Vermont Ambient Surface Water Pesticide Monitoring, 2017 – 2021

Vermont Agency of Agriculture, Food & Markets

Public Health & Resource Management Division

2022

Executive Summary

The Public Health and Agricultural Resource Management Division of the Vermont Agency of Agriculture, Food & Markets has been monitoring select surface water sites throughout high agricultural use areas of the state for pesticides over the last five years. The sites were routinely sampled during critical times of the growing season each year. The Vermont Agriculture and Environmental Laboratory analyzed water samples for neonicotinoids, glyphosate, and other commonly used corn herbicides and their derivatives.

- 2 common corn herbicides found at levels above the most conservative EPA aquatic life benchmarks at which no observable adverse effects were seen (NOAEC): atrazine and metolachlor
    - However, atrazine levels did not average above benchmark of 10 ppb for a 60-day period.
    - Mean concentration of metolachlor from 74 national sites and years 2013-2017 was 264 ppb (Stackpoole, Shoda, Medalie, & Stone, 2021). Whereas the Vermont mean metolachlor concentration from 32 state sites and years 2017-2021 was 0.836 ppb.
    - Only one detection of corn herbicides exceeded the Lowest Observable Adverse Effect Concentration (LOAEC) EPA toxicity threshold value for aquatic invertebrates – Metolachlor at 30.4ppb was detected at the Jewett Brook – 01 site in Franklin County in 2019.
- 2 common neonicotinoid insecticides found at levels above the most conservative EPA aquatic life NOAEC benchmarks: clothianidin and imidacloprid
    - 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.
    - Overall detection frequency and concentration (maximum: median) of neonicotinoids across all sites and years followed similar trend as previous research in Midwest US: clothianidin (3.6%, 1.4 ppb: 0.238 ppb) > thiamethoxam (2.4%, 0.575 ppb: 0.198 ppb) > imidacloprid (0.3%, 0.203 ppb: 0.149 ppb)
        - In Iowa, 79 water samples were tested in 2013 for neonicotinoids: clothianidin (75%, 0.257 ppb: 0.008 ppb) > thiamethoxam (47%, 0.185 ppb: <0.002 ppb) > 23% (0.0427 ppb: <0.002 ppb) (Hladik, Kolpin, & Kuivila, 2014)
            - This study had much lower detection limits (3.6 – 6.2 ppt) compared to our reporting limit (50 ppt)
    - None of the clothianidin detections exceeded the LOAEC toxicity threshold value for aquatic invertebrates.
        - The 2 detections of imidacloprid over the five year monitoring period (0.2 ppb in 2017 and 0.09 ppb in 2020) exceeded the NOAEC and LOAEC benchmark toxicity values for aquatic invertebrates and were both detected in Jewett Brook in Franklin County.
- There is a decreasing trend in number of detections found for atrazine, metolachlor, clothianidin, imidacloprid, and thiamethoxam from 2017 to 2021.
- 37 out of 38 detections above the most conservation EPA NOAEC benchmarks were in Franklin County
    - 1 Clothianidin detection in 2021 was above the EPA chronic NOAEC benchmark in Addison County

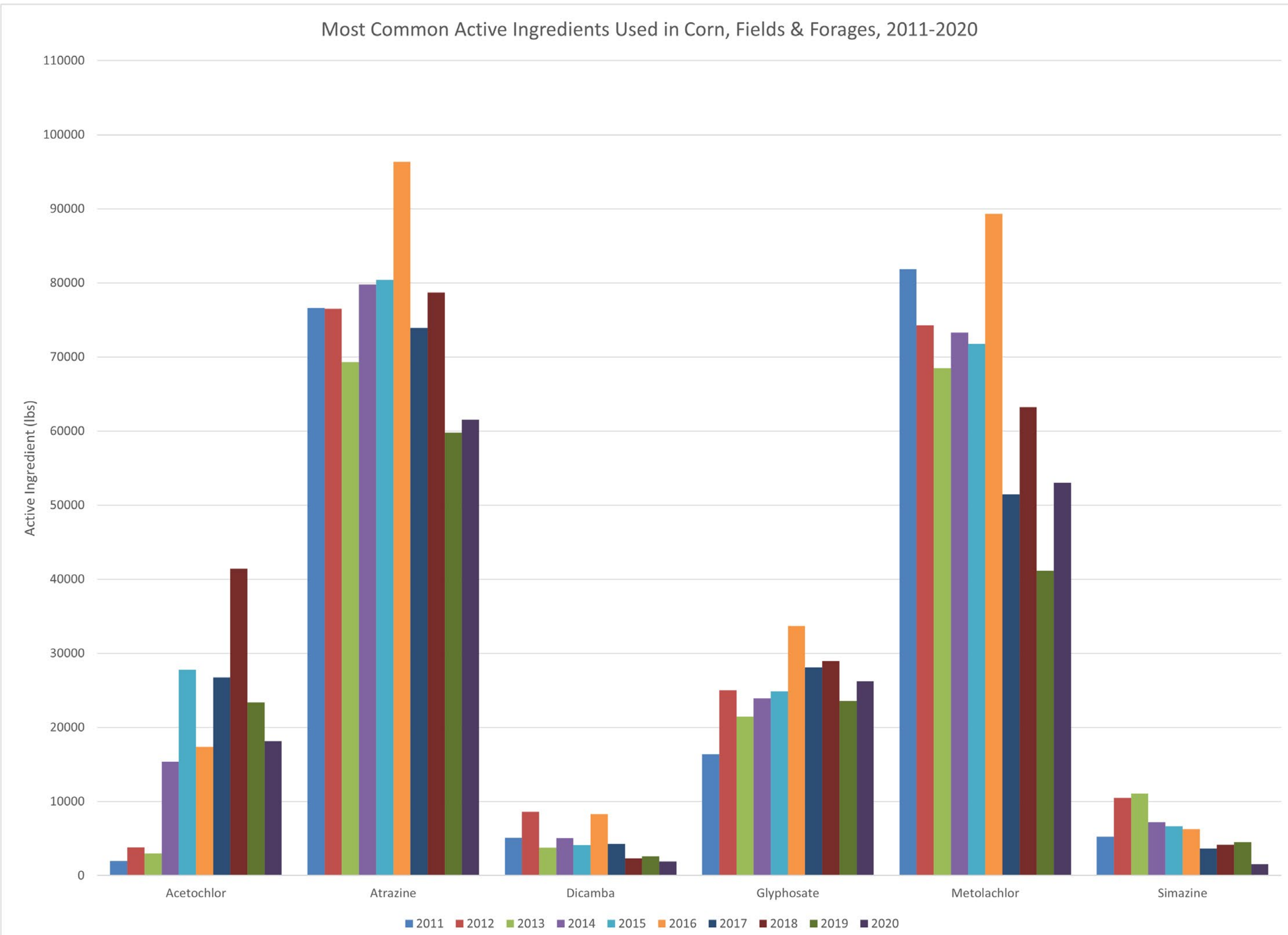
The level of pesticide detections in Vermont's surface water sampling is relatively low, however the data justify continued surveillance. Increased monitoring and expanded testing are warranted in specific locations and are planned in Franklin County in 2022. To fully understand the effects of pesticide 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 of impact on aquatic and other wildlife.

