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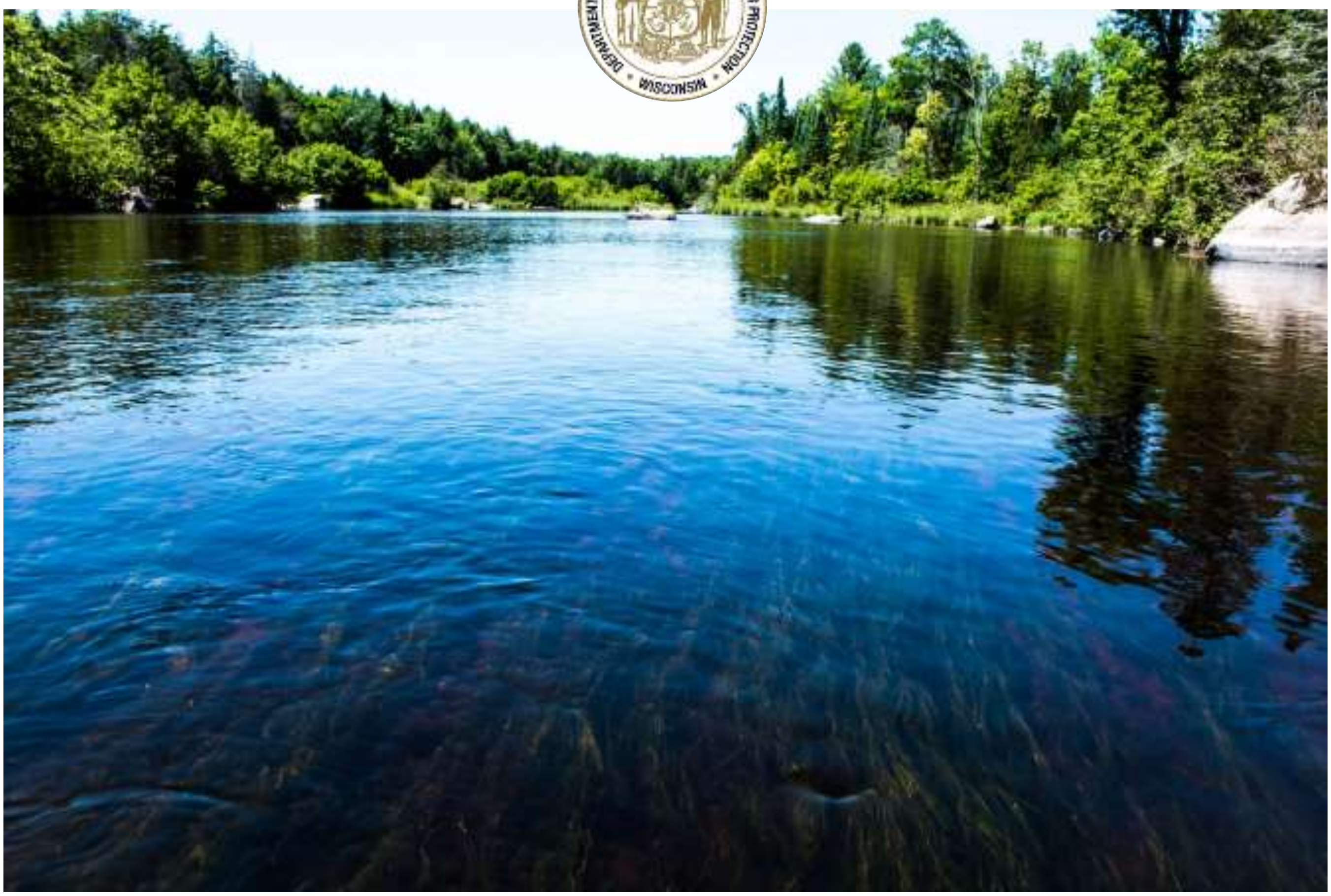
2020 Surface Water Pesticide Sampling Program Annual Report

ANNUAL REPORT



Wisconsin Department of Agriculture, Trade and Consumer Protection

Agricultural Resource Management Division

Environmental Quality Unit

Final (11-15-2022)

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Introduction

In 2020, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP), in cooperation with the Wisconsin Department of Natural Resources (DNR), continued the Surface Water Sampling Program to document the effect pesticide use is having on nine select rivers and streams and one spring in Wisconsin. 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 2021 Surface Water Sampling Program plan.

Purpose of Surface Water Sampling

Agriculture contributes $104.8 billion[1] annually to Wisconsin's economy. 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. DATCP's Surface Water Sampling Program was initiated in 2007 with the first monthly sampling occurring in 2008.

The goal of the ongoing Surface Water Sampling Program is to document what impact pesticide use is having on surface water quality in Wisconsin. 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 provide an indication of how the timing of pesticide application is related to surface water quality. During the 2020 sampling season, ten monthly samples were collected from each selected river, stream or spring; depending on ice conditions, laboratory availability, and sampler availability.

Program Approach and Selection Criteria

Perennial streams and rivers that were selected for the annual sampling program have changed many times for one reason or another. Streams for DATCP's program were selected predominately based on proximity to agricultural land in each watershed. Initially, streams were selected based on their inclusion in DNR's "wadeable" stream sampling project. Some years the focus was sampling on rivers with large watersheds and other years was focusing 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 Sampling 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 elevated nitrate, pesticides or other unusual test results;
- Areas where the same crops are grown year after year on the same fields or area (e.g. corn, cranberry, ginseng), increasing the likelihood of repetitive pesticide use in area;

[1] Contribution-of-Ag-to-WI-Econ-4-Update.pdf [wisc.edu])

- Areas where crops typically require extensive chemical or fertilizer inputs or irrigation;
- Areas where pesticides with known characteristics of high mobility and resistance to degradation are used; or
- At the request of one of the partnering agencies.

Over the years, the Surface Water Sampling Program has evolved to a mix of continuous monthly sampling to build a seasonal and annual database, and sampling a couple of new locations 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 conduct the majority of the sampling, time commitment and willingness is necessary for the annual 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.

Over the past three years, the program has generally consisted of collecting surface water samples from ten locations - 50% are repeat locations and 50% are new locations to the program. In 2020, most samples were collected at long-term repeat locations to continue to build the database and measure annual variability. Long-term repeat locations included the following:

- Wisconsin River at Muscoda;
- Mississippi River at Lock and Dam #9;
- Milwaukee River at Estabrook Park in Milwaukee County;
- Tenmile Creek at Evergreen in Portage County within the Central Sands Agricultural Region;
- Fourteen Mile Creek in Adams County within the Central Sands Agricultural Region;
- Leola Ditch at Aniwa in Adams County within the Central Sands Agricultural Region; and
- Seyene Spring in Dane County.

New or historical repeat locations for 2020 included the following:

- West Branch of the Sugar River in Dane County (a repeat from prior years);
- Root River at 8-Mile Road in Racine County (a repeat from prior years); and
- Duncan Creek at 157th Avenue, just south of the City of Bloomer.

2020 PROGRAM SPECIFICS

A total of nine perennial rivers and streams and a Dane County spring were selected for the 2020 sampling program. A total of 66 samples were collected between March and December for chemical analysis of pesticides and nitrogen as nitrate/nitrite. Table 1 lists the 2020 surface water sampling program locations, and Figure 1 shows the ten locations relative to State of Wisconsin and county boundaries. Table 2 includes a summary of watershed size and land use for 2020 for all but the largest watersheds (Mississippi and Wisconsin Rivers) using data provided by the U.S. Department of Agriculture's (USDA) Agricultural Statistics Service.

Table 1: 2020 Surface Water Sampling Program Rivers and Streams

River / Stream Name	SWIMS ID	County	Program Years
West Branch of the Sugar River at CTH M in Dane County	10017221	Dane	3
Duncan Creek at 157th Avenue	93072	Chippewa	1
Root River at 8-Mile Road	10039425	Racine	3
Fourteen Mile Creek at County Road D	013173	Adams	4
Leola Ditch at Aniwa	10009165	Adams	4
Milwaukee River at Estabrook Park	413640	Milwaukee	3
Mississippi River at L&D #9	123016	Crawford	8
Seyene Spring	10051622	Dane	2
Tenmile Creek at Evergreen	10016427	Portage	6
Wisconsin River at Muscoda	223282	Grant	8

