Vermont Ambient Surface Water Pesticide Monitoring: 2022 Data Summary

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Vermont Agency of Agriculture, Food & Markets

Public Health & Agricultural Resource Management Division

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Executive Summary

The Public Health and Agricultural Resource Management (PHARM) Division of the Vermont Agency of Agriculture, Food & Markets (VAAFM) has been monitoring select surface water sites throughout high agricultural use areas of the state for pesticides over the last seven years. These sites are routinely sampled during critical times of the growing season each year. The Vermont Agriculture and Environmental Laboratory (VAEL) analyzes water samples for neonicotinoids, glyphosate, and other commonly used corn herbicides and their degradates. This report summarizes the results from the 2022 growing season sampling efforts.

- In 2022, 187 water samples were collected from 26 Vermont rivers, streams, and lakes.
- Samples were analyzed for 8 pesticides and 6 pesticide degradates.
    - 6 pesticides and 4 degradates were detected at least once.
    - 4 pesticides and 3 degradates were detected in 10% or fewer of the samples.
- The herbicides bicyclopyrone, mesotrione, and glyphosate were detected in 2.1%, 3.7%, and 0.5% of samples, respectively, and all detections were concentration levels below the most conservative EPA aquatic life benchmark value at which no observable adverse effects were seen (the no observable adverse effects concentration [NOAEC] level for sensitive species).
- Degradates of the herbicides atrazine, metolachlor, alachlor, and acetochlor were detected in 9.1%, 73.8%, 11.8%, and 33.2% of samples, respectively. All detections were below the NOAEC benchmark values. The degradate of glyphosate was not detected in any of the samples collected.
- Atrazine was detected in 20.3% of the samples, and because the most conservative benchmark, the NOAEC EPA acute value for nonvascular plants, is less than 1 ppb, potentially all of these positive detections reach or exceed this threshold. There were 2 sample values greater than the most conservative chronic benchmark, the NOAEC EPA chronic value for fish (5 ppb).
    - The samples that exceeded the NOAEC EPA chronic benchmark were both collected from Jewett Brook in August. Levels did not measure above the benchmark for longer than 30 days.
    - No samples with detected atrazine levels exceeded the lowest observable adverse effect concentration (LOAEC) for chronic exposure to sensitive fish species, 50 ppb.
- Metolachlor was detected in 17.6% of the samples and 7 values were greater than the most conservative EPA benchmark (NOAEC chronic value for invertebrates, 1 ppb).
    - The samples that exceeded the NOAEC EPA benchmark were all collected in Franklin County (Jewett Brook, Hungerford Brook, and Mill River Tributary).
        - Hungerford Brook and Mill River Tributary had 1 sample each, collected on June 27, 2022, that exceeded 1 ppb, but no subsequent samples exceeded the NOAEC benchmark.
            - The Mill River Tributary sample contained the maximum concentration of metolachlor found in 2022 (12.4 ppb). It also exceeded the LOAEC chronic value for fish.
        - Jewett Brook samples collected on June 1, June 13, June 27, July 1, and August 10 exceeded the benchmark, but were either non-detect or detected below 1 ppb for the rest of the season (August 17 – October 3, 2022).

        - Mean concentration of metolachlor from 74 national sites collected from 2013 through2017 was 264 ppb (Stackpoole, Shoda, Medalie, & Stone, 2021), whereas the Vermont mean metolachlor concentration from 26 high agricultural use sites was 1.15 ppb in 2022.
- Clothianidin was the only neonicotinoid insecticide detected in 2022, with 6.4% of samples with concentration levels above the reporting limit of 0.05 ppb. The most conservative EPA aquatic life NOAEC benchmark value for invertebrates is <0.05 ppb and the LOAEC value is 0.05 ppb. Therefore, all detections met or exceeded the LOAEC benchmark.
    - This corresponds to previous monitoring results in Vermont, as well as surface water monitoring in Minnesota, where clothianidin was more frequently detected in water samples from agricultural areas compared with other neonicotinoids (Berens, Capel, & Arnold, 2020).
    - All clothianidin detections occurred in Franklin County. Jewett Brook had at least one detection in the months of June, July, August, and October, whereas Hungerford Brook only measured detections in samples collected in June, and Mill River Tributary had one June sample detection of clothianidin above the reporting limit.
        - Vermont data show most detections in June, coinciding with 3-6 weeks after the typical date corn is planted in the state, similar to other neonicotinoid surface water studies ((Schaafsma, Limay-Rios, Baute, Smith, & Xue, 2015).
- The reporting limit for samples tested for imidacloprid in this study was 0.05 ppb (50 ppt). However, the EPA aquatic life NOAEC benchmark is 0.01 ppb (10 ppt) and LOAEC benchmark is 0.03 ppb. Therefore, results are potentially an underrepresentation of detection frequency and detections exceeding the EPA aquatic benchmarks.