The Public Health and Agricultural Resource Management Division of the Vermont Agency of Agriculture, Food & Markets 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 derivatives (Figure 1). Data from 2017 through 2021 were analyzed and compared to EPA Aquatic Life Benchmarks and Ecological Risk Assessments for registered pesticides (U.S. Environmental Protection Agency, 2021).

Figure 1. Vermont Usage data 2011-2020: Common Active Ingredients used in corn, fields and forages



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

Methods

Samples were collected from 32 sites (some sites changed over the course of the five-year study) by Field Specialists from both Agency of Agriculture, Food & Markets and Department of Environmental Conservation. For routine sampling there were 8 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 taken in both June and July, two weeks apart; and one sample in each month, August, September, and October. Samples collected after rain-fall 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 the Vermont Agriculture and Environmental Laboratory with mostly internally developed methods.

Table 1. Methods and Reporting Limits for Pesticide Active Ingredients Tested, 2017-2021

Pesticide Analyte	Reporting Limit (ppb)[a]	Analysis Method
Acetochlor	0.1	VAEL-Neonic-CHMetabs internal method
Acetochlor ESA	0.05	VAEL-Neonic-CHMetabs internal method
Alachlor	0.1	VAEL-Neonic-CHMetabs internal method
Alachlor ESA	0.05	VAEL-Neonic-CHMetabs internal method
Atrazine	0.05	VAEL-Neonic-CHMetabs internal method
Desethylatrazine	0.05	VAEL-Neonic-CHMetabs internal method
Bicyclopyrone	0.05	VAEL-Neonic-CHMetabs internal method
Clothianidin	0.05	VAEL-Neonic-CHMetabs internal method
Dimethenamid	0.1	VAEL-Neonic-CHMetabs internal method
Dimethenamid ESA	0.05	VAEL-Neonic-CHMetabs internal method
Glyphosate	10	USGS 01-454
AMPA	10	USGS 01-454
Imidacloprid	0.05	VAEL-Neonic-CHMetabs internal method
Mesotrione	0.05	VAEL-Neonic-CHMetabs internal method
Metolachlor	0.05	VAEL-Neonic-CHMetabs internal method
Metolachlor ESA	0.05	VAEL-Neonic-CHMetabs internal method
Simazine	0.1	VAEL-Neonic-CHMetabs internal method
Thiamethoxam	0.05	VAEL-Neonic-CHMetabs internal method

[a] Reporting limit is the smallest concentration of analyte that can be reported by a laboratory

Sampling Sites

Figure 2. Surface Water Collection Sites (Routine Sampling and Post-Rainfall Event Sampling), 2017-2021

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) Missisquoi Bay Lake Champlain (Highgate) Missisquoi Bay Central Lake Champlain (Quebec) Lake Champlain (Burlington) Pike River (Quebec)[a] Missisquoi River (St. Albans)[a] Rock River (Highgate)[a] St. Albans Bay Lake Champlain (St. Albans)	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) Calendar Brook (Sutton) King George Road Stream (Sutton) Station Road Stream (Sutton) Sheffield Road Culvert (Sutton) Burke Road Culvert (Sutton)
Northeast	**Southwest**
Black River (Coventry) Mississquoi 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 rain-fall event sample site

[ab] indicates post rain-fall event sample site and routine sampling site

Routine Sampling Site Descriptions

Hungerford Brook (Highgate)

Samples taken from small pool on north side of road where medium sized stream crosses Wood's Hill Road in Highgate. Upstream landscape consists of primarily agricultural fields (largely corn) with only shrub/perennial grass buffers mixed with some small tracts of forest.

Jewett Brook (Lower Newton Road, St. Albans)

Samples taken from a pool just south of Lower Newton Road where the brook exits a large culvert at a USGS stream monitoring station. Upstream landscape consists of primarily agricultural fields (largely corn) with only shrub/perennial grass buffers mixed with some small tracts of forest.

