



## Leaching of insecticides used in blueberry production and their toxicity to red worm



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### H I G H L I G H T S

- Insecticide leaching from rainfall wash-off were not lethal to *E. foetida*.
- Carbaryl showed the highest level of toxicity to *E. foetida*.
- Insecticide recovery generally declined as soil depth increased.

### A R T I C L E I N F O

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### A B S T R A C T

Soil columns were collected from a blueberry field, and insecticide solutions were allowed to leach through these columns. Insecticides from four different chemical classes were applied at two different rates: the concentration at which the insecticides wash off blueberries under rainfall conditions and the labeled field rate at which they are sprayed. The soil columns were divided into thirds; top, middle and bottom. Soil bioassays using *Eisenia foetida* Savigny, as an indicator species, were set up to determine the toxicity of the insecticides at a top, middle and bottom layer of the soil column. The mass of *E. foetida* was also measured after the bioassay experiment was completed. The concentrations at which insecticides wash-off of blueberries from rainfall were not lethal to *E. foetida*. In order to support mortality data, insecticide residues were quantified in the soil layers for each insecticide. Under field rate leaching conditions, carbaryl showed the high levels of toxicity in the top and middle layers of soil suggesting that it has the highest risk to organisms from leaching. This study will help blueberry growers make informed decisions about insecticide use, which can help minimize contamination of the environment.

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### 1. Introduction

Agricultural intensification has been a worldwide trend over the past several decades. This was done by expanding the land area used for agriculture, using higher yielding varieties, and increasing the use of fertilizers and pesticides (Matson et al., 1997). Increased use of pesticides is of concern because only about 1% of pesticides may reach the target organism with the rest drifting to or leaching

into other areas of the environment (PSAC, 1965; Pimentel and Edwards, 1982). Studies show that air-blast sprayers are a relatively inefficient way to deliver pesticides, with only 29–56% of the applied spray solution reaching the canopy of the tree and the rest of the product drifting to ground or other off-target endpoints (Steiner, 1969; Reichard et al., 1979; Zhu et al., 2006; Perry et al., 1998). Lack of effective control against disease and insect pests can cause enormous damage to the crops. Often, economic factors such as consumer preferences and food industry restrictions create standards for food products that are difficult to achieve without the use of pesticides for production. Specialty crop industries have a zero tolerance standard for insect contamination at pack-out. This

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creates additional challenges for growers of fruit crops, such as blueberry, which have pests present during harvest time. The pressure on growers to deliver clean fruit at the time of harvest is large and reliance on conventional insecticide applications is common.

Conventional synthetic pesticides developed in the twentieth century are generally known to present greater risks for environmental contamination because of their stability in the environment. Organochlorines such as DDT and dieldrin are far more persistent in the environment than organophosphates, such as parathion or phosmet, and carbamates such as carbaryl (Eichelberger and Lichtenberg, 1971). Modern insecticides are likely to degrade over days and weeks, whereas older compounds may persist in the environment long enough to have impacts for years.

Microbial activity, photolysis, and hydrolysis are the main sources of insecticide degradation (Eichelberger and Lichtenberg, 1971; Zepp and Cline, 1977; Gupta et al., 2008). Some insecticides have physical properties which allow them to bind to particles of soil and remain relatively immobile, while others are more susceptible to leaching. Insecticides pose the greatest risk if they do not readily degrade and do not bind to the soil. Insecticides with these characteristics may leach and eventually reach groundwater or other larger bodies of water. Insecticides that remain in the soil for days or weeks after application can also be a source of risk due to their impact on the soil fauna.

It is well known that insecticide applications can have adverse effects on beneficial organisms in agroecosystems (Pimentel, 1995; Grue et al., 1997). Integrated Pest Management (IPM) attempts to use pesticides in ways which minimize negative impacts to beneficial organisms (Elzen, 2001; Michaud and Grant, 2003; Michaud and McKenzie, 2004). Beneficial organisms within subterranean agro-ecosystems can be affected by insecticide applications as well (Gyldenkerne and Jørgensen, 2000). *E. foetida* has been widely used as a representative organism for evaluating toxicity impacts of contaminated soils on beneficial organisms (Neuhauser et al., 1983; Wilborn et al., 1997). There has been considerable work done on how pesticides leach through various soils (Sakata et al., 1986; Zhou et al., 1997; Gupta et al. 2002, 2008; Wauchope et al., 2004). These studies have focused on how single insecticides behave, but not in soil suitable for growing blueberries.