Notes: SWIMS - Surface Water Integrated Monitoring System

Figure 1: 2020 Surface Water Sampling Program Rivers and Streams Locations

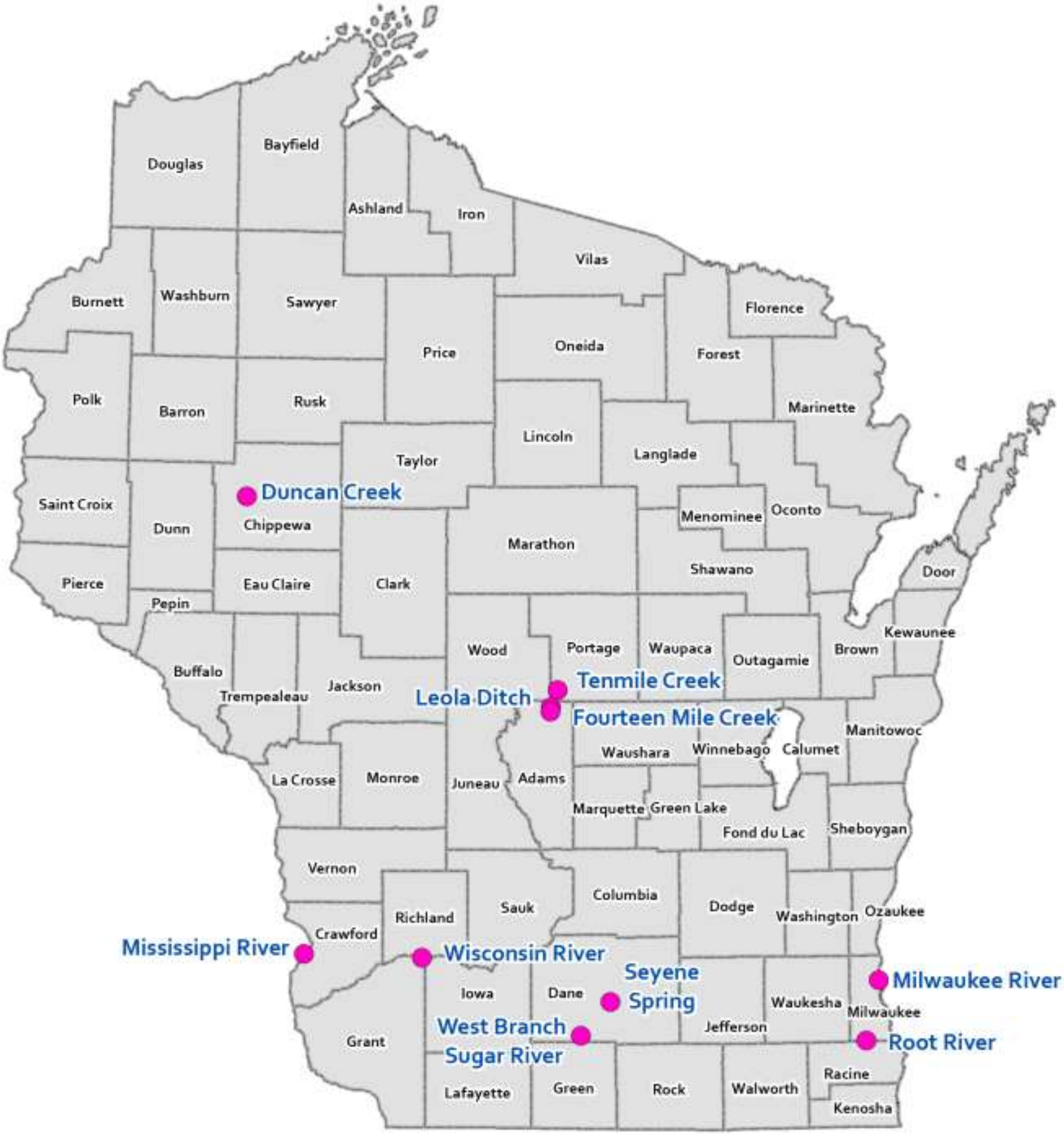

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Table 2:
2020 Surface Water Sampling Program Rivers and Streams Land Use Summary and Watershed Size

River/Stream Name	Forest	Wetland	Developed or Open	Corn	Alfalfa, Grass or Pasture	Soy or Dry Beans	Potatoes	Watershed Size (Acres)
West Branch of Sugar River	10,530 (24.6%)	1,082 (2.5%)	2,612 (6.1%)	9,533 (22.3%)	13,001 (30.4%)	5,488 (12.8%)	0 (0.0%)	42,813
Duncan Creek	15,793 (20.6%)	3,626 (4.7%)	6,283 (8.2%)	21,440 (27.9%)	14,896 (19.4%)	12,472 (16.2%)	0 (0.0%)	76,783
Fourteen Mile Creek	17,620 (31.8%)	5,944 (10.7%)	4,759 (8.6%)	6,726 (12.1%)	7,565 (13.6%)	3,859 (7.0%)	4,990 (9%)	55,468
Leola Ditch	3,206 (17.6%)	2,443 (13.4%)	887 (4.9%)	3,171 (17.4%)	4,251 (23.3%)	2.021 (11.1%)	2,280 (12.5%)	18,259
Milwaukee River	10,006 (9.4%)	14,779 (13.9%)	53,614 (50.4%)	5,266 (5.0%)	12,647 (11.9%)	3,795 (3.6%)	0 (0%)	106,339
Mississippi River (1) (L&D #9)								
Seyene Spring	Capture size is unknown							
Tenmile Creek	25,124 (25.6%)	6,079 (6.2%)	4,573 (4.7%)	18,954 (19.3%)	15,175 (15.5%)	14,187 (14.5%)	6,694 (6.8%)	97,987
Wisconsin River (1)								
Root River	10,937 (13.0%)	7,158 (8.5%)	39,759 (47.1%)	8,005 (9.5%)	6,928 (8.2%)	8,877 (9.3%)	0 (0.0%)	84,453

Notes: 1 *Too large of a watershed to make a meaningful calculation.*

This is the third consecutive year for sampling the Seyene Spring. Four years ago, the Wisconsin Geologic and Natural History Survey (WGNHS) completed a study evaluating water quality of Wisconsin's natural springs. Initial analytical results of water samples collected from Seyene Springs indicated elevated levels of pesticides, specifically atrazine, was affecting the water quality. This was of great concern since the Seyene Spring and its likely watershed is located within an atrazine Prohibition Area. We would not expect to see these type of atrazine concentrations in the area's surface or spring water. DATCP wanted to further confirm the atrazine existence and identify trends, if any, thus, included the site in our 2018, 2019 and 2020 surface water quality monitorin program.

Sample Collection and Analysis

Surface water samples are collected using DNR standard protocols[2] and DATCP standard operating procedures[3], which is designed to collect surface water samples in an unbiased fashion with respect to flow, weather, and other factors. All samples were collected in free flowing, well-mixed areas of the rivers and streams.

[2] Monitoring During Open Water Season-Standard Operating Procedure #4—Water Resources Monitoring Protocols, EGAD #3200-2018-23
[3] Surface Water Sampling Procedures dated 11/30/20

Surface water samples were collected by directly filling two laboratory-provided one-liter amber-colored glass sampling bottles at the designated sampling location. Bottles were then placed in a cooler on ice along with a properly completed sample collection form. Packages were then either shipped to BLS using an overnight delivery service or hand-delivered to BLS. There were no reported shipping issues or bottle breakage with the 2020 program. However, no surface water samples were collected in April and May due to COVID-19 travel restriction protocols for State employees. A summary of all analytical data for the 2020 program is included in a table located in Appendix A. Actual analytical reports are available upon request.

BLS performed all surface water analytical testing using GC/MS/MS and LC/MS/MS methods in accordance with ISO 17025 accreditation standards. All samples were tested for 107 pesticides (and certain metabolites) and nitrogen as nitrate and nitrite. The table include in Appendix A lists the parameters along with corresponding laboratory reporting limits.

Results and Discussion

A total of 66 surface water samples were collected and submitted for chemical analysis as a part of the DATCP's 2020 Surface Water Sampling Program. The table in Appendix A summarizes the 2020 Surface Water Sampling Program results and provides comparative risk values. The surface water data is compared to benchmark values to assess potential risk to human health and the environment. The risk values are sourced from the Wisconsin Administrative Code (Wis. Admin. Code) ch. NR 140 groundwater standards for groundwater qualitative health standard limits, and a listing of the U.S. Environmental Protection Agency (EPA) Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticide Registrations.

The following bulleted items are a summary of the sampling results. A detailed narrative for the 2020 data follows.

- Of the 107 pesticide analytes included in the laboratory testing methods, 30 were detected above laboratory reporting limits in the surface water samples. Detections include 15 herbicides, 10 herbicide metabolites, four insecticides, and one fungicide.
- At least one pesticide analyte was detected in excess of laboratory reporting limits in every surface water sample for every monthly sampling event from all locations.
- The most frequently detected compound in surface water samples is Metolachlor ethanesulfonic acid (ESA). It was detected less than laboratory reporting limits in all samples collected.
- Alachlor ESA was the second most frequently detected compound, and it was detected in excess greater than laboratory reporting limits in nearly 75% of the samples collected.
- Atrazine, or one of its breakdown products (de-ethyl atrazine, de-isopropyl atrazine and di-amino atrazine) was detected in excess of laboratory reporting limits in nearly 57% of the samples collected. This is the highest annual percentage of detections compared to prior years of monitoring.
- More pesticide analytes were detected in excess of laboratory reporting limits in June compared to any other month, which coincides with the primary pesticide application season. This has been consistent with each prior annual surface water sampling results.
- The presence of pesticides in samples collected every month suggests that most pesticides detected in surface water are the results of groundwater discharge (base flow) to surface water bodies rather than overland flow.
- Three neonicotinoid compounds were detected in numerous surface water samples collected from the Central Sands Agricultural Region (Fourteen Mile Creek, Leola Ditch, and Tenmile Creek) during 2020. Clothianidin and thiamethoxam were detected in 100% of samples, and imidacloprid was detected in 78% of samples collected from Fourteen Mile Creek, Leola Ditch, and Tenmile Creek. Because these compounds

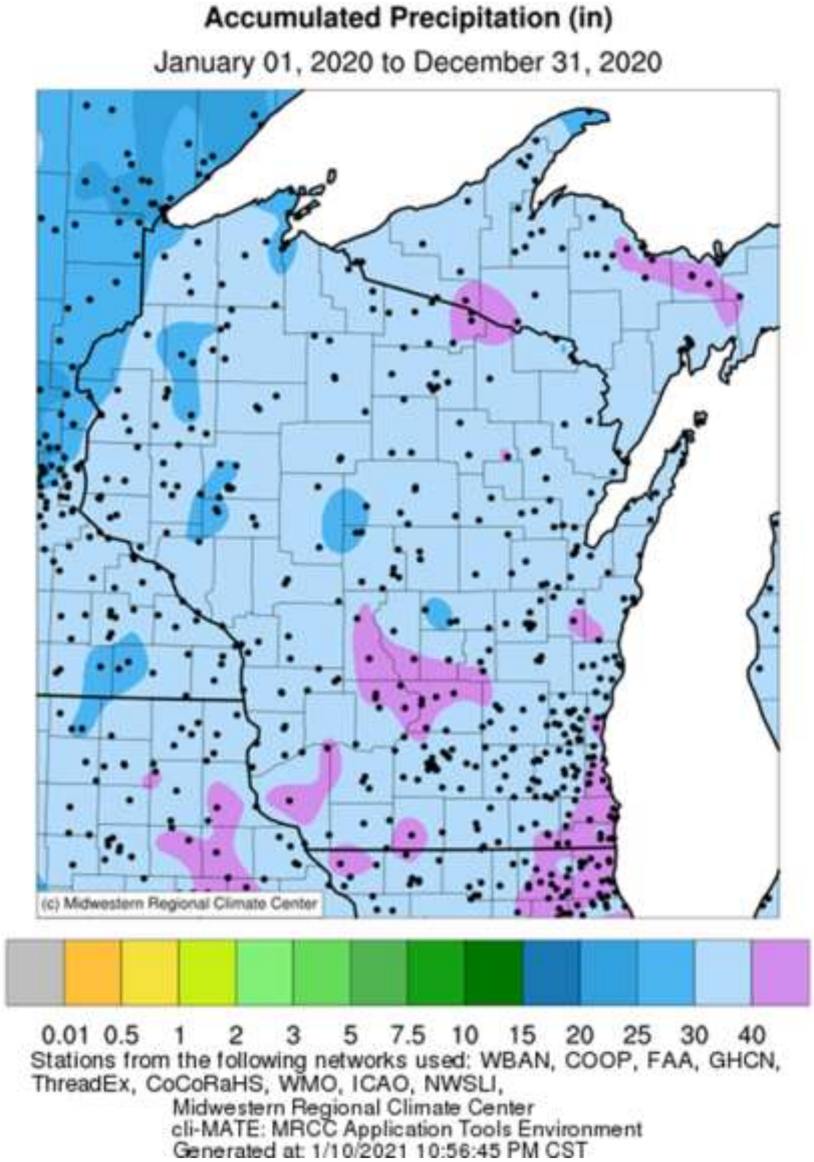
are also detected in groundwater samples collected from the Central Sands Agricultural Region for other programs, results suggest that there is a relationship between this neonicotinoid class of insecticides migration to groundwater and surface water quality in these watersheds. Neonicotinoids detected in surface water are likely the result of base flow for regional aquifers to surface water bodies within the Central Sands Agricultural Region.

