# Vermont Ambient Surface Water Pesticide Monitoring: 2023 Data Summary

Vermont Agency of Agriculture, Food & Markets

Public Health & Agricultural Resource Management Division

Initial Reporting, 2024

## **Executive Summary**

Over the last 8 years, the Public Health and Agricultural Resource Management (PHARM) Division of the Vermont Agency of Agriculture, Food & Markets (VAAFM) has monitored select surface water sites throughout high agricultural use areas of the State for pesticides. Surface water quality monitoring is conducted for the purpose of evaluating the impact from the routine application of agricultural chemicals on surface water in Vermont. The sites monitored are routinely sampled during critical times of the growing season each year. The Vermont Department of Environmental Conservation (DEC) also monitors surface waters, including Lake Champlain and rivers and streams, throughout the state for pesticides and overall water quality parameters. The Vermont Agriculture and Environmental Laboratory (VAEL) analyzes the water samples collected by both VAAFM and DEC for neonicotinoids, glyphosate, and other commonly used corn herbicides and their degradates. This report summarizes the results from the 2023 growing season sampling efforts.

- In 2023, 155 water samples were collected from 25 Vermont rivers, streams, and lakes.
- Samples were analyzed for 8 pesticides and 6 pesticide degradates.
  - o 7 pesticides and 4 degradates were detected at least once.
  - o 6 pesticides and 1 degradate were detected in 10% or fewer of the samples.
- There were no detections of glyphosate or its degradation product, aminomethylphosphonic acid (AMPA).
- The herbicides bicyclopyrone and mesotrione, were detected in 1.9% and 3.9% of samples, respectively, and all detections were concentration levels below the most conservative Environmental Protection Agency (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 3.9%, 71.0%, 9.7%, and 41.3% of samples, respectively. All detections were below the NOAEC benchmark values that are established.
- Atrazine was detected in 6.5% of the samples, and because the most conservative benchmark, the NOAEC EPA acute value for nonvascular plants, is defined as less than 1 ppb, potentially all of these positive detections reach or exceed this threshold. There were no detection values greater than the most conservative chronic benchmark, the NOAEC EPA chronic value for fish (5 ppb).
  - 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 19.4% of the samples and 2 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 collected in Jewett Brook located in Franklin County on June 22, 2023 and July 11, 2023.
    - Jewett Brook samples did not exceed the LOAEC chronic or acute benchmark values (10 ppb or 8 ppb, respectively).
    - Jewett Brook measured elevated flow on both of these dates due to coinciding rain events.
    - The mean concentration of metolachlor detections was 0.48 ppb (1.15 ppb mean in 2022).

- There was at least one detection of each of the neonicotinoid insecticide analytes.
  - Clothianidin was detected in 6.5% of samples. The most conservative EPA aquatic life NOAEC benchmark value is for invertebrates at <0.05 ppb and the LOAEC value is 0.05 ppb. Therefore, because VAEL's reporting limit is 0.05 ppb, all reported detections met or exceeded the NOAEC and LOAEC benchmarks.
    - Nine out of ten clothianidin detections occurred in Franklin County, with one June 19 detection from Little Otter Creek in Addison county. Jewett Brook had at least one detection in the months of June, July, and September. Hungerford Brook and Mill River Tributary had one detection each, measured in samples collected on June 22. Rock River had one detection from a July 11 sample.
  - There were two thiamethoxam detections on June 28, 2023 in Addison County, both the Little Otter Creek and Otter Creek samples had detections of 0.08 ppb and 0.06 ppb, respectively. These detections are below the most conservative NOAEC benchmark, the chronic benchmark value for invertebrates at 0.74 ppb.
  - Imidacloprid was detected at 0.06 ppb in one 2023 DEC sample from Little Otter Creek in Addison county on July 11. 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. VAEL has developed new methods for imidacloprid detections that have a reduced reporting limit of 0.01 ppb (10 ppt) which will be utilized in the 2024 sampling season.

The level of pesticide detections in Vermont's surface water sampling justifies continued surveillance. The 2023 sampling resulted in increased detection frequencies for some of the analytes and reduced detection of others. The PHARM Division will continue to sample our established sites through 2024, in coordination with DEC, to understand if the increased detections are an anomaly due to extreme weather/high precipitation conditions seen in the last few years, or a consistent trend.

