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Research Article
Field Evaluation and Modeling Approaches Used to Understand the Transport of Pyrethroid Insecticides out of Pennsylvania Vineyards

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Abstract

Background and Objective: Pyrethroid insecticides are commonly deployed across the globe to combat grape pests, yet little is known regarding the environmental risk associated with runoff from vineyards. Therefore, the objective was to quantify accumulation, transport, and environmental fate of a common-use pyrethroid (bifenthrin) administered to concord grapes in a research vineyard in northwestern Pennsylvania. **Materials and Methods:** Bifenthrin was applied to concord grape vines at three recommended application rates three times during the growing season (July, August, September), with soil samples collected at one- and 14-days post-spray. Using 24 h single-point Tenax extractions, the bioaccessible fraction of bifenthrin in soil samples was analyzed. Furthermore, the potential risk of runoff and transport into local waterbodies was modeled. To validate the results of the model, sediment and water samples were collected from three local streams in close proximity to vineyards. **Results:** Bifenthrin in field-collected soils increased over the growing season, with higher detection frequencies in rows with higher application rates. While the model predicted runoff to adjacent water bodies and potential toxicity to non-target species, no bifenthrin was detected in field-collected stream samples (water and sediment). **Conclusion:** The hydrology of local streams likely protects from bifenthrin accumulation, thus reducing the environmental risk of pyrethroid use in Pennsylvania vineyards.

INTRODUCTION

Insecticides used in urban and agricultural applications are known to accumulate in surrounding freshwater environments, causing toxicity to non-target aquatic organisms. The environmental transport and fate of agrochemicals are highly dependent upon the chemical properties, with the insecticidal class being a strong factor in dictating environmental risk. One class of insecticides that is of environmental concern both nationally and globally are pyrethroids[1-7]. Functioning as potent neurotoxins, pyrethroid insecticides are widely applied in both urban and agricultural applications to control pest invertebrate species while posing little risk to co-exposed mammals and birds[8-16]. Through spray drift during application and runoff of surface soils during rain events, pyrethroids often enter freshwater environments, where they pose a significant risk to non-target invertebrate species[7,13]. For example, an analysis of sediments collected from water bodies surrounding agricultural areas in California revealed 75% of samples were contaminated with pyrethroid insecticides; these environmental concentrations caused significant toxicity to aquatic invertebrates during laboratory tests[17]. Similar phenomena have been observed in aquatic ecosystems across the United States, including Tennessee, Texas, Illinois, Massachusetts and Wisconsin[11,14,18-19]. Such contamination is expected to alter the health of aquatic ecosystems by affecting the invertebrate community structure, potentially leading to pyrethroid resistance in non-target invertebrate species. The evolution of resistance in primary consumers could result in biomagnification through the aquatic food web, posing risk to higher-order species traditionally thought to be protected from such hydrophobic chemicals.

Within the viticulture industry, pyrethroid insecticides are commonly applied to grapevines in order to control populations of pest invertebrate species[20-23]. To combat the decline in crop yield caused by the presence of pests, viticulturists traditionally apply insecticides multiple times per year, the timing of which is based on the emergence of adult insects. The frequent application of insecticides leads to the potential for unintended transport of such chemicals into surrounding freshwater ecosystems through field runoff, as well as the contamination of groundwater by vertical transport through the soil. Considering the recreational and commercial value of freshwater ecosystems and the well-documented risk of pyrethroid usage[1-7,11,14,18-19], investigating the degree to which these insecticides migrate from vineyards to freshwater ecosystems is a justified concern. Therefore, the goal of the current research was to quantify the accumulation, transport and environmental fate of a common-use pyrethroid insecticide, bifenthrin, administered at three recommended application rates using field sampling and modeling approaches.

MATERIALS AND METHODS

Experimental design: To document the accumulation of bifenthrin in soils of Pennsylvania vineyards and local streams, a commonly used pesticide formulation containing bifenthrin (Sniper (Loveland Products, Inc., Loveland, CO, USA)) was applied to concord grapes grown at a research vineyard (North East, PA, USA) in July, August and September of 2018, soil samples were collected in June, July, August and September of 2018 and local streams were sampled in September 2019 (Fig. 1). Three application rates were applied using a block design to document any effect that the application rate had on pyrethroid accumulation within surface soils (Fig. 2). Each application rate treatment was replicated three times (Fig. 2). Preliminary soil sampling was conducted in June 2018 prior to the first spray event to determine any residual bifenthrin concentrations present within the soil from the previous growing season. The specific dates on which spray events occurred and when soil samples were collected are documented in Supplemental Information (Supplemental Table S1).