- US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides in freshwater were exceeded for three compounds:
    - Clothianidin was detected in the June sample collected from the Root River. It was detected at a concentration of 0.164 micrograms per liter (ug/L) exceeding the Chronic Exposure on Invertebrates value of 0.05 ug/L,
    - Imidacloprid was detected in 21 samples at concentrations greater than the 0.01 µg/L laboratory reporting limit collected from Tenmile Creek, Leola Ditch, Fourteen Mile Creek, and Root River. Concentrations ranged from 0.0118 to 0.318 ug/L, exceeding the Chronic Exposure on Invertebrates value of 0.01 ug/L, and
    - Metolachlor was detected in the June sample collected from the Root River at a concentration of 6.44 ug/L, exceeding the Chronic Exposure on Invertebrates value of 1.0 ug/L. This is the first time metolachlor was detected at a concentration exceeding a surface water benchmark since the Surface Water Sampling Program began in 2007.
- There were no Wis. Admin. Code ch. NR 140 Enforcement Standard (ES) exceedances for groundwater quality standards. However, there were exceedances of Wis. Admin. Code ch. NR 140 Preventive Action Limits (PALs) for acetochlor, atrazine, di-amino atrazine and total chlorinated residue (TCR) of atrazine. This is the first time acetochlor was detected at a concentration greater than a PAL standard since the Surface Water Sampling Program began.
- The Wisconsin Department of Health Services (DHS) has developed drinking water health advisories for 15 pesticides. Imidacloprid was the only compound to exceed a DHS pesticide drinking water health advisory. Imidacloprid concentrations were detected in the surface water samples collected in June and July (0.318 and 0.274 µg/L, respectively) from the Root River in excess of the of 0.2 µg/L health advisory.
- Analytical data associated with water samples collected from the Seyene Spring continue to identify several pesticides and their metabolites plus total nitrogen as nitrate/nitrite concentrations greater than reporting limits. This includes concentrations of atrazine and it metabolites greater than several regulatory standards. Atrazine in these samples is also a regulatory concern for DATCP because the watershed for this area is within an atrazine Prohibition Area.

2020 PRECIPITATION MEASUREMENTS

Greater surface water runoff conditions usually correlate well with above normal precipitation, especially when ground surface is exposed (lack of vegetation), which was recorded throughout the state during 2020. This could result in greater pesticide concentrations in surface water. Wisconsin averages about 33.5 inches of precipitation annually. In 2020, the majority of the state accumulated more than 30 inches of annual precipitation, and some areas exceeded 40 inches of precipitation. Figure 2 shows the accumulated precipitation in inches for Wisconsin.

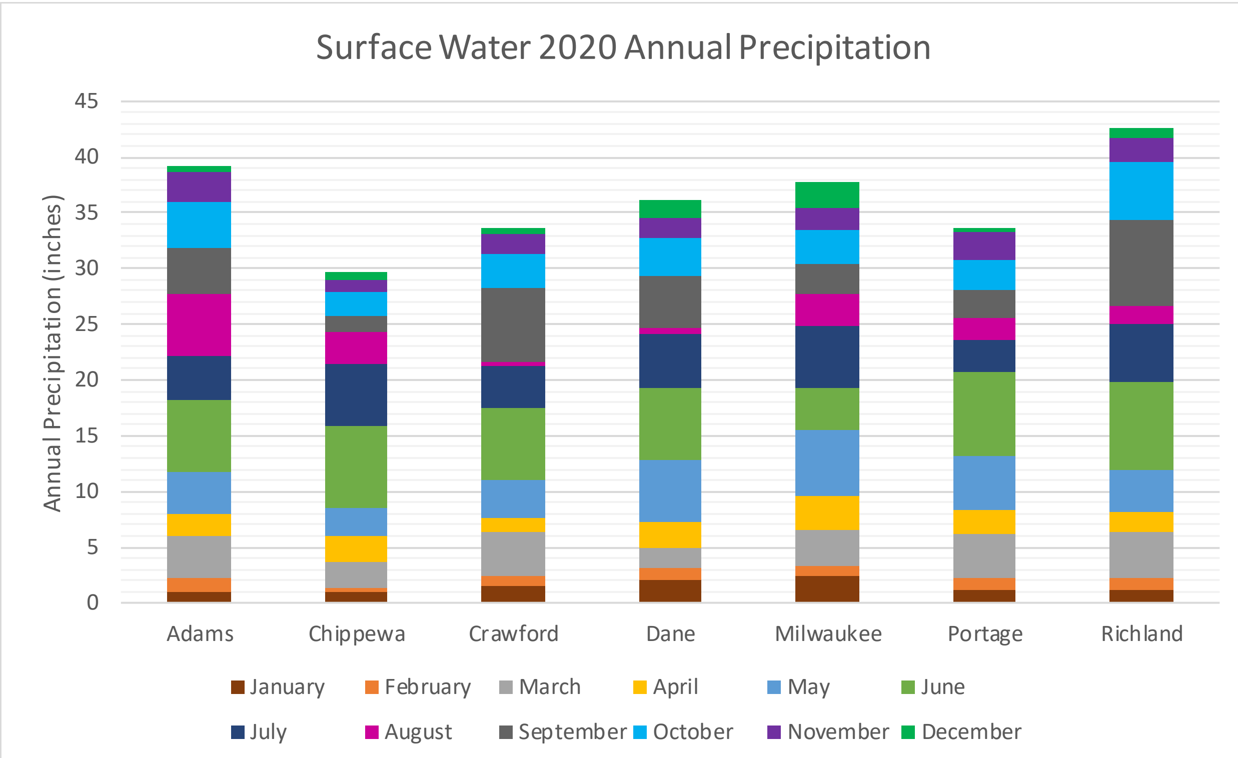
Figure 2: Accumulated Precipitation from Monthly Climate Watch Archive



As reported by the National Centers for Environmental Information and their *National Climate Report - Annual 2020*, Wisconsin experienced numerous winter storm and heavy snow events January through April. In early February, a winter snow storm produced four to 10 inches of snow across the western region. As the snow melted, it produced a flooding event in early April along portions of the Mississippi and Yellow Rivers. This event caused the rivers to crest over 0.5 ft. above the flood stage. Thunderstorm events with strong winds primarily occurred throughout the year from April through August. In early June, Wisconsin experienced the remnants of Hurricane Cristobal in the western region of the state, which caused flash flooding events across Trempealeau, Taylor, and Buffalo Counties. In late June, another flash flood event occurred in central Wisconsin. This event produced 1.5 to two times above the normal flash flood guidance value. In late August, a heavy rain event produced three to five inches of precipitation in Juneau and Adams Counties, which caused flash flooding to occur. The remainder of the year from October through December primarily consisted of strong wind and normal winter weather storm events.

As recorded by NOAA, Figure 3 summarizes the total annual precipitation in the counties where Program surface water samples are collected. The various colors indicate the monthly precipitation data at each location. The data indicates that precipitation was above average for four of the seven counties where surface water samples were collected in 2020.

Figure 3: Accumulated Precipitation from Monthly Climate Watch Archive



Monthly state-wide precipitation departure from the historical normal was obtained from the Wisconsin State Climatology Office and is displayed on Figure 4. During 2020, January, March, May through July, and October showed a positive departure from normal, meaning that there was an increase in precipitation in those months. These range from 0.2 to 1.4 inches above normal. Conversely, February, April, August through September, November and December showed a negative departure from normal, meaning there was a decrease in precipitation in those months. These values are less than one inch. *Based on these* data points, it appears greater than average precipitation was occurring during the usual pesticide application season.