A majority of the sites in which we have consistently seen positive detections of pesticides are also streams monitored by DEC and listed on Part A of the 303(d) List of Impaired Waters. As of July 2022, the source of impairment associated with these waters is listed as sedimentation and nutrients from agricultural runoff. To fully understand the potential contribution of pesticide applications and runoff in high agricultural use areas on impaired water quality and biota, we recommend future studies exploring the potential correlation between rain events, flow rates and analyte concentrations.

#### Methods

Samples were collected from 26 sites by staff from VAAFM and DEC. 2023 VAAFM routine sampling efforts were hindered by significant flooding events. As a result of the flooding, the sites were sampled less than in previous years noting limited samples taken in June, July, and August. There were three to five visits per site and, when sampling was safe, the collections were coordinated with agricultural events throughout the year: after thaw, before planting, in late April or early May; after planting throughout the growing season in June, July, August, and September; and during or after harvest in October. Tributary samples are collected by DEC in streams after rainfall events when there was an observed significant increase in flow, and also three times throughout the year when tributaries are at

low-flow levels. DEC sample results are not distinguished between collection at high-flow or low-flow levels and samples may be collected at all stream sites even if the observed increase in flow was only in one area. Lake Champlain samples are collected by DEC on a routine basis, with frequency averaging between two and three weeks between sampling events.

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

### Sampling Sites

Table 1. Surface Water Collection Sites (Routine Sampling and Post-Rainfall Event Sampling), 2023

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

<sup>&</sup>lt;sup>a</sup> indicates DEC sample site

#### Results and Discussion

There were detections of the following active ingredients and degradates that were routinely tested for in 2023: atrazine, desethylatrazine, acetochlor ethanesulfonic acid (ESA), alachlor ESA, bicyclopyrone, clothianidin, imidacloprid, mesotrione, metolachlor, metolachlor ESA, and thiamethoxam. There were no detections that exceeded laboratory reporting limits for dimethenamid ESA, glyphosate or the glyphosate degradate aminomethyl phosphoric acid (AMPA) (Table 3).

The highest detection frequency (percentage of samples having a detection exceeding the reporting limit) was seen in metolachlor ESA, the degradate of metolachlor, at 71.0% of samples having a positive detection. However, with detections ranging from 0.05–8.6 ppb, detections were well below the only established EPA Aquatic Life Benchmark for the analyte, 24,000 ppb, the acute benchmark value for fish

<sup>&</sup>lt;sup>ab</sup> indicates DEC and VAAFM sample site

(U.S. Environmental Protection Agency, 2024). Metolachlor was detected in 19.4% of the samples tested.

One herbicide concentration and two neonicotinoid insecticide concentrations exceeded the most conservative NOAEC EPA Aquatic Life Benchmarks: metolachlor, clothianidin and imidacloprid, respectively. The samples that resulted in at least one analyte detection exceeding the NOAEC EPA Aquatic Life Benchmark were from Addison and Franklin Counties. In Franklin County samples that resulted in metolachlor and/or clothianidin detections exceeding the NOAEC benchmark were taken from Jewett Brook, Hungerford Brook, Rock River, and Mill River Tributary throughout the growing season in June, July, and September. In Addison County, samples from Little Otter Creek had single detections exceeding the NOAEC of clothianidin and imidacloprid in June and July, respectively.

When compared to previous years' detections, the 2023 detection frequencies are similar or increasing for some chemicals but decreasing for other analytes. A clear trend of increasing detections cannot be supported to date (Table 4). Compared with the previous year's results, the 2023 sample data show a decrease in positive detections for atrazine and its degradate desethylatrazine (atrazine DEA), as well as a decrease in detections of degradates metolachlor ESA and alachlor ESA. There was an increase in detection frequency of the herbicides mesotrione and metolachlor, and the degradate analyte acetochlor ESA. The neonicotinoid insecticides monitored, clothianidin, imidacloprid and thiamethoxam, each saw an increase in detection frequency in 2023.

When comparing precipitation monthly totals (data available for Burlington, VT) from previous sampling years, there may be an association with higher detection frequencies and higher rainfall levels in June, July, August and October (Table 2). However, there is not an obvious and consistent link between higher precipitation measured in Burlington and higher detection frequencies elsewhere in the state. When comparing daily precipitation measured in Burlington compared to normal daily precipitation values, there were days when rainfall exceeded normal values that may have led to increased agricultural runoff and more positive pesticide detections (Figure 1). There was significant flooding on July 11, 2023 and DEC sampled on that date due to the increased corresponding stream flow. These samples led to positive detections in Franklin and Addison Counties.