Mill River Tributary (Georgia)

Samples taken from the south side of Polly Hubbard Road from a medium sized tributary that feeds into the Mill River about 1,000 feet downstream. Upstream landscape consists of a mix of agricultural fields (largely tiled corn fields) interspersed with small, forested tracts.

Otter Creek (Middlebury)

Samples site is on main river at confluence with Middlebury River. Upstream landscape consists of agricultural use areas.

Middlebury River (Middlebury)
Sample Site is approximately 1 mile upstream from Otter Creek site. Upstream landscape consists of agricultural use areas. This site was only sampled in 2021.

Winooski River (Middlesex)
Sample site is on Rt. 2 in Middlesex, approx. 450' south of where rt. 2 intersects rt. 100b. There is a farmstead across the river and slightly upstream that is agricultural land that is no longer in use and cornfields approximately 750' upstream. Buffer consists of perennial vegetation that is narrowest in places along Rt. 2.

Lamoille River (Morristown)
Sample site is in Morrisville at the Morrisville Rotary Access on VT 15. Upstream consists of forested land and areas of agricultural lands (primarily corn).

Little Otter Creek (Ferrisburgh)
Samples taken approximately 3/4 mi. east of Rt. 7 on Satterly Road in Ferrisburgh. Runs through agricultural land (primarily corn) and wetlands. Is characterized as a river with high turbidity.

White River, 2nd Branch (Brookfield)
Samples taken approximately 300 ft. west of Rt. 14 on McKeage Rd. in Brookfield. Upstream buffers consist of wetlands and cropland (largely corn).

Calendar Brook (Sutton)
Samples taken from small, fast moving, shallow book near roadside. Site is downstream from intensive dairy operation and corn fields.

King George Road Stream (Sutton)
Station Road Stream (Sutton)
Sheffield Road Culvert (Sutton)
Burke Road Culvert (Sutton)
Roadside very small stream sampling sites closer to intensive agricultural land area in Sutton.

Black River (Coventry)
Sample site is where Hi-Acres Rd and US Route 5 intersect in Coventry. Upstream landscape is predominantly agricultural lands (corn) and some forested land.

Missisquoi River (Troy)
Sample site is on the River Rd in Troy just south of Big Falls at the intersection with Brown Rd. The large river at this site is very fast moving and well aerated. Site is downstream from a mixture of agricultural land and forested land. There are a significant number of small organic farms along this river.

Passumpsic River (St. Johnsbury)
Sample site is in St. Johnsbury where US Route 5 and Pierce Rd intersect. Upstream landscape consists of agricultural (largely corn), forested, and developed lands.

Battenkill River (Arlington)
Sample site is at the small boat/swimming access on the west side of the covered bridge located on Covered Bridge Rd, just off RT 313. Mixed use of fruit, vegetable, silage corn and forages within 1-2 miles upstream.

Mettawee River (Pawlet)
Samples collected from this shallow, fast moving gravel bed area of the river along the River Rd. Approx. 550 ft. west of the intersection of Betts Bridge Rd and River Rd. in Pawlet. Upstream buffers consist of agricultural (primarily corn) and forested land.

Connecticut River (Newbury)
Sample taken from where the river flows beneath the Newbury Crossing Road. Upstream is mostly agricultural land buffered with woody vegetation.

Williams River (Chester)
Samples taken from this medium sized river adjacent to a corn field.

West River (Brattleboro)
Samples taken, starting in 2021, at a very broad and deep section of this large river. Upstream landscape consists of agricultural (largely corn), forested, and developed lands.

Alburgh Center Lake Champlain [station 46] (Alburgh)
Missisquoi Bay Lake Champlain [station 50] (Swanton)
Missisquoi Bay Central Lake Champlain [station 53] (Philipsburg, Quebec)
Lake Champlain [station 19] (Burlington)
St. Albans Bay Lake Champlain [station 40] (St. Albans)
Diamond Island Lake Champlain [station 09] (Ferrisburgh)
Lake Champlain sampling sites are considerably offshore and accessible by boat only. These sites were sampled every 2 weeks and correspond to numbered lake monitoring stations with the Lake Champlain Long-Term Water Quality and Biological Monitoring Program.

Post Rain-Fall / High Flow Event Sampling Site Descriptions

Pike River (Pike River, Quebec)
Samples taken from a tributary stream monitoring station (PIKE01) established with the Lake Champlain Long-Term Water Quality and Biological Monitoring Program.

Missisquoi River (St. Albans)
Samples taken from a tributary stream monitoring station (MISS01) established with the Lake Champlain Long-Term Water Quality and Biological Monitoring Program.

Rock River (Highgate)
Samples taken from a tributary stream monitoring station (ROCK02) established with the Lake Champlain Long-Term Water Quality and Biological Monitoring Program.

Little Otter Creek (Ferrisburgh)
Samples taken upstream from the bridge on Satterly Road in Ferrisburg. Area upstream is mostly wetlands with some ag fields mixed in. Site corresponds to stream monitoring station LOTT03 established with the Lake Champlain Long-Term Water Quality and Biological Monitoring Program.

Jewett Brook (Lower Newton Road, St. Albans)
Samples taken from a pool just south of Lower Newton Road where the brook exits a large culvert at a USGS stream monitoring station (JEWE02). Upstream landscape consists of primarily agricultural fields (largely corn) with only shrub/perennial grass buffers mixed with some small tracts of forest.

Results & Discussion

There were detections of all the active ingredients and degradates that were routinely tested over the five years of the study: atrazine, desethylatrazine, acetochlor ethanesulfonic acid (ESA), alachlor ESA, bicyclopyrone, clothianidin, glyphosate, imidacloprid, mesotrione, metolachlor, metolachlor ESA, and thiamethoxam (Table 2).