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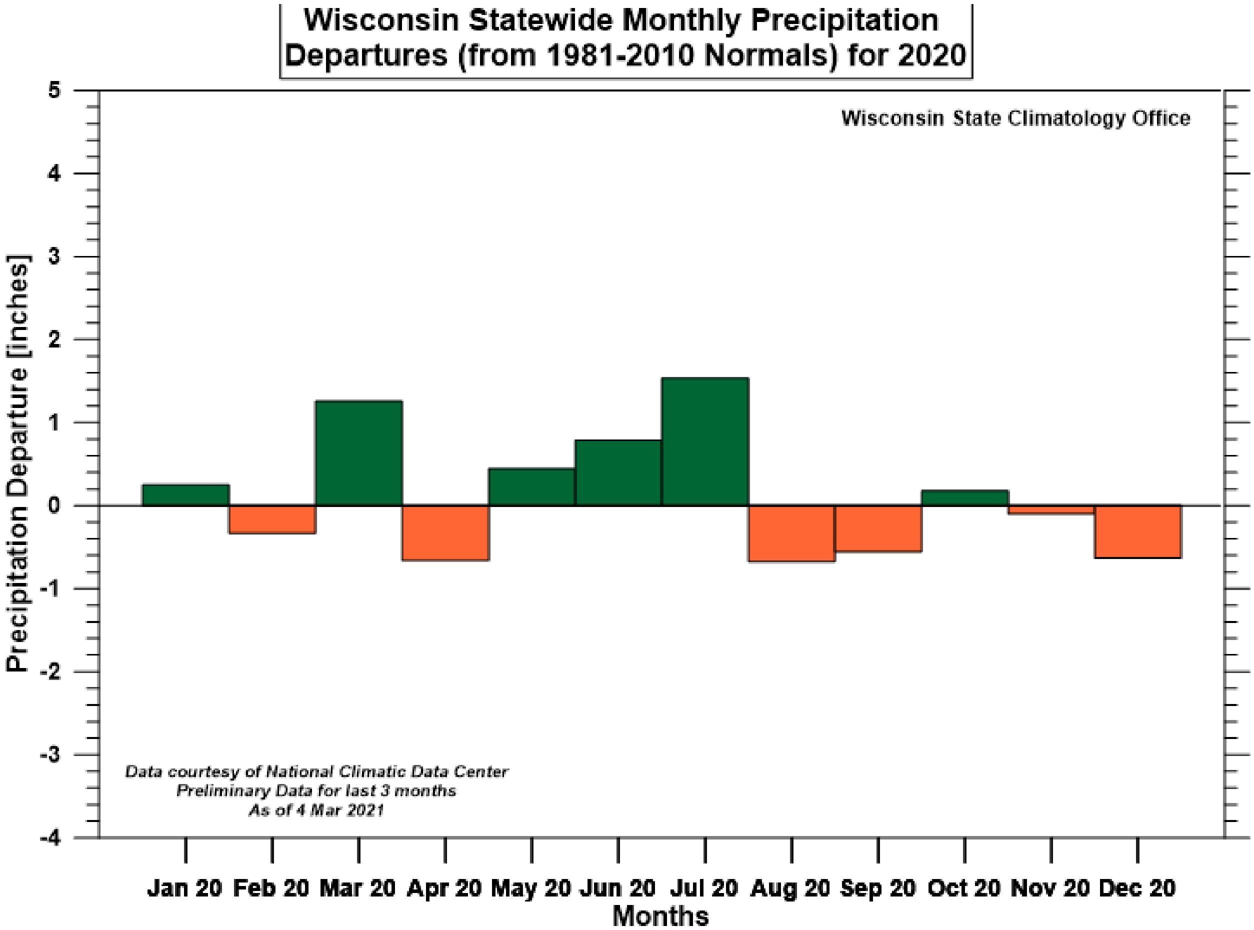
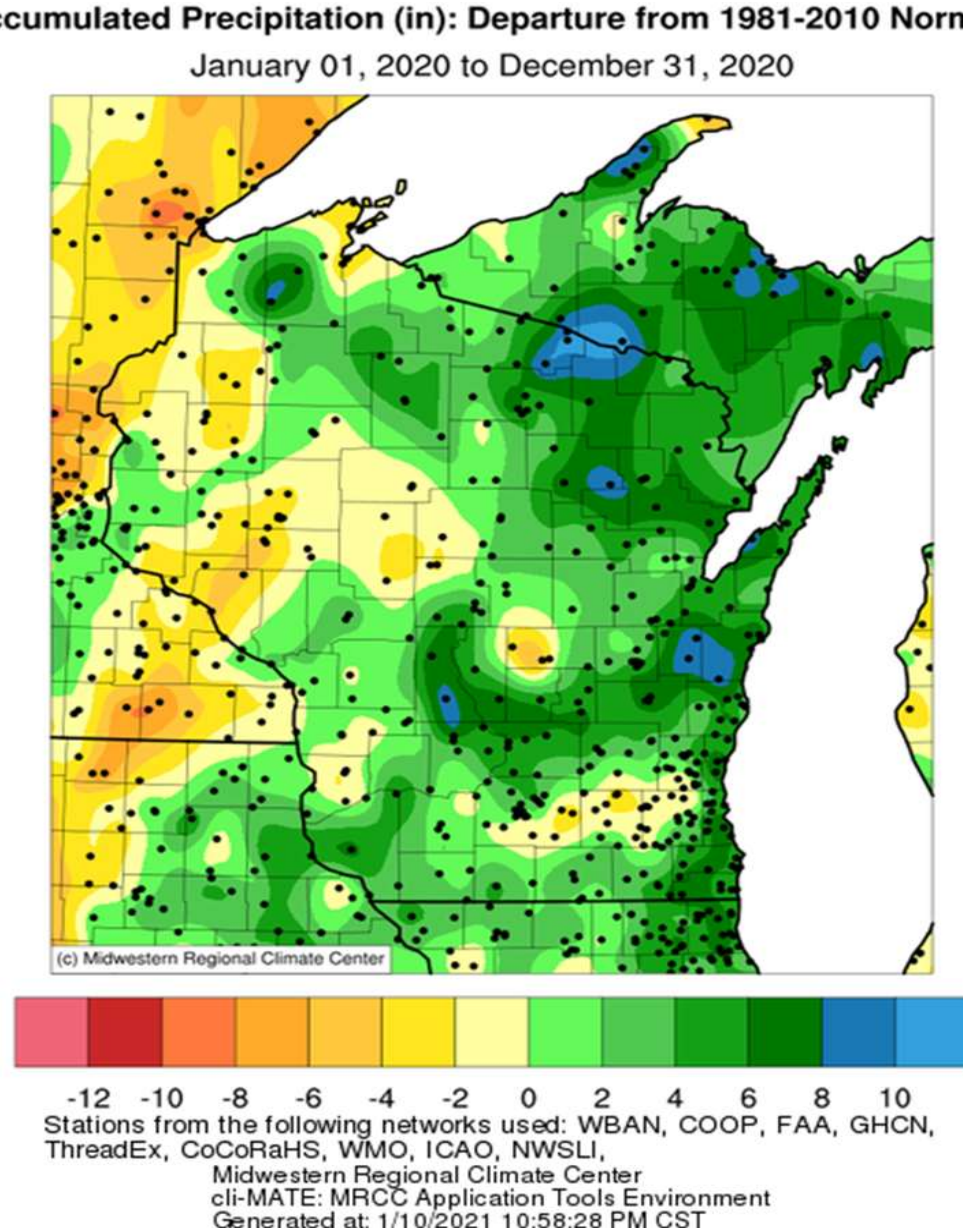
Figure 4: Monthly Precipitation Departures from Average



Similarly, Figure 5 shows the departure from normal for the accumulated precipitation regarding 2020 data. Positive values, indicated by the green and blue colors, show that the total precipitation was greater than normal. The negative values, indicated by the yellows and orange colors, show that the total precipitation was less than normal for 2020. Overall, this Figure also indicates that Wisconsin experienced greater than average precipitation levels. According to NOAA's Annual 2020 National Climate Report, Wisconsin accrued greater than one inch in excess of normal conditions. This is the eighth consecutive year Wisconsin has experienced above normal precipitation conditions.

Figure 5: Statewide Map of the Accumulated Precipitation Departure from Normal



PESTICIDE DETECTED FREQUENCY

Of the 107 analytes included in DATCP's Surface Water Sampling Program testing methodology, 30 pesticides were detected (77 not detected) in excess of laboratory reporting limits. These results are similar to prior years. However, a few pesticides that were not detected in prior years were detected in 2020. Pesticides first detected in 2020 surface water samples include clopyralid, dicamba and prometone.

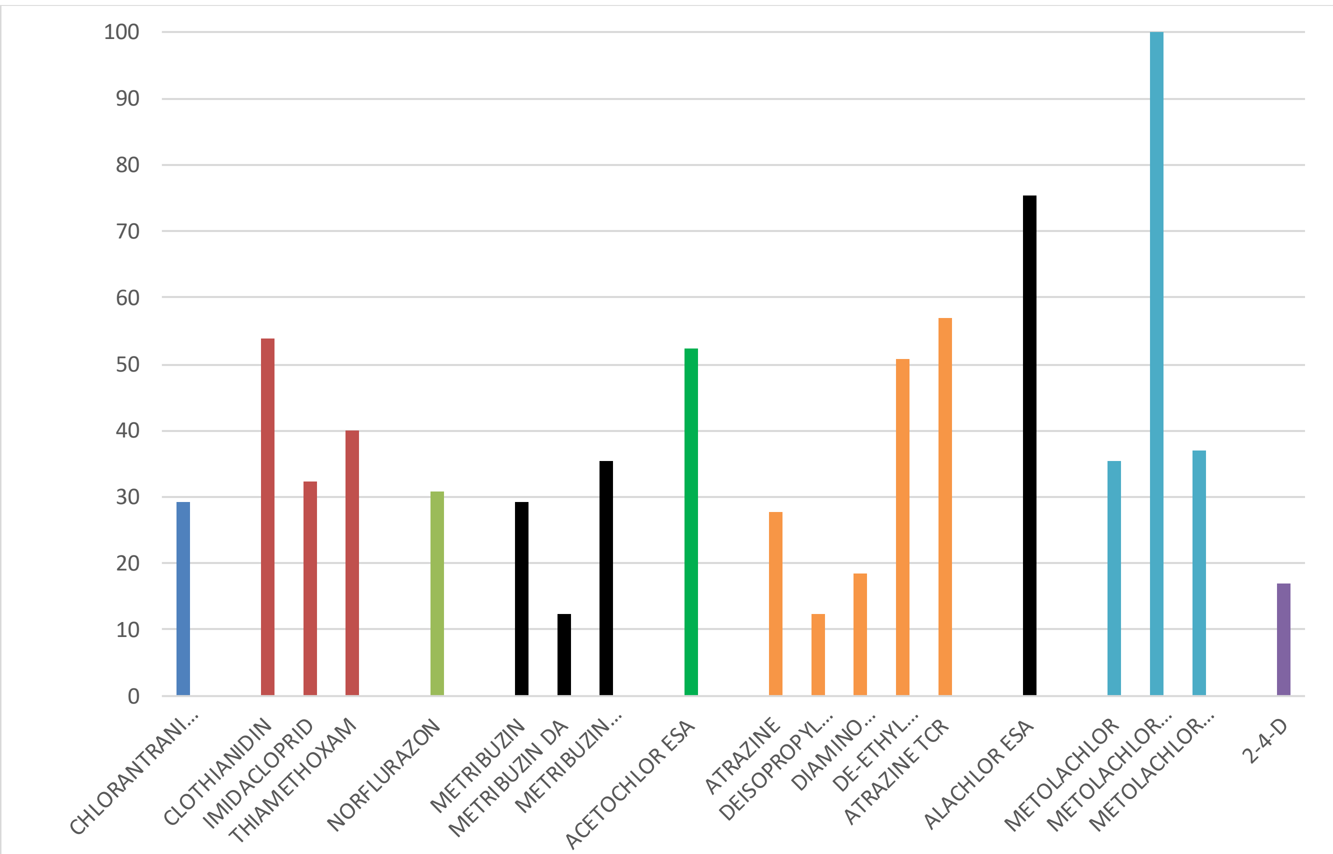
At least one pesticide concentration was detected in excess of laboratory reporting limits in every river, stream, or spring sample for every monthly event. This is the second year in a row regarding this observation. Historically, few to no pesticides were detected in surface water samples collected in the months prior to the pesticide application season greater than laboratory reporting limits.

Groundwater discharge is believed to contribute to stream flow at many of the gaining streams that are included in the Surface Water Sampling Program. Because pesticides are detected at statistically-similar concentrations in surface water samples throughout the year, it is reasonable to conclude that groundwater discharge contributes to pesticide detections in surface water, rather than seasonal influence from (surface) runoff.

The pesticide most frequently detected in excess of laboratory reporting limits was metolachlor ESA. This is a breakdown product of metolachlor, which is an active ingredient in corn herbicide such as Dual, Halex GT, Lumax and many others. Metolachlor ESA concentrations were detected in all 2020 river, stream or spring samples collected. This is very similar to the frequency of metolachlor ESA observed in DATCP program groundwater samples. Alachlor ESA was the second most frequently detected compound, found in 75% of the surface water samples collected in 2020.