Table 2. Monthly Total Precipitation for Burlington, VT (NOAA Online Weather Data), 2019-2023

# Monthly Total Precipitation for Burlington Area, VT (ThreadEx)

Year Jan Feb Mar Jul Oct Dec Annual Apr May Jun Aug Sep Nov 4.99 2019 3.29 2.31 1.91 2.77 3.71 8.50 2.34 3.53 5.15 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 2023 2.70 3.40 1.55 2.81 1.97 3.93 5.89 4.90 2.91 6.41 2.53 5.78 44.78 Mean 2.39 2.02 2.08 3.21 2.82 3.46 3.98 4.42 3.69 5.29 2.95 2.61 38.91 3.40 2.37 2.70 4.21 5.15 4.99 5.89 6.46 8.50 3.61 5.78 44.78 6.61 Max 2023 2022 2023 2022 2019 2019 2023 2020 2022 2019 2022 2023 2023 0.94 1.55 1.02 1.84 1.42 1.88 1.91 2.77 2.29 2.62 2.08 31.38 1.27 Min 2022 2021 2021 2020 2021 2020 2019 2019 2020 2022 2020 2020 2020

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

Figure 1. Mean precipitation measured compared to normal precipitation by day for Burlington Area, VT (NOAA)

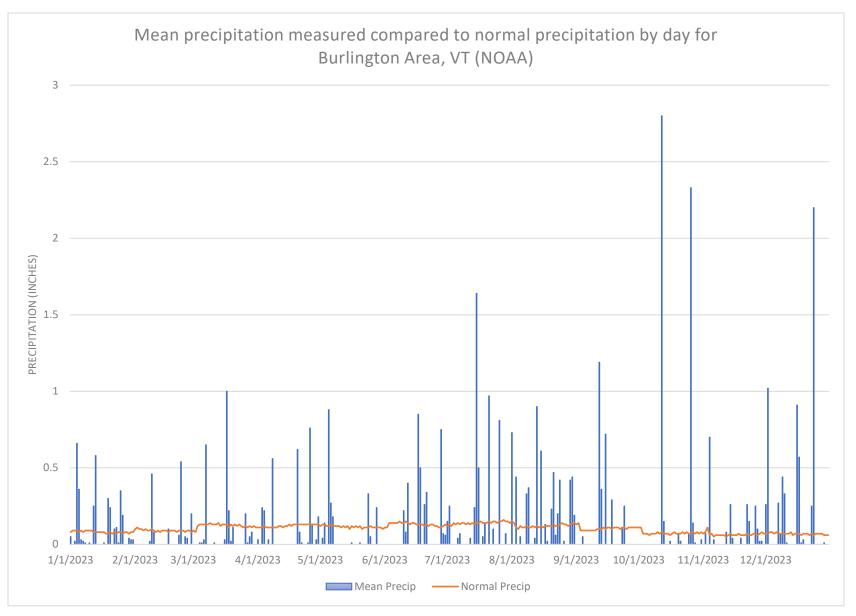


Table 3. Surface water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA Aquatic Life Benchmark values, 2023