Blueberries are an important economic crop for Michigan (NASS - National Agricultural Statistics Service, 2011). Michigan blueberry growers rely on insecticides in their IPM programs, including organophosphates, carbamates, neonicotinoids, and synthetic pyrethroids (Wise et al., 2011). The average monthly rainfall during the blueberry growing season in Michigan ranges from approximately 50 mm–100 mm (Michigan Automated Weather Network, 2011). The application of insecticides in combination with the high likelihood of rainfall presents both a production challenge for growers and a potential contamination problem when insecticides are carried by precipitation and leach into soils. Spraying blueberry fields with air-blast sprayers may also result in drift to the soil surface and other off-target locations.

The aim of this study was to determine if insecticides used in blueberry production leach through soils appropriate for growing blueberries, and measure their impact on non-target beneficial organisms. This was done by leaching four different insecticides from different chemical classes through soil columns taken from a blueberry field in south-west Michigan. The insecticides were leached at two different rates: one which simulates wash-off by rain, and one which simulates non-target drift of field rate insecticides to the ground. Red worms, *Eisenia foetida* Savigny, were used in soil bioassays as a measure of toxicity.

## 2. Materials and methods

### 2.1. Worms

*E. foetida* adults were purchased from Carolina Biological Supply Company, Burlington, NC in July 2010. Upon arrival, the worms were placed in the culturing container. The culturing container comprised of a 35.6 × 45.7 × 20.3 cm plastic bin with a layer of damp shredded newspaper in the bottom and full of potting soil. Oats were mixed into the soil to provide the *E. foetida* with food until they were needed for the bioassay experiments. Over the top of the culturing container, a damp towel was placed to keep the contents moist. Water was lightly sprayed in the chamber once a week to maintain the dampness of the soil. Healthy adult *E. foetida* were selected for the bioassay experiments.

### 2.2. Soil columns and treatment applications

Fifty soil columns were collected from a blueberry field at the Michigan State University Trevor Nichols Research Center in Fennville, MI (+42° 36' 12.59", -86° 9' 13.86"). The soil columns were comprised of PVC pipes approximately 50 cm in length and 7.62 cm in diameter. The soil column depth was similar to the depth of blueberry root systems, thus the most relevant zone for studying leaching and impact on beneficial organisms, including *E. foetida*. The PVC pipes were hammered into the ground at the field site using a sledgehammer. Once the pipes had been hammered to a depth of 25 cm, they were removed from the ground with the soil column still in the PVC pipe. The soil was characterized by the Michigan State University Soil and Plant Nutrient Laboratory as sandy loam and had the following composition: % Sand = 74.7, % Silt = 13.5, % Clay = 11.8, TKN (Total Kjeldahl Nitrogen) = 0.09%, pH = 3.8, % OM (Organic Matter) = 2.8, and CEC (Cation Exchange Capacity) = 8.2 me/100 g. The bottoms of the soil columns were placed in bins of water to allow the water to partition up through the soil over 24 h, and then allowed to drain for 24 h before the insecticide treatment, to ensure uniform water concentration in all of the soil columns.

Two different concentrations of each insecticide were applied to the soil columns. The concentrations of the first application were calculated by using the observed wash off of the insecticides active ingredient (AI) from simulated rainfall (Hulbert et al., 2012) (Table 1). The second concentration (AI) was equal to the amount at which each insecticide is labeled for use in blueberries, based on spraying in 468 L/Ha (50 gallons per acre) diluent (Wise et al., 2011). The volume of treatment solution applied was equivalent to 25.4 mm (1 inch) of rain over an area equal to the area of the opening of the soil column (45.604 cm<sup>2</sup>), calculated based on figures from the U.S. Geological Survey website (Rain and precipitation, 2010). It was calculated that 117.2 mL of water is equivalent to 25.4 mm of rain over a surface area of 45.604 cm<sup>2</sup>. This volume of distilled water was allowed to flow through the soil columns with the concentrations of insecticides listed in Table 1. Untreated control soil columns had 117.2 ml of distilled water poured into them. Funnels with spray bottle nozzles attached were used to drip the insecticide solutions onto the soil columns to approximate the natural rate of rainfall. After the insecticide application, the soil columns were allowed to sit in a cool, dark area overnight until they were prepared for the next part of the experiment.

After 24 h (same waiting period as used in Hulbert et al., 2012), the soil columns were cut into 3 equal segments laterally, each 8.3 cm in length, corresponding to "top", "middle" and "bottom" as per their orientation to the soil surface. These segments were then cut in half longitudinally so that half of the soil at a particular depth

**Table 1**

Formulated compounds, field rates and concentrations used for bioassay experiments and residue analysis.

