2018 Surface Water Sampling Summary Report

ANNUAL REPORT

Wisconsin Department of Agriculture, Trade and Consumer Protection

Agricultural Resource Management Division

Environmental Quality Unit

Final (5-8-2019)

Introduction

In 2018, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP), in a cooperative effort with the Wisconsin Department of Natural Resources (DNR) and Prairie Island Indian Community, continued the Surface Water Sampling Program to document the effect pesticide use is having on nine select rivers and streams in Wisconsin. Surface water samples were collected monthly from February to 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 2019 Surface Water Sampling Program plan.

Purpose of Surface Water Sampling

It is estimated that agriculture contributes $88-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 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 2018 sampling season, between nine and twelve 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 stream 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, likely public access locations;
- Watershed has susceptible geologic conditions like sandy soils with shallow groundwater, shallow depth to bedrock or karst features;
- Prior testing by others (federal government, university, other state agencies, etc.) indicated elevated nitrate, pesticides or other unusual test results;
- Same crops grown year after year on same fields/area (e.g. corn, cranberry, ginseng) increasing the likelihood of repetitive pesticide-use in area;
- Crops grown in area typically require extensive chemical or fertilizer inputs and/or irrigation;
- Pesticides used in area have characteristics of high mobility and resistance to degradation; or

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- At the request of one of the partnering agencies.

Using this criteria, over the past several years, the Surface Water Sampling Program has evolved to a mix of sampling consistent locations 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 can accept samples (usually in February) after annual maintenance. 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. Over the past two years, the program has generally consisted of collecting surface water samples from nine locations; 50% are repeat locations with 50% are new locations to the program. The repeat locations are the following:

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

2018 PROGRAM SPECIFICS

A total of nine perennial rivers and streams were selected for the 2018 sampling program. A total of 90 samples were collected from February to December for chemical analysis. Table 1 lists the 2018 surface water sampling program locations and Figure 1 depicts the nine locations relative to State of Wisconsin and county boundaries. Size of the watershed and a summary of land use for calendar year 2018 for all but the largest watersheds (Mississippi and Wisconsin Rivers) using data provided by the Wisconsin Agricultural Statistics Service is presented on Table 2.

Table 1: 2018 Surface Water Sampling Program Rivers and Streams

River / Stream Name	SWIMS ID	County
Fourteen Mile Creek at County Road D	013173	Adams
Leola Ditch at Aniwa	10009165	Adams
Milwaukee River at Estabrook Park	413640	Milwaukee
Mississippi River at L&D 3	483027	Pierce
Mississippi River at L&D 9	123016	Crawford
Root River in Oak Creek	413913	Milwaukee
Tenmile Creek at Evergreen	10016427	Portage
Wisconsin River at Muscoda	223282	Grant
Kickapoo River at Steuben Bridge 123017 Crawford	123017	Crawford