	Detection	EPA <u>Chronic</u>		Detection	EPA <u>Acute</u>		Detection	
Daniel da Amalana	Detection	<b>NOAEC Aquatic</b>	<b>EPA Benchmark</b>	Frequency Above	<b>Aquatic Life</b>	<b>EPA Benchmark</b>	Frequency Above	Range of
Pesticide Analyte	Frequency	Life Benchmark	Type	EPA Chronic	Benchmark	Type	EPA Acute	Detections (ppb)
	(%)	(ppb)		Benchmark (%)	(ppb)		Benchmark (%)	
Acetochlor	NT	22.1	USEPA Chronic (i)	n/a	1.43	USEPA Acute (n)	n/a	n/a
Acetochlor ESA	41.3	-	-	n/a	9900	USEPA Acute (n)	0	0.05 - 2.08
Alachlor	NT	110	USEPA Chronic (i)	n/a	1.64	USEPA Acute (n)	n/a	n/a
Alachlor ESA	9.7	-	-	n/a	3600	USEPA Acute (n)	0	0.05 - 0.3
Atrazine	6.5	5	USEPA Chronic (f)	0	1	USEPA Acute (n)	0	0.07 - 0.93
Desethylatrazine	3.9	-	-	n/a	-	-	n/a	0.07 - 0.32
Bicyclopyrone	1.9	10000	USEPA Chronic (f)	0	13	USEPA Acute (v)	0	0.06 - 0.37
Clothianidin	6.5	0.05	USEPA Chronic (i)	6.5	11	USEPA Acute (i)	0	0.06 - 0.63
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	0.0	25700	USEPA Chronic (f)	0	11900	USEPA Acute (v)	0	n/a
AMPA	0	-	-	n/a	249500	USEPA Acute (f)	0	n/a
Imidacloprid	0.6	0.01	USEPA Chronic (i)	0.6 <sup>a</sup>	0.385	USEPA Acute (i)	0	0.06
Mesotrione	3.9	3055	USEPA Chronic (i)	0	4.8	USEPA Acute (v)	0	0.06 - 0.58
Metolachlor	19.4	1	USEPA Chronic (i)	1.3	8	USEPA Acute (n)	0	0.05 - 4.48
Metolachlor ESA	71.0	-	-	n/a	24000	USEPA Acute (f)	0	0.05 - 8.6
Thiamethoxam	1.3	0.74	USEPA Chronic (i)	0	17.5	USEPA Acute (i)	0	0.06 - 0.08

NT analyte not tested

Benchmark Sources: U.S. Environmental Protection Agency, 2024. 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

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

<sup>(</sup>f) benchmark value for fish

<sup>(</sup>i) benchmark value for invertebrates

<sup>(</sup>n) benchmark value for nonvascular plants

<sup>(</sup>v) benchmark value for vascular plants

<sup>&</sup>lt;sup>a</sup> may underrepresent detections because chronic aquatic life benchmark is lower than reporting limit of 0.05 ppb

Table 4. Surface water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA Aquatic Life Benchmark values, 2019-2023

Pesticide Analyte	De	tectio	n Freqı	uency	(%)	EPA <u>Chronic</u> NOAEC Aquatic Life Benchmark (ppb)	EPA Benchmark Type			•	ency Al chmar		EPA <u>Acute</u> Aquatic Life Benchmark	EPA Benchmark Type			•	ency Ab hmark	
	2019	2020	2021	2022	2023			2019	2020	2021	2022	2023			2019	2020	2021	2022	2023
Acetochlor	NT	NT	NT	NT	NT	22.1	USEPA Chronic (i)	n/a	n/a	n/a	n/a	n/a	1.43	USEPA Acute (n)	n/a	n/a	n/a	n/a	n/a
Acetochlor ESA	28.3	19.2	20.3	33.2	41.3	-	-	n/a	n/a	n/a	n/a	n/a	9900	USEPA Acute (n)			0	0	0
Alachlor	NT	NT	NT	NT	NT	110	USEPA Chronic (i)	n/a	n/a	n/a	n/a	n/a	1.64	USEPA Acute (n)	n/a	n/a	n/a	n/a	n/a
Alachlor ESA	11.1	12.2	7.7	11.8	9.7	-	-	n/a	n/a	n/a	n/a	n/a	3600	USEPA Acute (n)	0	0	0	0	0
Atrazine	12.2	12.2	7.0	20.3	6.5	5	USEPA Chronic (f)	0.6	1.3	0	1.1	0	1	USEPA Acute (n)	0.6	1.9	0.7	5.3	0
Desethylatrazine	1.1	7.7	2.1	9.1	3.9	-	-	n/a	n/a	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	1.9	10000	USEPA Chronic (f)	0	0	0	0	0	13	USEPA Acute (v)	0	0	0	0	0
Clothianidin	3.9	3.8	0.7	6.4	6.5	0.05	USEPA Chronic (i)	3.9	3.8	0.7	6.4	6.5	11	USEPA Acute (i)	0	0	0	0	0
Dimethenamid	NT	NT	NT	NT	NT	120	USEPA Chronic (f)	n/a	n/a	n/a	n/a	n/a	8.9	USEPA Acute (v)	n/a	n/a	n/a	n/a	n/a
Dimethenamid ESA	0	0	0	0	0	-	-	n/a	n/a	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	0.0	25700	USEPA Chronic (f)	0	0	0	0	0	11900	USEPA Acute (v)	0	0	0	0	0
AMPA	0	0	0	0	0	-	-	n/a	n/a	n/a	n/a	n/a	249500	USEPA Acute (f)	0	0	0	0	0
Imidacloprid	0	0.6	0	0	0.6	0.01	USEPA Chronic (i)	0 <sup>a</sup>	0.6 <sup>a</sup>	0 <sup>a</sup>	<b>0</b> <sup>a</sup>	0.6 <sup>a</sup>	0.385	USEPA Acute (i)	0	0	0	0	0
Mesotrione	1.7	3.8	2.1	3.7	3.9	3055	USEPA Chronic (i)	0	0	0	0	0	4.8	USEPA Acute (v)	0	0	0	0	0
Metolachlor	17.8	14.7	6.3	17.6	19.4	1	USEPA Chronic (i)	1	2	0	3.7	1.3	8	USEPA Acute (n)	0.6	0	0	0.5	0
Metolachlor ESA	72.8	75.6	51.7	73.8	71.0	-	-	n/a	n/a	n/a	n/a	n/a	24000	USEPA Acute (f)	0	0	0	0	0
Thiamethoxam	1.7	0.6	0	0	1.3	0.74	USEPA Chronic (i)	0	0	0	0	0	17.5	USEPA Acute (i)	0	0	0	0	0