Chemicals: Bifenthrin and octachlorobiphenyl (polychlorinated biphenyl (PCB)-204) were purchased as individual compounds from AccuStandard, Inc. (New Haven, CT, USA) and were used for analytical chemistry (e.g., calibration curves, matrix spikes). Bifenthrin-d6, which was used as an internal standard, was purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA). Tenax (60-80 mesh) was purchased from Scientific Instrument Services, Inc. (Ringoes, NJ, USA). Anhydrous sodium sulfate, hexane and acetone (Optima grade) and acetic acid (glacial grade) were purchased from Thermo-Fisher Scientific (Waltham, MA, USA).

Collection of soil samples: To document bifenthrin accumulation within soils of Pennsylvania vineyards, soil

Table S1: Dates when Sniper was applied to treatment rows within the vineyard at LERGREC, as well as dates of subsequent soil sample collection

Spray date	Sample date post spray 1-d	Sample date post spray 14-d
July 04, 2018	July 05, 2018	July 20, 2018
August 3, 2018	August 4, 2018	August 17, 2018
August 31, 2018	September 1, 2018	September 18, 2018

Fig. 1: Map of research vineyard
A visual depiction of the location of the Lake Erie Regional Grape Research and Extension Center (LERGREC) in North East, Pennsylvania. Map was generated using images from Google Maps (Map data: Google, Maxar Technologies, © 2020)

Fig. 2: Experimental application of bifenthrin to the grape vines within the research plot
Each block contains replicate rows of the three experimental application rates separated by buffer rows that received no pyrethroid sprays to minimize spray drift. Each block of treatment rows was separated by three untreated buffer rows ("block buffers")
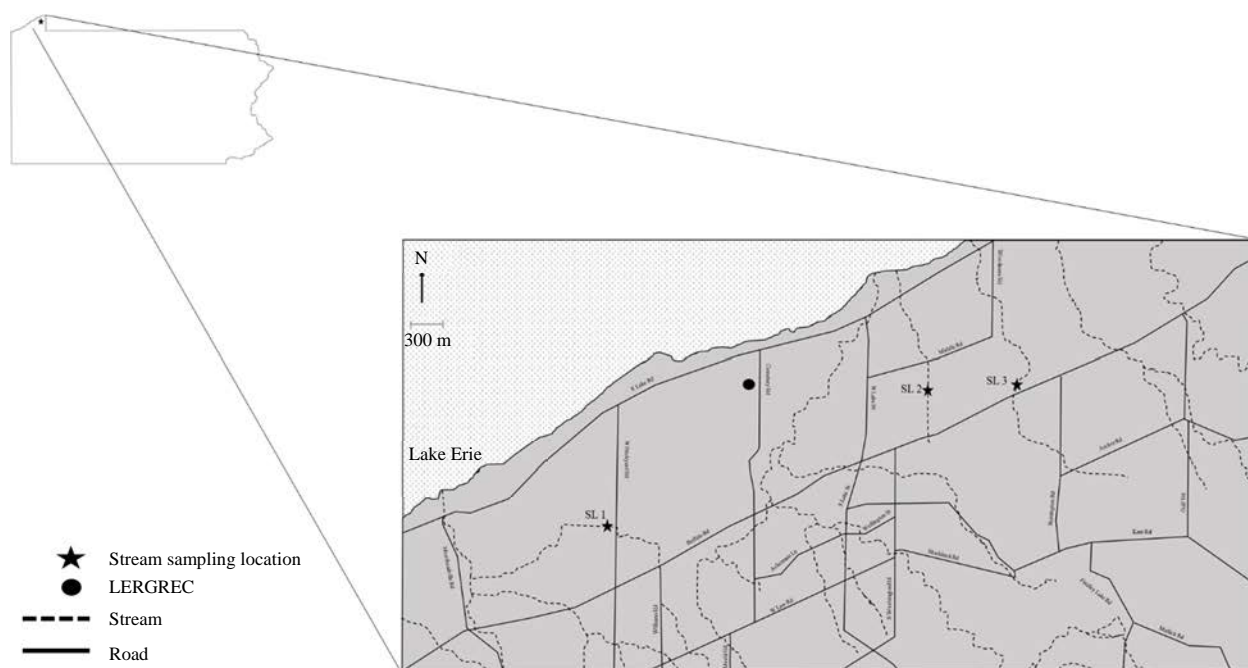
Fig. 3: Map of stream sampling locations within North East, Pennsylvania
Map was generated using images from Google Maps (Map data: Google, Maxar Technologies, © 2020)

samples were collected from all treatment rows (excluding block buffer rows) 1- and 14-days post spray (Fig. 2). Within each treatment row, three locations were haphazardly selected and surface soil samples (<2 cm in depth) were scooped into glass jars using a stainless-steel trowel. Soil samples were passed through a 2 mm sieve to remove large debris and stored at 4°C until analysis. Soil organic carbon (OC) content was determined by Midwest Laboratories, Inc. (Omaha, NE, USA) using the Association of Occupational and Environmental Clinics method (AOEC, 993.13).