Figure 1: 2018 Surface Water Sampling Program Rivers and Streams Locations

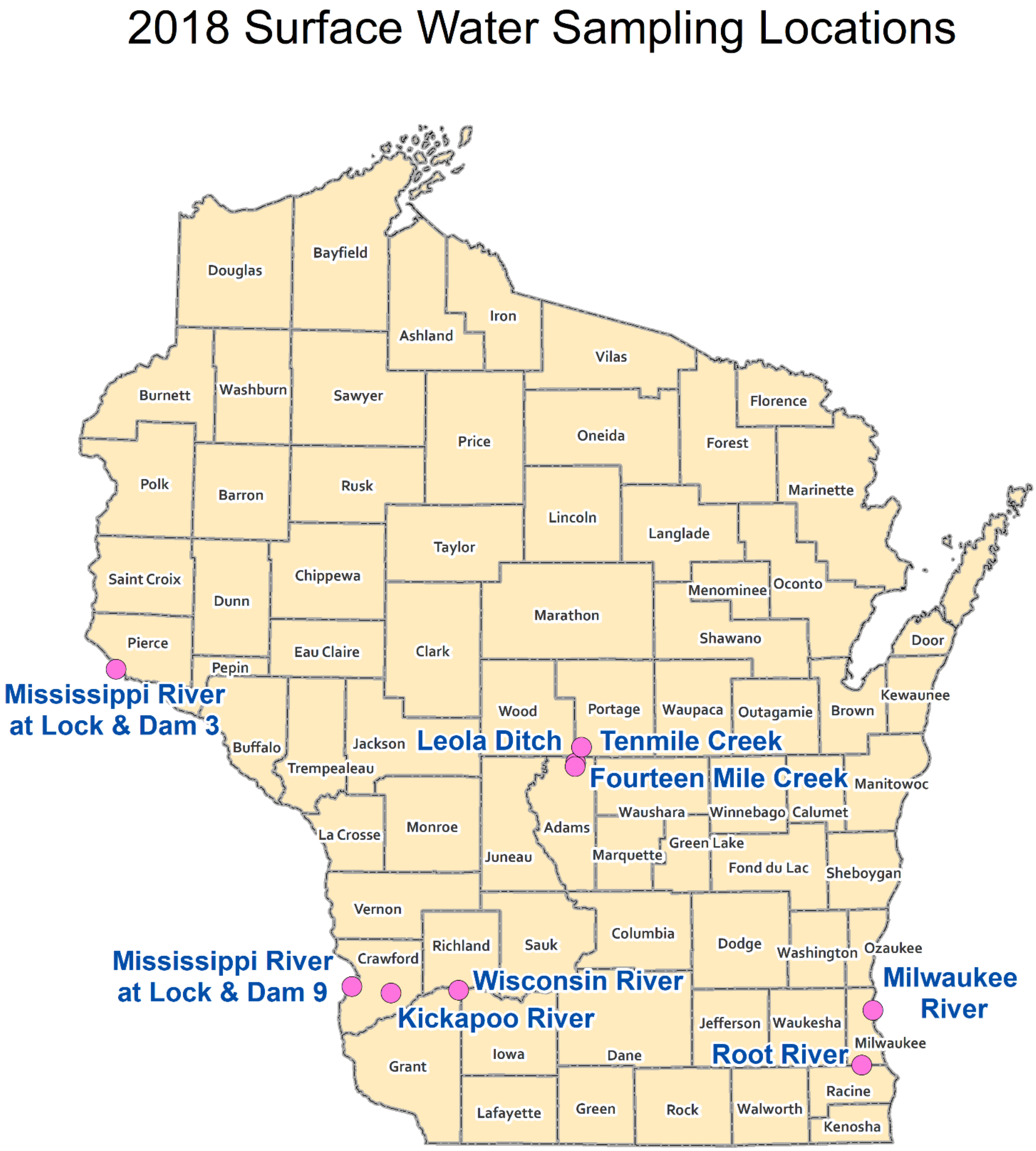

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Table 2: 2018 Surface Water Sampling Program Rivers and Streams Land Use Summary and Watershed Size

River/Stream Name	Forest	Wetland	Developed or Open	Corn	Alfalfa, Grass or Pasture	Soy or Dry Beans	Potatoes	Watershed Size (Acres)
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 (9.0%)	55,468
Leola Ditch	3,206 (17.6%)	2,443 (13.4%)	887 (4.9%)	3,171 (17.4%)	4,251 (23.2%)	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 #3)								
Mississippi River (1) (L&D #9)								
Root River	12,410 (14.7%)	4,723 (5.6%)	40,131 (47.5%)	7,471 (8.8%)	7,588 (9.0%)	9,204 (10.9%)	0 (0%)	84,452
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)								
Kickapoo River	55,850 (58.2%)	3,503 (3.7%)	4,094 (4.3%)	8,258 (8.6%)	17,930 (18.7%)	5,486 (5.7%)	0 (0%)	95,935

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

It should be noted that that during the 2018 late summer and into the fall season, the southern half, and most notability the southwestern portion of the state, received greater-than-normal precipitation. Greater than average surface water runoff and higher to flood stage surface water levels were encountered within a number of watersheds, including the Milwaukee, Root, Wisconsin and Kickapoo Rivers.

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 1-liter amber glass sampling bottles at the designated sampling location. Bottles were then placed in an ice-filled cooler along with a properly completed chain-of-custody record. 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 2018 program. A summary of all analytical data for the 2018 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 100 pesticides and nitrogen as nitrate and nitrite. The table include in Appendix A lists the parameters along with corresponding reporting limits.

Results

A total of 90 surface water samples were collected and submitted for chemical analysis as a part of the DATCP's 2018 Surface Water Sampling Program. The table in Appendix A surmises' the 2018 Surface Water Sampling Program results and provides comparative risk values. The surface water data is compared to the 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 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 2018 data follows.