Overall, there is an increase in the number and frequency of pesticides detected in 2020 samples compared to prior years. In particular, a continual increase in neonicotinoid detections is occurring on an annual basis. A further discussion regarding this trend is provided below. Figure 6 shows all pesticides that were detected above the laboratory reporting limits in more that 10% of samples collected in 2020.

Figure 6: Percentage of Pesticide Detected in 2020 Samples (includes all analytes detected in more than 10% of samples)



Notes: Atrazine TCR - Total chlorinated residues of atrazine includes the sum of atrazine plus its metabolites de-ethyl atrazine, de-isopropyl atrazine, and di-amino atrazine

It is worth noting that metolachlor ESA is also the most widely reported pesticide (metabolite) detected in drinking water wells according to the 2016 Statewide Survey (32% of all wells), which is followed by alachlor ESA (21.5% of all wells).

MONTHLY PESTICIDE DETECTIONS

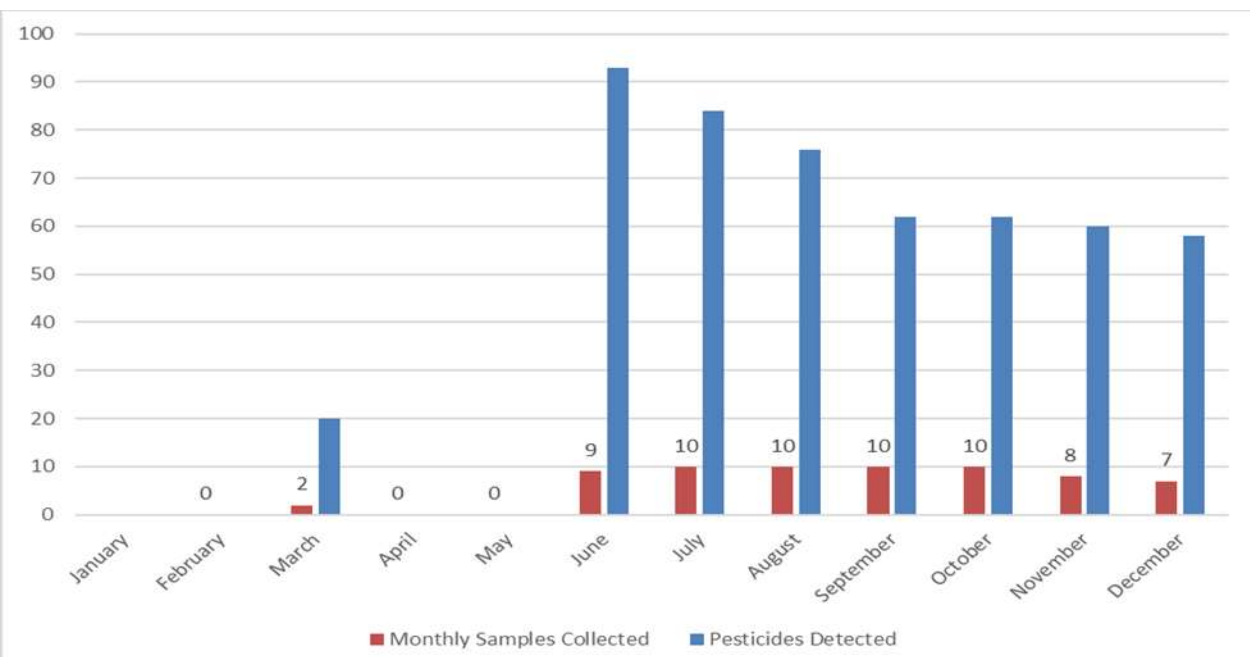
One of the Program's objectives is to evaluate the relationship between pesticide application and seasonal impacts to surface water quality. Figure 7 shows the number of pesticides detected by month for 2020. The monthly total includes all detections greater than laboratory detection limits for samples collected each month. As shown, surface water sampling was not completed in January and February and limited in March because the BLS lab not operating at full capacity while new and upgraded equipment was installed. Additionally, no sampling was completed in April and May because of state-imposed travel restrictions due to COVID-19.

The February through April timeframe is considered to be prior to the primary pesticide application season. In 2020, only a few surface water samples were collected due to laboratory unavailability and COVID-19 travel restrictions.

May through July are the months considered to be the primary pesticide application season for agricultural fields. The greatest number of pesticide detections occurred in June, with subsequent decreases July and August. The maximum number of pesticides detected in excess of laboratory reporting limits (93) was observed in June 2020. The number of pesticides then detected declined to 85 in July. (The number of pesticides detected in June number could have been higher in another sample was collected; only nine samples were collected in June compared to 10 samples in July and August.) Reduced surface water runoff due to crop cover and plant maturity likely contribute to this decline.

Pesticides detected in surface water would be expected to gradually decrease in the months following the primary pesticide application season. However, in 2020 (and as observed for this same timeframe during previous years), the number of pesticides detected above laboratory reporting limits remained relatively consistent in samples collected between August and December. Pesticides detection for August (76), September (51), October (51), November (50), and December (49) are shown below in Figure 7.

Figure 7: Number of Pesticide Analytes Detected by Month During the 2020 Sampling Program



Notes: There were no surface water samples collected in January due to the lab shut down for annual maintenance.

Monthly pesticide data was also evaluated to determine if concentrations are influenced by seasonal runoff or by groundwater discharge (base flow). Expectations for seasonal runoff would consist of analyte concentration fluctuations throughout the year. The greatest concentrations in surface water would be expected during the pesticide applications months (May through August), followed by a decline in the following months (September through October), and a continued decline over the winter months until the cycle is repeated the next application season. For groundwater discharge, a consistent number of analytes and consistent concentrations would be expected throughout the year. The base flow would reflect pesticide concentrations within the watershed aquifer that discharges to surface water throughout the year.

The greatest concentrations of metolachlor ESA detected in surface water samples were collected from the Central Sands Agricultural Region. This observation is consistent with surface water results from prior years and observations for other DATCP groundwater monitoring and drinking water pesticide data. Because metolachlor ESA was frequently detected all in aquifers within drainage basins where surface water was collected and it was detected in all 2020 surface water samples, it is likely that groundwater discharge from shallow aquifers as base flow is contributing to pesticides detected in surface water samples collected in 2020.

The following is a list of pesticides detected within each watershed that are likely influenced by groundwater discharge.

- Fourteen Mile Creek at County Road D
  - Alachlor ESA fluctuated between 0.289 to 0.492 µg/L throughout the year;
  - Chlorantraniliprole fluctuated between 0.133 to 0.493 µg/L throughout the year;
  - Clothianidin fluctuated between 0.0106 to 0.0471 µg/L throughout the year (first detected in 2020);
  - Metolachlor ESA fluctuated between 1.20 to 2.04 µg/L throughout the year;
  - Metolachlor OA fluctuated between 0.525 to 0.999 µg/L throughout the year;
  - Metribuzin DADK fluctuated between 0.613 to 0.854 µg/L throughout the year;
  - Norflurazon fluctuated between 0.120 to 1.04 µg/L throughout the year; and
  - Thiamethoxam fluctuated seasonally between 0.0241 to 0.236 µg/L.
- Leola Ditch at Aniwa
  - Alachlor ESA fluctuated between 0.322 to 0.994 µg/L throughout the year;
  - Chlorantraniliprole fluctuated between 0.0866 to 0.311 µg/L throughout year;
  - Clothianidin fluctuated between 0.0254 to 0.0365 µg/L throughout the year (first detected in 2020);
  - Metolachlor ESA fluctuated between 1.23 to 2.25 µg/L throughout the year;
  - Metolachlor OA fluctuated between 0.503 to 1.01 µg/L throughout the year;
  - Metribuzin DADK fluctuated between 0.533 to 0.909 µg/L throughout the year; and
  - Thiamethoxam fluctuated between 0.0978 to 0.359 µg/L throughout the year (first detected in 2020).
- Duncan Creek at 157th Avenue
  - Acetochlor ESA fluctuated between 0.131 to 0.156 µg/L throughout the year;
  - Alachlor ESA fluctuated between 0.155 to 0.300 µg/L throughout the year;
  - De-Ethyl Atrazine fluctuated between 0.0535 to 0.0842 µg/L for six of the seven samples collected; and
  - Metolachlor ESA fluctuated between 0.707 to 0.992 µg/L throughout the year.

- Milwaukee River at Estabrook Park
  - Metolachlor ESA fluctuated between 0.0761 to 0.302 µg/L throughout the year.
- Mississippi River at L & D #9
  - Acetochlor ESA fluctuated between 0.0692 to 0.364 µg/L throughout the year; and
  - Metolachlor ESA fluctuated between 0.207 to 0.376 µg/L throughout the year.
- Root River at 8-Mile Road
  - Metolachlor ESA fluctuated between 0.128 to 0.448 µg/L throughout the year.
- Tenmile Creek at Evergreen
  - Alachlor ESA fluctuated between 0.381 to 0.494 µg/L throughout the year;
  - Clothianidin fluctuated between 0.0238 to 0.0394 µg/L throughout the year (new in 2020);
  - Imidacloprid fluctuated between 0.0216 to 0.0308 µg/L throughout the year (new in 2020):
  - Metolachlor ESA fluctuated between 1.13 to 1.92 µg/L throughout the year;
  - Metolachlor OA fluctuated between 0.531 to 0.855 µg/L throughout the year;
  - Metribuzin fluctuated between 0.106 to 0.193 µg/L throughout the year;
  - Metribuzin DADK fluctuated between 0.508 to 0.715 µg/L throughout the year;
  - Norflurazon fluctuated between 0.126 to 1.25 µg/L throughout the year; and
  - Thiamethoxam fluctuated between 0.137 to 0.246 µg/L throughout the year.
- West Branch of the Sugar River
  - Acetochlor ESA fluctuated between 0.0788 to 0.177 µg/L for the year;
  - Clothianidin fluctuated between 0.0102 to 0.0175 µg/L for six of the seven samples;
  - De-Ethyl Atrazine fluctuated between 0.0706 to 0.168 µg/L for six of the seven samples collected;
  - Diamino Atrazine fluctuated between 0.203 to 0.433 µg/L for six of the seven samples collected; and
  - Metolachlor ESA fluctuated between 0.325 to 1.91 µg/L for the year.
- Wisconsin River at Muscoda
  - Alachlor ESA fluctuated between 0.0669 to 0.107 µg/L for the year; and
  - Metolachlor ESA fluctuated between 0.211 to 0.268 µg/L for the year.