The highest detection frequency (percentage of samples with a detection above the reporting limit) was seen in metolachlor ESA, the degradate of metolachlor, at 72.7% of samples with a positive detection. However, with detections ranging from 0.05 – 16.7 ppb, detections were well below the only established EPA Aquatic Life Benchmark for the analyte. Metolachlor was detected in 15.0% of the samples tested.

Two herbicide and two neonicotinoid insecticide concentrations exceeded the most conservative, No Observable Adverse Effects Concentration (NOAEC) EPA aquatic life benchmarks: atrazine and metolachlor, and clothianidin and imidacloprid, respectively. 37 out of 38 detections above the most conservative NOAEC EPA benchmarks were in Franklin County. And one clothianidin detection in 2021 above the chronic benchmark was in Addison County (Table 3).

In 2021, there were detections of fewer active ingredients and degradates that were routinely tested, and the detection frequencies were lower across the board (Table 4).

Similar trends were seen among the detection frequencies of analytes in 2021 as with previous years. However, only clothianidin was detected with a concentration exceeding the EPA aquatic life NOAEC benchmark.

Table 2. Surface Water monitoring study (routine and post-rainfall event sampling) data summary in comparison to U.S. EPA Aquatic Life benchmark values, 2017-2021

Pesticide Analyte	Samples	Detections	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 (%)	Range of Detections (ppb)
Acetochlor	10	0	0	22.1	USEPA Chronic (i)	0	1.43	USEPA Acute (n)	0	n/a
Acetochlor ESA	584	133	22.8	-	-	n/a	9900	USEPA Acute (n)	0	0.055 - 4.11
Alachlor	11	0	0	110	USEPA Chronic (i)	0	1.64	USEPA Acute (n)	0	n/a
Alachlor ESA	584	52	8.9	-	-	n/a	3600	USEPA Acute (n)	0	0.05 - 0.996
Atrazine	647	88	13.6	10	USEPA CE-LOC	**0.5**	n/a	n/a	n/a	0.037 - 21.8
Desethylatrazine	638	30	4.7	-	-	n/a	-	-	n/a	0.06 - 0.871
Bicyclopyrone	594	4	0.7	10000	USEPA Chronic (f)	0	13	USEPA Acute (v)	0	0.059 - 0.858
Clothianidin	638	23	3.6	0.05	USEPA Chronic (i)	**3.6**	11	USEPA Acute (i)	0	0.059 - 1.4
Dimethenamid	9	0	0	120	USEPA Chronic (f)	0	8.9	USEPA Acute (v)	0	n/a
Dimethenamid ESA	584	0	0	-	-	n/a	-	-	n/a	n/a
Glyphosate	650	2	0.3	25700	USEPA Chronic (f)	0	11900	USEPA Acute (v)	0	12 - 22
AMPA	650	0	0	-	-	n/a	249500	USEPA Acute (f)	0	n/a
Imidacloprid	638	2	0.3	0.01	USEPA Chronic (i)	**0.3**[a]	0.385	USEPA Acute (i)	0	0.094 - 0.203
Mesotrione	594	17	2.9	3055	USEPA Chronic (i)	0	4.8	USEPA Acute (v)	0	0.05 - 0.816
Metolachlor	647	97	15.0	1	USEPA Chronic (i)	**1.5**	8	USEPA Acute (n)	**0.2**	0.05 - 30.4
Metolachlor ESA	638	464	72.7	-	-	n/a	24000	USEPA Acute (f)	0	0.05 - 16.7
Simazine	9	0	0	40	USEPA Chronic (i)	0	6	USEPA Acute (n)	0	n/a
Thiamethoxam	638	15	2.4	0.74	USEPA Chronic (i)	0	17.5	USEPA Acute (i)	0	0.052 - 0.575

[-] 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

CE-LOC = Aquatic plant Concentration Equivalent Level of Concern 10ppb over 60 days

[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. (2021, August 31). 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

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

Table 3. Detection Frequency Above Most Conservative NOAEC Benchmark by Region and Year (Routine and Post-Rainfall Event Sampling), 2017-2021

Pesticide Analyte	Northwest					North / Central				
	2017	2018	2019	2020	2021	2017	2018	2019	2020	2021
Acetochlor	0	0	n/a	n/a	n/a	0	0	n/a	n/a	n/a
Acetochlor ESA	n/a	0	0	0	0	n/a	0	0	0	0
Alachlor	0	0	n/a	n/a	n/a	0	0	n/a	n/a	n/a
Alachlor ESA	n/a	0	0	0	0	n/a	0	0	0	0
Atrazine	0	0	**1.2**	**3.6**	0	0	0	0	0	0
Desethylatrazine	-	-	-	-	-	-	-	-	-	-
Bicyclopyrone	n/a	0	0	0	0	n/a	0	0	0	0
Clothianidin	**20**	**3.3**	**8.4**	**10.7**	0	0	0	0	0	**2.2**
Dimethenamid	0	n/a	n/a	n/a	n/a	0	n/a	n/a	n/a	n/a
Dimethenamid ESA	-	-	-	-	-	-	-	-	-	-
Glyphosate	0	0	0	0	0	0	0	0	0	0
AMPA	0	0	0	0	0	0	0	0	0	0
Imidacloprid	**2.9**[a]	0	0	**1.8**[a]	0	0	0	0	0	0
Mesotrione	n/a	0	0	0	0	n/a	0	0	0	0
Metolachlor	**14.3**	0	**2.4**	**5.4**	0	0	0	0	0	0
Metolachlor ESA	0	0	0	0	0	0	0	0	0	0
Simazine	0	n/a	n/a	n/a	n/a	0	n/a	n/a	n/a	n/a
Thiamethoxam	0	0	0	0	0	0	0	0	0	0