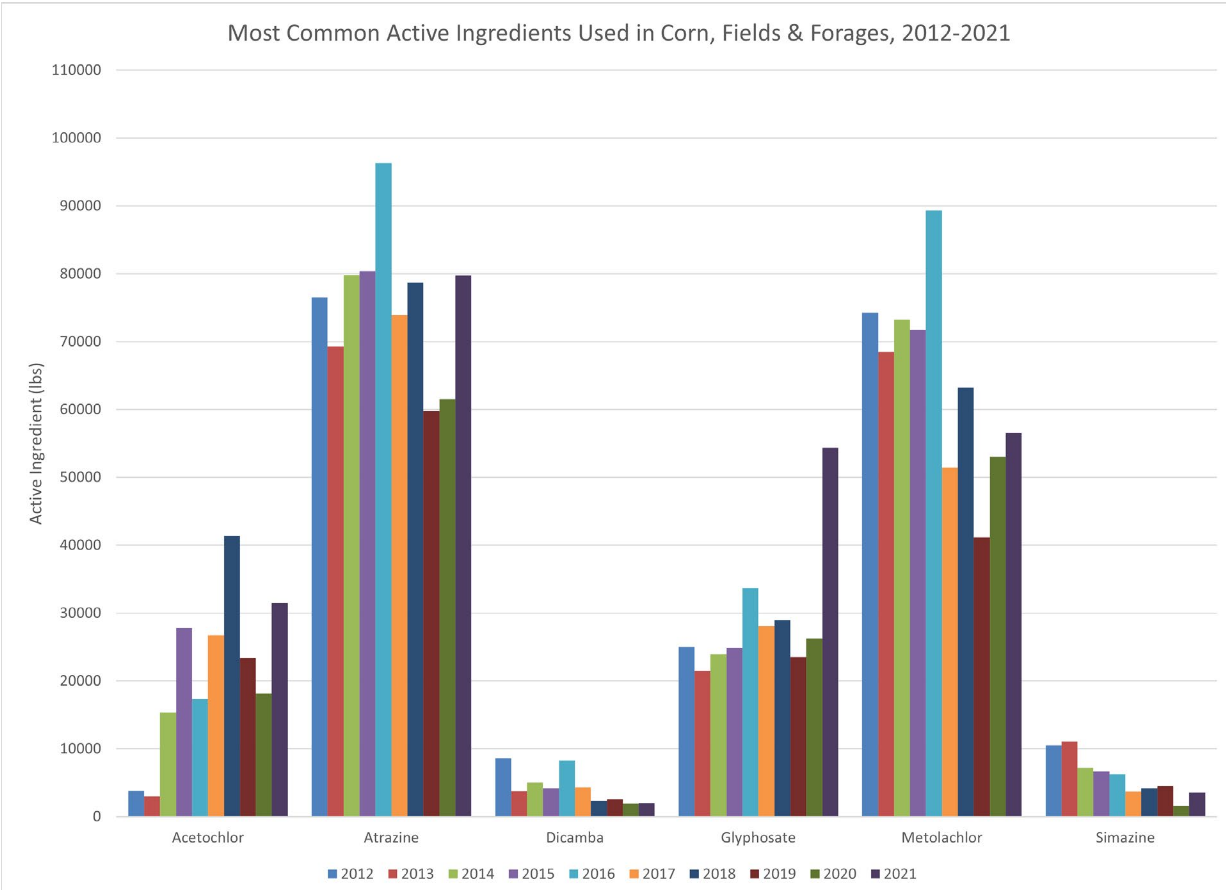
The level of pesticide detections in Vermont's surface water sampling is relatively low, however the data justify continued surveillance. Our 2022 sampling resulted in increased detection frequencies for many of the analytes, therefore the PHARM Division will continue to sample our established sites through 2023 to understand if the increased detections are an anomaly or a consistent trend. Increased monitoring and expanded testing are warranted in specific locations, like Jewett Brook, and were planned at the Franklin County site in Fall of 2021 and 2022. However, the macroinvertebrate bioassessment of Jewett Brook, conducted by the Vermont Department of Environmental Conservation, has been postponed both years because water levels were too low to representatively sample the macroinvertebrates populations at the site. To fully understand the effects of pesticide applications on the water quality and biota in ambient surface water in Vermont high agricultural use areas, we recommend future studies exploring new analytes, method development for lower reporting limits of neonicotinoid active ingredients, and the potential correlation between flow rates and analyte concentrations.

Introduction

Vermont uses fewer pesticide active ingredients and less total pesticides per acre than other agricultural states, however it is important to monitor for our high-use agricultural active ingredients in the environment because of the risk for impact on aquatic and other wildlife.

The PHARM Division conducted environmental surveillance of surface waters in high agricultural use areas around the state by monitoring for neonicotinoids, glyphosate, and other commonly used corn herbicides and their degradates (Figure 1). Data from 2022 sampling were analyzed and compared to EPA Aquatic Life Benchmarks and Ecological Risk Assessments for registered pesticides (U.S. Environmental Protection Agency, 2022).

Figure 1. Vermont Usage Data 2012-2021*: Common Active Ingredients Used in Corn, Fields and Forages



*2022 usage data is being processed at time of report publication.

The objective of this study is to monitor Vermont's surface waters for high-use pesticide active ingredients because of the potential risk to aquatic and other wildlife. The results provide current characterization of the presence or absence of pesticides within high agricultural use areas of the state and will inform future studies.

Methods

Samples were collected from 26 sites by staff from VAAFM and the Vermont Department of Environmental Conservation. For routine sampling there were eight visits per site during the year and timing was coordinated with agricultural events throughout the year: one sample was taken after thaw, before planting, in late April or early May; two samples were taken in both June and July, two weeks apart; and one sample was taken in August, September, and October. Samples collected after rainfall events were taken at stream sites when there was an observed significant increase in flow. However, samples were collected at all stream sites even if the increase in flow was only in one area.

Samples were processed and analyzed by VAEL with mostly internally developed methods.

Sampling Sites

Figure 2. Surface Water Collection Sites (Routine Sampling and Post-Rainfall Event Sampling), 2022

Northwest	North/Central
Hungerford Brook (Highgate) Jewett Brook - 01 (Lower Newton Road St. Albans) [a] Jewett Brook - 02 (Lower Newton Road St. Albans) Mill River Tributary (Georgia) Alburgh Center Lake Champlain (Alburgh) [a] Missisquoi Bay Lake Champlain (Highgate) [a] Missisquoi Bay Central Lake Champlain (Quebec) [a] Lake Champlain (Burlington) [a] Pike River (Quebec) [a] Missisquoi River (St. Albans) [a] Rock River (Highgate) [a] St. Albans Bay Lake Champlain (St. Albans) [a]	Otter Creek (Middlebury) Middlebury River (Middlebury) Winooski River (Middlesex) Lamoille River (Morristown) Little Otter Creek (Ferrisburgh) [ab] White River, 2nd Branch (Brookfield) Diamond Island Lake Champlain (Ferrisburgh) [a]
Northeast	**Southwest**
Black River (Coventry) Missisquoi River (Troy) Passumpsic River (St. Johnsbury)	Battenkill River (Arlington) Mettawee River (Pawlet)
East/Southeast	
Connecticut River (Newbury) Williams River (Chester) West River (Brattleboro)	

[a] indicates post-rainfall event sample site

[ab] indicates post-rainfall event sample site and routine sample site

Results and Discussion

There were detections of the following active ingredients and degradates that were routinely tested for in 2022: atrazine, desethylatrazine, acetochlor ethanesulfonic acid (ESA), alachlor ESA, bicyclopyrone, clothianidin, glyphosate, mesotrione, metolachlor, and metolachlor ESA. There were no detections that exceeded laboratory reporting limits for dimethenamid ESA, thiamethoxam, imidacloprid, or the glyphosate degradate aminomethyl phosphoric acid (AMPA) (Table 1).