Based on data from DATCP's 2020 Surface Water Sampling Program for Tenmile Creek, Leola Ditch and Fourteen Mile Creek, it appears that several pesticides are unique to Central Sands Agricultural Region watersheds. These pesticides include chlorantraniliprole, metribuzin and metabolites, norflurazon and thiamethoxam. With the exception of alachlor ESA and metolachlor ESA, these constituents were not observed in historic down river samples collected from the Wisconsin River at the Muscoda sampling location. These observations indicate that pesticides present within the Central Sands Agricultural Region watershed appear to have a minimal impact on downstream surface water quality. It is likely that the presence of pesticides in Central Sands Agricultural Region watersheds is a localized condition, and influenced by groundwater discharges to surface water.

Additional interpretation of pesticide data from multiple years is needed to validate these observations. This includes comparing agrichemical groundwater data associated with DATCP's Field-Edge Groundwater

Monitoring Program and surface water data from the same watersheds. This evaluation will be performed as part of the detailed comprehensive report documenting DATCP's Surface Water Sampling Program 2008-2021.

COMPARISON TO STANDARDS

Detected pesticide concentrations identified during DATCP's 2020 Surface Water Sampling Program were compared to two published environmental surface water or groundwater quality standards;

- U.S. EPA's Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides for freshwater; and
- Wis. Admin. Code ch. NR 140 - Groundwater Quality.

The table in Appendix A provides the two standards alongside the range of the detected pesticide analyte concentrations identified as part of the 2020 Surface Water Sampling Program. As labeled in the Appendix A table, several pesticides and their metabolites do not have aquatic life benchmarks (19 out of 107) or established Wis. Admin. Code ch. NR 140 ES and PAL standards (72 out of 107). Also listed are DHS drinking water advisories for 15 pesticides.

Of the 30 pesticide analytes detected in 2020 samples in excess of the laboratory reporting limits, six have no aquatic life benchmark (acetochlor OA, atrazine metabolites, metribuzin metabolites, and prometone) and nine have no established Wis. Admin. Code NR 140 ES or PAL standard. Of the 15 pesticides with DHS drinking water advisories, six analytes (clothianidin, thiamethoxam, imidacloprid, chlorantraniliprole, fomesafen, and sulfentrazone) were detected at concentrations greater than laboratory reporting limits.

U.S. EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides for freshwater were only exceeded for three compounds:

- Clothianidin
  - The June 2020 sample collected from the Root River detected clothianidin at a concentration of 0.164 µg/L, which exceeds the 0.05 µg/L Chronic Exposure on Invertebrates value;
- Imidacloprid
  - Twenty-one samples collected from Root River, Tenmile Creek, Leola Ditch, and Fourteen Mile Creek detected impidacloprid at concentrations ranging from 0.0118 to 0.0318 µg/L, which exceeds the Chronic Exposure on Invertebrates value of 0.01 µg/L; and
- Metolachlor
  - The June 2020 sample collected from the Root River detected metolachlor at a concentration of 6.44 µg/L, which exceeds the 1.0 µg/L Chronic Exposure on Invertebrates value.

Since Wisconsin does not have surface water standards established for pesticides, groundwater standards are used as substitues for evaluation purposes. An important part of Wisconsin's groundwater protection laws was the creation of groundwater 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 parts, an Enforcement Standard (ES) and Preventative Action Limit (PAL). The ES is a level 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 all other 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.

No pesticides or pesticide metabolites were detected at concentrations exceeding existing Wis. Admin. Code ch. NR 140 ES levels. However, the June and July 2020 samples collected from the Root River had detections of imidacloprid at concentrations of 0.318 and 0.274 µg/L, respectively, which exceeds the DHS drinking water advisory of 0.2 µg/L. Concentrations of acetochlor, atrazine, di-amino atrazine and atrazine TCR (total chlorinated residues, which are the sum of atrazine plus its metabolites de-ethyl atrazine, de-isopropyl atrazine, and di-amino atrazine) were detected above the Wis. Admin. Code ch. NR 140 PAL standards in

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several locations over multiple months. Table 3 identifies the pesticides and the metabolite exceedances for Wis. Admin. Code Ch. NR 140 ES and PAL standards and DHS drinking water health advisory levels.

Table 3: Summary of Pesticides and Metabolites Exceeding Wisconsin Admin. Code Chapter NR 140 Groundwater Quality Standards and Drinking Water Health Advisories

Compound	ES (µg/L)	PAL (µg/L)	Location	Date	Detection (µg/L)
Acetochlor	7	0.7	Root River	6/30/2020	3.34
Atrazine	3	0.3	Root River	6/30/2020	0.72
Di-Amino Atrazine	3	0.3	Seyene Spring	6/19/2020	0.374
				8/19/2020	0.407
				9/16/2020	0.418
				11/17/2020	0.432
				12/9/2020	0.394
			West Branch of Sugar	7/15/2020	0.433
Atrazine TCR	3	0.3	Duncan Creek	7/8/2020	0.3066
			Root River	6/30/2020	1.0422
			Seyene Spring	6/19/2020	0.703
				8/19/2020	0.7346
				9/16/2020	0.737
				10/23/2020	0.4366
				11/17/2020	0.7368
				12/9/2020	0.7092
			West Branch of Sugar River	7/15/2020	0.7541
				9/16/2020	0.3034
Imidacloprid	0.2*		Root River	6/30/2020	0.318
				7/28/2020	0.274

Notes: ES - Wisconsin Administrative Code, Chapter Natural Resources 140 - Enforcement Standard.
PAL - Wisconsin Administrative Code, Chapter Natural Resources 140 - Preventive Action Limits
µg/L - micrograms per liter or parts per billion.
Atrazine TCR - Total chlorinated residues of atrazine includes the sum of atrazine plus its metabolites de-ethyl atrazine, de-isopropyl atrazine, and di-amino atrazine
** - Wisconsin Department of Health Services Drinking Water Health Advisory.*

Comparing a detected pesticide (including metabolites) to the regulatory standards may not fully identify the total risk to human health and environment. Published surface water quality standards or benchmarks are based on concentrations for the occurrence of a single compound. Currently, there are no calculations to predict a comprehensive total potential risk when multiple compounds are present. Because this current approach does not account for potential cumulative risk, toxicity may be underestimated.

OTHER NOTABLE OBSERVATIONS

Neonicotinoids:

There has been interest in the neonicotinoid class of insecticides in recent years due to possible adverse effects on pollinators. DATCP began testing for these compounds in 2008 with thiamethoxam. BLS now analyzes for six neonicotinoid compounds. Three of these compounds (clothianidin, imidacloprid and thiamethoxam [CIT]) were each detected in surface water samples collected in 2020. The remaining three neonicotinoid compounds (acetamiprid, dinotefuran and thiacloprid) were not detected in any surface water samples. The detection of CIT is not unexpected, as these compounds are known to readily leach in sandy soils. They are present in insecticide products that are labeled for use on most crops grown in the state including corn, soybeans, potatoes, many other vegetables, as well as fruit crops, and most small grains.

Thiamethoxam and imidacloprid have been detected in DATCP's Surface Water Sampling Program since 2014. As observed during prior years, both of these compounds were detected in 2020 samples collected within the Central Sands Agricultural Region. However, the detected concentrations did not exceed DHS drinking water health advisories, which is consistent with historical data.

For the first time in 2020, both neonicotinoid compounds were detected in surface water samples collected outside the Central Sands Agricultural Region. As described above, both compounds were detected in Root River samples collected in June, July and August 2020. Imidacloprid was also detected in the June and July 2020 samples collected from the Root River at concentrations of 0.318 and 0.274 µg/L, respectively, which exceeds the DHS drinking water health advisory of 0.2 µg/L.

The concentrations of neonicotinoid compounds in surface water samples does not appear to fluctuate with season applications. Rather it appears that surface water concentrations are more associated with year round groundwater discharge rather than surface water runoff.

The U.S. EPA Office of Pesticide Programs benchmark for Chronic Exposure on Invertebrates was exceeded by two neonicotinoids in 2020:

- Clothianidin
  - The June 2020 sample collected from the Root River detected clothianidin at a concentration of 0.164 µg/L, which exceeds the 0.05 µg/L Chronic Exposure on Invertebrates value; and
- Imidacloprid
  - There were 21 samples collected from Root River, Tenmile Creek, Leola Ditch, and Fourteen Mile Creek that detected impidacloprid at concentrations ranging from 0.0118 to 0.0318 µg/L, which exceeds the Chronic Exposure on Invertebrates value of 0.01 µg/L.

These benchmarks were also exceeded in surface water samples collected from the same Central Sands Agricultural Region streams in prior years.

Atrazine:

Atrazine is a restricted-use herbicide. To protect groundwater, its use is prohibited within 101 atrazine prohibition areas (PAs) covering approximately 1.2 million acres within the state. 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 more than ten years, atrazine and its metabolite concentrations in surface or spring water should be low, if present at all. With the exception of the Milwaukee River, all streams sampled as part of the 2020 Surface Water Sampling Program either flow through or are adjacent to a PA. It would be expected that no atrazine use in these PAs would have an influence on the water quality at these surface water sample locations. However, atrazine was detected in 56% (37 of 66 samples) of the 2020 surface water samples. This is an increase compared to prior years. Every 2020 monitoring location had at least one surface water sample with an atrazine concentration above laboratory reporting limits. Either the parent material atrazine, or one of its metabolites (de-ethyl atrazine, de-isopropyl atrazine and di-amino atrazine) were detected in several stream and river samples.

The following is a summary of the atrazine findings for each river or stream.

- The greatest concentration of parent material atrazine and atrazine Total Chlorinated Residue (TCR, which is the combined sum of the parent material atrazine and its metabolites) was detected in a surface water sample collected in the June 2020 Root River sample at concentrations of 0.72 µg/L and 1.0422 µg/L, respectively. This is the same surface water sample that also contained the highest concentrations for several neonicotinoids.

- The parent material atrazine was detected in three of the seven monthly samples collected from Duncan Creek (June, July and September samples).
- Surface water samples from the West Branch of the Sugar River detected atrazine TCR concentrations throughout the year. However, the highest concentrations were identified in July 0.7541 µg/L. Concentration declined in subsequent samples to 0.2967 µg/L, indicating a seasonal fluctuation at this monitoring location.
- Fourteen Mile Creek samples had sporadic detections of de-ethyl atrazine throughout the year (in June, July, November and December samples). It was detected at low concentrations, ranging from 0.0502 to 0.069 µg/L, which is slightly in excess of the 0.05 µg/L reporting limit.
- Atrazine and de-ethyl atrazine were detected in Leola Ditch samples in June, August, November and December at concentrations ranging from 0.0529 µg/L to 0.0718 µg/L. As observed at Fourteen Mile Creek, these detections were also slightly above of the 0.05 µg/L laboratory reporting limit.
- The Milwaukee, Mississippi, and Wisconsin Rivers showed seasonal influence in the summer and fall seasons with most detections consisting of the atrazine parent material.
- Seyene Spring showed sustained levels of atrazine throughout the year (ranging from 0.0676 µg/L to 0.7368 µg/L). It exceeded the Wis. Admin. Code ch. NR 140 PAL of 0.3 µg/L in all but the July sample.