Detection frequency calculated from total number of tests from the sites within the region for each year

No detections above the benchmark were seen in Northeast, Southwest, or East/Southeast regions

[-] no available benchmark for comparison

[n/a] testing was not conducted

[a] May underrepresent detections because most conservative 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, 2021

Pesticide Analyte	Samples	Detections	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 (%)	Range of Detections (ppb)
Acetochlor	0	n/a	n/a	22.1	USEPA Chronic (i)	n/a	1.43	USEPA Acute (n)	n/a	n/a
Acetochlor ESA	143	29	20.3	-	-	n/a	9900	USEPA Acute (n)	0	0.07 - 0.91
Alachlor	0	n/a	n/a	110	USEPA Chronic (i)	n/a	1.64	USEPA Acute (n)	n/a	n/a
Alachlor ESA	143	11	7.7	-	-	n/a	3600	USEPA Acute (n)	0	0.07 - 0.19
Atrazine	143	10	7.0	10	USEPA CE-LOC	0	n/a	n/a	n/a	0.06 - 1.01
Desethylatrazine	143	3	2.1	-	-	n/a	-	-	n/a	0.06 - 0.46
Bicyclopyrone	143	1	0.7	10000	USEPA Chronic (f)	0	13	USEPA Acute (v)	0	0.24
Clothianidin	143	1	0.7	0.05	USEPA Chronic (i)	**0.7**	11	USEPA Acute (i)	0	0.07
Dimethenamid	0	n/a	n/a	120	USEPA Chronic (f)	n/a	8.9	USEPA Acute (v)	n/a	n/a
Dimethenamid ESA	143	0	0	-	-	n/a	-	-	n/a	n/a
Glyphosate	143	1	1	25700	USEPA Chronic (f)	0	11900	USEPA Acute (v)	0	22.0
AMPA	143	0	0	-	-	n/a	249500	USEPA Acute (f)	0	not detected
Imidacloprid	143	0	0	0.01	USEPA Chronic (i)	0[a]	0.385	USEPA Acute (i)	0	not detected
Mesotrione	143	3	2.1	3055	USEPA Chronic (i)	0	4.8	USEPA Acute (v)	0	0.11 - 0.24
Metolachlor	143	9	6.3	1	USEPA Chronic (i)	0	8	USEPA Acute (n)	0	0.05 - 0.48
Metolachlor ESA	143	74	51.7	-	-	n/a	24000	USEPA Acute (f)	0	0.05 - 16.7
Simazine	0	n/a	n/a	40	USEPA Chronic (i)	n/a	6	USEPA Acute (n)	n/a	n/a
Thiamethoxam	143	0	0	0.74	USEPA Chronic (i)	0	17.5	USEPA Acute (i)	0	not detected

[-] 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

CE-LOC = Aquatic plant Concentration Equivalent Level of Concern 10ppb over 60 days

[n/a] testing was not conducted

[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. (2021, August 31). 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

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

The data of samples taken during routine sampling (base flow conditions) were analyzed separately from samples taken after rain-fall events (high flow conditions) to see if the collection after rain-fall events skewed towards higher detections. There were slightly lower detection frequencies, but 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. Since the high flow events were not specifically tied to an amount of rain, and all sites were sampled even if one showed an increase in flow, there isn't clear data to show that the timing of sampling influenced detections. A future study correlating flow rates with detection concentrations could more specifically answer the question of if rain-fall events cause higher pesticide presence in surface water or if the higher flow rates result in increased dilution of pesticides in surface water.

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, 2021). The values reflect the No Observable Adverse Effect Concentration (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 sensitive long duration of exposure. To evaluate risk to aquatic resources, the LOAEC, or Lowest Observable Adverse Effect Concentration, 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)

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	3.4	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

[a]Source: U.S. Environmental Protection Agency. (2021, August 31). 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 this surface water pesticide monitoring data is revisited and compared to LOAEC values, there are only 3 total detections exceeding this more practical benchmark for the active ingredients that exceeded NOAEC values (Table 6). Metolachlor had one detection exceed the LOAEC value for aquatic invertebrates. The sample was taken at the Jewett Brook – 01 site in Franklin County in 2019. The two imidacloprid detections from 2017 and 2020 also exceeded the LOAEC value, because this benchmark also falls below the reporting limit of 0.05 ppb.

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, 2017-2021

Pesticide Analyte	Samples	Detections	Detection Frequency (%)	EPA Chronic LOAEC Aquatic Life Benchmark (ppb)[a]	EPA Benchmark Type	Detection Frequency Above EPA Chronic LOAEC Benchmark (%)	Range of Detections (ppb)
Atrazine	647	88	13.6	50	USEPA Chronic (f)	0	0.037 - 21.8
Metolachlor	647	97	15.0	10	USEPA Chronic (i)	**0.2**	0.05 - 30.4
Clothianidin	638	23	3.6	3.4	USEPA Chronic (i)	0	0.059 - 1.4
Imidacloprid	638	2	0.3	0.03	USEPA Chronic (i)	**0.3**[b]	0.094 - 0.203