Collection of stream water and sediment samples: Three streams adjacent to local vineyards were selected as sites for pyrethroid analysis (Fig. 3). At each site, sediment and water samples were collected in glass jars and samples were stored at 4°C until analysis.

Single-point tenax extractions (24 h): Twenty-four-hour single-point Tenax extractions were used to determine the bioaccessible concentration[24] of bifenthrin present within the soil, sediment and water samples following methods adapted from Nutile *et al*.[25] Briefly, three grams (dry weight) of soil/sediment was weighed into a glass vial, mixed with moderately hard water (MHW)[26] and 0.5 g of Tenax and

rotated for 24 h. Water samples (15 mL) were mixed with 0.5 g of Tenax in a glass vial and rotated for 24 h. Technical replicates (n = 2) of each sample were extracted. Matrix spike and laboratory blank samples (n = 3) were included with every 30 samples for quality control purposes and prepared in the same manner as field-collected samples, with the use of clean reference soil/sediment in place of field-collected soil/sediment. After 24 h, the Tenax beads were removed and placed in glass scintillation vials containing 5 mL of acetone. To ensure complete extraction and recovery of any pyrethroids bound to the Tenax beads, 50 ng of surrogate, PCB-204, was added to each collection vial, including all field and quality control samples. Matrix spike samples also received 50 ng of bifenthrin. The bifenthrin sorbed to the Tenax beads was removed using four washes with organic solvents (acetone, acetone: hexane) and sonication. Samples were concentrated under a steady stream of nitrogen, solvent exchanged with to hexane and concentrated. To remove water from the samples, the solvent layer was transferred to a clean vial and the aqueous layer was washed twice with hexane. Samples were then mixed with 0.5 g of sodium sulfate, concentrated to 1 mL under a steady stream of nitrogen, quantitatively transferred to gas chromatography (GC) vials and concentrated to 1 mL for final analysis. All

samples were acidified with 1 µL acetic acid prior to analysis with a GC-MS to stabilize isomer ratios.

Pyrethroid concentration analysis via. GC-MS: To determine the bifenthrin concentration present within each sample, a 7890B Agilent Gas Chromatograph equipped with a 5977 mass spectrometer (Agilent Technologies, Palo Alto, CA, USA), operated in electron ionization (EI) mode, was used following methods adapted from Nutile *et al.*[25] Deuterated (d-6) bifenthrin was used as an internal standard for standardization of response in calibration standards and field-collected/quality control samples. The surrogate, PCB-204, was quantified using an external calibration curve with no internal standard. Bifenthrin, the internal standard and the surrogate were identified using known retention times, the respective quantitation ion for each compound, specific ion ratios and at least one qualifier ion for each compound.

Modeling of bifenthrin runoff from pennsylvania vineyards: Pesticide in Water Calculator (PWC) Modeling Software (Version 1.52, United States Environmental Protection Agency (USEPA), Washington, DC, USA) was used to evaluate the potential for runoff containing bifenthrin was modeled using the three application rates utilized in the current study. Estimated runoff to a USEPA Standard Pond (1 ha, 20,000 m³, 2.00 m deep water body) and USEPA Index Reservoir (5.26 ha, 146,630 m³, 2.74 m deep water body) draining from a 10-hectare vineyard located in New York, USA, the closest location available within the scenarios of the model, was used to predict the accumulation of bifenthrin in water bodies surrounding vineyards of northwestern Pennsylvania. The specific chemical properties and application rates utilized in the model are summarized for bifenthrin in Supplemental Table S2.

Table S2: Pesticide Water Concentration (PWC) model parameters for bifenthrin applied to a standard New York vineyard at three application rates

Parameter	Input value
Scenario	NYGrapesSTD
Organic carbon to water partition coefficient (K_{OC})	776,247.12 mL g^{-1}
Benthic half-life at 20°C	365 d
Photolysis half-life @ at 42.1292° Latitude	316 d
Soil half-life at 20°C	85 d
Molecular weight	422.87 g mol^{-1}
Vapor pressure	1.335E-8 torr
Solubility	0.1 mg L^{-1}
Henry's constant	3.04E-6
Application rate (Low)	0.056 kg/hA A.I.
Application rate (Moderate)	0.084 kg/hA A.I.
Application Rate (High)	0.112 kg/hA A.I.

RESULTS

Quality control and assurance: Average surrogate recovery from soil samples ranged from 62.62 to 182.9%. The wide variability in surrogate recovery is likely due to either over-enrichment (recoveries>120%) or under-enrichment (recoveries<80%) during sample processing, or matrix interactions during sample analysis. Recovery of bifenthrin from matrix spike samples ranged from 90.18 to 152.32%, which is more in line with expected recoveries (80 to 120%). Matrix interference from reference sediment made quantification of bifenthrin in some quality control samples difficult. The average surrogate recovery of sediment and water samples ranged from 78.46 to 87.45%. The average recovery of bifenthrin from matrix spike samples was 91.26±4.67% (mean±standard deviation, n = 3).

Presence of pyrethroids in vineyard soils: The bifenthrin soil concentrations measured from samples collected during pre- and post-spray events are summarized in Table 1. Bifenthrin was not detected in June soil samples (Table 1). Similarly, no bifenthrin was detected in any of the soil samples collected from the buffer rows during the growing season (Table 1). The presence of bifenthrin in the treatment rows, however, increased throughout the growing season (Table 1). During July sampling, bifenthrin was found only in the High treatment row of Block III, while August sampling revealed bifenthrin in the High and Low treatment rows of Block I, the High, Medium and Low treatment rows of Block II and the High and Medium treatment rows of Block III (Table 1). During September sampling, bifenthrin was detected in all three treatment rows of the three Blocks during at least one of the two sampling events (Table 1). When bifenthrin was detected in treatment rows, however, the concentrations did not show any clear trend in relation to soil collection date post-spray or application rate (Table 1).

Modeled and measured accumulation of bifenthrin stream sediments and waters: Bifenthrin concentrations within the USEPA Standard Pond estimated according to the PWC model at the three application rates are summarized in Table 2. As expected, the bifenthrin concentrations in the Standard Pond declined as the application rate declined, with peak (1-in-10 year) bifenthrin concentrations of 10.1, 7.61 and 5.07 ng mL^{-1} in the high, moderate and low application treatments, respectively (Table 2).

The bifenthrin concentrations accumulating within the waters of the USEPA Standard Reservoir estimated by the PWC

Table 1: Concentration of bifenthrin in soil samples collected from experimental blocks and treatment rows from the vineyard (LERGREC)

Block	Treatment	June	July PS-1	July PS-14	August PS-1	August PS-14	September PS-1	September PS-14
I	High	ND	ND	ND	6.682 (13.61)[b]	ND	30.109 (21.15)[c]	ND
	Medium	ND	ND	ND	ND	ND	ND	4.688 (111.20)[c]
	Low	ND	ND	ND	ND	4.722 (16.85)[b]	8.977 (23.64)[b]	1.840 (1.526)[d]
	Buffer 1	ND	ND	ND	ND	ND	ND	ND
	Buffer 2	ND	ND	ND	ND	ND	ND	ND
II	High	ND	ND	ND	3.447 (46.67)[b]	1.370 (138.50)[b]	7.811 (27.54)[c]	5.487 (80.09)[d]
	Medium	ND	ND	ND	ND	3.554 (118.30)[c]	3.908 (3.98)[b]	2.475 (66.96)[c]
	Low	ND	ND	ND	ND	1.650 (24.92)[b]	ND	2.082 (47.98)[b]
	Buffer 1	ND	ND	ND	ND	ND	ND	ND
	Buffer 2	ND	ND	ND	ND	ND	ND	ND
III	High	ND	ND	2.677 (8.85)[b]	3.515 (2.725)[d]	3.671 (11.41)[b]	11.725 (4.280)[d]	6.488 (63.83)[c]
	Medium	ND	ND	ND	ND	2.951 (79.41)[c]	2.359 (849.3)[d]	ND
	Low	ND	ND	ND	ND	ND	3.829 (14.72)[d]	ND
	Buffer 1	ND	ND	ND	ND	ND	ND	ND
	Buffer 2	ND	ND	ND	ND	ND	ND	ND

Pre- And Post-Spray Events PS1, PS 14, All concentrations are reported as µg g^{-1} organic carbon (dry weight), [a]ND: Not detected, pyrethroid was not detected in soils according to mass spectrum and retention times of these compounds, [b]Present: Pyrethroid was detected in two technical replicates from one of three soil samples collected from treatment row, values in parentheses represent relative percent difference between technical replicates, [c]Present: Pyrethroid was detected in two technical replicates from two of three soil samples collected from treatment row, values in parentheses represent relative percent difference between average concentrations of sample jars (n = 2), [d]Present: Pyrethroid was detected in two technical replicates from three of three soil samples collected from treatment row, values in parentheses represent standard deviation between average concentrations of sample jars (n = 3)

Table 2: Estimated environmental bifenthrin concentration in a United States Environmental Protection Agency standard pond

Environmental concentration	High application rate	Moderate application rate	Low application rate
Peak (1-in-10 year)	10.1	7.61	5.07
4-d Average (1-in-10 year)	0.728	0.547	0.364
21-d Average (1-in-10 year)	0.386	0.290	0.193
60-d Average (1-in-10 year)	0.320	0.240	0.160
365-d Average (1-in-10 year)	0.271	0.204	0.136
Entire Simulation Mean	0.205	0.154	0.103

All concentrations are reported as ppb (ng mL^{-1})

Table 3: Estimated environmental bifenthrin concentration in a United States Environmental Protection Agency standard reservoir

Environmental concentration	High application rate	Moderate application rate	Low application rate
Peak (1-in-10 year)	23.9	18.0	12.0
4-d Average (1-in-10 year)	2.38	1.79	1.19
21-d Average (1-in-10 year)	1.24	0.929	0.618
60-d Average (1-in-10 year)	1.03	0.775	0.516
365-d Average (1-in-10 year)	0.873	0.655	0.436
Entire Simulation Mean	0.658	0.494	0.329

All concentrations are reported as ppb (ng mL^{-1})

Table 4: Concentration of bifenthrin in water and stream samples collected from around Northeast, Pennsylvania

Stream ID	Sediment concentration	Water concentration
1	[a]ND	ND
2	ND	ND
3	ND	ND

All concentrations are reported as ppb (Sediment: ng g^{-1}, Water: ng mL^{-1}), [a]ND: Not detected, bifenthrin was not detected in soils according to mass spectrum and retention times of these compounds

model at the three application rates are summarized in Table 3. Similar to the USEPA Standard Pond, bifenthrin concentrations accumulating within the Standard Reservoir decreased with the application rate (Table 3). The peak (1-in-10 year) bifenthrin concentrations in the Standard Reservoir were 23.9, 18.0 and 12.0 ng mL^{-1} in the high, moderate and low application treatments, respectively (Table 3).

The measured bifenthrin concentrations in sediment and water samples were taken from local streams in North East, PA are reported in Table 4. Bifenthrin was not detected in local streams surrounding vineyards in northwestern PA when water and sediment samples were analyzed from the three study locations (Table 4).

DISCUSSION

Despite model predictions of bifenthrin accumulation in water bodies adjacent to vineyards, the risk for bifenthrin

runoff from vineyards in North East, PA is low based on empirical evidence from soil and stream samples. The presence of bifenthrin in soils collected from the research vineyard was sporadic and seemingly random, suggesting the uneven distribution of the pesticide within treatment rows, even at the highest application rates (Table 1). Similarly, no insecticide was detected in any buffer row samples collected over the course of the study (Table 1), suggesting minimal spray drift or horizontal movement was occurring during or after application. As most insecticide that is delivered to freshwater habitats from agricultural practices occurs through either leaching, runoff, or spray drift[17,27-29], the empirical data suggest that it was unlikely that bifenthrin was reaching local streams, which was supported by the lack of bifenthrin detected in sediment or water samples (Table 4). This was in direct contrast to the PWC model predictions, which suggested bifenthrin would peak in an agricultural pond or reservoir at concentrations high enough to cause acute toxicity to aquatic invertebrates (Table 2-3).

As the growing season progressed, the presence of bifenthrin in soils increased accordingly (Table 1). The increased detection of bifenthrin in soils may be due to the increased growth of the leaf canopy encompassing the vines. Concord grapes have large leaves by the end of the growing season, but during the earlier summer months, the canopy cover is significantly smaller. Insecticide application to the grapes involves dissolving the formulations in water and spraying this mixture on the vines. As the growing season progresses and the density of the canopy surrounding the vines increases, the amount of water collecting on the leaves increases. The water and insecticide on the leaves then drip to the soil, creating highly localized hotspots of active ingredient[30]. This agrees with previous research that has demonstrated that soil concentrations of similar pesticides increased as the growing season of corn progressed, contributing to increased accumulation of chemicals within runoff and groundwater samples[31-33]. Similarly, DDT applied to grapevines reached the highest concentrations in soils where drips from vines and deposits from foliage accumulated in soils[30]. This could explain, in part, why the presence of bifenthrin in the soils increased as the growing season progressed. This increased presence of bifenthrin in the soil samples over the course of the growing season did not, however, correlate with increased risk to surrounding water bodies based on modeling and field sampling results.

In comparison to previous research, bifenthrin concentrations estimated within the Standard Pond and Reservoir by the PWC were similar to those recorded in natural water bodies from other states around the United States. For example, bifenthrin concentrations in sediments collected from waterways around Central Valley, CA peaked at 32 ppb[7]. In Texas, measured bifenthrin concentrations averaged 740 ppb, with maximum concentrations reaching 2,900 ppb[18]. Bifenthrin in waterways of Illinois ranged from 2.2 to 46 ppb[14]. The presence of these chemicals in water bodies surrounding agricultural areas raises concern in regard to the health of the aquatic habitats, as pyrethroids are highly toxic to non-target invertebrate species. Previous evaluations of the toxicity of field contaminated sediments under laboratory conditions have demonstrated that when pyrethroids are present, the toxicity can be largely attributed to the presence of pyrethroids, even when complex mixtures of contaminants were detected[11,18,34]. Consequently, the results of the PWC modeling are somewhat concerning considering the potential risk to native streams. Even with the lowest application rate, peak bifenthrin concentrations in the standard pond and reservoir exceed the 10-d median lethal concentration (LC_{50}) for sensitive species such as *Hyalella azteca* (Bifenthrin LC_{50}: 9.3 ppt)[35-36]. Considering the environmental persistence of these chemicals in aquatic systems, the risk to native aquatic invertebrates in streams surrounding vineyards is high, assuming the model results were accurate; however, this is called into question when considering the lack of bifenthrin detection in local streams surrounding vineyards in North East, PA (Table 4). The lack of bifenthrin accumulation in local streams could be explained by the hydrology of these areas. The streams least likely to be impacted by insecticide runoff are mostly headwater streams, with benthic zones composed of shale bedrock containing little organic matter. When entering aquatic habitats, the hydrophobic chemicals such as bifenthrin tend to partition strongly to organic matter within sediments[37]. This partitioning can create reservoirs of chemicals, maintaining elevated water concentrations as chemical partitions from sediment to water over time[38-40]. In the streams evaluated in the current study, such organic-rich sediments were scarce, with most of the stream bottom composed of shale bedrock. With nothing to hold the insecticides in the streams, it is likely that any bifenthrin washed into these habitats was rapidly flushed downstream and out of the system entirely. Coupled with the flashy nature of such headwater streams, the half-life of bifenthrin in these habitats is likely short.

The results of the current study suggest surface accumulation and transport of bifenthrin from vineyards to local waterways is low. The accumulation and transport of bifenthrin in and through groundwater, however, is not understood based on the current results and will require further research. Similarly, future research evaluating the

degree to which the insecticide formulation penetrates grape canopy and the means by which bifenthrin is delivered to soil (i.e., runoff from leaves directly after application or rinsing from leaves during rain events) would better inform these conclusions related to the sporadic nature of the presence of bifenthrin in soil samples.

CONCLUSION

Conclusively, minimal transport of pyrethroids out of Pennsylvania vineyards is expected. While bifenthrin detection and concentrations in vineyard soils increased with increasing application rates and repeated applications throughout the growing season, the insecticide was not detected in adjacent streams. Model predictions would suggest that concentrations in stagnant water bodies may exceed thresholds of risk for sensitive macroinvertebrate species, but considering the structure of local water bodies (i.e. headwater streams), accumulation of hydrophobic insecticides is unlikely. This does not mean that there is no cause for concern as it is plausible that such insecticides could leach into groundwater habitats or receiving bodies of water, such as Lake Erie. Based on the field-collected data, however, it is expected that little risk is posed by the transport of common-use pyrethroid insecticides from vineyards in northwestern Pennsylvania.

SIGNIFICANCE STATEMENT

This study discovered the potential for accumulation and transport of pyrethroid insecticides out of Pennsylvania vineyards to local streams using field and modeling approaches. This information could be beneficial for viticulturists that apply insecticides to protect crop yield and risk assessors and ecologists evaluating the health of aquatic environments surrounding Pennsylvania vineyards. This study will help researchers to uncover critical factors controlling accumulation and leaching of pyrethroid insecticides from vineyards to surrounding aquatic habitats, as well as highlight the importance of considering the role of local hydrology in influencing environmental risk. Thus, this information can better inform estimates of risk concerning insecticide runoff in the context of different agricultural applications.