NT analyte not tested

Benchmark Sources: U.S. Environmental Protection Agency, 2024. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. Retrieved from https://www.epa.gov/pesticidescience-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

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

<sup>(</sup>f) benchmark value for fish

<sup>(</sup>i) benchmark value for invertebrates

<sup>(</sup>n) benchmark value for nonvascular plants

<sup>(</sup>v) benchmark value for vascular plants

<sup>&</sup>lt;sup>a</sup> may underrepresent detections because chronic aquatic life benchmark is lower than reporting limit of 0.05 ppb

#### 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, 2024). 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 5).

Table 5. U.S. EPA Aquatic Life Benchmarks NOAEC & LOAEC values (ppb)

									Nonvascular	Vascular
Pesticide	Year	CAS number		Fish		l	Invertebrate	S	Plants	Plants
College	Updated	CAS Hamber		Chronic	Chronic		Chronic	Chronic		
			<b>Acute</b> <sup>a</sup>	NOAEC <sup>b</sup>	LOAEC	Acute <sup>d</sup>	NOAECe	LOAEC	<b>A</b> cute <sup>g</sup>	Acute <sup>h</sup>
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 <sup>i</sup>	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
Bicyclopyrone	2016	352010-68-5	> 46700	10000	> 10000	> 46650	103700	> 103700	2000	13
Mesotrione	2021	104206-82-8	> 60000	11000	23000	67000	3055	6614	> 820	4.8

<sup>&</sup>lt;sup>a</sup> for acute fish, toxicity value is generally the lowest 96-hour LC<sub>50</sub> in a standardized test (usually with rainbow trout, fathead minnow, or bluegill)

U.S. Environmental Protection Agency, 2024. 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

When the surface water pesticide monitoring data are revisited and compared with LOAEC values, there are 10 detections exceeding this more practical benchmark for the active ingredients that exceeded NOAEC values (Table 6). The 10 detections are out of 155 total samples and out of the 13 samples that exceeded NOAEC values. Because the reporting limit for imidacloprid is 0.05 ppb, the analysis method does not measure detections that would potentially meet or exceed both the NOAEC and LOAEC for this analyte. Likewise, 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 2023 are equivalent to or exceed the LOAEC and were found in samples taken in Franklin County (Jewett Brook, Hungerford Brook, Rock River, and Mill River Tributary) and in Addison County (Little Otter Creek).

