest nitrogen concentration observed in 2021 was 11.6 mg/L detected in the sample collected at Syene Spring in April.

The following is a summary of nitrogen results for 2021 river and stream samples.

- At Syene Sping, 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 11.6 mg/L.
- In September, nitrogen was found at concentrations of 20.6, 17, and 14.3 mg/L at the North Branch of Ten Mile Creek at Isherwood, the North Branch of Ten Mile Creek Ditch 5 at Taft Rd, and the South Branch of Ten Mile Creek, respectively. These concentrations exceeded the Wis. Admin. Code NR 140 ES of 10 mg/L
- In surface water samples collected from the Bad Axe River, Ten Mile Creek at Evergreen Rd, Ten Mile creek at Ct U, Fourteen Mile Creek Leola Ditch, West Branch of the Sugar River, and Duncan Creek nitrogen was found at concentrations ranging from 1.93 mg/L to 8.12 mg/L. With the exception of one sample collected in August at the Duncan Creek, the remaining concentrations exceeded the 2 mg/L Wis. Admin. Code NR 140 PAL.
- The Duncan Creek represented the location with the largest variation in nitrogen values among the sites sampled through 2021 for the DATCP Surface Water Sampling program. Nitrogen concentrations varied from 1.93 to 4.26 mg/L, with peaks in November and December.
- Overall Mormon Coulee Creek, Root River, and Mississippi River samples recorded nitrogen concentrations below the Wis. Admin. Code NR 140 PAL of 2.0 mg/L. However, during the winter months each of these locations had single exceedances of the Wis. Admin. Code NR 140 PAL of 2.0 mg/L, with samples concentrations of 2.01, 2.15, and 2.01 mg/L, respectively.
- Surface water samples collected from the Milwaukee River generated consistent concentrations ranging from below the reporting limit to 1.95 mg/L, which are less than the Wis. Admin. Code NR 140 PAL of 2.0 mg/L.
- None of the samples collected from the Wisconsin River contained nitrogen concentrations exceeding the Wis. Admin. Code NR 140 PAL of 2.0 mg/L. Nitrogen concentration ranged from below reporting limit to 1.23 mg/L at this location.

Table 5 includes a summary of the DATCP's 2021 Surface Water Sampling Program detections for nitrate plus nitrite as N.

Sample Location	Nitrogen (Nitrate + Nitrite) Concentration Range (mg/L)
Duncan Creek	1.93-4.26
Fourteen Mile Creek	3.85
Leola Ditch at Aniwa	3.1
Milwaukee River	ND-1.95
Mississippi River	ND-2.01
Mormon Coulee Creek - Bridge #6 at County Rd YY	1.32-2.01
Root River	ND-2.15
Syene Spring	10.7-11.6
South Fork Bad Axe River	2.2-2.9
Ten Mile Creek at Evergreen Rd	3.01
North Branch of Ten Mile Creek at Isherwood	20.6
Ten Mile Creek at County Rd U	8.12
North Branch of Ten Mile Creek - Ditch 5 at Taft Rd	17
South Branch of Ten Mile Creek at Taft Rd	14.3
West Branch Sugar River at CTH PB	4.42-5.55
Wisconsin River	ND-1.23

Table 5: 2021 Surface Water Sampling Program Nitrogen (Nitrate and Nitrite) Analytical Results

Notes: mg/L - milligrams per liter

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

2022 Program Goals and Objectives

DATCP's Surface Water Sampling Program will continue in 2022. It is expected that the following tasks will be completed.

- Collection of monthly surface water samples at 13 stream or river locations for the calendar year to include:
 - Collect monthly samples from 11 locations sampled in 2021, and
 - Collect monthly samples from four new locations.
- Prepare a 2022 Data Summary Report to be completed by 3rd Quarter of 2023, and
- Share report(s) with 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.

For 2022, surface water sampling will be continued at the following locations:

- Wisconsin River near Muscoda;
- Mississippi River at Lock and Dam #9;
- Syene Spring in Dane County;
- West Branch of the Sugar River;
- Root River;
- Milwaukee River at Estabrook Park;
- Mormon Coulee Creek Bridge #6 at County Rd YY;
- South Fork of the Bad Axe River;
- The three streams that flow within the Central Sands Region,
 - Ten Mile Creek at Evergreen Rd;
 - Fourteen Mile Creek at County Rd D; and

Leola Ditch at Aniwa.

2022 surface water results will provide additional information for these locations. 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. Long-term 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.

For 2022, sampling will be repeated at the following four historical locations last sampled in 2014:

- Pecatonica River in Martintown;
- Wisconsin River at Wisconsin Dells;
- Wisconsin River at Biron Dam; and
- Rock River in Afton.

Acknowledgments

DATCP's Bureau of Agrichemical Management's (ACM) financial information includes the state fiscal year (FY) 2021 from July 1, 2020 through June 30, 2021. Federal grants operated October 1, 2020 through September 30, 2021. 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 <u>DATCPGW@wisconsin.gov</u> 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)
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
ЕРА	U.S. 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	U.S. Department of Agriculture
WGNHS	Wisconsin Geological and Natural History Survey
Wis. Admin. Code	Wisconsin Administrative Code

DEFINITIONS

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

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

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)