(f) LOAEC benchmark value for fish

(i) LOAEC benchmark value for invertebrates

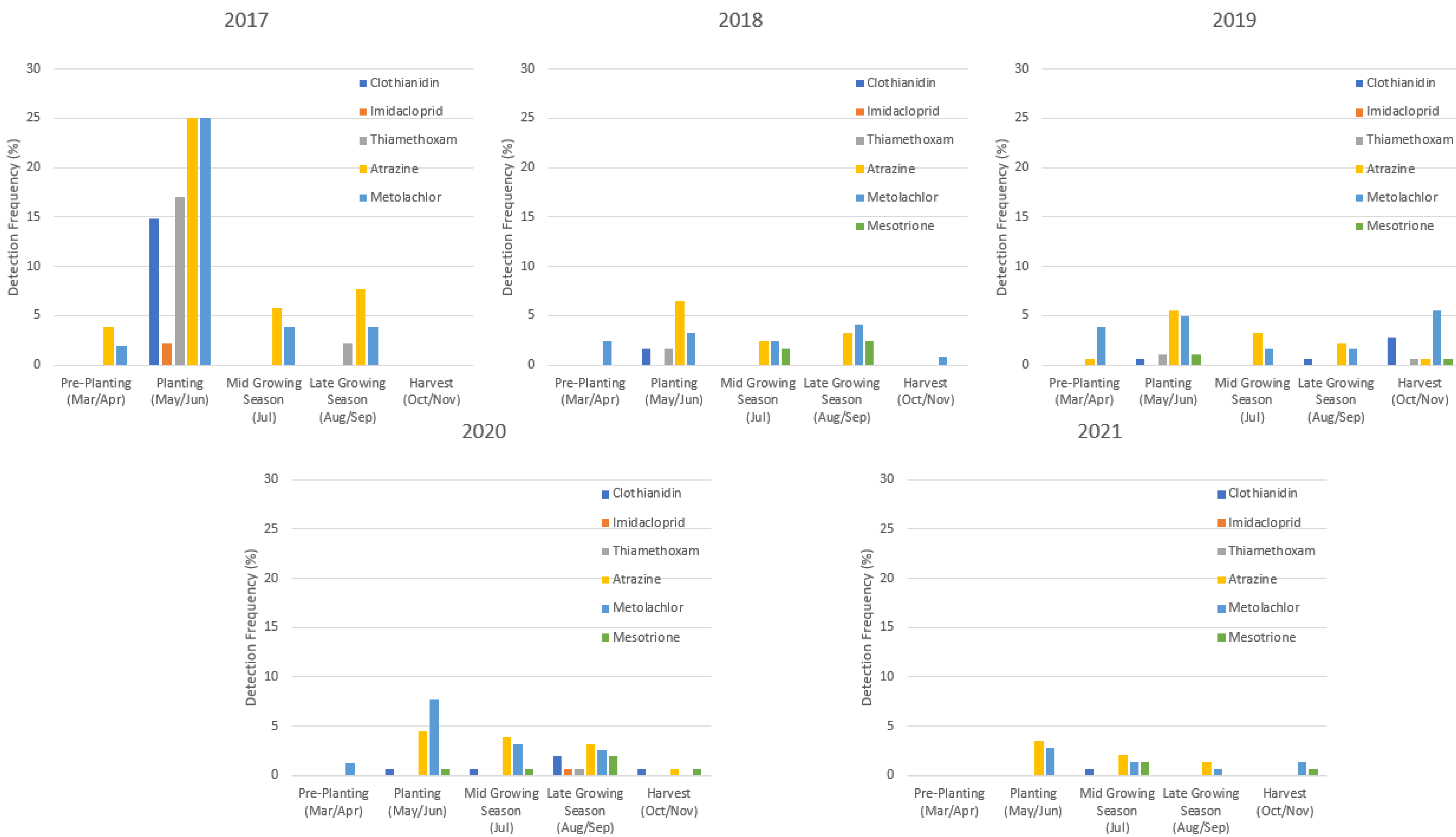
[a]Source: U.S. Environmental Protection Agency. (2021, August 31). Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. Retrieved from https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

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

Seasonal Patterns

Detection frequencies for the parent pesticides that were most commonly found in this study were analyzed to see if there was a seasonal pattern (Figure 3). Atrazine was detected more frequently during planting time (May/June) with decreasing detections as the growing season progressed. A similar trend was seen with metolachlor, except for in 2019 when there was an outlier increase in detection frequency during harvest time. The neonicotinoid insecticides had lower detection frequencies and did not show as clear of a seasonal pattern.

Figure 3. Seasonal Patterns in Detection Frequency of Parent Pesticides, 2017-2021



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 a lot of homeowner use. Because it has become an issue of public concern, surveillance efforts were greatly increased in the past few years. There were two detections of glyphosate, one in 2020 found in Franklin County and one in 2021 in Orleans County. The concentrations found (12 - 22 ppb) were significantly below both chronic and acute EPA aquatic life benchmarks (25.7 ppm, 11.9 ppm). There have not been any detections of aminomethylphosphonic acid (AMPA), a degradate of glyphosate over the last five years. The surface water monitoring program in Minnesota detected glyphosate in 15% of samples in 2020, which is significantly higher than Vermont's 0.3% statewide detection frequency (Bischof, et al., 2021).