Active Ingredient	Formulated Name	Chemical Class	Log $K_{ow}$	ppm <sup>a</sup>	ppm <sup>b</sup>	Company
Phosmet	Imidan® 70 WP	Organophosphate	2.95	33.350	2180	Gowan Company, Yuma, AZ
Carbaryl	Sevin XLR® 4L	Carbamate	2.36	39.843	4793	Bayer CropScience, Pittsburgh, PA
Zeta-cypermethrin	Mustang Max® 0.8 EC	Pyrethroid	5.5	1.168	60	FMC Corp., Princeton, NJ
Imidacloprid	Provado® 1.6 SC	Neonicotinoid	0.57	1.237	293	Bayer CropScience, Pittsburgh, PA

<sup>a</sup> Insecticide AI concentrations calculated from wash-off studies (Hulbert et al., 2012).<sup>b</sup> Insecticide AI concentrations based on labeled field rates in 468 L/Ha diluent.

could be used for bioassays and the other half could be used for residue analysis. For each insecticide and the untreated control, there were five soil columns for both of the insecticide concentrations. All five columns from each insecticide treatment were used to provide soil for five replicates of the bioassay experiment, while the first three columns from each treatment were used to provide soil for the residue analysis portion of the study.

### 2.3. Bioassays

Bioassays were used to determine the toxicity of the four insecticides against *E. foetida* at the three different soil depths. Half of the soil column at a particular depth (~190 cm<sup>3</sup>) was placed into a glass 1-pint canning jar (Ball Corporation, Broomfield, CO). The lid was placed on upside down so that a seal was not created. Each of these containers was considered an experimental unit in the bioassays, replicated five times.

Ten randomly selected healthy adult *E. foetida* were placed in each bioassay chamber, which were held in the laboratory at 21 °C and a photoperiod of 16:8 (L:D) h. There were five replicates for each insecticide treatment and each of two concentrations (wash-off ppm and field rate ppm), and soil column depth (top, middle, bottom) combination. The number of *E. foetida* alive and dead was recorded after 0, 24, 168 and 336 h (0, 1, 7, 14 d). The bioassays were evaluated by dumping the contents onto a clean sheet of paper and a probe was used to find the worms in the soil. The worms were lightly probed to determine whether they were living. After the final bioassay evaluation at 336 h, the total mass of *E. foetida* in the bioassays were measured.

### 2.4. Statistical analyses

The mean mass of the worms was compared among insecticide treatment at the same depth, and across depths within an insecticide treatment using analysis of variance (ANOVA). Mean separation was done using Tukey's honestly significant difference (HSD) test. The mortality data were analyzed by logistic regression to determine the time at which half of the organisms reached an immobile condition (LT<sub>50</sub>) (Robertson et al., 2007). Logistic regression analyses were performed at every insecticide treatment and depth combination. An overlap test of the 95% confidence intervals was used to determine significant differences in insecticide toxicity. These analyses were conducted in R version 2.12.1 (R Development Core Team, 2010) using the MASS library (Venables, W. N. & Ripley, B. D. 2002), the ltmtest library (Zeileis and Hothorn, 2002), and the do By library (Søren Højsgaard, Ulrich Halekoh with contributions from Ulrich Halekoh, Jim Robison-Cox, Kevin Wright and Alessandro A. Leidi, 2011).

### 2.5. Insecticide residue analysis

A ten g sample was taken from each homogenized column segment designated for residue analysis, then were placed in 150 ml of high-performance liquid chromatography (HPLC)-grade

acetonitrile (EMD Chemicals, Inc., Gibbstown, NJ) and sonicated for 10–15 s. The acetonitrile was decanted through 5 g of reagent-grade anhydrous sodium sulfate (EMD Chemicals, Inc.) to remove water. The samples were dried via rotary evaporation and brought up in acetonitrile for HPLC analysis. The remaining soil samples were ground in 50 ml of HPLC grade dichloromethane (Burdick & Jackson, Muskegon, MI). The extracts were passed through 5 g of anhydrous sodium sulfate. The samples were dried via rotary evaporation and brought up in acetonitrile. Any remaining particulates were removed by passing the sample through a 0.45-µm Acrodisc 13-mm syringe filter (Pall, East Hills, NY). For each compound, standard grade materials were placed into a volumetric flask and weighed, then brought to full volume with acetonitrile. Working standards were prepared from the standard stock solutions.

Samples were analyzed for insecticide residue with a Waters 2690 Separator Module HPLC equipped with a Waters 2487 Dual Wavelength Absorbance Detector (Waters, Milford, MA) set at 270 nm, and a C18 reversed-phase column (150 by 4.6 mm bore, 5 µm particle size, Restek, Bellefonte, PA) (Bayer 1998). The mobile phase was run at 1 mL/min with water/acetonitrile, and at isocratic conditions (80:20) at 55 °C, and the injection volume was 10 mL. US Pesticide Data Program Guidelines were used to determine Limits of Detection (LOD) and Limits of Quantification (LOQ) (Table 2).