- At least one pesticide analyte was detected in excess of laboratory reporting limits in every surface water sample for every monthly sampling event, with the exception of a sample collected from the Kickapoo River in February 2018.
- Sixteen herbicides, 10 herbicide metabolites, five insecticides, and one fungicide were detected in excess of laboratory reporting limits as part of the 2018 surface water sampling program.
- It appears that some of the pesticide detections in surface water are associated with the aquifer's baseline flow rather than just seasonal influence on groundwater quality.
- Metolachlor ethanesulfonic acid (ESA) concentrations in excess of laboratory reporting limits was detected in nearly 99% of all samples collected. This is an increase in the frequency of detections compared to years past.
- Alachlor ESA was the second most detected compound in excess of laboratory reporting limits identified in nearly 48% of the samples collected. This is an increase in the frequency of detections compared to years past.
- Atrazine concentrations 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 21% of the samples collected. This is a decrease in detection frequency compared to years past.
- More pesticides products were detected in excess of laboratory reporting limits in June compared to any other month, coincident with the primary pesticide application season.
- One of the neonicotinoid compounds thiamethoxam was detected in excess of laboratory reporting limits in over 80% (through-out the year) of surface water sample collected from the three streams flowing through the Central Sands Agricultural Region, which would be a characteristic of the aquifer's baseline flow.
- Of the 100 pesticide analytes included in the laboratory testing methods, 32 were detected in excess of laboratory reporting limits in the surface water samples. This is an increase in detectable compounds compared to years past.
- US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides in freshwater were exceeded for three compounds in only one sample collected from the Root River on June 27, 2018:
  - Clothianidin concentration of 0.0556 µg/L exceeded the Chronic Exposure on Invertebrates value of 0.05 µg/L;
  - Imidacloprid concentration of 0.0637 µg/L exceeded the Chronic Exposure on Invertebrates value of 0.05 µg/L; and

    - Metolachlor concentration of 1.61 µg/L exceeded the Chronic Exposure on Invertebrates value of 1.0 µg/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 and total chlorinated residue (TCR) of atrazine.

PESTICIDE DETECTED FREQUENCY

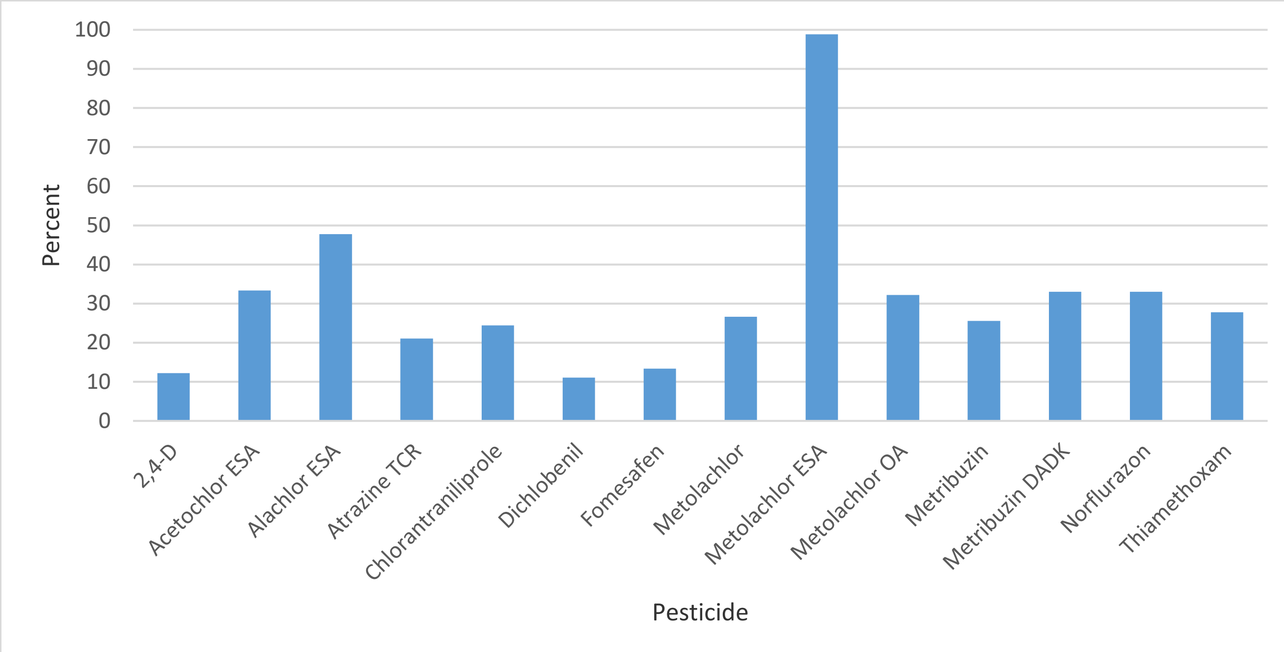
Of the 100 analytes tested for, there were 32 pesticides detected (68 not detected) in excess of laboratory reporting limits associated with the DATCP's 2018 Surface Water Sampling Program. This is an increase compared to previous years. However, this may be explained due to the laboratory having lesser reporting limits and/or that surface water samples are being collected from different land-use watersheds than previous years. It is not thought that this is due to the higher than normal precipitation encountered during the latter half of the year. The newly detected analytes included:

- Chlorantraniliprole – an insecticide (Altacor) used on apples, orchids and potato and cranberry fields;
- Clothianidin – an insecticide in the neonicotinoid family of pesticides used as a seed treatment on corn;
- Dimethenamid – a herbicide to control annual grasses, certain broadleaf weeds and sedges on corn and soybean fields;
- Saflufenacil – a herbicide to control broadleaf weeds on corn and soybean fields; and
- Sulfentrazone – a herbicide (Dismiss and Solitare) to control broadleaf weeds and sedges for turf grasses and right-of-ways.