The highest detection frequency (percentage of samples having a detection exceeding the reporting limit) was seen in metolachlor ESA, the degradate of metolachlor, at 73.8% of samples having a positive detection. However, with detections ranging from 0.05–13.5 ppb, detections were well below the only established EPA Aquatic Life Benchmark for the analyte, 24,000 ppb, the acute benchmark value for fish (U.S. Environmental Protection Agency, 2022). Metolachlor was detected in 17.6% of the samples tested.

Two herbicide concentrations and one neonicotinoid insecticide concentration exceeded the most conservative NOAEC EPA Aquatic Life Benchmarks: atrazine and metolachlor, and clothianidin, respectively. All the samples that resulted in at least one analyte detection exceeding the NOAEC EPA

Aquatic Life Benchmark were from Franklin County. They were sampled from Hungerford Brook, Jewett Brook, and Mill River Tributary and had detections exceeding the NOAEC throughout the growing season with concentrations exceeding the benchmark in June, July, August, September, and October.

Compared with the previous year's results, the 2022 sample data show an increase in positive detections for atrazine and its degradate desethylatrazine (atrazine DEA), bicyclopyrone, clothianidin, mesotrione, and metolachlor and its degradate metolachlor ESA. There was also an increase in detection frequency of the degradate analytes acetochlor ESA and alachlor ESA. However, the 2022 detection frequencies are similar to 2019 and 2020, therefore a clear trend of increasing detections cannot be supported to date (Table 2). There are no new analytes detected that exceed the chronic or acute benchmarks in 2022 compared with previous years. When comparing precipitation monthly totals from previous sampling years, there is not a clear link between higher precipitation and higher detection frequencies, therefore increased runoff from agricultural fields owing to precipitation cannot explain the increased detections seen in 2022 (Figure 3). VAAFM will evaluate 2023 data to determine if the detection frequency increases are an anomaly or a trend.

Figure 3. Monthly Total Precipitation for Burlington, VT (NOAA Online Weather Data), 2019-2022

Monthly Total Precipitation for Burlington Area, VT (ThreadEx)

Click column heading to sort ascending, click again to sort descending.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
2019	3.29	2.34	2.31	3.53	5.15	4.99	1.91	2.77	3.71	8.50	3.38	1.59	43.47
2020	2.61	2.30	2.01	1.84	2.61	1.88	2.45	6.61	2.29	3.43	2.08	1.27	31.38
2021	1.72	1.55	1.02	3.64	1.42	2.36	5.61	4.40	3.06	5.49	3.17	1.71	35.15
2022	0.94	2.37	2.35	4.21	2.93	4.15	4.04	3.40	6.46	2.62	3.61	2.69	39.77
Mean	2.14	2.14	1.92	3.31	3.03	3.35	3.50	4.30	3.88	5.01	3.06	1.82	37.44
Max	3.29 2019	2.37 2022	2.35 2022	4.21 2022	5.15 2019	4.99 2019	5.61 2021	6.61 2020	6.46 2022	8.50 2019	3.61 2022	2.69 2022	43.47 2019
Min	0.94 2022	1.55 2021	1.02 2021	1.84 2020	1.42 2021	1.88 2020	1.91 2019	2.77 2019	2.29 2020	2.62 2022	2.08 2020	1.27 2020	31.38 2020

The data from samples taken during routine sampling (base flow conditions) were analyzed separately from samples taken after rainfall events (high flow conditions) to see if the collection after rainfall events skewed toward higher detections. Some analytes had slightly lower detection frequencies, whereas others had higher detection frequencies when sampled at high flow conditions. This could be because the tributaries sampled during high flow events are all in Franklin County, where most of the routine sampling detections were found as well. Because the high flow events were not specifically tied to an amount of rain, and all sites were sampled even if one site showed an increase in flow, there aren't clear data to show that the timing of sampling influenced detections. A future potential study correlating flow rates with detection concentrations could more specifically answer the question of whether rainfall events cause higher pesticide presence in surface water or if the higher flow rates result in increased dilution of pesticides in surface water.

Table 1. Surface Water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA Aquatic Life benchmark values, 2022

Pesticide Analyte	Detection Frequency (%)	EPA Chronic NOAEC Aquatic Life Benchmark (ppb)	EPA Benchmark Type	Detection Frequency Above EPA Chronic Benchmark (%)	EPA Acute Aquatic Life Benchmark (ppb)	EPA Benchmark Type	Detection Frequency Above EPA Acute Benchmark (%)	Range of Detections (ppb)
Acetochlor	NT	22.1	USEPA Chronic (i)	n/a	1.43	USEPA Acute (n)	n/a	n/a
Acetochlor ESA	33.2	-	-	n/a	9900	USEPA Acute (n)	0	0.05 - 2.02
Alachlor	NT	110	USEPA Chronic (i)	n/a	1.64	USEPA Acute (n)	n/a	n/a
Alachlor ESA	11.8	-	-	n/a	3600	USEPA Acute (n)	0	0.05 - 0.88
Atrazine	20.3	5	USEPA Chronic (f)	**1.1**	1	USEPA Acute (n)	**5.3**	0.06 - 27.4
Desethylatrazine	9.1	-	-	n/a	-	-	n/a	0.06 - 1.39
Bicyclopyrone	2.1	10000	USEPA Chronic (f)	0	13	USEPA Acute (v)	0	0.10 - 0.26
Clothianidin	6.4	0.05	USEPA Chronic (i)	**6.4**	11	USEPA Acute (i)	0	0.06 - 4.54
Dimethenamid	NT	120	USEPA Chronic (f)	n/a	8.9	USEPA Acute (v)	n/a	n/a
Dimethenamid ESA	0	-	-	n/a	-	-	n/a	n/a
Glyphosate	0.5	25700	USEPA Chronic (f)	0	11900	USEPA Acute (v)	0	21
AMPA	0	-	-	n/a	249500	USEPA Acute (f)	0	n/a
Imidacloprid	0	0.01	USEPA Chronic (i)	0[a]	0.385	USEPA Acute (i)	0	n/a
Mesotrione	3.7	3055	USEPA Chronic (i)	0	4.8	USEPA Acute (v)	0	0.05 - 0.14
Metolachlor	17.6	1	USEPA Chronic (i)	**3.7**	8	USEPA Acute (n)	**0.5**	0.05 - 30.4
Metolachlor ESA	73.8	-	-	n/a	24000	USEPA Acute (f)	0	0.05 - 13.5
Thiamethoxam	0.0	0.74	USEPA Chronic (i)	0	17.5	USEPA Acute (i)	0	n/a