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

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

Appendix B

2021 Surface Water Sampling Program Analytical Results, Summary

2021 Surf	ace Water Sampling I	Program Ro	esults (μg/L)	Wisconsin / Chapte	Admin. Code r NR 140	Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchma Pesticide (µg/L)				nchmarks for	
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (PAL) (µg/L)	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
2,4-D	Herbicide	13	0.05	0.0509-0.725	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	2	0.05	0.0565-0.0783	0.7	7		190	130	4100	22.1	1.43	3.4
Acetochlor ESA	Metabolite	41	0.05	0.0525-0.187	46	230		>90000		>62500		9900	
Acetochlor OA or OXA	Metabolite	ND	0.3		46	230							
Acetochlor Metabolites	Sum of Acetochlor ESA and Acetochlor OA	41	0.05	0.0525-0.187	46	230							
Acifluorfen	Herbicide	1	0.05	0.0837									
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	2	0.25	0.253-0.377				>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	16	0.05	0.06-1.5	0.3	3		2650	5	360	60	<1	4.6
De-ethyl atrazine	Metabolite	48	0.05	0.0535-0.234	0.3	3							
De-isopropyl atrazine	Metabolite	10	0.05	0.0509-0.0929	0.3	3							
Di-amino atrazine	Metabolite	14	0.2	0.209-0.503	0.3	3							
Atrazine TCR	Sum of Atrazine and Atrazine metabolites	49		0.0535-1.7849	0.3	3							

2021 Surface Water Sampling Program Results (µg/L)				Wisconsin A Chapter	sconsin Admin. Code Chapter NR 140 Wisconsin Department of Health Services US EPA Office of Pesticide Programs - Aquatic Life E Pesticide (µg/L)					quatic Life Be .)	nchmarks for		
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (PAL) (µg/L)	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
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	5	0.05	0.0592-0.44	60	300		95000	9830	31150	101200	4500	5350
Bicyclopyrone	Herbicide	ND	0.05					>46700	10000	>46650	103700	2000	13
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	5	0.05	0.0517-0.722			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	ND	0.05					51500	10000	116500	4700	6900	90300
Clothianidin	Insecticide	15	0.01	0.0101-0.268			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	1	0.5	0.545			70						
Dacthal Mono-acid	Metabolite	ND	0.5				70						
Dacthal Total	Sum of Dacthal , Dacthal Di-acid, and Dacthal Mono-acid	1	0.5	0.545			70						

2021 Surface Water Sampling Program Results (µg/L)					Wisconsin A Chapter	Visconsin Admin. Code Chapter NR 140 Wisconsin Department of Health Services US EPA Office of Pesticide Programs - Aquatic Life Be Pesticide (µg/L)					nchmarks for		
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (PAL) (µg/L)	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
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		>50000		61	>3250
Dichlobenil	Herbicide	2	0.05	0.109-0.244				2465	<330	3100	560	1500	30
Dimethenamid	Herbicide	ND	0.05		5	50		3150	120	6000	1360	14	8.9
Dimethenamid ESA	Metabolite	2	0.05	0.0675-0.0703									
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
ЕРТС	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	ND	0.05				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
АМРА	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	7	0.01	0.0118-0.0886			0.2	114500	9000	0.385	0.01		
Isoxaflutole	Herbicide	ND	0.05				3	>850	80	>750	350	110	4.9

2021 Surface Water Sampling Program Results (μg/L)					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticide (µg/L)						
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (PAL) (µg/L)	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	
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	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	
МСРА	Herbicide	ND	0.05					>34000		>92000				
МСРВ	Herbicide	ND	0.1	-				1960	<530	25100	2510	1370	200	
МСРР	Herbicide	1	0.05	0.0566				>46500		>45500	50800	14	1300	
Mesotrione	Herbicide	ND	0.1					>60000	11000	67000	3055	>820	4.8	
Metalaxyl	Fungicide	3	0.05	0.0785-0.109			800	65000	9100	14000	1200		85000	
Methyl Parathion	Insecticide	ND	0.05	-				925	<10	0.485	0.25	15000	18000	
Metolachlor	Herbicide	23	0.05	0.0507-2.56	10	100		1600	30	11750	3200	8	14	
Metolachlor ESA	Metabolite	79	0.05	0.0699-6.36	260	1300		24000		>54000		>99450	43000	
Metolachlor OA or OXA	Metabolite	15	0.27	0.277-5.19	260	1300		>46550		7700		57100	>95400	
Metolachlor Metabolites	Sum of Metolachlor ESA and Metolachlor OA	79		0.0699-11.55	260	1300								
Metribuzin	Herbicide	5	0.05	0.0662-0.664	14	70		21000	<3000	2100	1290	8.1	130	
Metribuzin DA	Metabolite	3	0.1	0.104-0.15										
Metribuzin DADK	Metabolite	7	0.12	0.329-1.34										
Metsulfuron methyl	Herbicide	ND	0.05					>75000	4500	>75000		31	0.36	
Nicosulfuron	Herbicide	ND	0.05					>500000		>500000	43000			
Norflurazon	Herbicide	4	0.05	0.102-2.88				4050	770	>7500	1000	9.7	58.2	
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	

2021 Surface Water Sampling Program Results (µg/L)					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticide (µg/L)						
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (PAL) (µg/L)	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	
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	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	0.0232-0.443			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	1	0.05	0.0636				58500		66450		32500		
Trifluralin	Herbicide	1	0.05	0.0782	0.75	7.5		9.25	1.9	125.5	2.4	21.9	49.7	

Notes:

--- Indicates that Health Advisory Level value in Wisconsin not established or acceptable aquatic toxicity values are not available.

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, or in excess of any Aquatic Life benchmark values.

Indicates detects in excess of Wisc. Admin. code Ch. NR 140 PAL and respective Aquatic Life benchmark values.

Website Used for EPA Aquatic Benchmarks for Registered Pesticides (Accessed 1/4/2023)

https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk