2019 Surface Water Pesticide Sampling Program Annual Report

ANNUAL REPORT

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

In 2019, 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 February 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 2020 Surface Water Sampling Program plan.

Purpose of Surface Water Sampling

It is estimated that agriculture contributes $105-billion annually to Wisconsin's economy. Growers 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 2019 sampling season, between nine and eleven monthly samples were collected from each selected river or stream; dependent 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 having a great percentage of 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 grown year after year on the same fields/area (e.g. corn, cranberry, ginseng) increasing the likelihood of repetitive pesticide use in area;
- Areas where crops grown in area 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, or at the request of one of the partnering agencies.

Over the past 10 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 conducts the majority of the sampling, time commitment and willingness is necessary for the annual programs 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 two years, the program has generally consisted of collecting surface water samples from ten locations; 50% are repeat locations with 50% are new locations to the program. Repeat locations include the following:

- Wisconsin River at Muscoda;
- Mississippi River at Lock and Dam #9;
- Milwaukee River at Estabrook Park;
- Tenmile Creek at Evergreen within the Central Sands Agricultural Region; and
- Fourteen Mile Creek also within the Central Sands Agricultural Region.

New locations for 2019 include the following:

- Embarrass River at CTH M;
- Embarrass River at Hayman Falls Lane;
- North Branch of Embarrass River at North Branch Road;
- Leola Ditch at Aniwa;
- Seyene Spring; and
- Porcupine Creek.

2019 PROGRAM SPECIFICS

A total of nine perennial rivers and streams (including one river with three different sampling locations) and a Dane County spring were selected for the 2019 sampling program. Additionally, for comparative purposes, two seasonal surface water samples were collected from a stream in northwest Wisconsin, the Porcupine Creek, to provide background data. A total of 103 samples were collected between February and December for chemical analysis of pesticides and nitrogen as nitrate/nitrite. Table 1 lists the 2019 surface water sampling program locations and Figure 1 depicts the eleven locations relative to State of Wisconsin and county boundaries. Table 2 includes a summary of watershed size and a summary of land use for 2019 for all but the largest watersheds (Mississippi and Wisconsin Rivers) using data provided by the Wisconsin Agricultural Statistics Service.

Table 1: 2019 Surface Water Sampling Program Rivers and Streams

River / Stream Name	SWIMS ID	County	Program Years
Embarrass River at CTH M	593168	Shawano	1
Embarrass River at Hayman Falls Lane	10052089	Shawano	1
North Branch of Embarrass River at North Branch Road	10022027	Shawano	1
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
Porcupine Creek**	10020966	Bayfield	1

Note: *** - Porcupine Creek was sampled twice to identify comparative background concentrations.*

Figure 1: 2019 Surface Water Sampling Program Rivers and Streams Locations

Table 2: 2019 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)
Embarrass River	58,500 (36.6%)	52,262 (32.7%)	7,359 (4.6%)	17,193 (10.7%)	17,212 (10.8%)	4,439 (2.8%)	109 (0.1%)	159,966
North Branch of Embarrass River	7,370 (32.3%)	9,611 (42.2%)	928 (4.1%)	1,782 (7.8%)	2,636 (11.6%)	457 (2.0%)	2 (0.0%)	22,787
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)								
Porcupine Creek**	14,287 (74.2%)	3,227 (16.8%)	1,681 (8.7%)	28 (0.15%)	29 (0.15%)	2 (0.01%)	0	19,254

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

*** - Background sample*

The sampling from the Embarrass River was in coordination with a WDNR Northeast Region investigation. Over the past couple of years, the WDNR has been observing a die-off of mussels in a certain stretch of the Embarrass River. They do not know the reason for the die-off. WDNR requested DATCP to evaluate monthly surface water samples from this specific stretch of the Embarrass River to determine if pesticide concentrations are elevated in the water and could be a contributing factor to the die-off. It would also be beneficial to DATCP since we did not have any pesticide data from the Embarrass River.

This is the second consecutive year for sampling the Seyene Spring. Three 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 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, including the site in our 2018 and 2019 surface water quality monitoring program.

Sample Collection and Analysis

Surface water samples are collected using DNR standard protocols, 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.

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 2019 program. However, based on analytical data and historical concentration trends, it appears the surface water samples collected from the Wisconsin River and Seyene Spring in October may have been switched and mislabeled. The October data results were not included in the evaluation and reporting. A summary of all analytical data for the 2019 program is included 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 104 pesticides and nitrogen as nitrate and nitrite. The table include in Appendix A lists the parameters along with corresponding laboratory reporting limits.

Results

A total of 103 surface water samples were collected and submitted for chemical analysis as a part of the DATCP's 2019 Surface Water Sampling Program. The table in Appendix A summarizes the 2019 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 (WAC) Ch. NR 140 groundwater standards for groundwater qualitative health standard limits, and a listing of the US 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 2019 data follows.

- Of the 104 pesticide analytes included in the laboratory testing methods, 25 were detected in excess of laboratory reporting limits in the surface water samples. Detections include nine herbicides, 10 herbicide metabolites, five insecticides, and one fungicide.
- There were no pesticide detections in excess of laboratory reporting limits for both background samples collected from the Porcupine Creek.
- There were no pesticide detections in excess of laboratory reporting limits for both background samples collected from the Porcupine Creek.
- Metolachlor ethanesulfonic acid (ESA) concentrations in excess of laboratory reporting limits was detected in all collected samples (excluding background samples).
- Alachlor ESA was the second most frequently detected compound in excess of laboratory reporting limits identified in nearly 55% 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 32% of the samples collected.
- 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.

- The presence of pesticides in samples collected every month suggests that most pesticide detected in surface water are the results of groundwater discharge (baseline 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 during 2019. Clothianidin was detected in 70% of samples, imidacloprid was detected in almost almost 67% of samples, and thiamethoxam was detected in almost 87% of samples collected from Fourteenmile Creek, Leola Ditch, and Tenmile Creek. Only one other neonicotinoid compound was detected in excess of laboratory detection limits in the remaining surface water samples outside the Central Sands Agricultural Region; clothianidin was detected in the August Mississippi River sample. 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 baseline 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 two compounds:
  - Clothianidin was detected in the September sample collected from the Fourteen Mile Creek. It was detected at a concentration of 0.0535 micrograms per liter (ug/L) exceeding the Chronic Exposure on Invertebrates value of 0.05 ug/L.
  - Imidacloprid was detected in 20 samples (all samples that exceeded 0.01 µg/L laboratory reporting limits) collected from Tenmile Creek, Leola Ditch, and Fourteen Mile Creek, at concentrations ranging from 0.0138 to 0.0315 ug/L exceeding the Chronic Exposure on Invertebrates value of 0.01 ug/L.
- There were no WAC Ch. NR 140 Enforcement Standard (ES) exceedances for drinking water and groundwater quality health standards/advisory levels. However, there were exceedances of WAC Ch. NR 140 Preventive Action Limits (PAL) for atrazine, di-amino atrazine and total chlorinated residue (TCR) of atrazine.
- The Wisconsin Department of Health Services (DHS) has proposed groundwater standards for seven pesticides as part of the WAC Ch. 140 Cycle 10 recommendations. Only concentrations of imidacloprid exceeding the proposed PAL standard of 0.02 ug/L were detected in nine samples at concentrations ranging from 0.0203 to 0.0315 µg/L; four from Fourteen Mile Creek (during June, July, September, and October), one from Leola Ditch (in October), and four from Tenmile Creek (during June, July, September, and October).
- Analytical data associated with surface water samples collected from the Embarrass River did identify several pesticides and their metabolites plus total nitrogen as nitrate/nitrite concentrations in excess of laboratory reporting limits. However, the concentrations detected are unlikely to impose a risk to the mussel population.
- 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 in excess of reporting limits. This includes atrazine and it metabolites concentrations in excess of several regulatory standards. Atrazine is a regulatory concern for DATCP because the watershed for this area is within an atrazine Prohibition Area.

PESTICIDE DETECTED FREQUENCY

Of the 104 analytes included in the testing methodology, there were 25 pesticides detected (79 not detected) in excess of laboratory reporting limits associated with the DATCP's 2019 Surface Water Sampling Program.

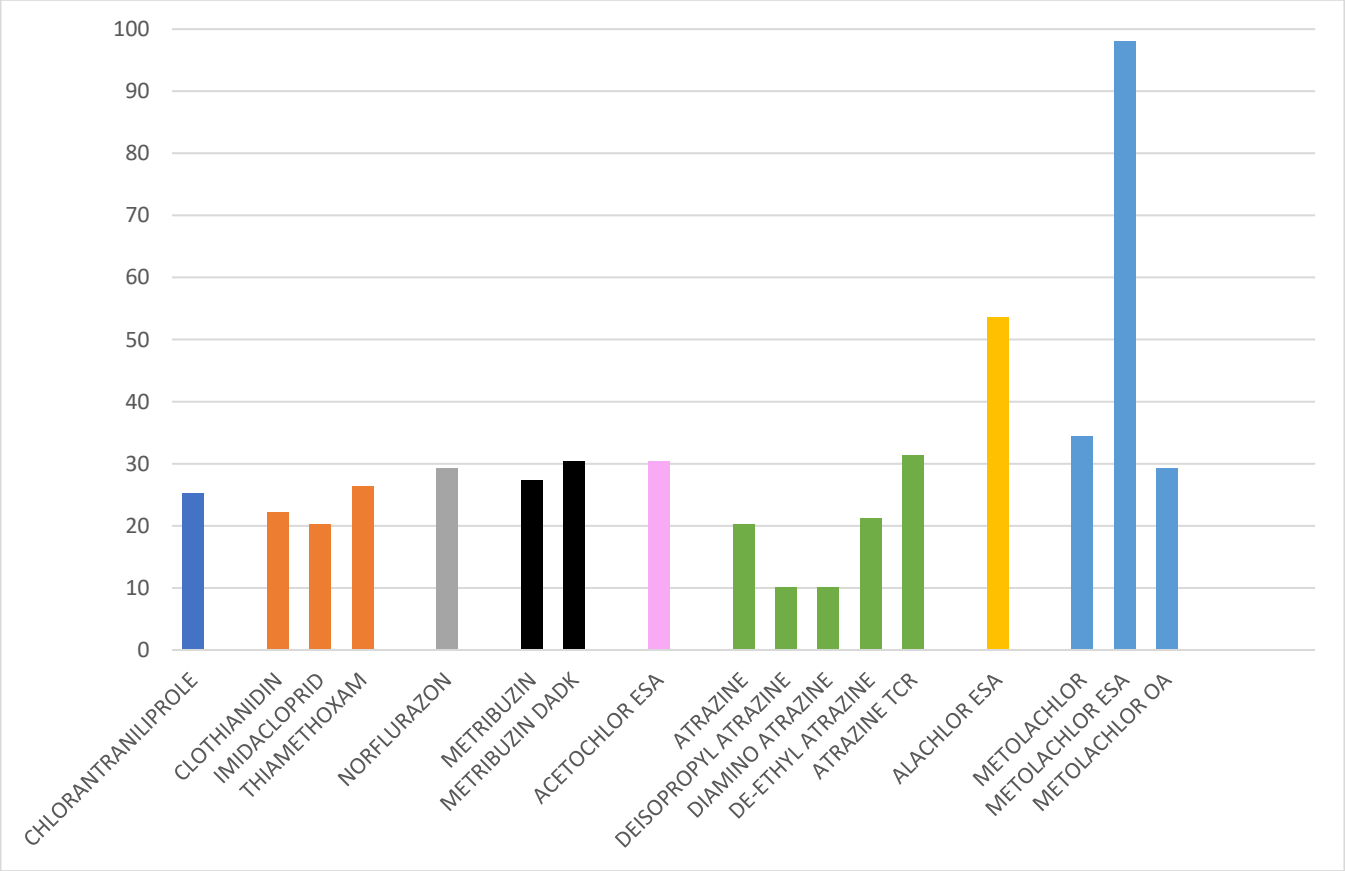
This is a decrease of analytes detected compared to prior years. There were no new pesticides detected compared to previous years.

At least one pesticide concentration was detected in excess of laboratory reporting limits in every river, stream, or spring sample for every monthly event, with the exception of the background samples collected from Porcupine Creek. These results suggest an increasing trend in the presence of pesticides detection compared to previous years. Historically, little to no pesticides were detected in excess of laboratory reporting limits in surface water samples collected in the months prior to the pesticide application.

Groundwater discharge is believed to contribute to stream flow as baseline flow at many of these gaining streams are included in the Program. Because pesticides are detected at 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 runoff.

The most frequently detected pesticide analyte 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 river, stream or spring samples collected. Only the two background samples from the Porcupine River did not have any detectable concentrations. Alachlor ESA was the second most frequently detected compound in excess of laboratory reporting limits identified in nearly 55% of the samples collected. Table 3 depicts the pesticide analytes that were detected at a concentration greater than the laboratory reporting limit at a frequency of greater than 10%.

Table 3: Percentage of 2019 Samples that contained Detectable Concentrations of the Respective Pesticide (only showing analytes detected greater than 10%)



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

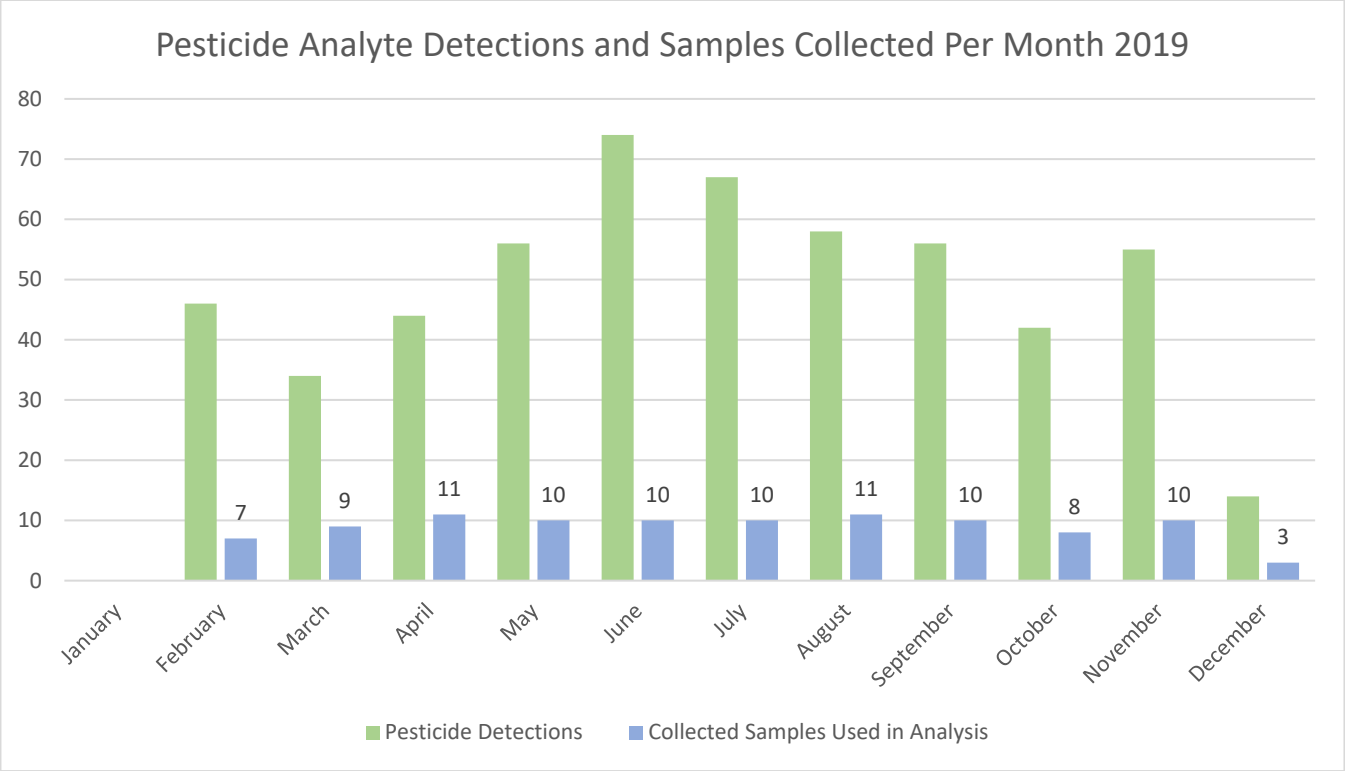
One of the Program's objectives is to evaluate the relationship between pesticide application and seasonal impacts to surface water quality. Table 4 depicts the number of pesticides detected by month for 2019. The monthly total includes all detections in excess of the laboratory detection limits in samples collected each month.

The 2019 February through April data, months that are considered to be prior to the primary pesticide application season, reflected an expected trend of analyte detections. The February data likely reflects conditions typical of winter snow melt (little infiltration due to frost in the ground, and increased overland flow). Increased runoff likely results in the mobilization of pesticides to streams and rivers. March likely reflects a low for spring season (before pesticides are applied to new crops) followed by a slow monthly increase for April as more pesticides are applied, and infiltration results in an increase in groundwater discharge to surface water.

May through July are the months considered to be the main pesticide application season for agricultural fields, As can be expected, the number of pesticide detections increased during these months. The maximum number of pesticides detected in excess of laboratory reporting limits (74) was observed in June 2019. The number of pesticides then detected declined to 67 in July. Reduced surface water runoff due to crop cover and plant maturity likely contribute to this decline.

August through December surface water samples can be expected to gradually decrease because this timeframe is past the primary pesticide application season. However, in 2019 (and for this timeframe during previous years), the number of pesticides detected in excess of laboratory reporting limits remained relatively consistent for August (58), September (56), and November (55). In October, the number of detections declined to 42, most likely in response to fewer samples used for this evaluation. Only 14 detections were observed for December, but only three samples (the Mississippi River, Seyene Spring and the Wisconsin River) were collected. It is likely that if samples were collected from all locations in December the pesticide detection count be similar to the previous four months.

Table 4: Number of Pesticide Analytes Detected by Month During the 2019 Sampling Program



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

October samples for the Wisconsin River and Seyene Spring were not included due to a possible labeling mistakes.

Porcupine Creek data was used for background comparative purposes; that data is not included in the chart.

Monthly pesticide data was also evaluated to determine if concentrations are influenced by seasonal surface water flows or by groundwater/aquifer discharge (base flow). A seasonal flow would have the analyte concentrations fluctuating throughout the year with greatest concentrations in the surface water during the pesticide applications months (May through August), followed by a decline in the following months (September through October), and then a continued decline over the winter months until the cycle is repeated the next application season. A baseline aquifer flow would have a consistent number of analytes and consistent concentrations likely throughout the year. The baseline flow would reflect pesticide concentrations within the watershed aquifer that discharges to surface water throughout the year.

Based on the above expected observations, it appears metolachlor ESA would be considered a primary baseline compound found in all of the aquifers that discharge to the streams and rivers that were sampled. The greatest concentrations of metolachlor ESA detected in surface water samples were located within the Central Sands Agricultural Region. This observation is consistent with other groundwater and drinking water pesticide data from other DATCP monitoring programs.

The following is a list of pesticides detected within each watershed that likely represent baseline aquifer flow.

- Embarrass River (sampled stretch)
  - Metolachlor ESA concentration range of 0.0663 to 0.41 µg/L for the year.
  - Fourteen Mile Creek at County Road D
  - Alachlor ESA concentration range of 0.421to 0.783 µg/L for the year;

- Chlorantraniliprole concentration range of 0.0825 to 0.468 µg/L for the year;
- Metolachlor concentration range of 0.0521 to 0.0988 µg/L (for nine of the 10 months with no detect in August);
- Metolachlor ESA concentration range of 1.33 to 2.72 µg/L for the year;
- Metolachlor OA concentration range of 0.509 to 1.05 µg/L for the year;
- Metribuzin concentration range of 0.0569 to 0.146 µg/L for the year;
- Metribuzin DADK concentration range of 0.62 to 0.918 µg/L for the year;
- Norflurazon concentration range of 0.0559 to 0.633 µg/L for the year with a seasonal variation; and
- Thiamethoxam concentration range of 0.11 to 0.328 µg/L for the year with a seasonal variation.

- Leola Ditch at Aniwa
  - Alachlor ESA concentration range of 0.161 to 1.21 µg/L for the year;
  - Chlorantraniliprole (potentially) concentration range of 0.0546 to 0.199 µg/L (for nine of the 10 months of sampling with no detect in March);
  - Metolachlor ESA concentration range of 0.343 to 2.31 µg/L for the year with a seasonal variation;
  - Metolachlor OA concentration range of 0.277 to 0.893 µg/L (for nine of the 10 months);
  - Metribuzin DADK concentration range of 0.247 to 0.809 µg/L for the year; and
  - Norflurazon concentration range of 0.0729 to 1.14 µg/L (for nine out of the 10 months with an apparent seasonal variation).
- Milwaukee River at Estabrook Park
  - Metolachlor ESA concentration range of 0.178 to 0.317 µg/L for the year.
- Mississippi River at L & D #9
  - Acetochlor ESA concentration range of 0.0639 to 0.381 µg/L for the year with a seasonal variation; and
  - Metolachlor ESA concentration range of 0.154 to 0.575 µg/L for the year.
- Tenmile Creek at Evergreen
  - Alachlor ESA concentration range of 0.399 to 0.645 µg/L for the year;
  - Metolachlor ESA concentration range of 0.938 to 1.66 µg/L for the year;
  - Metolachlor OA concentration range of 0.324 to 0.591 µg/L for the year;
  - Metribuzin concentration range of 0.0781 to 0.166 µg/L for the year;
  - Metribuzin DADK concentration range of 0.386 to 0.64 µg/L for the year;
  - Norflurazon concentration range of 0.0513 to 0.371 µg/L for the year; and
  - Thiamethoxam concentration range of 0.0532 to 0.0939 µg/L (for nine of the 10 months of sampling with no detect in March).
- Wisconsin River at Muscoda
  - Alachlor ESA concentration range of 0.0532 to 0.106 µg/L for the year; and
  - Metolachlor ESA = concentration range 0.164 to 0.323 µg/L for the year.

Based on data from DATCP's 2019 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 results 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 related to 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 common-located watersheds. This evaluation will be performed as part of the detailed comprehensive report documenting DATCP's Surface Water Sampling Program 2008-2018 Report, which is scheduled to be prepared in the fall of 2020.

COMPARISON TO STANDARDS

Detected pesticide concentrations identified during DATCP's 2019 Surface Water Sampling Program were compared to two published environmental surface water/groundwater quality standards;

- US EPA's Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides for freshwater; and
- WAC Ch. NR 140 – ES and PAL for Drinking Water and Groundwater Quality Health Standards/Advisory Levels.

The table in Appendix A provides the two standards alongside the range of the detected pesticide analyte concentrations identified as part of the 2019 Surface Water Sampling Program. As labeled in the Appendix A table, several pesticides and their metabolites do not have aquatic life benchmarks (17 out of 104) or established WAC NR 140 ES and PAL standards (72 out of 104). Also listed, currently, the DHS has proposed WAC NR 140 ES and PAL standards for an additional seven pesticides.

In regards to the 2019 data, of the 25 pesticide analytes detected in excess of laboratory reporting limits, six do not have an aquatic life benchmark (atrazine metabolites, dimethenamid metabolites, and metribuzin meatbolites) and nine do not have a WAC NR 140 ES or PAL standard. Of the seven pesticide analytes with proposed standards, four of the analytes had detected concentrations in excess of laboratory reporting limits.

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

- Clothianidin
  - The September 2019 sample collected from the Fourteen Mile Creek in detected clothianidin at a concentration of 0.0535 µg/L, which exceeds the 0.05 µg/L Chronic Exposure on Invertebrates value; and
- Imidacloprid
  - Twenty samples collected from Tenmile Creek, Leola Ditch, and Fourteen Mile Creek detected impidacloprid at concentrations ranging from 0.0138 to 0.0315 µg/L, which exceeds the Chronic Exposure on Invertebrates value of 0.01 µg/L.

An important part of Wisconsin's groundwater protection laws was the creation of water quality standards for different substances, outlined in WAC 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 ES and 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 any of the WAC ch. NR 140 ES levels. However, concentrations of 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 in excess of the WAC NR 140 PAL standards in several locations over multiple months. Imidacloprid was detected in excess of WAC NR 140 Cycle 10 Proposed PAL standard in surface water samples collected from the three streams located in the Central Sands Agricultural Region. Table 5 identifies the pesticides and the metabolite exceedances for WAC NR 140 PAL standards and proposed standards.

Table 5: Summary of Pesticides and Metabolites Exceeding Wisconsin Admin. Code NR 140 Existing and Proposed (Cycle 10) Groundwater Quality Standards

Compound	ES (µg/L)	PAL (µg/L)	Location	Date	Detection (µg/L)
Atrazine	3	0.3	Mississippi River	7/10/2019	0.371
Di-amino Atrazine	3	0.3	Seyene Spring	2/14/2019	0.415
				4/12/2019	0.334
				6/20/2019	0.381
				7/12/2019	0.394
				8/8/2019	0.44
				11/14/2019	0.455
				12/12/2019	0.447
Atrazine TCR	3	0.3	Mississippi River	7/10/2019	0.4629
			Seyene Spring	2/14/2019	0.7454
				3/14/2019	0.3671
				4/12/2019	0.5974
				5/9/2019	0.5249
				6/20/2019	0.7058
				7/12/2019	0.6995
				8/8/2019	0.7471
				9/12/2019	0.375
				11/14/2019	0.7497
				12/12/2019	0.7788
Imidacloprid	0.2*	0.02*	Fourteen Mile	6/11/2019	0.0294
				7/16/2019	0.0266
				9/18/2019	0.0315
				10/24/2019	0.0227
			Leola Ditch	10/24/2019	0.0219
			Tenmile Creek	6/11/2019	0.0244
				7/16/2019	0.0216
				9/18/2019	0.0204
				10/24/2019	0.0203

Notes: *ES - Wisconsin Administrative Code, Natural Resources 140 - Enforcement Standard.*

PAL - Wisconsin Administrative Code, 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 Administrative Code Cycle 10 Proposed PAL or ES*

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 the total potential comprehensive risk when multiple compounds are present. This current approach does not account for potential cumulative risk, and may underestimate toxicity.

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 2019. 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. The compounds were detected in samples collected within the Central Sands Agricultural Region. Only one other neonicotinoid detection in excess of laboratory reporting limits was identified outside the Central Sands Agricultural Region; clothianidin was detected in a Mississippi River sample collected in August 2019. No neonicotinoid compounds were detected in excess of laboratory reporting limits in both background samples collected from Porcupine Creek.

The presence of some neonicotinoid compounds in surface water samples was observed to fluctuate seasonally. Clothianidin and imidacloprid concentration fluctuations increase between April and July, which indicate a mass influx concurrent with the pesticide application season. However, concentration trends for monthly water samples collected from Tenmile and Fourteen Mile Creeks remain consistent throughout the year.

The US EPA Office of Pesticide Programs benchmark for Chronic Exposure on Invertebrates was exceeded by two neonicotinoids in 2019:

- Clothianidin
  - The September 2019 sample collected from the Fourteen Mile Creek detected clothianidin at a concentration of 0.0535 µg/L, which exceeds the 0.05 µg/L Chronic Exposure on Invertebrates value, and
- Imidacloprid
  - Imidachloprid was detected in excess of laboratory reporting limits in 20 samples collected from Tenmile Creek, Leola Ditch, and Fourteen Mile Creek at concentrations ranging from 0.0138 to 0.0315 µg/L. It exceed the 0.01 µg/L Chronic Exposure on Invertebrates in all samples collected exceeding the reporting limit.

This is the first time these benchmarks were exceeded by surface water samples collected from these Central Sands Agricultural Region streams.

There were no CIT concentration exceedances of the proposed WAC ch. NR 140 ES in the 2019 surface water samples. However, the 0.02 µ/L proposed PAL standard for imidacloprid was exceeded in the following 2019 surface water collected from Central Sands Agricultural Region streams:

- Fourteen Mile Creek (June, July, September and October samples at concentrations ranging from 0.0227 µg/L to 0.0315 µg/L);
- Leola Ditch (October sample at 0.0219 µg/L); and
- Tenmile Creek (June, July, September and October samples at concentrations ranging from 0.0202 µg/l to 0.0244 µg/L).

Atrazine:

Atrazine is a restricted use herbicide. To protect groundwater, its use is prohibited within 101 atrazine 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. In non-PAs, atrazine use is restricted but not prohibited. Because 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, if not present at all.

With the exception of the Embarrass, Porcupine and Milwaukee River, all streams sampled as part of the 2019 Surface Water Sampling Program either flow through or are adjacent to a PA. It would be expected that the PAs would have influence on the water quality at these surface water sample locations.

Atrazine concentrations were detected in 30% (31 samples) of the 2019 collected river, stream or spring water samples. The two background samples collected from the Porcupine Creek did not contain any atrazine or any metabolite concentrations in excess of laboratory reporting limits. Tenmile Creek is the only monitoring location where no atrazine was detected in excess of laboratory reporting limits in any of the 2019 water samples. Either the parent material atrazine, or one of its metabolites (de-ethyl atrazine, de-isopropyl atrazine and di-amino atrazine) were detected in excess of laboratory reporting limits in the remaining stream and river samples. The following is a summary of the atrazine findings for each river or stream.

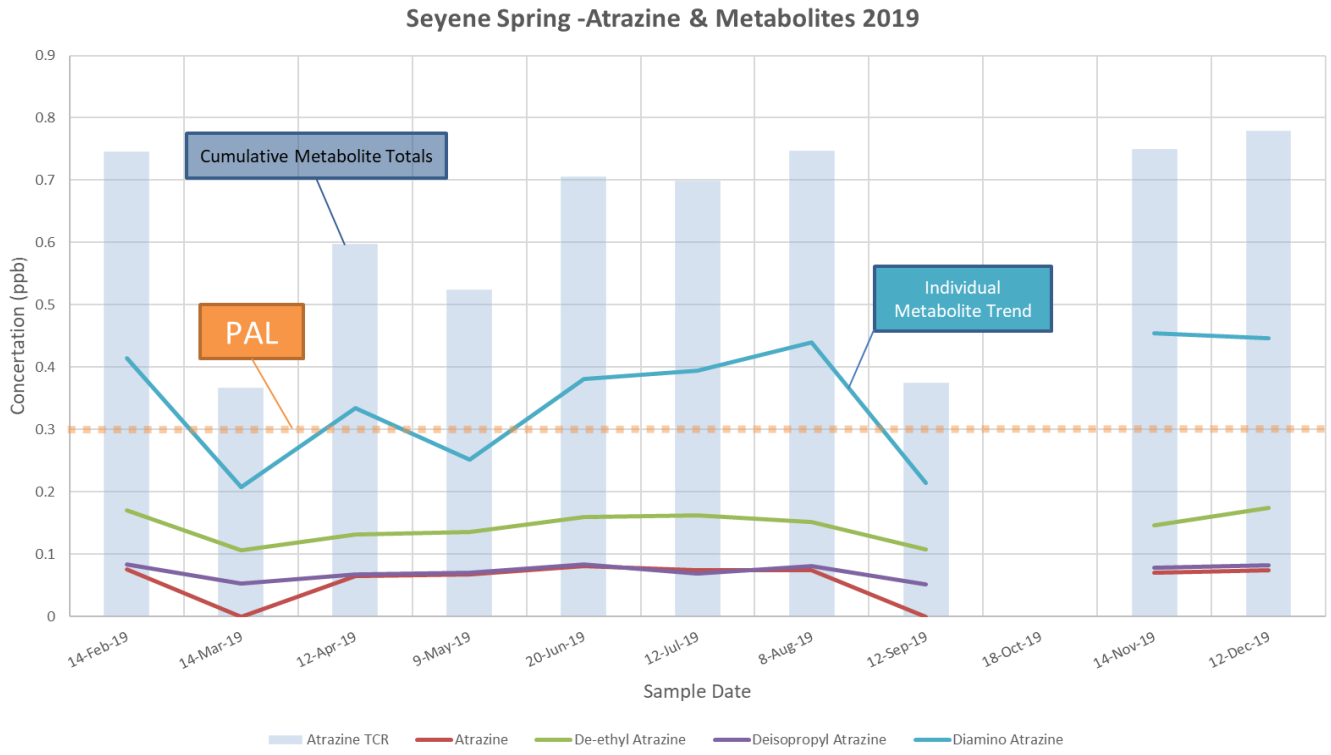
- Embarrass River water samples detected only the parent material atrazine in each of the three test locations. All three detections occurred in June water samples.
- Fourteen Mile Creek had sporadic detections of de-ethyl atrazine throughout the year (in February, May, July, September and November samples). It was detected at low concentrations ranging from 0.0527 to 0.0545 µg/L, slightly in excessive of the 0.05 µg/L reporting limit.
- Leola Ditch detected de-ethyl atrazine in February, September, October and November water samples at concentrations ranging from 0.0559 to 0.0627 µg/L. As observed at Fourteen Mile Creek, these detections were also slightly in excess 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, which was consistently in excess of the WAC ch. NR 140 PAL of 0.3 µg/L.

It does appear the atrazine concentrations we are observing in the surface water samples are typically associated with pesticide application season, thus seasonally influencing 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 whether the atrazine contributions are coming from inside or from outside the PA areas.

Seyene Spring was included in the 2019 sampling program because of an atrazine concentration (0.78 µg/L) identified in a spring water sample collected in 2018 as part of a WGNHS project. This spring is located within a PA and would be expected to be void of atrazine. The 2019 surface water data indicated a trend of

consistent atrazine and metabolite concentrations in excess of the WAC ch. NR 140 PAL for atrazine TCR of 0.03 ug/L for every month sampled.

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. Figure 2 depicts the metabolite trends over time. Figure 2: 2019 Atrazine and Metabolite Trend for Seyene Spring



Sustained concentrations of atrazine and its metabolites throughout the year indicate that there is a nearby source area for atrazine, and that the atrazine plume has migrated and is discharging to the spring. Because metabolites are present at higher concentration that 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 2019 surface water samples. Alachlor ESA is a breakdown product of alachlor, an active ingredient of Lasso or Temic. It was detected in excess of laboratory reporting limits in nearly 55% of 2019 surface water samples at concentrations between 0.0532 and 1.21 µg/L. This is an increase in the frequency of detections compared to years past. The two background samples collected from the Porcupine Creek did not contain any alachlor or its metabolite concentrations in excess of laboratory reporting limits.

Although alachlor ESA was widely detected in surface water and groundwater samples collected throughout the state, the parent alachlor was not detected in excess of laboratory reporting limits in any 2019 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.

Nitrate:

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

Nitrate was detected in excess of laboratory reporting limits in 93 of the 103 surface water samples collected for DATCP's 2019 Surface Water Sampling Program. No nitrate was detected in excess of laboratory reporting limits in both background samples collected from the Porcupine Creek indicating that the primary source for nitrate is anthropogenic.

The greatest nitrate concentration observed in 2019 was 11.4 parts per million (ppm) detected in the February and November samples collected at Seyene Spring. Seyene Spring was the only location with multiple nitrate detections (six) in excess of the 10 mg/L NR 140 ES and the remaining samples (four) exceeding the 2.0 mg/L NR 140 PAL.

The following is a summary of nitrate results for 2019 river and stream samples.

- August and November samples collected from the three Embarrass River locations contained nitrate at concentrations in excess of the 2.0 mg/L PAL. Water samples collected in April from the three locations did not contain any detects in excess of laboratory reporting limits.
- Every water sample that was collected from the three Central Sands Agricultural Region waterways (Fourteen Mile Creek, Leola Ditch and Tenmile Creek) contained nitrate in excess of the 2.0 mg/l PAL. This is the first year that all three creeks have contained nitrate concentrations in excess of the PAL throughout the year since DATCP began collecting surface water samples in 2008.
- None of the water samples collected from the Wisconsin River contained nitrate concentrations in excess of the PAL.
- The February sample collected from the Milwaukee River contained nitrate concentrations in excess of the PAL; it was not detected or detected below the PAL in the remaining nine samples.
- Nitrate exceeded the PAL in five of the 11 samples collected from the Mississippi River.

Table 6 includes a summary of the DATCP's 2019 Surface Water Sampling Program detections for nitrate.

Table 6: 2019 Surface Water Sampling Program Nitrogen as Nitrate and Nitrite Analytical Results

Sample Location	Nitrogen-Nitrate/ Nitrite Concentration Range (mg/L)
Embarrass River at CTH M	ND - 2.64
Embarrass River at Hayman Falls Lane	ND - 2.51
Embarrass River North Branch Road	ND - 2.97
Fourteen Mile Creek at County Road D	2.92 - 6.41
Leola Ditch at Aniwa	2.93 - 8.81
Milwaukee River at Estabrook Park	ND - 2.48
Mississippi River at L&D #9	0.696 - 2.73
Seyene Spring	7.45 - 11.4
Tenmile Creek at Evergreen	4.2 - 7.89
Wisconsin River at Muscoda	0.758 - 1.8
Porcupine Creek	ND

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 in excess of laboratory reporting limits

2020 Program Goals and Objectives

DATCP's Surface Water Sampling Program will continue in 2020. In response to the Covid virus and work restrictions, adjustments to the sampling were made. Regardless, it is expected that the following task will be performed.

- Collection of monthly surface water samples at ten stream or river locations for the calendar year to include:
- Continue to collect monthly sample from seven locations and add to existing database, and
- Continue monthly samples from three new locations.
- Prepare a 2019 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.

For 2020, surface water sampling will be continued at the following locations:

- To provide an early warning system to detect new agrichemical compounds in groundwater before widespread contamination can occur in underlying aquifers;

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

2020 surface water results will provide additional information to existing databases for these locations. The intent is to evaluate water quality data over time, and identify impacts from agricultural land use. In additional to groundwater data, surface water date 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 2020, the following three new surface water sampling locations be added:

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

The Sugar River was selected because due to heavy agriculture land use within the watershed. Most of the watershed area lies within a PA, and atrazine is not expected to be found in these samples. The Root River was added to the 2020 sampling program because it was previously included in DATCP's Surface Water Monitoring Program. The new information obtained in 2020 will be compared to the historic data to evaluate changes in water quality. Duncan Creek was selected because it is near a pesticide release investigation and it flows from a PA area.

ADDITION PROGRAM ACTIVITIES

In 2020 there will be additional or continued effort and focus beyond just the surface water sampling and reporting;

- Continue to partner with university, state and federal agencies regarding the potential use of Polar Organic Integrative Samplers (POCIS);
- Finalize a Surface Water Sampling Program Charter;
- Finalize a 10-Year Surface Water Sampling Program 2008 – 2018 Report and distribute appropriately; and
- Continue to implement a program outreach and branding plan.

These proposed activities were included in the 2020 Surface Water Program Work Plan.

Mike Miller of DNR intends to pilot test the POCIS for surface water in 2021. DNR has asked DATCP for assistance with pilot testing at several of DATCP's sampling locations. The tentative plan is to set up the POCIS, and collect the monthly surface water samples from the same location. Both samples would be analyzed for pesticides; monthly grab samples will be analyzed by BLS, and POCIS samples will be analyzed at UW-Stevens Point. The data would then be compared to evaluate the effectiveness and applicability of the POCIS. The work associated with the POCIS pilot test would be funded by EPA. DNR has submitted a funding application to EPA for consideration.

A *Surface Water Sampling Program Charter* will be finalized to document the program's purpose, benefits, components and history. The Surface Water Sampling Program was developed in 2007 with the first set of samples collected in 2008. Over time, program goals and objectives have evolved. A proposed short-term (1 to 3 year) and long-term vision will be provided. The charter will also include:

- A preliminary delineation of roles and responsibilities:
- Outline the program objectives,
- Identify stakeholders,
- Identify deliverables and intended audiences, and
- Define the authority of the program team.

The document is intended to be for internal purposes. The first draft for review is proposed to be available late 3rd quarter 2020.

DATCP intends to complete a *10-Year Surface Water Sampling Program 2008 – 2018 Report*. This work was been initiated in 2019. There has been 10 years of data/information complied since DATCP's Surface Water Sampling Program inception, but no overall comprehensive report summarizing the findings/conclusions and development of recommendations. This will complete one of the elements as required in the Program Charter. The report will be developed with the intent of being publically available. The first draft will be provided 3rd quarter of 2020 for internal review.

It appears the DATCP Surface Water Sampling Program is not widely known to the stakeholders, officials and citizens of the State. Evaluation of program data to date has produced significant findings and conclusions that may aid with evaluating other programs and development of policy for regulatory compliance. In 2019, several presentation for internal audiences were completed by Bureau staff. The intent was to share with DATCP and/or DNR staff the program work that is being completed and what their role is within the program. The second deliverable planned for 2020 would be a second presentation intended for an outside audience, and a short memo listing potential presentation opportunities. The presentation would be more technically based with a focus on a science-based audience. The conference and/or organization events would be intended for the 2020 and 2021 year. Approval of the presentation content and intended conferences or organizations will be a part of this action.

APPENDIX A

2019 Surface Water Sampling Program Analytical Results, Summary

2018 Surface Water Project Results (all concentrations in ug/l)					Wisconsin Admin. Code Chapter NR 140		US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticide (ug/l)					
Pesticide Name	Pesticide Class	Number Detects	Reporting Limit	Concentration Range	Enforcement Standard	Preventive Action Limit	Acute (Fish)	Chronic (Fish)	Acute (Invert.)	Chronic (Invert.)	Acute (Non-vascular Plants)	Acute (Vascular Plants)
2,4-D	Herbicide	11	0.05	1.11 - 0.873	70	70	--	--	12,500	--	--	--
2,4-DB	Herbicide	0	0.57	--	--	--	1000	--	7500	--	1100	--
2,4-DP	Herbicide	0	0.058	--	--	--	--	--	--	--	--	--
2,4,5-T	Herbicide	0	0.05	--	--	--	--	--	--	--	--	--
2,4,5-TP	Herbicide	0	0.05	--	50	5	--	--	--	--	--	--
Acetamiprid	Insecticide	0	0.05		--	--	> 50000	19200	10.5	2.1	> 1000	> 1000
Acetochlor	Herbicide	6	0.05	0.265 - 0.0662	7	0.7	190	130	4100	22.1	1.43	3.4
Acetochlor ESA	Herbicide	30	0.05	0.742 - 0.0531	230	46	> 90000	--	> 62500	--	9900	--
Acetochlor OA	Herbicide	2	0.3	0.455 - 0.342	230	46	--	--	--	--	--	--
Acifluorfen	Herbicide	0	0.056	--	--	--	--	--	--	--	--	--
Alachlor	Herbicide	0	0.05	--	2	0.2	900	187	1250	110	1.64	2.3
Alachlor ESA	Herbicide	43	0.05	0.832 - 0.0679	20	4	> 52000	--	> 52000	--	3600	>120000
Alachlor OA	Herbicide	0	0.25	--	--	--	> 500000	--	> 47500	--	--	--
Aldicarb Sulfone	Insecticide	0	0.059	--	--	--	21000	--	140	--	--	--
Aldicarb Sulfoxide	Insecticide	0	0.13	--	--	--	3570	--	21.5	--	--	--
Aminopyralid	Herbicide	0	0.05	--	--	--	> 50000	1360	7500	102000	18000	> 88000
Atrazine	Herbicide	12	0.05	0.411 - 0.067	3	0.3	2650	5	360	60	< 1*	4.6
De-ethyl atrazine	Herbicide	14	0.05	0.11 - 0.05	3	0.3	--	--	--	--	--	--
De-isopropyl atrazine	Herbicide	1	0.05	0.0658	3	0.3	--	--	--	--	--	--
Di-amino atrazine	Herbicide	0	0.28	--	3	0.3	--	--	--	--	--	--
Atrazine (TCR)	Herbicide	19	--	0.5858 - 0.0508	3	0.3	--	--	--	--	--	--
Azoxystrobin	Fungicide	3	0.05	0.154 - 0.0692	--	--	235	147	130	44	49	3400
Benfluralin	Herbicide	0	0.05	--	--	--	34.85	1.9	1090	15.5	> 100	
Bentazon	Herbicide	0	0.05	--	300	60	95000	9830	31150	101200	4500	5350
Bicyclopyrone	Herbicide	0	0.05	--	--	--	> 46700	10000	> 46650	103700	2000	13
Bromacil	Herbicide	0	0.084	--	--	--	18000	3000	60500	8200	6.8	45
Carbaryl	Insecticide	0	0.067	--	40	4	110	6	0.85	0.5	660	1500
Carbofuran	Insecticide	0	0.051	--	40	8	44	5.7	1.115	0.75	--	--
Chloramben	Herbicide	0	0.57	--	150	30	--	--	--	--	--	--
Chlorantraniliprole	Insecticide	22	0.2	0.97 - 0.0703	--	--	> 600	110	5.8	4.47	1780	>2000
Chlorothalonil	Fungicide	0	0.16	--	--	--	5.25	3	1.8	0.6	6.8	630
Chlorpyrifos	Insecticide	0	0.05	--	2	0.4	0.9	0.57	0.05	0.04	140	
Chlorpyrifos Oxon	Insecticide	0	0.05	--	--	--	--	--	--	--	--	--
Clomazone	Herbicide	0	0.05	--	--	--	1450	350	2700	2200	167	30200
Clopyralid	Herbicide	0	0.078	--	--	--	51750	--	116500	--	6900	--
Clothianidin	Insecticide	1	0.067	0.0556	--		> 50750	9700	11	0.05	64000	>280000
Cyclaniliprole	Insecticide	0	2	--	--	--	>68.5	200	40.4	9.6	>99	>187
Cyfluthrin	Insecticide	0	0.1	--	--	--	0.034	0.01	0.0125	0.0074	> 181	--
lambda- Cyhalothrin	Insecticide	0	0.05	--	--	--	--	--	--	--	--	--
Cypermethrin	Insecticide	0	0.15	--	--	--	0.195	0.14	0.21	0.069	--	--
Cyprosulfamide	Safener	0	0.074	--	--	--	--	--	--	--	--	--
Dacthal	Herbicide	0	0.05	--	70	14	15000	--	13500	--	> 11000	> 11000
Diazinon	Insecticide	0	0.05	--	--	--	45	< 0.55	0.105	0.17	3700	--
Diazinon oxon	Insecticide	0	0.05	--	--	--	--	--	--	--	--	--
Dicamba	Herbicide	0	0.89	--	300	60	14000	--	>50000	--	61	>3250
Dichlobenil	Herbicide	10	0.05	0.455 - 0.054	--	--	2465	< 330	3100	560	1500	30
Dichlorvos	Insecticide	0	0.076	--	--	--	91.5	5.2	0.035	0.0058	14000	
Dimethenamid	Herbicide	1	0.05	0.0508	50	5	3150	300	6000	1020	14	8.9
Dimethenamid ESA	Herbicide	3	0.05	0.0612 - 0.0565	--	--	--	--	--	--	--	--
Dimethenamid OA	Herbicide	0	0.054	--	--	--	--	--	--	--	--	--
Dimethoate	Insecticide	0	0.05	--	2	0.4	3100	430	21.5	0.5	20000	>92600
Dinotefuran	Insecticide	0	0.05	--	--	--	> 49550	> 6360	> 484150	> 95300	> 97600	> 110000
Diuron	Herbicide	2	0.18	0.0785 - 0.062	--	--	200	26.4	80	200	2.4	15
EPTC	Herbicide	0	0.05	--	250	50	7000		3250	800	1400	5600
Esfenvalerate	Insecticide	0	0.05	--	--	--	0.035	0.035	0.025	0.017	--	--
Ethalfluralin	Herbicide	0	0.074	--	--	--	16	0.4	30	24	25	7.3
Ethofumesate	Herbicide	0	0.05	--	--	--	5760	2560	147000	300	> 2760	3900
Flumetsulam	Herbicide	1	0.17	0.0763	--	--	> 146500	197000	127000	111000	3.52	3.1
Flupyradifurone	Insecticide	0	0.05	--	--	--	--	--	--	--	--	--
Fluroxypyr	Insecticide	0	0.32	--	--	--	7150	--	> 50000	--	> 100000	--

Fomesafen	Insecticide	12	0.05	0.163 - 0.05	--	--	63000	9400	188000	50000	92	210
Halosulfuron methyl	Insecticide	0	0.08	--	--	--	--	--	--	--	4.1	0.042
Hexazinone	Herbicide	0	0.05	--	--	--	137000	17000	75800	20000	7	37.4
Imazapyr	Herbicide	2	0.05	0.0759 - 0.0555	--	--	> 50000	43100	> 50000	97100	12200	24
Imazethapyr	Herbicide	1	0.05	0.207	--	--	120000	--	--	--	11500	18
Imidacloprid	Insecticide	1	0.05	0.0637	--		114500	9000	0.385	0.01	> 10000	--
Isoxaflutole	Herbicide	0	0.32	--	--	--	> 850	96	> 750	84	110	4.9
Isoxaflutole DKN	Herbicide	0	0.47	--	--	--	>15300	--	>29800	--	5000	75
Linuron	Herbicide	0	0.087	--	--	--	1500	5.58	60	0.09	13.7	2.5
MCPA	Herbicide	0	0.05	--	--	--	>34000	--	>92000	--	--	--
MCPB	Herbicide	0	0.21	--	--	--	1950	--	25000	--	380	210
MCPP	Herbicide	2	0.055	0.158 - 0.0576	--	--	--	--	>45500	50800	--	--
Malathion	Insecticide	0	0.05	--	--	--	2.05	8.6	0.049	0.06	2400	> 9630
Mesotrione	Herbicide	0	0.18	--	--	--	> 60000	11000	420000	< 97000	1900	17.7
Metalaxyl	Fungicide	0	0.05	--	--	--	65000	9100	14000	100	140000	92000
Methyl Parathion	Insecticide	0	0.078	--	--	--	925	< 10	0.485	0.25	15000	18000
Metolachlor	Herbicide	24	0.05	1.61 - 0.052	100	10	1900	30	550	1	8	21
Metolachlor ESA	Herbicide	89	0.05	2.52 - 0.0648	1,300	260	24000	--	> 54000	--	> 99450	43000
Metolachlor OA	Herbicide	29	0.27	1.01 - 0.341	1,300	260	>46550	--	7700	--	57100	>95400
Metribuzin	Herbicide	23	0.05	0.138 - 0.0569	70	14	21000	3000	2100	1290	8.7	130
Metribuzin DA	Herbicide	7	0.1	0.145 - 0.103	--	--	--	--	--	--	--	--
Metribuzin DADK	Herbicide	30	0.12	0.885 - 0.307	--	--	--	--	--	--	--	--
Metsulfuron methyl	Herbicide	0	0.094	--	--	--	> 75000	4500	> 75000	--	31	0.36
Nicosulfuron	Herbicide	0	0.05	--	--	--	> 500000		> 500000	43000	--	--
Norflurazon	Herbicide	30	0.058	4.43 - 0.0886	--	--	4050	770	> 7500	1000	9.7	58.2
Oxadiazon	Herbicide	0	0.05	--	--	--	600	33	1090	33	5.2	41
Pendimethalin	Herbicide	0	0.05	--	--	--	69	6.3	140	14.5	5.2	12.5
Picloram	Herbicide	0	0.05	--	500	100	2750	550	17200	11800	34900	--
Prometone	Herbicide	0	0.05	--	100	20	6000	19700	12850	3450	98	--
Prometryn	Herbicide	0	0.05	--	--	--	1455	620	4850	1000	1.04	11.9
Propiconazole	Fungicide	0	0.055	--	--	--	425	95	650	260	21	3500
Saflufenacil	Herbicide	1	0.2	0.075	--	--	> 54000	997	4250	1330	42	87
Simazine	Herbicide	0	0.05	--	4	0.4	3200	60	500	40	6	67
Sulfentrazone	Herbicide	7	0.75	0.586 - 0.0668	--	--	46900	2950	30200	200	31	28.8
Sulfometuron methyl	Herbicide	0	0.05	--	--	--	> 74000		> 75000	97000	4.3	0.45
Tebupirimphos	Insecticide	0	0.05	--	--	--	44.5	130	0.039	0.011	630	8800
Tembotrione	Herbicide	0	0.21	--	--	--	> 50000	604	24450	5100	310	5.2
Thiacloprid	Insecticide	0	0.067	--	--	--	12600	918	18.9	0.97	45000	> 95400
Thiamethoxam	Insecticide	25	0.067	0.216 - 0.055	--	--	> 50000	20000	17.5	0.74	> 97000	> 90000
Thiencarbazone methyl	Herbicide	0	0.38	--	--	--	> 52000	4800	> 47000	3540	298	0.8
Triclopyr	Herbicide	7	0.1	0.219 - 0.0515	--	--	58500	--	66450	--	32500	
Trifluralin	Herbicide	0	0.05	--	7.5	0.75	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. 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

Indicates no detects in excess of laboratory reporting limits.

Indicates detects in excess of laboraotry reporting limits, but not in excess of any benchmark values.

Indicates detects in excess of laboraotry reporting limits and WAC ch. NR 140 Preventive Action Limit, but not in excess of any benchmark values.

Indicates detects in excess of laboraotry reporting limits and respective benchmark value.