Corn Herbicides, and their degradates, accounted for most of the detections in this study. Atrazine has a half-life in soil around 60 days, but this can vary based on soil characteristics. Half-life of atrazine can range from 39 to 261 days (Hartzler, n.d.). Atrazine, and its degradate desethylatrazine, were detected in 13.6% and 4.7% of samples tested over the five-year study, respectively. Most of these samples were detected early in the growing season (May/June). This is significantly lower in comparison to the 2020 Minnesota surface water data of a statewide detection frequency of 61% (Bischof, et al., 2021). The EPA currently regulates on an aquatic plant Concentration Equivalent Level of Concern of 10 ppb average concentration over 60 days (U.S. Environmental Protection Agency, 2021). The detection above the level of concern in 2019 was sampled at the Jewett Brook – 01 site on June 21 (21.8 ppb) and the next sample taken from this site that measured above the detection limit was 103 days later, on October 2 at 0.095 ppb. Therefore, the average over 60 days was below the level of concern. The atrazine detections above 10 ppb in 2020 were measured in Hungerford Brook on June 1 (11.8 ppb) and Jewett Brook on August 6 (21 ppb). However, the Hungerford Brook was sampled three additional times over the next 60 days and the average concentration of atrazine detected was 3.16 ppb. The Jewett Brook was only sampled 34 days later and averaged 11.8 ppb, but if we assume the similar trend of decreasing concentrations and detections as the growing season progresses it is highly possible that detections would be below the level of concern after 60 days. There were no detections that exceeded the LOAEC chronic benchmark values indicating that risk to aquatic resources from atrazine toxicity is very low.

Table 7. Atrazine detections by year and site (routine and post-rainfall event sampling), 2017-2021

	Samples	Detections	Detections above CE-LOC benchmark	Site of detection above benchmark	Date
2017	52	22	0	n/a	n/a
2018	116	15	0	n/a	n/a
2019	180	22	1	Jewett Brook - 01[a]	6/21/2019
2020	156	19	2	Hungerford Brook Jewett Brook - 02	6/1/2020 8/6/2020
2021	143	10	0	n/a	n/a

[a] indicates post rain-fall event sample

no detections exceeded chronic LOAEC benchmarks

Metolachlor is characterized as moderately persistent to persistent in soil with 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 87% over this five-year study. This is consistent with other surface water pesticide monitoring studies for the Northeast region of the U.S. (Stackpoole, Shoda, Medalie, & Stone, 2021) as well as with data from the 2020 Minnesota surface water monitoring program (Bischof, et al., 2021). The most conservative EPA chronic aquatic life benchmark is for invertebrates at 1 ppb, the lowest concentration at which there were no observed adverse effects over a life-cycle test with select invertebrates. The Jewett Brook – 01 site (sampled at high flow events) averaged above this benchmark throughout the growing seasons of 2017, 2019 and 2020, but was below 1 ppb in 2018 and 2021. The other tributary sites sampled during high flow events, Rock River and Pike River, in addition to Hungerford Brook and routine sampling on Jewett Brook, resulted in metolachlor concentrations above this threshold during this study. These results correlate to regional surface water data throughout the U.S. Metolachlor, with the second highest herbicide usage in US (2013-2017), was present in high enough concentrations to exceed chronic invertebrate benchmarks in over 40% of the national sites (Stackpoole, Shoda, Medalie, & Stone, 2021). However, the mean concentration from these 74 national sites and years 2013-2017 was 264 ppb. Whereas the Vermont mean concentration from 32 state sites and years 2017-2021 was 0.836 ppb. One detection, sampled in 2017, exceeded the LOAEC chronic aquatic benchmark, but this concentration level of metolachlor was not consistently found.

Table 8. Metolachlor Detections by year and site (routine and post-rainfall event sampling), 2017-2021

	Samples	Detections	Detections above NOAEC benchmark	Site of detection above benchmark	Date
2017	52	18	5	Rock River[a]	6/7/2017
				Jewett Brook - 01[a]	6/7/2017, 6/20/2017, 6/30/2017
				Pike River[a]	6/20/2017
2018	116	16	0	n/a	n/a
2019	180	32	2	Rock River[a]	6/6/2019
				Jewett Brook - 01[a]	**6/21/2017[b]**
2020	156	23	3	Hungerford Brook	6/1/2020
				Jewett Brook - 02	8/6/2020
				Jewett Brook - 01[a]	8/5/2021
2021	143	7	0	n/a	n/a

[a] indicates post rain-fall event sample

[b]detection concentration exceeds LOAEC value (30.4 ppb)

Neonicotinoid insecticide usage in Vermont is significantly lower than in top corn and soybean producing states. However, since this class of insecticide is under increased scrutiny recently for potentially adversely affecting pollinators, it is important to monitor to determine if the pesticides are traveling off-site.

Overall detection frequency and concentration (maximum: median) of neonicotinoids followed similar trend as previous research in Iowa: clothianidin (3.6%, 1.4 ppb: 0.238 ppb) > thiamethoxam (2.4%, 0.575 ppb: 0.198 ppb) > imidacloprid (0.3%, 0.203 ppb: 0.149 ppb). In Iowa, the top producer of corn and soybeans in U.S., 79 surface water samples were tested for neonicotinoids in 2013: clothianidin (75%, 0.257 ppb: 0.008 ppb) > thiamethoxam (47%, 0.185 ppb: <0.002 ppb) > 23% (0.0427 ppb: <0.002 ppb) (Hladik, Kolpin, & Kuivila, 2014). However, this study had much lower detection limits (3.6 – 6.2 ppt) compared to our reporting limit (50 ppt), potentially inflating their detection frequencies, and lowering concentration medians. The trend in detection frequency and concentration seen in Vermont does not correspond to the average yearly (2017-2020) usage of these insecticides in the state: imidacloprid (1028 lbs/yr) > clothianidin (15.7 lbs/yr) > thiamethoxam (7.9 lbs/yr). This could be because clothianidin is extremely persistent in the environment compared to the other two neonicotinoid compounds with a half-life range of 148 to 1,155 days (Federoff, Liu, Patrick, & Khan, 2009).