Indifferent from prior years, at least one pesticide concentration was detected in excess of laboratory reporting limits in every river or stream sample for every monthly event, with the exception of a sample collected from the Kickapoo River on February 28, 2018. This type of occurrence likely reflects area aquifer quality rather than seasonal fluctuations related to agricultural practices. It appears that some of the pesticide detections in surface water are associated with the aquifer's baseline flow rather than just seasonal influence on groundwater quality.

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 nearly 99% of all samples collected. Only the February 28, 2018 sample from the Kickapoo River did not have a detectable concentration. This is an increase in the frequency of detections compared to years past. Alachlor ESA was the second most detected compound in excess of laboratory reporting limits identified in nearly 48% of the samples collected. This also is an increase in the frequency of detections compared to years past. 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%. Historically, these are the herbicide analytes typically identified at the higher frequency, with the exception of thiamethoxam. This is the first time this analyte has been detected at a frequency greater than 10%.

Table 3: Percentage of 2018 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).

PESTICIDE DETECTED TIMING

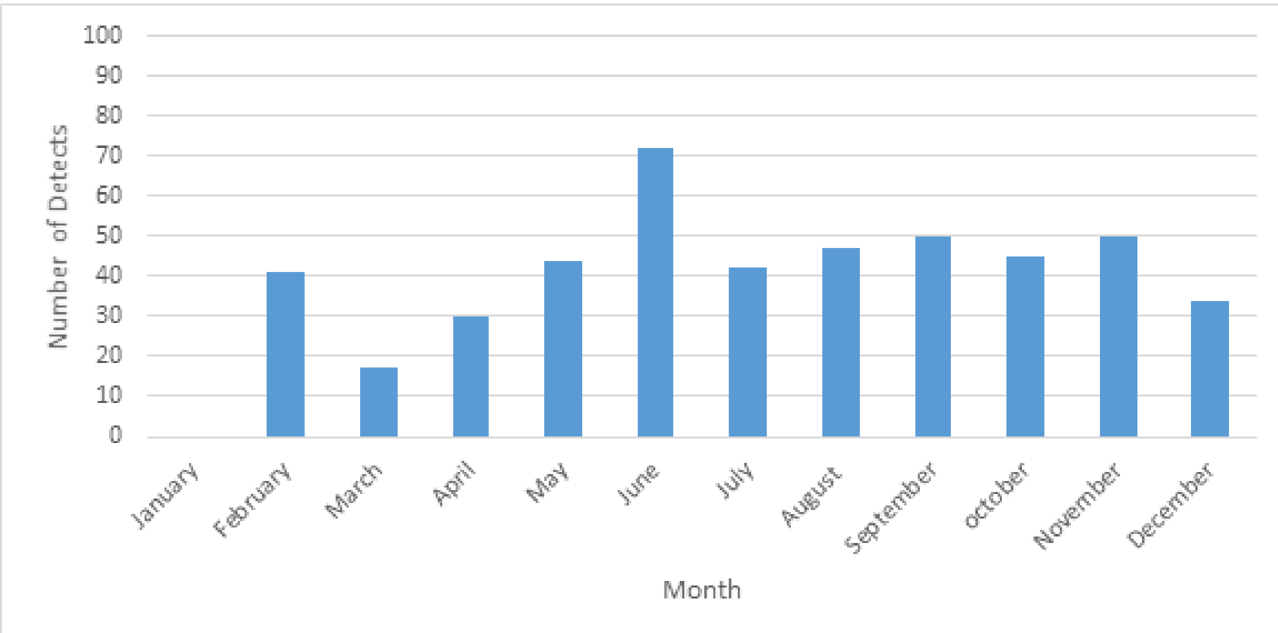
One of the DATCP's Surface Water Sampling Program objectives is to evaluate the typical timing of pesticide application and its relationship to surface water quality respective to those agrichemicals. Table 4 depicts the 2018 total pesticide count within a given month for detects in excess of laboratory reporting limits in the surface water samples.