## 3. Results

### 3.1. Bioassays

- Wash-off simulated rates: There were no observable toxic effects on the worms when the precipitation wash-off rates of insecticides were leached through the soil columns.
- Field-rate simulated study: In the top layer of soil, imidacloprid had a significantly lower LT<sub>50</sub> value than phosmet which had a significantly lower LT<sub>50</sub> value than both zeta-cypermethrin and the untreated control (Table 3). In the middle layer of soil, carbaryl had a significantly lower LT<sub>50</sub> value than zeta-cypermethrin. In the bottom layer of soil, none of the treatments had significantly different LT<sub>50</sub> values.

The top layer of soil treated with phosmet had a significantly lower LT<sub>50</sub> value than the bottom layer of soil treated with phosmet. Layers of soil treated with zeta-cypermethrin had similar LT<sub>50</sub>

**Table 2**

The limit of detection (LOD) and limit of quantitation (LOQ) values for each treatment compound in residue analysis. The LOD and LOQ recoveries ranged from 50 to 150%.

Chemical	LOD (ug/g)	LOQ (ug/g)
Phosmet	0.03	0.1
Zeta-cypermethrin	0.003	0.01
Imidacloprid	0.002	0.005
Carbaryl	0.001	0.003

**Table 3**  
LT<sub>50</sub> values for insecticides leached through soil at the different soil depths for *E. foetida* adults.

Insecticide	Depth	n	Slope (+SE)	LT <sub>50</sub>	95% CI	Chi square
UTC	Top	50	-0.009 (+0.002)	367	(297.34, 436.15)	<0.0001
	Middle	50	-0.004 (+0.003)	980	(-119.18, 2078.41)	0.1608
	Bottom	50	-0.005 (+0.002)	727	(239.41, 1214.25)	0.0345
Phosmet	Top	50	-0.009 (+0.001)	135	(104.07, 164.98)	<0.0001
	Middle	50	-0.003 (+0.002)	1107	(-292.29, 2506.57)	0.1895
	Bottom	50	-0.005 (+0.002)	744	(225.95, 1262.48)	0.0379
Zeta-cypermethrin	Top	50	-0.006 (+0.002)	455	(319.67, 589.81)	<0.0001
	Middle	50	-0.004 (+0.002)	778	(184.29, 1371.04)	0.0473
	Bottom	50	-0.006 (+0.002)	542	(321.06, 762.74)	0.0017
Imidacloprid	Top	50	-0.030 (+0.004)	78	(65.85, 90.60)	<0.0001
	Middle	50	-0.001 (+0.002)	1423	(-336.01, 4182.62)	0.3662
	Bottom	50	-0.004 (+0.002)	798	(172.24, 1423.73)	0.0562
Carbaryl	Top	50	-0.324 (+62.600)	67	(-810.81, 1944.89)	0.9959
	Middle	50	-0.007 (+0.001)	134	(98.62, 169.35)	<0.0001
	Bottom	50	-0.003 (+0.001)	602	(211.16, 992.90)	0.0247

values. The top layer of soil treated with imidacloprid had a significantly lower LT<sub>50</sub> value than the bottom layer. The middle layer of soil treated with carbaryl had a significantly lower LT<sub>50</sub> value than the bottom layer.

The mass of live *E. foetida* in each bioassay at the end of the bioassay experiment was measured as another measure of toxicity. In the untreated (UTC) soil columns, the results of the overall ANOVA across depth was  $F = 4.19$ ;  $df = 2, 12$ ;  $P = 0.04$ , but none of the individual comparisons using Tukey's HSD were significant at  $\alpha = 0.05$  (Table 4). Within bioassays with soil treated with phosmet, there was a significant difference between the masses of *E. foetida* across soil depths ( $F = 9.77$ ;  $df = 2, 12$ ;  $P = 0.003$ ). Within bioassays treated with zeta-cypermethrin there was no significant difference between the masses of *E. foetida* across soil depth ( $F = 1.47$ ;  $df = 2, 12$ ;  $P = 0.26$ ). Within bioassays treated with imidacloprid, there was a significant difference between the masses of *E. foetida* across soil depth ( $F = 26.57$ ;  $df = 2, 12$ ;  $P < 0.001$ ). Within bioassays treated with carbaryl, there was a significant difference between the masses of *E. foetida* across depth ( $F = 25.77$ ;  $df = 2, 12$ ;  $P < 0.001$ ).