ACKNOWLEDGMENTS

REFERENCES

1. Mokry, L.E. and K.D. Hoagland, 1990. Acute toxicities of five synthetic pyrethroid insecticides to *Daphnia magna* and *Ceriodaphnia dubia*. Environ. Toxicol. Chem., 9: 1045-1051.
2. Amweg, E.L., D.P. Weston and N.M. Ureda, 2005. Use and toxicity of pyrethroid pesticides in the central valley, California, USA. Environ. Toxicol. Chem., 24: 966-972.
3. Maul, J.D., A.A. Brennan, A.D. Harwood and M.J. Lydy, 2008. Effect of sediment-associated pyrethroids, fipronil and metabolites on *Chironomus tentans* growth rate, body mass, condition index, immobilization and survival. Environ. Toxicol. Chem., 27: 2582-2590.
4. Cui, W., C. Fang, Z. Quan and F. Zhuo, 2009. Chronic toxicity and cytotoxicity of synthetic pyrethroid insecticide *cis*-bifenthrin. J. Environ. Sci., 21: 1710-1715.
5. Harwood, A.D., P.F. Landrum and M.J. Lydy, 2013. Bioavailability-based toxicity endpoints of bifenthrin for *Hyalella azteca* and *Chironomus dilutus*. Chemosphere, 90: 1117-1122.
6. Li, H., B. Sun, X. Chen, M.J. Lydy and J. You, 2013. Addition of contaminant bioavailability and species susceptibility to a sediment toxicity assessment: Application in an urban stream in China. Environ. Pollut., 178: 135-141.
7. Weston, D.P., Y. Ding, M. Zhang and M.J. Lydy, 2013. Identifying the cause of sediment toxicity in agricultural sediments: The role of pyrethroids and nine seldom-measured hydrophobic pesticides. Chemosphere, 90: 958-964.
8. Casida, J.E., D.W. Gammon, A.H. Glickman and L.J. Lawrence, 1983. Mechanisms of selective action of pyrethroid insecticides. Annu. Rev. Pharmacol. Toxicol., 23: 413-438.
9. Siegfried, B.D., 1993. Comparative toxicity of pyrethroid insecticides to terrestrial and aquatic insects. Environ. Toxicol. Chem., 12: 1683-1689.
10. Liu, W., J. Gan, S. Lee and I. Werner, 2005. Isomer selectivity in aquatic toxicity and biodegradation of bifenthrin and permethrin. Environ. Toxicol. Chem., 24: 1861-1866.
11. Weston, D.P., R.W. Holmes, J. You and M.J. Lydy, 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. Environ. Sci. Technol., 39: 9778-9784.
12. Weston, D.P., M. Zhang and M.J. Lydy, 2008. Identifying the cause and source of sediment toxicity in an agriculture-influence creek. Environ. Toxicol. Chem., 27: 953-962.
13. Weston, D.P., R.W. Holmes and M.J. Lydy, 2009. Residential runoff as a source of pyrethroid pesticides to urban creeks. Environ. Pollut., 157: 287-294.
14. Ding, Y., A.D. Harwood, H.M. Foslund and M.J. Lydy, 2010. Distribution and toxicity of sediment-associated pesticides in urban and agricultural waterways from Illinois, USA. Environ. Toxicol. Chem., 29: 149-157.

15. Weston, D.P. and M.J. Lydy, 2010. Focused toxicity identification evaluations to rapidly identify the cause of toxicity in environmental samples. Chemosphere, 78: 368-374.

16. Harwood, A.D., P.F. Landrum, D.P. Weston and M.J. Lydy, 2012. Using SPME fibers and Tenax to predict the bioavailability of pyrethroids and chlorpyrifos in field sediments. Environ. Pollut., 173: 47-51.

17. Weston, D.P., J. You and M.J. Lydy, 2004. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's central valley. Environ. Sci. Technol., 38: 2752-2759.

18. Hintzen, E.P., M.J. Lydy and J.B. Belden, 2009. Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. Environ. Pollut., 157: 110-116.

19. Kemble, N.E., D.K. Hardesty, C.G. Ingersoll, J.L. Kunz and P.K. Sibley *et al.*, 2012. Contaminants in stream sediments from seven united states metropolitan areas: part ii-sediment toxicity to the amphipod *Hyalella azteca* and the midge *Chironomus dilutus*. Arch. Environ. Contam. Toxicol., 64: 52-64.

20. Coyle, D., J. Chong and B.A. Blaauw, 2019. Spotted lanternfly management in nurseries, orchards, vineyards and natural areas in South Caroline and Georgia. Land-Grant Press by Clemson Extension: LGP 1003.