The 2018 January 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 early season snow melt/overland flow and pesticide loading into the area stream and rivers. March likely reflects a low for the calendar year followed with a slow monthly increase for April as more pesticides are applied and an increase in water/groundwater discharge through the watershed. The 2018 data reflects this trend.

In May through August, the months considered to be the main agricultural pesticide application season, the number of pesticide detections continue to increase. The 2018 June data had 72 different detections in excess of laboratory reporting limits, the greatest for any month. The number of pesticides detected in July and August dropped, as expected, to 42 and 47, respectively.

Finally, in September through December, months past the primary agricultural pesticide application season, the number of pesticides detected in the surface water should gradually decrease. However, in 2018, we saw the number of pesticides detected in excess of laboratory reporting limits remained consistent; September 50, October 45 and November 50. (December had only 34 detects, but samples from the Root River, Mississippi River L&D#9 and Milwaukee River were not collected. If samples would have been collected from these three rivers in December and added to the pesticide detection count, it would be expected that the number would have been consistent to what was seen in the previous three months.) It is difficult to determine the actual effects of the greater-than-average precipitation that occurred in the latter half of 2018 in the southern half of the state. However, it is likely that the abundance of overland water flow and increase in groundwater discharge to steams and river could have contributed to the greater-than-expected pesticides detected during this timeframe.

Table 4: Number of Pesticide Analytes Detected in each Month During the 2018 Sampling Program



Notes: *There were no surface water samples collected in January 2018 due to the lab shut down for annual maintenance.*

No surface water samples were collected from Tenmile Creek, Leola Ditch and Fourteen Mile Creek in March.

No surface water samples were collected from Mississippi River L&D #3 in April and August.

No surface water samples were collected from Root River, Mississippi River L&D #9 and Milwaukee River in December.

The pesticide timing data was also evaluated to determine if we are observing seasonal flow or if the analyte concentrations represent an aquifer baseline flow. A seasonal flow would have the analyte concentrations cycling through the year with greatest concentrations in the surface water during the pesticide applications months (May through August), potentially shortly following (September through October) and then decreasing until the following application season. A baseline aquifer flow would have the analyte detected with consistent concentrations likely throughout the year. The baseline flow would represent the pesticide concentration within the watershed aquifer that discharges to that specific stream or river throughout the year. Based on this definition and DATCP's 2018 Surface Water Sampling Program data, it appears metolacher ESA would be considered as a baseline compound in all of the aquifers that discharge to the streams and rivers that were sampled, with the greatest concentrations located within the Central Sands Agricultural Region.

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

- Wisconsin River at Muscoda
  - Alachlor ESA = concentration range of 0.121 – 0.0776 µg/L (for 11 of the 12 months with no detect in June); and

- Metolachlor ESA = concentration range of 0.317 – 0.156 µg/L for the year.

- Root River at Estabrook Park
  - Acetochlor ESA = concentration range of 0.121 – 0.0776 µg/L (for 11 of the 12 months with no detect in May); and
  - Metolachlor ESA = concentration range of 0.317 – 0.156 µg/L for the year.
- Mississippi River at L&D #3
  - Acetochlor ESA = concentration range of 0.305 – 0.0531 µg/L (for nine of the 10 months with an outlier of 0.742 µg/L in November); and
  - Metolachlor ESA = concentration range of 0.465 – 0.259 µg/L for the year.
- Mississippi River at L&D #9
  - Acetochlor ESA = concentration range of 0.486 – 0.119 µg/L for the year; and
  - Metolachlor ESA = concentration range of 0.375 – 0.145 µg/L (for 10 of the 11 months with an outlier of 0.666 µg/L in November).
- Milwaukee River at Estabrook Park
  - Metolachlor ESA = concentration range of 0.401 – 0.103 µg/L for the year.
- Kickapoo River at Steuben Bridge
  - Metolachlor ESA = concentration range of 0.0894 – 0.0668 µg/L (for 10 of the 11 months with no detect in February).
- Tenmile Creek at Evergreen
  - Alachlor ESA = concentration range of 0.354 – 0.544 µg/L for the year;
  - Metolachlor ESA = concentration range of 1.146 – 0.635 µg/L for the year;
  - Metolachlor OA = concentration range of 0.502 – 0.341 µg/L for the year;
  - Metribuzin = concentration range of 0.138 – 0.0629 µg/L for the year;
  - Metribuzin DADK = concentration range of 0.601 – 0.389 µg/L for the year;
  - Norflurazon = concentration range of 0.212 – 0.0886 µg/L (for seven of the 10 months with an outlier of 0.391, 0.633 and 0.448 µg/L in June, October and December, respectively); and
  - Thiamethoxam (potentially) - concentration range of 0.105 – 0.055 µg/L (for eight of the 10 months with no detect in April and July).
- Leola Ditch at Aniwa
  - Alachlor ESA = concentration range of 0.832 – 0.215 µg/L for the year;
  - Chlorantraniliprole = concentration range of 0.97 – 0.0703 µg/L for the year;
  - Metolachlor ESA = concentration range of 1.91 – 0.469 µg/L for the year;
  - Metolachlor OA = concentration range of 0.784 – 0.403 µg/L (for nine of the 10 months with no detect in April);
  - Metribuzin DADK = concentration range of 0.782 – 0.307 µg/L for the year;
  - Norflurazon = concentration range of 1.51 – 0.112 µg/L (for eight of the 10 months with an outlier of 4.43 and 3.07 µg/L in November and December, respectively); and