### 3.2. Insecticide residue analysis

The patterns of insecticide recovery generally progressed to lower concentrations as depth increased (Table 5). Much higher concentrations were recovered in soils treated with the Field spray rates than the precipitation wash-off rates. In soil treated with phosmet at the wash-off rate, residue detection was approximately 90% less in the bottom layer than in the top layer. In soil treated with phosmet at the field rate, residue detection was more than 99% less in the middle layer than in the top layer. In soil treated with zeta-cypermethrin at the wash-off rate, detection only occurred in the top layer of soil. In soil treated with zeta-cypermethrin at the field rate, detected residues in the middle layer were approximately 98% less than in the top layer and detected residues were approximately 90% less in the bottom layer than in the middle layer. In soil treated with imidacloprid at the wash-off rate, residues detected in the middle and bottom layers

were more than 90% less than in the top layer. In soil treated with imidacloprid at the field spray rate, residues detected in the middle and bottom layers were approximately 99% less than in the top layer. In soil treated with carbaryl at the wash-off rate, detected residues were approximately 14% lower in the middle layer than the top layer, and 99% lower in the bottom layer than the middle layer. In soil treated with carbaryl at the field spray rate, residues detected in the middle layer were approximately 50% less than in the top layer and approximately 93% lower in the bottom layer than in the top layer.

## 4. Discussion

This study showed that when insecticides were leached through the soil at concentrations likely to occur after a rainfall, there were no toxic effects on the worms. Thus, the primary risk associated with rainfall is the loss of efficacy of these insecticides for the grower (Hulbert et al., 2012). When the insecticides were leached at concentrations that simulated off-target drift to the ground, there was evidence of toxic effects to worms by several compounds, varying by soil depth. Carbaryl was lethal to the worms at both top and middle layers of soil, while the toxicity effects of imidacloprid and phosmet were limited to the top layer of soil. Zeta-cypermethrin had no toxic effects on the worms. This has important implications for IPM and avoiding negative impacts on beneficial organisms and the environment.

This study suggests that neonicotinoid, pyrethroid, and organophosphate insecticides pose a lower risk of soil contamination than carbamates like carbaryl in blueberry production systems. When carbaryl was tested against other older insecticides such as DDT, dieldrin, and lindane it was found that carbaryl had lower adsorption on soil than the other insecticides (Sharom et al., 1980). While the majority of carbaryl remained near the soil surface, sufficient leaching occurred to cause higher levels of toxicity than the other insecticides tested in our experiment.

Water solubility and octanol-water partitioning coefficient Kow are properties which significantly correlate with the mobility of insecticides in soils and Kow has been found to be a better predictor

**Table 4**  
Average mass ( $\pm$ SE) of live *E. foetida* in the bioassay chambers for all insecticide at each depth. Upper case letters show significant differences across depths within a single insecticide treatment column. Mean separation was done using Tukey's HSD ( $P < 0.05$ ).

Soil depth	Untreated check	Phosmet	Zeta-cypermethrin	Imidacloprid	Carbaryl
Top	1.67 (0.39) A	0.70 (0.47) B	1.80 (0.33) A	0.01 (0.01) B	0.0 (0.0) B
Middle	2.79 (0.24) A	2.63 (0.21) A	2.28 (0.30) A	2.60 (0.34) A	0.80 (0.27) B
Bottom	2.83 (0.29) A	2.38 (0.24) A	2.48 (0.20) A	2.58 (0.36) A	2.51 (0.34) A

**Table 5**

Mean ( $\pm$ SE) insecticide residues recovered from blueberry soil across soil depth after the wash-off and labeled spray rate of insecticides applied to the soil. Residues are measured in micrograms per gram (ppm) of active ingredient per soil sample. ND = not detected.

Applied rate	Soil depth	Phosmet	Zeta-cypermethrin	Imidacloprid	Carbaryl
Wash-off	Top	0.54 (0.23)	0.29 (0.12)	0.026 (0.018)	0.43 (0.08)
	Middle	ND	ND	0.002 (0.002)	0.37 (0.2)
	Bottom	0.03 (0.03)	ND	0.001 (0.001)	0.003 (0.002)
Field rate	Top	15.8 (5.67)	3.22 (1.17)	6.04 (2.73)	173.2 (37.7)
	Middle	0.07 (0.07)	0.07 (0.06)	0.04 (0.003)	83.4 (33.7)
	Bottom	ND	0.007 (0.007)	0.06 (0.05)	4.9 (2.88)

than water solubility (Somasundaram et al., 1991).  $K_{ow}$  varies from approximately  $10^{-3}$  to  $10^7$  and is usually expressed as  $\log K_{ow}$  (Leo et al., 1971). Compounds with lower  $\log K_{ow}$  are polar and have high solubility in water. Compounds with higher  $\log K_{ow}$  are non-polar and have low water solubility and are lipophilic (Ragnarsdottir, 2000).