NT analyte not tested

[-] for some analytes, benchmark values have not been developed, identified, or evaluated

(f) benchmark value for fish

(i) benchmark value for invertebrates

(n) benchmark value for nonvascular plants

(v) benchmark value for vascular plants

[a] May underrepresent detections because chronic aquatic life benchmark is lower than reporting limit of 0.05 ppb

Benchmark Sources: U.S. Environmental Protection Agency. (2022, December 14). Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. Retrieved from https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

Table 2. Surface Water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA Aquatic Life benchmark values, 2019-2022

Pesticide Analyte	Detection Frequency (%)				EPA Chronic NOAEC Aquatic Life Benchmark (ppb)	EPA Benchmark Type	Detection Frequency Above EPA Chronic Benchmark (%)				EPA Acute Aquatic Life Benchmark	EPA Benchmark Type	Detection Frequency Above EPA Acute Benchmark (%)			
	2019	**2020**	**2021**	**2022**			**2019**	**2020**	**2021**	**2022**			**2019**	**2020**	**2021**	**2022**
Acetochlor	NT	NT	NT	NT	22.1	USEPA Chronic (i)	n/a	n/a	n/a	n/a	1.43	USEPA Acute (n)	n/a	n/a	n/a	n/a
Acetochlor ESA	28.3	19.2	20.3	33.2	-	-	n/a	n/a	n/a	n/a	9900	USEPA Acute (n)			0	0
Alachlor	NT	NT	NT	NT	110	USEPA Chronic (i)	n/a	n/a	n/a	n/a	1.64	USEPA Acute (n)	n/a	n/a	n/a	n/a
Alachlor ESA	11.1	12.2	7.7	11.8	-	-	n/a	n/a	n/a	n/a	3600	USEPA Acute (n)	0	0	0	0
Atrazine	12.2	12.2	7.0	20.3	5	USEPA Chronic (f)	**0.6**	**1.3**	0	**1.1**	1	USEPA Acute (n)	**0.6**	**1.9**	**0.7**	**5.3**
Desethylatrazine	1.1	7.7	2.1	9.1	-	-	n/a	n/a	n/a	n/a	-	-	n/a	n/a	n/a	n/a
Bicyclopyrone	1.7	0.0	0.7	2.1	10000	USEPA Chronic (f)	0	0	0	0	13	USEPA Acute (v)	0	0	0	0
Clothianidin	3.9	3.8	0.7	6.4	0.05	USEPA Chronic (i)	**3.9**	**3.8**	**0.7**	**6.4**	11	USEPA Acute (i)	0	0	0	0
Dimethenamid	NT	NT	NT	NT	120	USEPA Chronic (f)	n/a	n/a	n/a	n/a	8.9	USEPA Acute (v)	n/a	n/a	n/a	n/a
Dimethenamid ESA	0	0	0	0	-	-	n/a	n/a	n/a	n/a	-	-	n/a	n/a	n/a	n/a
Glyphosate	0.0	0.7	0.7	0.5	25700	USEPA Chronic (f)	0	0	0	0	11900	USEPA Acute (v)	0	0	0	0
AMPA	0	0	0	0	-	-	n/a	n/a	n/a	n/a	249500	USEPA Acute (f)	0	0	0	0
Imidacloprid	0	0.6	0	0	0.01	USEPA Chronic (i)	0[a]	**0.6**[a]	0[a]	0[a]	0.385	USEPA Acute (i)	0	0	0	0
Mesotrione	1.7	3.8	2.1	3.7	3055	USEPA Chronic (i)	0	0	0	0	4.8	USEPA Acute (v)	0	0	0	0
Metolachlor	17.8	14.7	6.3	17.6	1	USEPA Chronic (i)	**1**	**2**	0	**3.7**	8	USEPA Acute (n)	**0.6**	0	0	**0.5**
Metolachlor ESA	72.8	75.6	51.7	73.8	-	-	n/a	n/a	n/a	n/a	24000	USEPA Acute (f)	0	0	0	0
Thiamethoxam	1.7	0.6	0	0	0.74	USEPA Chronic (i)	0	0	0	0	17.5	USEPA Acute (i)	0	0	0	0

NT analyte not tested

[-] for some analytes, benchmark values have not been developed, identified, or evaluated

(f) benchmark value for fish

(i) benchmark value for invertebrates

(n) benchmark value for nonvascular plants

(v) benchmark value for vascular plants

[a] May underrepresent detections because chronic aquatic life benchmark is lower than reporting limit of 0.05 ppb

Benchmark Sources: U.S. Environmental Protection Agency. (2022, December 14). Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. Retrieved from https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

Comparison to Lowest Observable Adverse Effect Concentration Endpoints

Comparing monitoring data to the most conservative EPA aquatic benchmark values may not be the most appropriate evaluation of risk to Vermont's aquatic resources. The EPA aquatic chronic fish and invertebrate benchmarks reflect the lowest known value reported in literature (U.S. Environmental Protection Agency, 2022). The values reflect the NOAEC. This conservative endpoint often does not align with toxicity studies that would be selected for aquatic risk assessments because no effect was measured over a long duration exposure. To evaluate risk to aquatic resources, the LOAEC is a more appropriate endpoint to use. The LOAEC value represents a sensitive chronic toxicity test and is equivalent to a very low toxic concentration (Table 3).