- Thiamethoxam (potentially) - concentration range of 0.216 – 0.0509 µg/L (for eight of the 10 months with no detect in April and August).

- Fourteen Mile Creek at County Road D
  - Alachlor ESA = concentration range of 0.647 – 0.418 µg/L for the year;
  - Chlorantraniliprole = concentration range of 0.926 – 0.0734 µg/L for the year;
  - Metolachlor ESA = concentration range of 2.52 – 1.1 µg/L for the year;
  - Metolachlor OA = concentration range of 1.01 – 0.535 µg/L for the year;
  - Metribuzin DADK = concentration range of 0.885 – 0.585 µg/L for the year;
  - Norflurazon = concentration range of 0.552 – 0.131 µg/L for the year; and
  - Thiamethoxam (potentially) - concentration range of 0.202 – 0.0791 µg/L (for eight of the 10 months with no detect in February and April).

From the DATCP's 2018 Surface Water Sampling Program data, it appears the Central Sands Agricultural Region has several pesticide analytes consistently present in the local aquifer that discharges to nearby streams and rivers (Tenmile Creek, Leola Ditch and Fourteen Mile Creek). This is not new, but there appear to be additional analytes like chlorantraniliprole and thiamethoxam, in the aquifer baseline flow now affecting surface water quality. However, it does appear that the pesticide load within the Central Sands Agricultural Region watershed is not great enough to have affected the surface water quality consistently that was sampled from down river at the Wisconsin River at Muscoda, with the exception of alachlor ESA and metolachlor ESA.

Additional interpretation of pesticide data from multiple years would need to be completed to validate these observations. This includes comparing the groundwater agrichemical data associated with the DATCP's Field-Edge Groundwater Monitoring Program and surface water data from common-located watersheds. This will be evaluated as part of the detailed comprehensive report documenting DATCP's Surface Water Sampling Program 2008 – 2018 Report, which will be completed in 3rd Quarter 2019.

COMPARISON TO STANDARDS

Detected pesticide concentrations identified during DATCP's 2018 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 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 2018 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 100) or WAC NR 140 ES standards (72 out of 100) established at this time. In regards to the 2018 data, of the 32 pesticide analytes detected in excess of laboratory reporting limits, only six did not have a standard. All six of these detected compounds were metabolites (for either acetochlor, atrazine, dimethenamid, or metribuzin).

US EPA Office of Pesticide Programs - Aquatic Life Benchmarks for Pesticides for freshwater were only exceeded for three compounds. They all were comingled in one sample collected from the Root River on June 27, 2018:

- Clothianidin concentration of 0.0556 µg/L exceeded the Chronic Exposure on Invertebrates value of 0.05 µg/L;
- Imidacloprid concentration of 0.0637 µg/L exceeded the Chronic Exposure on Invertebrates value of 0.05 µg/L; and

- Metolachlor concentration of 1.61 µg/L exceeded the Chronic Exposure on Invertebrates value of 1.0 µg/L.

There were no other detected pesticide or pesticide metabolite concentrations exceeding any of the referenced surface water/groundwater quality standards, for aquatic life benchmarks or WAC NR 140 ES standards.

It should be noted that WAC NR 140 includes an additional drinking water/groundwater quality standard, Preventive Action Limits (PAL), which are either 5 or 10 times less than the ES, substance dependent. Table 5 identifies the pesticides and the metabolite exceedances for WAC NR 140 PAL standards. 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) was detected in excess of the WAC NR 140 PAL standards in two samples, one from the Mississippi River Lock and Dam #9 and the Root River.