<sup>&</sup>lt;sup>b</sup> 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)

<sup>&</sup>lt;sup>c</sup>for chronic fish, the LOAEC from the life-cycle or early life stage test (usually with rainbow trout or fathead minnow)

dfor acute invertebrate, toxicity value is usually the lowest 48- or 96-hour EC<sub>50</sub> or LC<sub>50</sub> 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)

<sup>&</sup>lt;sup>f</sup> for chronic invertebrates, the LOAEC from a life-cycle test with invertebrates (midge or mayfly)

<sup>&</sup>lt;sup>8</sup> for acute nonvascular plants, toxicity value is usually a short-term (<10 days) EC<sub>50</sub> (usually with green algae or diatoms)

<sup>&</sup>lt;sup>h</sup> for acute vascular plants, toxicity value is usually short-term (<10 days) EC<sub>50</sub> (usually with duckweed)

<sup>&</sup>lt;sup>1</sup>no effects were observed at highest test concentration

Table 6. Surface water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA LOAEC Aquatic Life Benchmark values, 2023

Pesticide Analyte	Detection Frequency (%)	EPA <u>Chronic</u> LOAEC Aquatic Life Benchmark (ppb)	EPA Benchmark Type	Detection Frequency Above EPA <u>Chronic</u> LOAEC Benchmark (%)	Range of Detections (ppb)
Atrazine	6.5	50	USEPA Chronic (f)	0	0.07 - 0.93
Clothianidin	6.5	0.05	USEPA Chronic (i)	6.5	0.07 - 0.63
Imidacloprid	0.6	0.03	USEPA Chronic (i)	0.6 <sup>a</sup>	0.06
Metolachlor	19.4	10	USEPA Chronic (i)	0	0.05 - 4.48
Thiamethoxam	1.3	2.23	USEPA Chronic (i)	0	0.06 - 0.08
Bicyclopyrone	1.9	10000	USEPA Chronic (f)	0	0.06 - 0.37
Mesotrione	3.9	6614	USEPA Chronic (i)	0	0.06 - 0.58

<sup>(</sup>f) benchmark value for fish

#### 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 2). Atrazine was detected more frequently during planting time and early season (May/June) with decreased detections in mid- and late-growing season. Metolachlor detections peaked during midgrowing season. Thiamethoxam was only detected in late June and the single detection of imidacloprid that was reported occurred after significant rainfall on July 11, 2023. Clothianidin was detected in June and again after that significant rainfall event in mid-July and in September.

<sup>(</sup>i) benchmark value for invertebrates

<sup>&</sup>lt;sup>a</sup> 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, 2024. 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

2023 10 9 Detection Freguency (%) 3 Pre-Planting **Planting** Mid Growing Late Growing Harvest (Mar/Apr) (May/Jun) (Oct/Nov) Season Season (Jul) (Aug/Sep) ■ Clothianidin ■ Imidacloprid ■ Thiamethoxam ■ Atrazine ■ Metolachlor ■ Mesotrione ■ Bicyclopyrone ■ Glyphosate

Figure 2. Seasonal Patterns in Detection Frequency of Parent Pesticides, 2023

#### 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 were no detections of glyphosate or of aminomethylphosphonic acid (AMPA), a degradate of glyphosate, in 2023, which is similar to the very limited to no detections over the past seven years.

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 6.5% and 3.9% of samples tested in 2023, respectively. Both of these detection frequencies are a reduction from 2022 detections of these compounds. Like 2022, most of the Vermont 2023 detections were detected early in the growing season (May/June), with a slight decrease in mid- and late-growing season samples (Figure 2). There were 10 detections of atrazine from 155 samples collected. Detections were in Addison and Franklin Counties (Table 7).

The maximum atrazine level detected in 2023 was collected from Hungerford Brook during routine sampling in June (0.93 ppb). Because the most conservative EPA benchmark, which is for acute exposure to sensitive species of

nonvascular plants includes all detections less than 1 ppb, all 10 positive detections of atrazine (6.5% detection frequency) may meet or exceed this value. 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 no detections in 2023 that exceed either the 3.4 ppb or 5 ppb threshold.

Table 7. Atrazine detections by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/8/2023	Jewett Brook - 02	0.07
6/19/2023	Little Otter Creek <sup>a</sup>	0.35
6/22/2022	Jewett Brook - 02	0.11
6/22/2023	Hungerford Brook	0.93
6/20/2022	Little Otter Creek	0.24
6/28/2023	Otter Creek	0.07
7/11/2023	Jewett Brook - 01 <sup>a</sup>	0.15
7/47/2022	Jewett Brook - 01 <sup>a</sup>	0.14
7/17/2023	Little Otter Creek <sup>a</sup>	0.07
8/9/2023	Otter Creek	0.08

<sup>&</sup>lt;sup>a</sup> indicates DEC sample

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 90.3% in 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 30 detections of metolachlor from 155 samples collected. There were two samples having concentrations exceeding the NOAEC EPA chronic benchmark, a reduction from seven samples exceeding the benchmark in 2022, and no samples exceeded the LOAEC value of 10 ppb for chronic exposure to sensitive invertebrate species (Table 8). The majority of detections occurred in Franklin County, but five detections were found in Addison County and one detection each in Orleans and Grand Isle Counties.