Table 3. U.S. EPA Aquatic Life Benchmarks NOAEC & LOAEC Values (ppb)

Pesticide	Year Updated	CAS number	Fish			Invertebrates			Nonvascular Plants	Vascular Plants
			Acute[a]	Chronic NOAEC[b]	Chronic LOAEC[c]	Acute[d]	Chronic NOAEC[e]	Chronic LOAEC[f]	Acute[g]	Acute[h]
Clothianidin	2016	210880-92-5	> 50750	9700	20000	11	<0.05	0.05	64000	> 280000
Imidacloprid	2017	138261-41-3	114500	9000	26900	0.385	0.01	0.03		
Thiamethoxam	2017	153719-23-4	> 57000	20000	n/a[i]	17.5	0.74	2.23	> 99000	> 90200
Atrazine	2016	1912-24-9	2650	5	50	360	60	140	< 1	4.6
Metolachlor	2016	51218-45-2	1900	30	56	550	1	10	8	21

[a]For acute fish, toxicity value is generally the lowest 96-hour LC_{50} in a standardized test (usually with rainbow trout, fathead minnow, or bluegill)

[b]For chronic fish, toxicity value is usually the lowest NOEAC from the life-cycle or early life stage test (usually with rainbow trout or fathead minnow)

[c]For chronic fish, the LOAEC from the life-cycle or early life stage test (usually with rainbow trout or fathead minnow)

[d]For acute invertebrate, toxicity value is usually the lowest 48- or 96-hour EC_{50} or LC_{50} in a standardized test (usually with midge, scud, or daphnids)

[e]For chronic invertebrates, toxicity value is usually the lowest NOAEC from a life-cycle test with invertebrates (usually with midge, scud, or daphnids)

[f]For chronic invertebrates, the LOAEC from a life-cycle test with invertebrates (midge or mayfly)

[g]For acute nonvascular plants, toxicity value is usually a short-term (<10 days) EC_{50} (usually with green algae or diatoms)

[h]For acute vascular plants, toxicity value is usually short-term (<10 days) EC_{50} (usually with duckweed)

[i]no effects were observed at highest test concentration

When the surface water pesticide monitoring data are revisited and compared with LOAEC values, there are 11 detections exceeding this more practical benchmark for the active ingredients that exceeded NOAEC values (Table 4). The 11 detections are out of 126 total samples and out of the 21 samples that exceeded NOAEC values. One detection of metolachlor exceeded the LOAEC value for aquatic invertebrates. The sample was taken at the Mill River Tributary in Franklin County. Because the reporting limit for clothianidin is 0.05 ppb, detections below the NOAEC cannot be measured and all detections exceeding the reporting limit will be at or above the LOAEC as well. All clothianidin detections in 2022 are equivalent to or exceed the LOAEC and were found in samples taken in Franklin County (Jewett Brook, Hungerford Brook, and Mill River Tributary).

Table 4. Surface Water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA LOAEC Aquatic Life benchmark values, 2022

Pesticide Analyte	Detection Frequency (%)	EPA Chronic LOAEC Aquatic Life Benchmark (ppb)	EPA Benchmark Type	Detection Frequency Above EPA Chronic LOAEC Benchmark (%)	Range of Detections (ppb)
Atrazine	11.9	50	USEPA Chronic (f)	0	0.08 - 27.4
Clothianidin	7.9	0.05	USEPA Chronic (i)	**7.9**	0.06 - 4.54
Imidacloprid	0	0.03	USEPA Chronic (i)	0[a]	n/a
Metolachlor	9.5	10	USEPA Chronic (i)	**0.8**	0.13 - 12.4
Thiamethoxam	0.0	2.23	USEPA Chronic (i)	0	n/a

(f) benchmark value for fish

(i) benchmark value for invertebrates

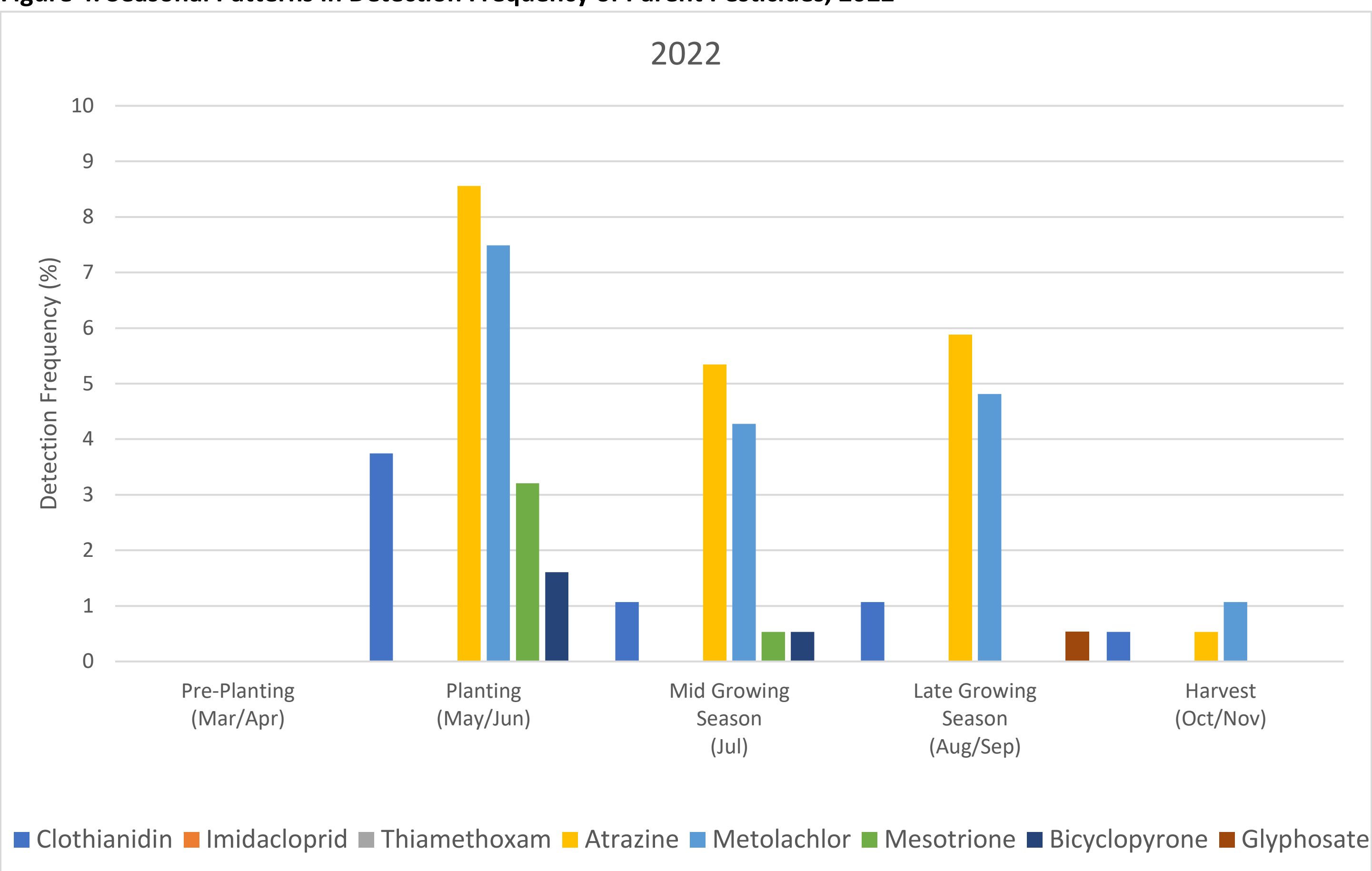
[a] May underrepresent detections because chronic LOAEC aquatic life benchmark is lower than reporting limit of 0.05 ppb