Table 5: Detected Concentrations of Pesticides and Metabolites Exceeding WAC NR 140 PAL Standards

Compound	ES (µg/L)	PAL (µg/L)	Location	Date	Detection (µg/L)
Atrazine	3.0	0.3	Mississippi River L&D #9	7/8/2018	0.411
Atrazine TCR	3.0	0.3	Mississippi River L&D #9	7/9/2018	0.5858
			Root River	6/27/2018	0.397

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

These comparisons may not be truly evaluating the total risk to human health and environment. The comparisons of detected pesticide and their metabolite concentrations to published surface water quality standards or benchmarks are based on the single compound. Currently, there are no calculations to predict the total potential comprehensive risk if there are multiple compounds present. This current approach does not account for potential cumulative risk; thus, potentially underestimating toxicity.

OTHER NOTABLE OBSERVATIONS

Neonicotinoids:

Interest in the neonicotinoid class of insecticides has increased greatly in recent years due to concerns over possible 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 2018. The other three neonicotinoid compounds; acetamiprid, dinotefuran and thiacloprid; were not detected in excess of laboratory reporting limits in any surface water sample. The detection of the three CIT compounds 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.

It is apparent that the CIT compounds are becoming more prevalent overtime, but not necessarily increasing in concentrations. Thiamethoxam and imidacloprid has been detected in DATCP's Surface Water Sampling

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Program, mostly in the Central Sands Agricultural Region, since 2014. (DATCP's Surface Water Sampling Program 2008 – 2018 Report will go into further detail regarding historical trends and observations.) An observation regarding the 2018 data suggests that the thiamethoxam is likely part of the aquifer's baseline flow in the Central Sands, and not associated with the seasonal fluctuations. For the first time, clothianidin has been detected in surface water samples from the Central Sands Agricultural Region. And for the first time as part of the Surface Water Sampling Program, these three compounds were also detected in a surface water sample collected outside of the Central Sands Agricultural Region; Root River sample on June 27, 2018.

In 2018, the US EPA Office of Pesticide Programs had lowered the benchmark for Chronic Exposure on Invertebrates for CIT. For the first time, published surface water quality benchmarks were exceeded for two neonicotinoids in a sample collected from the Root River on June 27, 2018:

- Clothianidin concentration of 0.0556 µg/L exceeded the Chronic Exposure on Invertebrates value of 0.05 µg/L; and
- Imidacloprid concentration of 0.0637 µg/L exceeded the Chronic Exposure on Invertebrates value of 0.05 µg/L.

Atrazine:

There are 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. In non-PAs, atrazine use is restricted but not prohibited. The PAs have been in-place for over ten years. It would be expected that atrazine and its metabolite concentrations in surface water would be limited, if not present at all. The stream and rivers, with the exception of the Root and Milwaukee River, sampled as part of the 2018 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 surface water quality at these surface water sample locations.

Atrazine concentrations were detected in a number of samples. Data did indicate some seasonal fluctuations (May through July) with atrazine concentrations in samples collected from the Wisconsin and Mississippi River. Otherwise, there were detections of atrazine in excess of laboratory reporting limits for only June in samples collected from the Root River, Milwaukee River, Kickapoo River, and Leola Ditch.

Total chlorinated residue (TCR) of atrazine, which includes the sum of atrazine plus its metabolites de-ethyl atrazine, de-isopropyl atrazine, and di-amino atrazine, was detected in excess of laboratory reporting limits in all the streams and rivers, with the exception of Tenmile Creek. All of these detections were identified during the typical pesticide application season, with the exception of Fourteen Mile Creek, which had inconsistent detects throughout the year.

We can interpret these observations as atrazine is still being over-applied to the agricultural fields, but at rates not great enough to influence aquifer quality on a baseline flow basis. A trend analysis would need to be completed with all the historical surface water data to determine if the atrazine TCR concentrations are decreasing as the PAs intended. This analysis will be completed as part of the DATCP's *Surface Water Sampling Program 2008 – 2018 Report*.

Alachlor:

As noted previously, alachlor ESA was the second most detected compound in excess of laboratory reporting limits identified in nearly 48% of the surface water samples collected. Concentrations ranged from 0.832 – 0.0679 ppb. This is an increase in the frequency of detections compared to years past. Alachlor ESA is a breakdown product of alachlor, an active ingredient of Lasso or Temic. Alachlor production ceased in December 2014 with field application no longer allowable after August 2018. In the 2018 surface water sampling program, there were no detectable concentrations in excess of laboratory reporting limits for the parent alachlor analyte. However, alachlor ESA is still widely detected in surface water and groundwater samples collected throughout the state. It would be expected that these metabolite concentrations would decline over time since the parent analyte can no longer be field applied.

Nitrate:

DATCP's Surface Water Sampling Program focuses on agrichemical impacts on surface water quality. Nitrogen and its metabolites use and impacts are the responsibility of DNR. However, we include nitrogen as nitrate and nitrite analyses as part of this program and share the information with DNR.