Phosmet has a  $\log K_{ow}$  of 2.95 (Table 1) meaning that phosmet has relatively low solubility in water and is lipophilic. Phosmet has been known to degrade rapidly in soil and phosmet hydrolysis is buffered at neutral and alkaline pH (Menn et al., 1965). Phosmet has also been found to degrade more rapidly in soils with higher organic content (Suter et al., 2002). These factors likely influenced the degradation over the course of our experiment.

Carbaryl has a  $\log K_{ow}$  of 2.36 that makes carbaryl relatively low in water solubility and is relatively lipophilic. Significant efforts have been made to assess how carbaryl degrades in soil and water and its environmental fate. (Kazano et al., 1972; Wolfe et al., 1978). Carbaryl can bond moderately with soil and may leach into groundwater. The degradation of carbaryl has been characterized in a sandy loam soil similar to the soil used in our experiment and it was found that hydrolysis was the main pathway of degradation (Kazano et al., 1972).

Zeta-cypermethrin has a  $\log K_{ow}$  of 5.5, indicating zeta-cypermethrin is relatively lipophilic. The insecticide is highly toxic to insects, which is why a relatively low rates are needed for effective pest control. The leaching potential of cypermethrin has been described as "limited" because of its low water solubility and adsorption to soil (Sakata et al., 1986). Mixtures of pyrethroids, including zeta-cypermethrin, are used with neonicotinoids to control termites in soil because the mixture has high toxicity to termites at low application rates and has "good soil mobility for a very effective continuous chemical barrier" (Ballard et al., 2008).

Imidacloprid is a systemic insecticide with  $\log K_{ow}$  of 0.57. Under high levels of simulated rainfall, imidacloprid has been found to have a high potential for leaching (Gupta et al., 2002), but other studies have found that under non-monsoon conditions, imidacloprid is relatively immobile (Hellpointer, 1998). Different formulations of this insecticide are also known to reduce the risk of leaching and contamination of imidacloprid (Fernández-Pérez et al., 1998). As stated above, imidacloprid, when mixed with a pyrethroid, has been used and studied for its control of termites in soils (Baskaran et al., 1999; Ballard et al., 2008).

It is important to recognize that the comparative patterns of toxicity and leaching seen in this study are based in part on the fact that label rates of each insecticides were applied to the soil columns. Carbaryl, which showed the highest degree of leaching as evidenced by ppms of residues recovered, was applied at a rate several times higher than phosmet, hundreds of times higher than that of imidacloprid and zeta-cypermethrin (Table 1). Identical concentrations of insecticides would have been used had the purpose of this study been to determine, based strictly on the physical properties of the compounds, which insecticide was most susceptible to leaching. The purpose, however, was to determine what is

more likely to occur in the field given normal blueberry production practices. The trend, in general, is that newer reduced-risk insecticides are active on target pests at much lower doses than older 20th-century tools (Perry 1998).

Insecticide leaching in soils is influenced by several factors, such as soil moisture, temperature, insecticide formulation, soil pH and composition among others. With this study, we hope to advance our understanding of insecticide mobility in blueberry soils, and the associated risks to soil organisms from off-target drift and insecticide wash-off from precipitation. This study showed that carbaryl would, in practice, have greater risks to subterranean beneficial organisms, such as worms and entomopathogenic nematodes, than imidacloprid. The results of this study can help blueberry growers make informed decisions about their insecticide use, and minimize risks to the environment.

#### Declaration of competing interest

The authors declare no conflict of interest.