Benchmark Sources: U.S. Environmental Protection Agency. (2022, December 14). Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. Retrieved from https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

Seasonal Patterns

Detection frequencies for the parent pesticide active ingredients that were tested in this study were analyzed to see if there was a seasonal pattern (Figure 4). Atrazine was detected more frequently during planting time (May/June) with decreased detections in mid- and late-growing season. A similar trend was seen with metolachlor detections. Clothianidin was the only neonicotinoid insecticide that was detected in 2022 and most of those detections occurred in samples taken at planting time.

Figure 4. Seasonal Patterns in Detection Frequency of Parent Pesticides, 2022



Active Ingredient Deep Dive

Glyphosate is relatively immobile and has a very short half-life compared with other corn herbicides. However, it is seeing increased use in the context of no-till and cover cropping agricultural practices, as well as from widespread homeowner use. Because it has become an issue of public concern, surveillance efforts have greatly increased in the past few years. There was one detection of glyphosate in 2022 in Jewett Brook in Franklin County. The concentration detected was 21.0 ppb, significantly below chronic and acute EPA Aquatic Life Benchmarks (25,700 ppb and 11,900 ppb, respectively). There were no detections of aminomethylphosphonic acid (AMPA), a degradate of glyphosate, in 2022, which is similar to findings of the past six years. The surface water monitoring program in Minnesota detected glyphosate in 4% of 864 monitoring samples in 2021, which is significantly higher than Vermont's 0.5% statewide detection frequency from 187 monitoring samples (Minnesota Department of Agriculture, 2023).

Corn Herbicides and their degradates accounted for most of the detections in this study. This finding correlates to the relatively high use of these products within Vermont agriculture compared with other active ingredients. Atrazine has a half-life in soil of approximately 60 days, but this can vary based on soil characteristics and environmental conditions. The half-life of atrazine can range from 39 to 261 days (Hartzler, n.d.). Atrazine and its degradate atrazine DEA were detected in 20.3% and 9.1% of samples tested in 2022, respectively. Vermont's detection frequency of atrazine is significantly lower when compared to the 2021 Minnesota surface water data's statewide detection frequency of 54% (Minnesota Department of Agriculture, 2023). Most of the Vermont 2022 detections were detected early in the growing season (May/June), with a slight decrease in mid- and late-growing season samples (Figure 3). There were 38 detections of atrazine from 187 samples collected. Only one of those 38 samples having a detectable level of atrazine was sampled outside of Franklin County, in Alburgh Center, Lake Champlain in Grand Isle County.

The maximum atrazine level detected in 2022 was seen in a sample collected from Jewett Brook during routine sampling in August (27.4 ppb). This concentration level exceeds the most conservative EPA NOAEC benchmark, which is for acute exposure to sensitive species of nonvascular plants (<1 ppb). Because this acute benchmark includes all detections less than 1 ppb, all 38 positive detections of atrazine (20.3% detection frequency) may meet or exceed this value (Table 5). The Refined Ecological Risk Assessment for Atrazine, published in 2016 by the EPA, states that average atrazine concentrations in water at, or exceeding, 5 ppb for several weeks are predicted to lead to reproductive effects in fish, whereas a 60-day average of 3.4 ppb has a high probability of impacting the aquatic plant community's primary productivity, structure and function (Farruggia, Rossmeisl, Hetrick, & Biscoe, 2016). There were two detections at, or exceeding, the 5 ppb threshold, Jewett Brook sampled routinely on August 10, 2022 (27.4 ppb) and Jewett Brook sampled after a rainfall event on August 17, 2022 (5.16 ppb). However, this sampling site did not have concentrations at or exceeding 5 ppb at the next sampling event less than a month later, making it unlikely that concentrations at the site were at, or exceeding, threshold values for several weeks. Looking at each of the sites with positive detections of atrazine, the Jewett Brook site that is routinely sampled is the only site that exceeded the 60-day average of 3.4 ppb, at which level there is a high probability of impacting the aquatic plant community (results averaged 5.2 ppb over the 124-day sampling season).

Table 5. Atrazine Detections by Site (routine and post-rainfall event sampling), 2022

Date	Site of detection above benchmark	Detected concentration (ppb)
5/31/2022	St. Albans Bay Lake Champlain[a]	0.07
6/1/2022	Hungerford Brook	1.21
	Mill River Tributary	0.08
	Jewett Brook - 02	0.23
6/7/2022	St. Albans Bay Lake Champlain[a]	0.06
	Missisquoi Bay Central Lake Champlain[a]	0.13
6/13/2022	Jewett Brook - 02	4.14
	Hungerford Brook	0.51
	Mill River Tributary	0.27
6/27/2022	Hungerford Brook	1.47
	Mill River Tributary	2.74
	Jewett Brook - 02	0.7
	St. Albans Bay Lake Champlain[a]	0.11
6/28/2022	Missisquoi Bay Lake Champlain[a]	0.12
	Missisquoi Bay Central Lake Champlain[a]	0.12
	Alburgh Center Lake Champlain[a]	0.12
7/1/2022	Jewett Brook - 01[a]	2.90
	Rock River[a]	0.12
	Missisquoi River[a]	0.16
7/18/2022	Jewett Brook - 02	2.14
	Hungerford Brook	0.19
7/19/2022	St. Albans Bay Lake Champlain[a]	0.07
	Missisquoi Bay Lake Champlain[a]	0.11
7/25/2022	Rock River[a]	0.25
	Jewett Brook - 01[a]	0.75
7/29/2022	St. Albans Bay Lake Champlain[a]	0.06
8/5/2022	Missisquoi Bay Lake Champlain[a]	0.1
	Missisquoi Bay Central Lake Champlain[a]	0.1
8/10/2022	Jewett Brook - 02	27.40[b]
	Hungerford Brook	0.08
8/17/2022	Jewett Brook - 01[a]	5.16[b]
	Rock River[a]	0.09
8/25/2022	Missisquoi Bay Lake Champlain[a]	0.06
	Missisquoi Bay Central Lake Champlain[a]	0.07
9/8/2022	Jewett Brook - 01[a]	1.02
9/12/2022	Jewett Brook - 02	1.42
9/20/2022	Jewett Brook - 01[a]	0.23
10/3/2022	Jewett Brook - 02	0.52