Imidacloprid poses a severe threat to aquatic invertebrates as evidence from the very conservative EPA chronic NOAEC and LOAEC invertebrate benchmark of 0.01 ppb (10 ppt) and 0.03 (30 ppt), respectively (U.S. Environmental Protection Agency, 2021). The reporting limit for samples tested for imidacloprid in this study was 0.05 ppb (50 ppt) and therefore results are potentially an underrepresentation of detection frequency and detections exceeding the EPA aquatic benchmarks. Method changes are in process to lower the reporting limit for this active ingredient for future monitoring studies in the state.

Clothianidin also is toxic to aquatic invertebrates and therefore has a very low EPA chronic NOAEC aquatic benchmark at 0.05 ppb (U.S. Environmental Protection Agency, 2021). Since this benchmark is equivalent to the reporting limit for this study, every detection of clothianidin exceeded the NOAEC benchmark. However, the same toxicity study that determined no observable adverse effects at 0.05 ppb found the Lowest Observable Adverse Effect Concentration (LOAEC) to be 3.4 ppb. No detections found in this study exceed this LOAEC benchmark.

There was a similar decreasing trend from 2017 through 2021 in overall detections for clothianidin and thiamethoxam. Thiamethoxam, however, had no detections exceed either the NOAEC or LOAEC chronic benchmark thresholds.

Table 9. Clothianidin detections by Year and Site (routine and post-rainfall event sampling), 2017-2021

	Samples	Detections	Detections above NOAEC benchmark[a]	Site of detection	Date of detection
2017	43	7	7	Rock River[b] Jewett Brook - 01[b] Pike River[b]	6/7/2017, 6/20/2017, 6/30/2017 6/7/2017, 6/20/2017, 6/30/2017 6/20/2017
2018	116	2	2	Hungerford Brook Hungerford Brook (Woods Hill Rd)	6/13/2018 6/26/2018
2019	180	7	7	Jewett Brook - 01[b] Mill River Tributary Hungerford Brook	6/21/2019, 10/2/2019, 10/18/2019, 11/1/2019 9/10/2019, 10/2/2019 10/2/2019
2020	156	6	6	Jewett Brook - 01[b] Hungerford Brook Jewett Brook - 02	8/5/2020 6/1/2020, 8/6/2020, 10/6/2020 7/14/2020, 8/6/2020
2021	143	1	1	Little Otter Creek	7/6/2021

[a] most conservative aquatic life benchmark (USEPA Chronic Invertebrate, 0.05 ppb) is equivalent to reporting limit

[b] indicates post rain-fall event sample

no detections exceeded chronic LOAEC benchmarks

Table 10. Imidacloprid detections by year and site (routine and post-rainfall event sampling), 2017-2021

	Samples	Detections	Detections above NOAEC benchmark[a]	Site of detection	Date of detection
2017	43	1	1	Jewett Brook - 01[b]	**6/7/2017[c]**
2018	116	0	0		
2019	180	0	0		
2020	156	1	1	Jewett Brook - 02	**8/6/2020[d]**
2021	143	0	0		

[a] most conservative aquatic life benchmark (USEPA Chronic Invertebrate, 0.01 ppb) is lower than reporting limit (0.05 ppb)

[b] indicates post rain-fall event sample

[c]detection concentration exceeds LOAEC value (0.203 ppb)

[d]detection concentration exceeds LOAEC value (0.094 ppb)

Table 11. Thiamethoxam detections by year and site (routine and post-rainfall event sampling), 2017-2021

	Samples	Detections	Detections above NOAEC benchmark[a]	Site of detection	Date of detection
2017	43	9	0	Mill River Tributary Pike River[b] Rock River[b] Jewett Brook - 01[b]	9/14/2017 6/7/2017, 6/20/2017, 6/30/2017 6/7/2017, 6/20/2017 6/7/2017, 6/20/2017, 6/30/2017
2018	116	2	0	Hungerford Brook Hungerford Brook (Woods Hill Rd)	6/13/2018 6/26/2018
2019	180	3	0	Jewett Brook - 01[b] Little Otter Creek	6/21/2019, 10/2/2019 6/21/2019
2020	156	1	0	Jewett Brook - 02	8/6/2020
2021	143	0	0		

[a] most conservative aquatic life benchmark (USEPA Chronic Invertebrate, 0.74 ppb)

[b] indicates post rain-fall event sample

no detections exceeded chronic LOAEC benchmarks

An identified gap in Vermont's usage data for neonicotinoids is the lack of data on seeds treated specifically with neonicotinoids. If this data is tracked in the future, there may be more correlations that can be made between usage and surface water active ingredient detection and concentration results.

Conclusions

Overall, the results of select pesticide monitoring in surface water samples from high agricultural use areas of the state from 2017-2021 justify continued surveillance is necessary. Knowing if there are contaminants in surface water can help guide decisions on where to focus our efforts, such as increased surveillance, remediation, or regulation. In order to fully understand the effects of pesticide applications on the water quality in ambient surface water in Vermont high agricultural use areas we recommend future studies: 1) correlate stream flow data with analyte concentrations to better understand effect of rain-fall events; 2) revise methods to detect lower levels of imidacloprid and clothianidin to be able to accurately determine toxicity to aquatic invertebrates; 3) continue to add analytes to test as new products are introduced and state usage changes; and 4) further investigate why Franklin county is location showing most detections exceeding the most conservative EPA aquatic life benchmarks.

References

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

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.

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. (2021, August 31). *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

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

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.