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#### References

- Ballard, J.B., Palmer, C.L., Watson, K., 2008. Liquid Termiticide Compositions of Pyrethroids and Neonicotinoids.
- Baskaran, S., Kookana, R.S., Naidu, R., 1999. Degradation of bifenthrin, chlorpyrifos and imidacloprid in soil and bedding materials at termiticidal application rates. *Pestic. Sci.* 1222–1228. [https://doi.org/10.1002/\(SICI\)1096-9063\(199912\)55:12<1222::AID-PS83>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1096-9063(199912)55:12<1222::AID-PS83>3.0.CO;2-7).
- Eichelberger, J.W., Lichtenberg, J.J., 1971. Persistence of pesticides in river water. *Environ. Sci. Technol.* 5, 541–544. <https://doi.org/10.1021/es60053a002>.
- Elzen, G.W., 2001. Lethal and sublethal effects of insecticide residues on *Orius insidiosus* (Hemiptera: anthocoridae) and *Geocoris punctipes* (Hemiptera: lygaeidae). *J. Econ. Entomol.* 94, 55–59. <https://doi.org/10.1603/0022-0493-94.1.55>.
- Fernández-Pérez, M., González-Pradas, E., Ureña-Amate, M.D., et al., 1998. Controlled release of imidacloprid from a lignin matrix: water release kinetics and soil mobility study. *J. Agric. Food Chem.* 46, 3828–3834. <https://doi.org/10.1021/jf980286f>.
- Grue, C.E., Gilbert, P.L., Seeley, M.E., 1997. Neurophysiological and behavioral changes in non-target wildlife exposed to organophosphate and carbamate pesticides: thermoregulation, food consumption, and reproduction. *Am. Zool.* 37, 369–388. <https://doi.org/10.1093/icb/37.4.369>.
- Gupta, S., Gajbhiye, V.T., Kalpana, Agnihotri, N.P., 2002. Leaching behavior of imidacloprid formulations in soil. *Bull. Environ. Contam. Toxicol.* 68, 502–508. <https://doi.org/10.1007/s00128-001-0283-8>.
- Gupta, S., Gajbhiye, V., Gupta, R., 2008. Soil dissipation and leaching behavior of a neonicotinoid insecticide thiamethoxam. *Bull. Environ. Contam. Toxicol.* 80, 431–437.
- Gyldenkerne, S., Jørgensen, S.E., 2000. Modelling the bioavailability of pesticides to soil-dwelling organisms. *Ecol. Model.* 132, 203–230, 16/S0304-3800(00)00241-