21. Čuš, F., H.B. Česnik, Š.V. Bolta and A. Gregorčič, 2010. Pesticide residues in grapes and during vinification process. Food Control, 21: 1512-1518.

22. Lentza-Rizos, C. and K. Kokkinaki, 2002. Residues of cypermethrin in field-treated grapes and raisins produced after various treatments. Food Addit. Contam., 19: 1162-1168.

23. Tang, W., D. Wang, J. Wang, Z. Wu, L. Li, M. Huang, S. Xu and D. Yan, 2018. Pyrethroid pesticide residues in the global environment: An overview. Chemosphere, 191: 990-1007.

24. Semple, K.T., K.J. Doick, K.C. Jones, P. Burauel, A. Craven and H. Harms, 2004. Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ. Sci. Technol., 38: 228A-231A.

25. Nutile, S.A., A.D. Harwood, F.L. Sinche, K.E.H. Hartz, P.F. Landrum and M.J. Lydy, 2017. The robustness of single-point Tenax extractions of pyrethroids: Effects of the Tenax to organic carbon mass ratio on exposure estimates. Chemosphere, 171: 308-317.

26. Smith, M.E., J.M. Lazorchak, L.E. Herrin, S. Brewer-Swartz and W.T. Thoeny, 1997. A reformulated, reconstituted water for testing the freshwater amphipod, *Hyalella azteca*. Environ. Toxicol. Chem., 16: 1229-1233.

27. Wauchope, R.D., 1978. The pesticide content of surface water draining from agricultural fields: A review. J. Environ. Qual., 7: 459-472.

28. Felsot, A.S., J.K. Mitchell and A.L. Kenimer, 1990. Assessment of management practices for reducing pesticide runoff from sloping cropland in Illinois. J. Environ. Qual., 19: 539-545.

29. Fawcett, R.S., B.R. Christensen and D.P. Tierney, 1994. The impact of conservation tillage on pesticide runoff into surface water: A review and analysis. J. Soil Water Conserv., 49: 126-136.

30. Taschenberg, E.F., G.L. Mack and F.L. Gambrell, 1961. Pesticide residues, DDT and copper residues in a vineyard soil. J. Agric. Food Chem., 9: 207-209.

31. Thorngren, J.L., A.D. Harwood, T.M. Murphy, K.E. Huff Hartz, C.Y. Fung and M.J. Lydy, 2017. Fate and risk of atrazine and sulfentrazone to nontarget species at an agriculture site. Environ. Toxicol. Chem., 36: 1301-1310.

32. Whiting, S.A., K.E. Strain, L.A. Campbell, B.G. Young and M.J. Lydy, 2014. A multi-year field study to evaluate the environmental fate and agronomic effects of insecticide mixtures. Sci. Total Environ., 497-498: 534-542.

33. Whiting, S.A. and M.J. Lydy, 2015. A site-specific ecological risk assessment for corn-associated insecticides. Integr. Environ. Asses. Manag., 11: 445-458.

34. Amweg, E.L., D.P. Weston, J. You and M.J. Lydy, 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. Environ. Sci. Technol., 40: 1700-1706.

35. Anderson, B.S., B.M. Phillips, J.W. Hunt, V. Connor, N. Richard and R.S. Tjeerdema, 2006. Identifying primary stressors impacting macroinvertebrates in the Salinas River (California, USA): Relative effects of pesticides and suspended particles. Environ. Pollut., 141: 402-408.

36. Deanovic, L.A., D. Markiewicz, M. Stillway, S. Fong and I. Werner, 2013. Comparing the effectiveness of chronic water column tests with the crustaceans *Hyalella azteca* (Order: Amphipoda) and *Ceriodaphnia dubia* (Order: Cladocera) in detecting toxicity of current-use insecticides. Environ. Toxicol. Chem., 32: 707-712.

37. DiToro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz *et al.*, 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem., 10: 1541-1583.

38. Pignatello, J.J., 1990. Slowly reversible sorption of aliphatic halocarbons in soils. I. Formation of residual fractions. Environ. Toxicol. Chem., 9: 1107-1115.

39. Pignatello, J.J, 1990. Slowly reversible sorption of aliphathic halocarbons in soils. II. Mechanistic aspects. Environ. Toxicol Chem., 98: 1117-1126.

40. Pignatello, J.J., 1991. Desorption of tetrachloroethene and 1,2-dibromo-3-chloropropane from aquifer sediments. Environ. Toxicol. Chem., 10: 1399-1404.