[a] indicates post-rainfall event sample

[b] detection concentration exceeds chronic NOAEC value for fish (5 ppb)

Metolachlor is characterized as moderately persistent to persistent in soil, having a half-life ranging from 3 to 292 days in surface soils (Sternberg & Koper, 2014). Metolachlor and its degradate, metolachlor ESA, had a combined detection frequency of 91.4% in 2022. This is consistent with other surface water pesticide monitoring studies for the northeast region of the United States (Stackpoole, Shoda, Medalie, & Stone, 2021) as well as being consistent with data from the 2021 Minnesota surface water monitoring program (Minnesota Department of Agriculture, 2023). The most conservative EPA chronic Aquatic Life Benchmark is for invertebrates at 1 ppb, the concentration at which there were no observed adverse effects over a life-cycle test with select invertebrates. There were 33 detections of metolachlor from 187 samples collected. Only one of those 33 samples having a detectable level of metolachlor was sampled outside of Franklin County, at Alburgh Center, Lake Champlain in Grand Isle County. There were seven samples having concentrations exceeding the NOAEC EPA chronic benchmark and one sample that exceeded the LOAEC value of 10 ppb for chronic exposure to sensitive invertebrate species (Table 6). Metolachlor was consistently found at levels exceeding the benchmark threshold in Jewett Brook throughout the season, whereas the maximum concentration detected was from a single detection in Mill River Tributary in June. These results correlate with regional surface water data throughout the United States. Metolachlor, having the second highest herbicide use in the United States from 2013 to 2017, was present in high enough concentrations to exceed chronic invertebrate benchmarks in more than 40% of the national sites sampled during this five year time period (Stackpoole, Shoda, Medalie, & Stone, 2021). However, the mean concentration from these 74 national sites between 2013 and 2017 was 264 ppb, whereas the mean concentration from 26 Vermont sites was 1.15 ppb in 2022.

Table 6. Metolachlor Detections Above EPA Aquatic Life NOAEC Benchmark by Site (routine and post-rainfall event sampling), 2022

Date	Site of detection above benchmark	Detected concentration (ppb)
6/1/2022	Jewett Brook - 02	1.31
6/13/2022	Jewett Brook - 02	1.19
6/27/2022	Jewett Brook - 02	6.62
	Hungerford Brook	2.14
	Mill River Tributary	**12.40**[b]
7/1/2022	Jewett Brook - 01[a]	2.13
8/10/2022	Jewett Brook - 02	5.03

[a] indicates post-rainfall event sample

[b]detection concentration exceeds LOAEC value

Neonicotinoid insecticide use in Vermont is significantly less than in top corn and soybean producing states. However, because this class of insecticides is under increased scrutiny recently for potentially adversely affecting pollinators, it is important to monitor to determine if these pesticides are traveling offsite.

Only clothianidin was detected at levels above reporting limits in 2022. These data correspond to previous monitoring results in Vermont as well as to surface water monitoring in Minnesota, where clothianidin was more frequently detected in water samples from agricultural areas compared with other neonicotinoids (Berens, Capel, & Arnold, 2020). This Minnesota study saw a seasonal trend of higher neonicotinoid concentrations detected in rivers, streams, and lakes coinciding with spring planting and elevated streamflow early in the season. A similar trend was seen in research conducted in southwestern Ontario, where water samples were collected within or around the perimeter of commercial corn fields. Residues of clothianidin (mean, 2.28; max, 43.6 ng/mL (ppb)) and thiamethoxam (mean, 1.12; max, 16.5 ng/mL(ppb)) were detected in 100% and 98.7% of water samples tested, respectively. The concentration of neonicotinoids in water within corn fields increased sixfold during the first five weeks after planting and returned to preplant levels seven weeks post-planting. However, water samples collected from outside the corn fields were similar throughout the sample period and were not so influenced by planting (Schaafsma, Limay-Rios, Baute, Smith, & Xue, 2015). Vermont data show most detections occurred in June, coinciding with three to six weeks after Vermont's typical corn-planting date, although Jewett Brook samples had detections of clothianidin throughout the growing season and into October.

The trend in neonicotinoid detection frequency and concentration seen in Vermont does not correspond with the 2021 state usage data for the three neonicotinoids tested during surface water monitoring. The 2021 usage data show imidacloprid with the highest annual total pounds applied (915.5 lb), followed by clothianidin (45.4 lb) and thiamethoxam (4.4 lb). This could be because clothianidin is extremely persistent in the environment compared with the other two neonicotinoid compounds, having a half-life range of 148 to 1,155 days (Federoff, Liu, Patrick, & Khan, 2009). However, Vermont pesticide usage data do not include the amount of active ingredient on treated seeds and therefore is potentially significantly underestimating the total pounds of clothianidin used in the state. If these data are tracked in the future, there may be more correlations that can be made between neonicotinoid use and surface water active ingredient detection and concentration results.

Clothianidin is extremely toxic to aquatic invertebrates and therefore has a very low EPA chronic NOAEC aquatic benchmark at <0.05 ppb and LOAEC value of 0.05 ppb for sensitive aquatic invertebrates (U.S. Environmental Protection Agency, 2022). Because these benchmark values are equivalent to the reporting limit for this study, every detection of clothianidin exceeded NOAEC and LOAEC benchmarks (Table 7).