6.  
Hellpointer, E., 1998. Lysimeter Study of Imidacloprid after Seed Treatment of Sugar Beet in Two Crop Rotations. The Lysimeter Concept. American Chemical Society, pp. 40–51.
- Hulbert, D., Isaacs, R., Vandervoort, C., Earhardt, S., Wise, J.C., 2012. Rainfastness of insecticides used to control Japanese beetle in blueberries. *J. Econ. Entomol.* 105, 1688–1693. <https://doi.org/10.1603/EC11412>.
- Kazano, H., Kearney, P.C., Kaufman, D.D., 1972. Metabolism of methylcarbamate insecticides in soils. *J. Agric. Food Chem.* 20, 975–979. <https://doi.org/10.1021/jf60183a029>.
- Leo, A., Hansch, C., Elkins, D., 1971. Partition coefficients and their uses. *Chem. Rev.* 71, 525–615.
- Matson, P.A., Parton, W.J., Power, A.G., Swift, M.J., 1997. Agricultural intensification and ecosystem properties. *Science* 277, 504–509. <https://doi.org/10.1126/science.277.5325.504>.
- Menn, J.J., McBain, J.B., Adelson, B.J., Patchett, G.G., 1965. Degradation of N-(mercaptomethyl) phthalimide-S-(O,O-dimethylphosphorodithioate) (imidan) in soils. *J. Econ. Entomol.* 58, 875–878.
- Michaud, J.P., Grant, A.K., 2003. IPM-compatibility of foliar insecticides for citrus: indices derived from toxicity to beneficial insects from four orders. *J. Insect Sci.* 3, 1–10.
- Michaud, J.P., McKenzie, C.L., 2004. Safety of a novel insecticide, sucrose octanoate, to beneficial insects in Florida citrus. *Fla. Entomol.* 87, 6–9. [https://doi.org/10.1653/0015-4040\(2004\)087\[0006:SOANIS\]2.0.CO;2](https://doi.org/10.1653/0015-4040(2004)087[0006:SOANIS]2.0.CO;2).
- Michigan automated weather Network. <http://www.agweather.geo.msu.edu/mawn/>, 2011–. (Accessed 8 October 2019).
- Nass - national agricultural statistics service. <http://www.nass.usda.gov/>, 2011–. (Accessed 8 October 2019).
- Neuhauser, E.F., Malecki, M.R., Loehr, R.C., 1983. Methods Using Earthworms for the Evaluation of Potentially Toxic Materials in Soils. *Hazardous and Industrial Solid Waste Testing: Second Symposium*. ASTM STP805.
- Perry, A., Yamamoto, I., Ishaaya, I., Perry, R., 1998. *Insecticides in Agriculture and Environment; Retrospects and Prospects*. Springer Publishing Ltd., Dordrecht, Heidelberg, London, New York, p. 261.
- Pimentel, D., 1995. Amounts of pesticides reaching target pests: environmental impacts and ethics. *J. Agric. Environ. Ethics* 8, 17–29. <https://doi.org/10.1007/BF02286399>.
- Pimentel, D., Edwards, C.A., 1982. Pesticides and ecosystems. *Bioscience* 32, 595–600. <https://doi.org/10.2307/1308603>.
- PSAC, 1965. *Restoring the Quality of Our Environment*. The White House, Washington DC.
- R Development Core Team, 2010. *A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. <http://www.R-project.org/>.
- Ragnarsdottir, K.V., 2000. Environmental fate and toxicology of organophosphate pesticides. *J. Geol. Soc.* 157, 859–876.
- Zhu, H., Derksen, R., Guler, H., Krause, C., Ozkan, H., 2006. Foliar deposition and off-target loss with different techniques in nursery applications. *ASABE* 49 (2), 325–334.
- Rain and Precipitation, 2010. USGS Water Science for Schools. [https://www.usgs.gov/special-topic/water-science-school/science/rain-and-precipitation?qt-science\\_center\\_objects=0#qt-science\\_center\\_objects](https://www.usgs.gov/special-topic/water-science-school/science/rain-and-precipitation?qt-science_center_objects=0#qt-science_center_objects). (Accessed 8 October 2019).
- Reichard, D.L., Fox, R.D., Brazee, R.D., Hall, R.R., 1979. Air velocities delivered by orchard airblast sprayers. *Trans. ASAE* 22, 69–74.
- Robertson, J., Russell, R.M., Preisler, H.K., Savin, N.E., 2007. *Bioassays with Arthropods*, second ed. CRC Press.
- Sakata, S., Mikami, N., Matsuda, T., Miyamoto, J., 1986. Degradation and leaching behavior of the pyrethroid insecticide cypermethrin in soils. *J. Pestic. Sci.* 11, 71–79.
- Sharom, M.S., Miles, J.R.W., Harris, C.R., McEwen, F.L., 1980. Behaviour of 12 insecticides in soil and aqueous suspensions of soil and sediment. *Water Res.* 14, 1095–1100. [10.1016/0043-1354\(80\)90158-X](https://doi.org/10.1016/0043-1354(80)90158-X).
- Somasundaram, L., Coats, J.R., Racke, K.D., Shanbhag, V.M., 1991. Mobility of pesticides and their hydrolysis metabolites in soil. *Environ. Toxicol. Chem.* 10, 185–194. <https://doi.org/10.1002/etc.5620100206>.
- Steiner, P.W., 1969. *The Distribution of Spray Material between Target and Non-target Areas of a Mature Apple Orchard by Air-Blast Equipment*. A master's thesis at Cornell University, pp. 1–57.
- Suter, H.C., White, R.E., Heng, L.K., Douglas, L.A., 2002. Sorption and degradation characteristics of phosmet in two contrasting Australian soils. *J. Environ. Qual.* 31, 1630. <https://doi.org/10.2134/jeq2002.1630>.
- Wauchope, R.D., Johnson III, W.C., Sumner, H.R., 2004. Foliar and soil deposition of pesticide sprays in peanuts and their washoff and runoff under simulated worst-case rainfall conditions. *J. Agric. Food Chem.* 52, 7056–7063.
- Wilborn, D.C., Bollman, M.A., Gillett, C.S., Ott, S.L., Linder, G.L., 1997. A Field Screening Method Using Earthworms (*Eiseniafoetida Andrei*) to Evaluate Contaminated Soils," *Environmental Toxicology and Risk Assessment: Modeling and Risk Assessment*, Sixth. ASTM STP 1317.
- Wise, J., Schilder, A., Zandstra, B., Hanson, E., Gut, L., Isaacs, R., Sundin, G., 2011. *Michigan Fruit Management Guide*. MSUE bulletin E-154.
- Wolfe, N.L., Zepp, R.G., Paris, D.F., 1978. Carbaryl, propham and chlorpropham: a comparison of the rates of hydrolysis and photolysis with the rate of biolysis. *Water Res.* 12, 565–571.
- Zeileis, A., Hothorn, T., 2002. Diagnostic checking in regression relationships. *R. News* 2, 7–10. URL <http://CRAN.R-project.org/doc/Rnews/>. (Accessed 8 October 2019).
- Zepp, R.G., Cline, D.M., 1977. Rates of direct photolysis in aquatic environment. *Environ. Sci. Technol.* 11, 359–366. <https://doi.org/10.1021/es60127a013>.
- Zhou, J.L., Rowland, S.J., Fauzi, R., et al., 1997. Desorption of tefluthrin insecticide from soil in simulated rainfall runoff systems—Kinetic studies and modelling. *Water Res.* 31, 75–84. [https://doi.org/10.1016/S0043-1354\(96\)00237-0](https://doi.org/10.1016/S0043-1354(96)00237-0).