Table 8. Metolachlor detections above EPA Aquatic Life NOAEC Benchmark by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/22/2023	Jewett Brook - 02	3.56
7/11/2023	Jewett Brook - 01 <sup>a</sup>	4.48

<sup>&</sup>lt;sup>a</sup> indicates DEC sample

In 2023, there were two additional corn herbicides detected during sampling events. Bicyclopyrone was detected on three collection dates from Jewett Brook in Franklin County (Table 9). When detection dates are plotted with the height of the brook at the United States Geological Survey (USGS) stream gage located at the collection point for Jewett Brook,

each positive sample was collected immediately during, or after a significant event that caused the stream height to peak. The most conservative EPA Aquatic Life Benchmark is for acute bicyclopyrone exposure to sensitive species of vascular plants (13 ppb), this benchmark was not exceeded in any of the samples collected.

Table 9. Bicyclopyrone detections by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/22/2023	Jewett Brook - 02	0.37
7/11/2023	Jewett Brook - 01 <sup>a</sup>	0.20
7/17/2023	Jewett Brook - 01 <sup>a</sup>	0.06

<sup>&</sup>lt;sup>a</sup> indicates DEC sample

The second corn herbicide detected in 2023 that was not detected in 2022 is mesotrione. There were six positive detections collected from Addison and Franklin Counties (Table 10). Again, some of these samples were collected after significant rainfall events throughout the state that could have led to runoff of pesticides due to erosion. No sample collected exceeded the most conservative EPA NOAEC benchmark concentration which is for chronic exposure to invertebrates (3055 ppb).

Table 10. Mesotrione detections by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/19/2023	Little Otter Creek <sup>a</sup>	0.11
6/22/2023	Hungerford Brook	0.08
0/22/2023	Jewett Brook - 02	0.58
6/28/2023	Little Otter Creek	0.07
7/11/2023	Jewett Brook - 01 <sup>a</sup>	0.11
//11/2023	Pike River <sup>a</sup>	0.06

<sup>&</sup>lt;sup>a</sup> indicates DEC sample

**Neonicotinoid** insecticides are under increased scrutiny recently for potentially adversely affecting pollinators, therefore it is important to monitor to determine if these pesticides are traveling offsite via water.

Clothianidin was the neonicotinoid monitored that had the most detections, with 10 out of 155 samples detected above the reporting limit of 0.05 ppb. Vermont data show slightly more detections in June, coinciding with three to six weeks after Vermont's typical (neonicotinoid treated) corn-planting date, although Jewett Brook samples had detections of clothianidin into September. 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, 2024). Because these benchmark values are equivalent to the reporting limit for this study, every detection of clothianidin exceeded both the NOAEC and LOAEC benchmarks (Table 11).

Table 11. Clothianidin detections by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/19/2023	Little Otter Creek <sup>a</sup>	0.13 <sup>b</sup>
	Hungerford Brook	0.28 <sup>b</sup>
6/22/2023	Jewett Brook - 02	0.63 <sup>b</sup>
	Mill River Tributary	0.09 <sup>b</sup>
7/11/2023	Jewett Brook - 01 <sup>a</sup>	0.48 <sup>b</sup>
7/11/2023	Rock River <sup>a</sup>	0.10 <sup>b</sup>
7/17/2023	Jewett Brook - 01 <sup>a</sup>	0.28 <sup>b</sup>
9/7/2023	Jewett Brook - 02	0.07 <sup>b</sup>
9/11/2023	Jewett Brook - 01 <sup>a</sup>	0.17 <sup>b</sup>
9/25/2023	Jewett Brook - 01 <sup>a</sup>	0.06 <sup>b</sup>

<sup>&</sup>lt;sup>a</sup> indicates DEC 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, 2024). 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 have been completed at VAEL to decrease the reporting limit for this active ingredient for the 2024 monitoring studies in Vermont. There was one detection of imidacloprid in 2023 above the reporting limit in Addison County (Table 12).