Table 7. Clothianidin Detections by Site (routine and post-rainfall event sampling), 2022

Date	Site of detection above benchmark	Detected concentration (ppb)
6/1/2022	Jewett Brook - 02	0.12
	Hungerford Brook	0.09
6/13/2022	Jewett Brook - 02	0.09
	Hungerford Brook	0.07
6/27/2022	Jewett Brook - 02	0.21
	Hungerford Brook	0.30
	Mill River Tributary	4.54
7/1/2022	Jewett Brook - 01[a]	0.26
7/18/2022	Jewett Brook - 02	0.07
8/10/2022	Jewett Brook - 02	0.07
9/20/2022	Jewett Brook - 01[a]	0.40
10/3/2022	Jewett Brook - 02	0.06

[a] indicates post-rainfall event sample

Imidacloprid also poses a severe threat to aquatic invertebrates as evident from the very conservative EPA chronic NOAEC and LOAEC invertebrate benchmark of 0.01 ppb (10 ppt) and 0.03 ppb (30 ppt), respectively (U.S. Environmental Protection Agency, 2022). The reporting limit for samples tested for imidacloprid in this study was 0.05 ppb (50 ppt); therefore, results are potentially an underrepresentation of detection frequency and detections exceeding the EPA aquatic benchmarks. Method changes are in process at VAEL to decrease the reporting limit for this active ingredient for future monitoring studies in Vermont.

Conclusions

Overall, the results of select pesticide monitoring in surface water samples from high agricultural use areas in Vermont in 2022 justify continued surveillance. Knowing whether there are contaminants in surface water can help guide decisions on where to focus efforts, such as increased monitoring, remediation, or regulation. To fully understand the effects of pesticide applications on water quality in ambient surface water in Vermont's high agricultural use areas, we recommend future studies: (1) correlate stream flow data with analyte concentrations to better understand effect of rainfall events; (2) revise methods to detect lower levels of imidacloprid and clothianidin to more accurately determine potential toxicity to aquatic invertebrates; (3) continue adding analytes to test as new products are introduced and usage changes; and (4) further investigate why Franklin county is the location showing more detections exceeding the most conservative EPA Aquatic Life Benchmarks.

References

Berens, M. J., Capel, P. D., & Arnold, W. A. (2020). Neonicotinoid Insecticides in Surface Water, Groundwater, and Wastewater Across Land-Use Gradients and Potential Effects. *Environmental Toxicology and Chemistry, 40*(4), 1017-1033.

Bischof, S., Bruening, B., Johnson, H., MacDonald, M., Matterson, S., Rassmussen, K., . . . VanRyswyk, B. (2021). *2020 Water Quality Monitoring Report.* Pesticide and Fertilizer Management Division. Saint Paul, MN: Minnesota Department of Agriculture. Retrieved from https://wrl.mnpals.net/islandora/object/WRLrepository%3A3746/datastream/PDF/view

Farruggia, F. T., Rossmeisl, C. M., Hetrick, J. A., & Biscoe, M. (2016). Refined Ecological Risk Assessment for Atrazine. *U.S. Environmental Protection Agency*, EPA-HQ-OPP-2013-0266-0315.

Federoff, N. E., Liu, L., Patrick, G., & Khan, F. A. (2009). *Environmental Fate and Ecological Risk Assessment for the Registration of Clothianidin for Use on Turfgrass, Tobacco, Apples, Pears, and Ornamentals.* Office of Pesticide Programs, Environmental Fate and Effects Division. Washington DC: U.S. Environmental Protection Agency. Retrieved from https://www3.epa.gov/pesticides/chem_search/cleared_reviews/csr_PC-044309_24-Nov-04_a.pdf

Hartzler, B. (n.d.). *Absorption of Soil-Applied Herbicides*. Retrieved from Iowa State University Extension and Outreach: https://crops.extension.iastate.edu/encyclopedia/absorption-soil-applied-herbicides#:~:text=Absorption%20of%20Soil-Applied%20Herbicides%20%20%20Herbicide%20,%20%2030%20%2015%20more%20rows%20

Hladik, M. L., Kolpin, D. W., & Kuivila, K. M. (2014). Widespread occurrence of neonicotinoud insecticides in streams in a high corn and soybean producing region, USA. *Environmental Pollution, 193*, 189-196.

Minnesota Department of Agriculture. (2023, June). Retrieved from Surface Water Pesticide Water Quality Monitoring: https://www.mda.state.mn.us/pesticide-fertilizer/surface-water-pesticide-water-quality-monitoring

Schaafsma, A., Limay-Rios, V., Baute, T., Smith, J., & Xue, Y. (2015). Neonicotinoid Insecticide Residues in Surface Water and Soil Associated with Commercial Maize (Corn) Fields in Southwestern Ontario. *PLoS ONE, 10*(2), 1-21.

Stackpoole, S. M., Shoda, M. E., Medalie, L., & Stone, W. W. (2021). Pesticides in US Rivers: Regional differences in use, occurrence, and environmental toxicity, 2013 to 2017. *Science of the Total Environment, 787*, 147147.

Sternberg, R., & Koper, C. M. (2014). *Registration Review Problem Formulation: Metolachlor and S-Metolachlor.* Office of Pesticides, Environmental Fate and Effects Division. Washington DC: U.S. Environmental Protection Agency.

U.S. Environmental Protection Agency. (1995). *Reregistration Eligibility Decision Fact Sheet, Metolachlor.* Retrieved from U.S. Environmental Protection Agency: https://www3.epa.gov/pesticides/chem_search/reg_actions/reregistration/fs_PC-108801_1-Apr-95.pdf

U.S. Environmental Protection Agency. (2020, January). Imidacloprid Proposed Interim Registration Review Decision. *Case Number 7605*, EPA-HQ-OPP-2008-0844.

U.S. Environmental Protection Agency. (2021, May). *Ingredients Used in Pesticide Products, Atrazine*. Retrieved from U.S. Environmental Protection Agency: https://www.epa.gov/ingredients-used-pesticide-products/atrazine

U.S. Environmental Protection Agency. (2022, December 14). *Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides*. Retrieved from https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

Wieben, C. M. (2020, May). *Estimated Annual Agricultural Pesticide Use by Major Crop or Crop Group for States of the Conterminous United States, 1992-2017.* Retrieved from U.S. Geological Survey data release: https://doi.org/10.5066/P9HHG3CT.