Nitrogen was detected in excess of laboratory reporting limits in 87 of the 90 surface water samples collected in DATCP's 2018 Surface Water Sampling Program. This represented aquifer baseline flow in each of the watersheds. None of the nitrogen detects exceeded the WAC Ch. NR 140 ES of 10 milligram per liter (mg/l or parts per million [ppm]). The greatest concentration was 8.11 ppm in a sample collected from the Leola Ditch on September 19, 2018. All of the surface water samples collected from the Mississippi River L&D #3 and Tenmile Creek sample locations had nitrogen detects exceeding the WAC Ch. NR 140 PAL 2.0 ppm criteria. None of the samples collected from the Kickapoo River and Wisconsin River at Muscoda had a WAC NR 140 PAL exceedance. Table 6 provides a summary of the DATCP's 2018 Surface Water Sampling Program detections for nitrogen.

Table 6: 2018 Surface Water Sampling Program Nitrogen as Nitrate and Nitrite Analytical Results

Sample Location	Nitrogen as Nitrate and Nitrite Concentration Range
Fourteen Mile Creek	6.83 – 1.1
Kickapoo River	1.81 - 0.917
Leola Ditch	8.11 – 1.81
Milwaukee River	2.16 – no detect
Mississippi River L&D #3	3.4 - 2.11
Mississippi River L&D #9	3.29 - 0.914
Root River	4.37 – 0.859
Tenmile Creek	6.77 – 4.16
Wisconsin River	1.46 – no detect

Notes: *Concentrations 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

2019 Program Goals and Objectives

In 2019, DATCP's Surface Water Sampling Program will continue. It is expected that:

- Ten stream or river locations will be sampled monthly as part of the program for the calendar year;
  - Will sample from six repeat locations to continue to build a database; and
  - Will sample from four new locations.
- Prepare a *2019 Data Summary Report* to be completed in 1st Quarter 2020; and

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- Share report(s) with DNR Bureau of Water Quality, surface water sampling team, and any other appropriate stakeholders as directed by Bureau Chief.

For 2019, the six repeat surface water sampling locations are the following:

- Wisconsin River at Muscoda;
- Mississippi River at Lock and Dam #9;
- 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.

This will provide additional information to the existing database for these locations. The intent is to evaluate the data over time and determine agrichemical trends. It will aid in determining the effectiveness of the PAs regarding surface water quality over the long term. The long-term surface water data will be compared to groundwater data from a common watershed to identify potential relationships between the two. It will also validate whether there are aquifer baseline flows or seasonal variations.

For 2019, the four new surface water sampling locations are the following:

- Syene Spring at South Syene Road in Dane County; and
- Three locations along the Embarrass River in Shawano County.

The Syene Spring was selected because of an atrazine concentration (0.78 µg/L) identified in a water sample collected from the spring in 2018 as part of a DNR project. The spring is located within a PA and would have expected to be void of atrazine. The Embarrass River in Shawano County was selected because of documented mussel die-off below the Pella dam. The reason for the die-off is unknown. Surface water samples will be collected from two tributaries upstream of the dam and a third sample will be collected near the die-off location below the dam.

ADDITION PROGRAM ACTIVITIES

In 2019 there will be additional effort and focus beyond just the surface water sampling and reporting;

- Partner with DNR regarding the potential use of Polar Organic Integrative Samplers (POCIS);
- Prepare a *Surface Water Sampling Program Charter*;
- Prepare a *10-Year Surface Water Sampling Program 20018 – 2018 Report* and distribute appropriately; and
- Develop and implement a program outreach and branding plan.

These proposed activities were included in the 2019 Work Plan.

Mike Miller of DNR is looking to pilot test the POCIS for surface water in 2019. He has requested DATCP to participate by conducting the pilot test at a couple of DATCP's sampling locations. The tentative plan would be to set up the POCIS and collect monthly surface water samples from the same location. Both samples would be chemically analized for pesticides, with the POCIS sample analized 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 DNR.

It appears the DATCP Surface Water Sampling Program has not been promoted (enough) to the stakeholders, officials and citizens of the State. There are significant findings and conclusions from the data that could aid with discussion and program/regulatory direction. Two deliverables are being proposed for this activity. The first would be the completion and shown of a PowerPoint presentation for internal audiences. The intent would be to share with DATCP and/or DNR staff the program work that is being completed and what their role is within the program. It would include some of the observations and conclusions associated with the 10-year report. The second deliverable would be a second PowerPoint presentation intended for an outside audience, and a short memo listing potential presentation opportunities. The presentation would be more technically based with the intent of 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.

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APPENDIX A

2018 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	--

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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.