Table 12. Imidacloprid detections by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/28/2023	Little Otter Creek <sup>a</sup>	0.08 <sup>b</sup>

<sup>&</sup>lt;sup>a</sup> indicates DEC sample

The third neonicotinoid analyte that water samples are tested for, thiamethoxam, has a slightly higher EPA NOAEC and LOAEC invertebrate benchmark than the other neonicotinoids tested, 0.74 ppb and 2.23 ppb, respectively. However, this benchmark is still indicative of high toxicity to aquatic invertebrates. There were two detections of thiamethoxam above the reporting limit, but below the NOAEC and LOAEC EPA benchmarks, in late June in Addison County (Table 13).

<sup>&</sup>lt;sup>b</sup> detection concentration exceeds NOAEC and LOAEC value (0.05 ppb)

<sup>&</sup>lt;sup>b</sup> detection concentration exceeds NOAEC (0.01 ppb) and LOAEC (0.03 ppb) values

Table 13. Thiamethoxam detections by site (routine and post-rainfall event sampling), 2023

Date	Site of detection above benchmark	Detected concentration (ppb)
6/28/2023	Little Otter Creek	0.08
0/ 20/ 2023	Otter Creek	0.06

## Correlation with Department of Environmental Conservation Water Quality Testing

The majority of sites in which we have consistently seen positive detections of pesticides are also streams monitored by DEC for water quality and biological conditions. Some have been subsequently listed on Part A of the 303(d) List of <a href="Impaired Waters">Impaired Waters</a> as of July 2022 for aquatic biota use impairment with the source problem listed as sedimentation nutrients from agricultural runoff (Table 14).

Table 14. Monitored Sites on 303(d) List of Impaired Waters

Northwest	North/Central
Jewett Brook - 01 (Lower Newton Road St. Albans)	Otter Creek (Middlebury)*
Jewett Brook - 02 (Lower Newton Road St. Albans)	Little Otter Creek (Ferrisburgh)
Rock River (Highgate)	

<sup>\*</sup> Otter Creek is listed on Part D of the 303(d) List of Impaired Waters for E.coli/contact recreation use and not impaired for aquatic biota

Hungerford Brook monitoring has shown mixed results in recent years, with some sites suggesting impairment and other sites meeting aquatic biota criteria. DEC is aware of the potential for future impairment of this stream and is planning to conduct ongoing assessments, including in 2024. A 2019 assessment of a Hungerford Brook passed biological criteria standards, with parameters just above minimum thresholds and a low relative abundance of sensitive species. A tributary of Hungerford Brook, sampled in 2019, received an assessment of Fair two years in a row, failing to meet aquatic biota criteria. This was primarily due to a very low richness of sensitive taxa and a macroinvertebrate community mainly comprised of enrichment tolerant organisms. The assessment of this tributary noted the stream is stressed due to adjacent land use activities, implying that nearby agricultural fields was potentially causing nutrient runoff. Monitoring in 2023 in lower Hungerford Brook met aquatic biota criteria and was assessed as 'Good', though also had relatively low richness values that kept the site from receiving a higher assessment rating.

Pike River was the only other site that had a positive detection of pesticides during 2023 monitoring. DEC has evaluated this site, but assessments have passed water quality standards. The positive detection at this site was on July 11, 2023, immediately after a major statewide flooding event and may not be correlated with persistent contamination.

#### Conclusions

Overall, the results of select pesticide monitoring in surface water samples from high agricultural use areas in Vermont in 2023 justify continued surveillance and coordination between the Agency of Agriculture, Food and Markets and the Department of Environmental Conservation. Knowing whether there are contaminants in surface water can help guide decisions on where to focus efforts, such as increased monitoring, runoff risk mitigation measures, remediation, or regulation. To better 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 the effect of rainfall events and potential runoff mitigation measures necessary; (2) continue adding analytes to test as new products are introduced and usage changes; (3) conduct agricultural pesticide use inspections to confirm pesticide use is in compliance with labels and the Vermont Rule for Control of Pesticides; and (3) further investigate, in conjunction with DEC, how pesticide use and regulations can help mitigate agricultural impact on impaired water ways in Franklin and Addison County.

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