It appears that atrazine concentrations observed in the surface water samples at some of the locations may be associated with pesticide application season and seasonally impacting surface water quality. Because the parent material was detected more frequently than metabolites, surface water detection are likely associated with material applied to fields the same year. However, it is unknown if the atrazine contributions are coming from inside or outside the PA areas.

Seyene Spring has been included in the DATCP Surface Water Monitoring Program since 2018 when an atrazine concentration (0.78 µg/L) was identified in a spring water sample as part of a WGNHS project. This spring is located within a PA and would be expected to be void of atrazine. The 2020 surface water data indicated a trend of consistent atrazine and metabolite concentrations in excess of the Wis. Admin. Code ch. NR 140 PAL for atrazine TCR of 0.03 ug/L for every month sampled.

The 2020 atrazine data for the Seyene Spring is very consistent with prior year's data. For the most part, atrazine and each (measured) metabolite were detected in almost every sample. Concentrations of atrazine parent compound, de-ethyl atrazine and deisopropyl atrazine were relatively constant throughout the year. Di-amino atrazine was the most dynamic metabolite accounting for most of the TCR atrazine concentration.

Sustained concentrations of atrazine at Seyene Spring and its metabolites throughout the year indicate that there is a nearby continued source area for atrazine, and that the atrazine plume has migrated and is discharging to the spring. Because metabolites are present at higher concentration than parent atrazine, the source is likely old and may be difficult to locate.

Alachlor:

As noted previously, alachlor ESA was the second most frequently detected compound in 2020 surface water samples. Alachlor ESA is a breakdown product of alachlor. It was detected above laboratory reporting limits in nearly 75% of 2020 surface water samples at concentrations ranging between 0.0568 and 0.994 µg/L. This is an increase in the frequency of detections compared to years past.

Although alachlor ESA was widely detected in surface water (and groundwater) samples collected throughout the state, the parent alachlor was not detected above laboratory reporting limits in any 2020 surface water samples. Alachlor production ceased in December 2014, and field application has not been allowed since

August 2018. It is expected that these metabolite concentrations should decline over time since the parent analyte is no longer in use.

Nitrogen:

In additional to pesticides, DATCP's Surface Water Sampling Program includes analyses for nitrogen as nitrate/nitrite to evaluate impacts to surface water quality from agriculture. Nitrogen and its metabolites use and impacts are the responsibility of DNR. However, BLS includes nitrogen analyses as part of this program and results are shared with DNR.

Nitrogen was detected in excess of laboratory reporting limits in 62 of the 66 surface water samples collected for DATCP's 2020 Surface Water Sampling Program. The highest nitrogen concentration observed in 2020 was 11.6 parts per million (ppm) detected in the September Seyene Spring sample. Seyene Spring was the only location with multiple nitrogen detections (five) that exceeded the Wis. Admin. Code ch. NR 140 ES of 10 mg/L. The remaining four samples exceeded the Wis. Admin. Code ch. NR 140 PAL of 2.0 mg/L.

The following is a summary of nitrogen results for 2020 surface water samples.

- Surface water samples collected from the West Branch of the Sugar River and Duncan Creek consistently detected nitrogen; concentrations ranged from 5.35 ppm to 5.79 ppm and 2.33 ppm to 4.31 ppm, respectively. All of these detections exceeded the Wis. Admin. Code ch. NR 140 PAL of 2.0 mg/L.
- No samples collected from the Wisconsin River detected nitrogen in excess of the 2.0 mg/L Wis. Admin. Code ch. NR 140 PAL.
- Surface water samples collected from the Milwaukee River consistently detected nitrogen in excess of laboratory reporting limits ranging from 0.772 ppm to 1.28, which are less than the Wis. Admin. Code ch. NR 140 PAL of 2.0 mg/L.
- Mississippi River surface water samples were consistent throughout the year ranging from 1.12 ppm to 1.39 ppm.

Table 4 includes a summary of the DATCP's 2020 Surface Water Sampling Program detections for nitrogen.

Table 4: 2020 Surface Water Sampling Program Nitrogen as Nitrate and Nitrite Analytical Results

Sample Location	Nitrogen-Nitrate/ Nitrite Concentration Range (mg/L)
Duncan Creek at 157th Ave	2.33 - 4.31
Fourteen Mile Creek at County Road D	0.698 - 4.94
Leola Ditch at Aniwa	4.44 - 9.25
Milwaukee River at Estabrook Park	0.772 - 1.28
Mississippi River at L&D #9	1.12 - 1.37
Root River	0.534 - 5.36
Seyene Spring	5.43 - 11.6
Tenmile Creek at Evergreen	5.72 - 8.27
West Branch of Sugar River	2.84 - 10.9
Wisconsin River at Muscoda	ND - 1.3

Notes: Concentrations are reported in parts per million.
Wisconsin Administrative Code, Natural Resources 140 - Enforcement Standard for Nitrate or Nitrate + Nitrite is 10 mg/l.
Wisconsin Administrative Code, Natural Resources 140 - Preventive Action Limits for Nitrate or Nitrate + Nitrite is 2 mg/l
mg/L- milligrams per liter or parts per million
ND - no detect above laboratory reporting limits

2021 Program Goals and Objectives

DATCP's Surface Water Sampling Program will continue in 2021. It is expected that the following tasks will be completed.

- Collection of monthly surface water samples at twelve stream or river locations for the calendar year to include:
  - Collect monthly sample from these same ten locations to add to the existing database, and
  - Collect monthly samples from two new locations.
- Prepare a 2021 Data Summary Report to be completed by 3rd Quarter 2020, and
- Share report(s) with DNR Bureau of Water Quality, surface water sampling team, and other appropriate stakeholders, and have report available to public via the DATCP website.

For 2021, surface water sampling will be continued at the following locations:

- Wisconsin River at Muscoda;
- Mississippi River at Lock and Dam #9;
- Seyene Spring at South Seyene Road in Dane County;

- West Branch of the Sugar River in Dane County;
- Root River at 8-mile Road in Racine County (a repeat from prior years);
- Duncan Creek at 157th Avenue, just south of Bloomer:
- Milwaukee River at Estabrook Park; and
- The three streams that flow within the Central Sands Agricultural Region,
  - Tenmile Creek at Evergreen;
  - Fourteen Mile Creek at County Road D; and
  - Leola Ditch at Aniwa.

2021 surface water results will provide additional results for these locations. The intent is to evaluate water quality data over time and identify impacts and trends from agricultural land use. In addition to groundwater data, surface water data will aid in evaluating the effectiveness of the 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 2021, the following two new surface water sampling locations will be added:

- Mormon Coulee Creek #6 at County Road YY; and
- South Fork of the Bad Axe River in La Crosse County.

The WDNR Bureau of Fisheries Management reported that they have observed a decline in trout populations and density in some of the trout streams in western Wisconsin with have no explanation. One hypothesis is that pesticides are present in streams at toxic levels that are affecting aquatic life, thus reducing trout populations. The pesticides could be affecting fish populations directly or food sources such as invertebrates and plant life. WDNR requested that DATCP add both monitoring locations to our surface water monitoring program to evaluate surface water quality impacts from pesticides. Neither of these stream's watershed area lies within a PA.

ADDITIONAL PROGRAM ACTIVITIES

In addition to surface water sampling and reporting in 2021, additional or continued efforts will include the following:

- Continue to partner with university, state and federal agencies regarding the potential use of Polar Organic Integrative Samplers (POCIS); and
- Continue to implement a program outreach and branding plan.

These proposed activities were included in DATCP's 2021 Surface Water Program Work Plan.

APPENDIX A

2020 Surface Water Sampling Program Analytical Results, Summary

2020 Surface Water Sampling Program Results (all concentrations in ug/l)					Wisconsin Admin. Code Chapter NR 140		Department of Health Services	US EPA Office of Pesticide Programs - Aquatic Life Benchmarks For Pesticide					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit	Concentration Range	Enforcement Standard	Preventive Action Limit	Drinking Water Health Advisory[1]	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Acute (Non-vascular Plants)	Acute (Vascular Plants)
2,4-D	Herbicide	11	0.05	0.0546 - 3.34	70	7	--	--	--	12,500	--	--	299.2
2,4-DB	Herbicide	ND	1.3	--	--	--	--	7250	1600	12500	1500	952	83
2,4-DP	Herbicide	ND	0.05	--	--	--	--	>45750	--	279000	180000	77	32000
2,4,5-T	Herbicide	ND	0.05	--	--	--	--	--	--	--	--	--	--
2,4,5-TP	Herbicide	ND	0.05	--	50	5	--	--	--	--	--	--	--
Acetamiprid	Insecticide	ND	0.01	--	--	--	--	>50000	19200	10.5	2.1	>1000	>1000
Acetochlor	Herbicide	1	0.05	0.0756 - 1.39	7	0.7	--	190	130	4100	22.1	1.43	3.4
Acetochlor ESA	Metabolite	14	0.05	0.0531 - 1.61	230	46	--	>90000	--	>42500	--	9900	--
Acetochlor OA	Metabolite	1	0.1	1.17	230	46	--	--	--	--	--	--	--
Acifluorfen	Herbicide	1	0.05	0.187	--	--	--	--	--	--	--	--	--
Alachlor	Herbicide	ND	0.05	--	2	0.2	--	900	187	1250	110	1.64	2.3
Alachlor ESA	Metabolite	53	0.053	0.0568 - 0.994	20	4	--	>52000	--	>52000	--	3600	>120000
Alachlor OA	Metabolite	ND	0.25	--	--	--	--	>50000	--	>47500	--	--	--
Aldicarb Sulfone	Insecticide	ND	0.05	--	--	--	--	21000	--	140	--	--	--
Aldicarb Sulfoxide	Insecticide	ND	0.071	--	--	--	--	3570	--	21.5	--	--	--
Aminopyralid	Herbicide	ND	0.15	--	--	--	--	>50000	1360	7500	102000	10000	>88000
Atrazine	Herbicide	18	0.05	0.0529 - 0.72	3	0.3	--	2650	5	360	60	<1*	4.6
De-ethyl atrazine	Metabolite	33	0.05	0.0501 - 0.101	3	0.3	--	--	--	--	--	--	--
De-isopropyl atrazine	Metabolite	6	0.05	0.0516 - 0.0912	3	0.3	--	--	--	--	--	--	--
Di-amino atrazine	Metabolite	12	0.1	0.100 - 0.431	3	0.3	--	--	--	--	--	--	--
Atrazine TCR		37		0.0500 - 1.0421	3	0.3	--	--	--	--	--	--	--
Azoxystrobin	Fungicide	2	0.05	0.059 - 0.0923	--	--	--	235	147	130	44	49	3400
Benfluralin	Herbicide	ND	0.05	--	--	--	--	34.25	1.9	1030	15.5	>100	
Bentazon	Herbicide	ND	0.05	--	300	60	--	95000	8630	31150	101200	4500	5350
Bicyclopyrone	Herbicide	ND	0.05	--	--	--	--	>46700	10000	>44650	103700	2800	13
Bromacil	Herbicide	ND	0.05	--	--	--	--	18000	3000	60500	8200	6.8	45
Bifenthrin	Insecticide	ND	0.005	--	--	--	--	0.075	0.04	0.8	0.0013	--	--
Carbaryl	Insecticide	ND	0.05	--	40	4	--	110	6	0.85	0.5	660	--
Carbofuran	Insecticide	ND	0.05	--	40	8	--	44	5.7	1.115	0.75	--	--
Chloramben	Herbicide	ND	0.32	--	150	30	--	--	--	--	--	--	--
Chlorantraniliprole	Insecticide	19	0.05	0.0503 - 1.577	--	--	14,000	>3500	110	5.8	4.47	1760	>2000
Chlorothalonil	Fungicide	ND	0.1	--	--	--	--	5.25	3	1.8	0.6	6.8	630
Chlorpyrifos	Insecticide	ND	0.05	--	2	0.4	--	0.9	0.57	0.05	0.04	140	
Chlorpyrifos Oxon	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Clomazone	Herbicide	ND	0.05	--	--	--	--	1450	350	2700	2200	167	30200
Clopyralid	Herbicide	1	0.05	0.0720	--	--	--	51750	--	116500	--	6900	--
Clothianidin	Insecticide	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cyantraniliprole	Insecticide	ND	0.05	--	--	--	--	>5000	10700	15.2	6.56	>10000	>12100
Cyclaniliprole	Insecticide	ND	0.2	--	--	--	--	>60.5	200	40.4	9.6	>99	>187
Cyfluthrin	Insecticide	ND	0.05	--	--	--	--	0.034	0.01	0.0125	0.0074	>181	--
lambda-Cyhalothrin	Insecticide	ND	0.02	--	--	--	--	0.029	0.031	0.0035	0.002	>310	--
Cypermethrin	Insecticide	ND	0.1	--	--	--	--	0.195	0.14	0.21	0.069	--	--
Cyprosulfamide	Safener	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dacthal	Herbicide	ND	0.05	--	70	14	--	15000	--	13500	--	>11000	>11000
Dacthal Di-acid	Metabolite	ND	0.5	--	70[2]	14[2]	--	--	--	--	--	--	--
Dacthal Mono-acid	Metabolite	ND	0.5	--	70[2]	14[2]	--	--	--	--	--	--	--
Diazinon	Insecticide	ND	0.05	--	--	--	--	45	<0.55	0.105	0.17	3700	--
Diazinon Oxon	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dicamba	Herbicide	1	0.6	3.41	300	60	--	14000	--	>50000	--	61	>3250
Dichlobenil	Herbicide	5	0.05	0.0549 - 0.122	--	--	--	2465	>330	3100	560	1500	30
Dimethenamid	Herbicide	ND	0.05	--	50	5	--	3150	300	6000	1320	14	8.9
Dimethenamid ESA	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dimethenamid OA	Metabolite	ND	0.05	--	--	--	--	--	--	--	--	--	--
Dimethoate	Insecticide	ND	0.05	--	2	0.4	--	3100	400	21.5	0.5	20000	>92000
Dinotefuran	Insecticide	ND	0.01	--	--	--	--	>49550	6360	>484150	>95300	>97600	>110000
Diuron	Herbicide	ND	0.05	--	--	--	--	200	26.4	80	200	2.4	15

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2020 Surface Water Sampling Program Analytical Results, Summary - Continued

EPTC	Herbicide	ND	0.05	--	250	50	--	7000	40	3250	800	1400	5600
Esfenvalerate	Insecticide	ND	0.025	--	--	--	--	0.035	0.035	0.025	0.017	--	--
Ethalfluralin	Herbicide	ND	0.05	--	--	--	--	18	0.4	30	24	25	7.3
Ethofumesate	Herbicide	ND	0.05	--	--	--	--	5760	2560	147000	300	> 2760	39500
Flumetsulam	Herbicide	ND	0.05	--	--	--	10,000	> 146500	157000	127000	111000	0.31	3.1
Flupyradifurone	Insecticide	ND	0.05	--	--	--	--	--	--	--	--	--	--
Fluroxypyr	Insecticide	ND	0.07	--	--	--	--	7150	--	> 50000	--	> 100000	--
Fomesafen	Insecticide	4	0.05	0.0574 - 0.112	--	--	1	65000	5400	188000	50000	92	213
Halosulfuron methyl	Insecticide	ND	0.05	--	--	--	--	--	--	--	--	4.1	0.042
Hexazinone	Herbicide	ND	0.05	--	--	--	400	137500	17000	75800	20000	7	37.4
Imazapyr	Herbicide	ND	0.05	--	--	--	--	> 50000	40100	> 50000	97100	12200	24
Imazethapyr	Herbicide	ND	0.05	--	--	--	--	120000	87000	>500000	103000	4770	6.1
Imidacloprid	Insecticide	31	0.01	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
Isoxaflutole	Herbicide	ND	0.05	--	--	--	1	> 850	96	> 750	84	110	4.9
Isoxaflutole DKN	Metabolite	ND	0.05	--	--	--	1	>15300	--	>29800	--	9800	75
Linuron	Herbicide	ND	0.05	--	--	--	--	1500	3.58	60	0.09	13.7	2.5
MCPA	Herbicide	ND	0.05	--	--	--	--	>34000	--	>92000	--	--	--
MCPB	Herbicide	ND	0.1	--	--	--	--	1950	--	25000	--	380	210
MCPP	Herbicide	1	0.05	0.0563	--	--	--	>46500	--	>45500	50800	14	1300
Malathion	Insecticide	ND	0.05	--	--	--	--	2.05	0.6	0.049	0.06	2040	24000
Mesotrione	Herbicide	ND	0.1	--	--	--	--	> 60000	11000	420000	> 87000	1900	17.7
Metalaxyl	Fungicide	ND	0.05	--	--	--	880	65000	9100	14000	1200		85000
Methyl Parathion	Insecticide	ND	0.05	--	--	--	--	925	< 10	0.405	0.25	15000	18000
Metolachlor	Herbicide	[illegible]	[illegible]	[illegible]	300	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Metolachlor ESA	Metabolite	65	0.05	0.0707 - 2.25	1,300	260	--	24000	--	> 54000	--	> 55450	40000
Metolachlor OA	Metabolite	24	0.27	0.271 - 1.81	1,300	260	--	>46550	--	7760	--	57180	>95400
Metribuzin	Herbicide	19	0.05	0.0525 - 0.193	70	14	--	21000	> 2000	2100	1290	8.1	130
Metribuzin DA	Metabolite	8	0.1	0.101 - 0.198	--	--	--	--	--	--	--	--	--
Metribuzin DADK	Metabolite	23	0.12	0.308 - 0.903	--	--	--	--	--	--	--	--	--
Metsulfuron methyl	Herbicide	ND	0.05	--	--	--	--	> 75000	4500	> 75000	--	31	0.36
Nicosulfuron	Herbicide	ND	0.05	--	--	--	--	> 500000		> 500000	43000	--	--
Norflurazon	Herbicide	20	0.05	0.0573 - 1.04	--	--	--	4050	778	> 7500	1000	9.7	58.2
Oxadiazon	Herbicide	ND	0.05	--	--	--	--	600	33	1000	33	5.2	42
Pendimethalin	Herbicide	ND	0.05	--	--	--	--	69	6.3	140	14.5	5.2	12.5
Permethrin	Insecticide	ND	0.03	--	--	--	--	0.395	0.0515	0.0195	0.0014	68	--
Picloram	Herbicide	ND	0.05	--	500	100	--	2750	550	17200	11800	84900	--
Prometon	Herbicide	1	0.05	0.0561	100	20	--	--	--	--	--	--	--
Prometryn	Herbicide	ND	0.05	--	--	--	--	1465	620	4050	1000	1.04	11.0
Propiconazole	Fungicide	ND	0.05	--	--	--	--	425	95	650	260	21	3500
Saflufenacil	Herbicide	ND	0.05	--	--	--	460	> 54000	997	4250	1000	42	87
Simazine	Herbicide	ND	0.05	--	4	0.4	--	3200	60	580	48	6	67
Sulfentrazone	Herbicide	3	0.05	0.0784 - 1.94	--	--	1,000	46900	2950	30300	200	31	28.8
Sulfometuron methyl	Herbicide	ND	0.05	--	--	--	--	> 74000	--	> 75000	97000	4.3	0.45
Tebupirimphos	Insecticide	ND	0.05	--	--	--	--	44.5	138	0.030	0.011	630	8000
Tembotrione	Herbicide	ND	0.1	--	--	--	--	> 50000	404	24450	5100	310	5.2
Thiacloprid	Insecticide	ND	0.01	--	--	--	--	12000	918	18.9	0.97	45000	> 95400
Thiamethoxam	Insecticide	26	0.01	0.0177 - 0.359	--	--	180	> 57000	20000	17.5	0.74	> 35000	> 90200
Thiencarbazone methyl	Herbicide	ND	0.05	--	--	--	880	> 52000	4800	> 47000	3540	290	3.8
Triclopyr	Herbicide	1	0.05	0.0741	--	--	--	58000	--	66450	--	32500	
Trifluralin	Herbicide	ND	0.05	--	7.5	0.75	--	9.25	1.9	125.5	14	21.9	49.7

Notes:

-- Indicates that Health Advisory Level value in Wisconsin is 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. Reflects an additive quantity of atrazine and its three metabolites (de-ethyl, de-isopropyl and di-amino atrazine).

* Value may underestimate toxicity; *Refined Ecological Risk Assessment for Atrazine*; April 12, 2016.

[1] Wisconsin Department of Health Services Drinking Water Health Advisory (June 2015, November 2020, revised February 2022).

Indicates no detections in excess of laboratory reporting limits.

Indicates detections in excess of laboratory reporting limits, and less than Health Advisory levels or benchmark values.

Indicates detections in excess of laboratory reporting limits and Wis. Admin. Code Ch. NR 140 Preventive Action Limit, but less than benchmark values.

Indicates detections in excess of laboratory reporting limits and respective benchmark value or drinking water health advisory.

Website Used for aquatic benchmarks:

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