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Author(s) :Daniel Hulbert, Rufus Isaacs, Christine Vandervoort, and John C. Wise
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Rainfastness and Residual Activity of Insecticides to Control Japanese Beetle (Coleoptera: Scarabaeidae) in Grapes

DANIEL HULBERT,[1,2] RUFUS ISAACS,[1] CHRISTINE VANDERVOORT,[3] AND JOHN C. WISE[1]

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ABSTRACT Field-based bioassays and residue profile analysis were used to determine the relative toxicity, rainfastness, and field degradation over time of five insecticides from five insecticide classes on adult Japanese beetles, *Popillia japonica* Newman (Coleoptera: Scarabaeidae), in grapes, *Vitis labrusca* L. Bioassays assessed Japanese beetle condition as alive, knockdown, or immobile when exposed for 24 h or 7-d field-aged residues of phosmet, carbaryl, bifenthrin, thiamethoxam, or indoxacarb after 0, 12.7, or 25.4 mm of rain had been simulated. We found that the two most toxic insecticides to Japanese beetle were phosmet and carbaryl, followed by bifenthrin, thiamethoxam, and then indoxacarb. The efficacy of phosmet decreased because of rainfall, but not because of field aging. The efficacy of carbaryl decreased because of rainfall and field aging. The efficacies of bifenthrin and thiamethoxam were not affected by rainfall but decreased because of field aging. The efficacy of indoxacarb was not affected by rainfall or field aging. This study will help vineyard managers make informed decisions on when reapplications of insecticides are needed with the aim of improving integrated pest management programs.

KEY WORDS rainfastness, residual activity, Japanese beetle, grapes, residue profile

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In eastern and central North America, the Japanese beetle, *Popillia japonica* Newman (Coleoptera: Scarabaeidae), is an invasive pest of ornamentals, turfgrass, fruits, and vegetables. Japanese beetles were first discovered in the United States 1916 in New Jersey and are now a major pest, causing US$450 million in damage to ornamental plants and turf in the eastern United States (Fleming 1972, Potter and Held 2002). The Japanese beetle is univoltine; the adults emerge in midsummer (depending on climate) and feed on plant foliage. During this time, females dig into the ground to lay eggs. The eggs hatch, and the larvae feed on plant roots for the remainder of the summer and then overwinter in the soil. During the spring, the larvae complete their development, and by early summer they emerge as adults. During the periods of adult emergence, late June to September in Michigan, Japanese beetles feed in aggregations on the foliage of their host plants. Japanese beetle adults feed on >300 plant species, including grapes (*Vitis* spp.) (Fleming 1972, Potter and Held 2002). The phenology and behavior of Japanese beetles make them difficult to control in the crops they favor.

On grape foliage, Japanese beetle feeding damage is evident as clusters of small holes in the leaf tissue. Grape vines are able to withstand some feeding damage, but too much defoliation can decrease and delay fruit set as well as reduce fruit quality (Boucher and Pfeiffer 1989). Defoliation also may decrease the cold hardiness of the buds and canes (Mansfield and Howell 1981). The grape industry is economically important to Michigan, with the value of the 2008 grape crop worth >US$26 million (USDA–NASS 2010). Currently, broad-spectrum insecticides such as organophosphates, carbamates, and pyrethroids are the most commonly used insecticides for Japanese beetle control in Michigan grapes (Agriculture Across Michigan 2009).

The rate and pattern of insecticide degradation in the environment varies for different compounds and is influenced by several key drivers such as temperature, UV light, plant metabolism, and mircoorganisms (Bertrand and Barceló 1991, Baskaran et al. 1999, Burrows et al. 2002, Sinderhauf and Schwack 2003, de Urzedo et al. 2007). Recent studies in fruit crops have shown that applications of organophosphate insecticides result in primarily surface residues on the fruit and foliage, whereas for neonicotinoid insecticides the portions of residues that penetrate plant tissues provide extended residual activity (Wise et al. 2006). The decline in insecticide active residues due to field aging is a concern to farmers, and the ultimate impact on plant protection varies by the specific pesticide, insect, and crop involved (Wise and Whalon 2009).

Michigan receives an average of 24.5–38.1 millimeters of rainfall during the grape growing season (Michigan Automated Weather Network 2011). This has important implications for the fate of insecticides sprayed. Overestimation of wash-off can cause unwar-

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[1] Department of Entomology, Michigan State University, East Lansing, MI 48824–1311.

[2] Corresponding author, e-mail: hulbertd@msu.edu.

[3] MSU Pesticide Analytical Laboratory, Michigan State University, East Lansing, MI 48824–1311.

ranted reapplications of insecticides, and underestimation may result in vine damage and crop loss. Insecticide wash-off also has important environmental and public safety implications (Pimentel et al. 1992). Research to date on the impact of precipitation on insecticides has primarily targeted older chemistries, such as organophosphates and carbamates, or is in the context of cotton and field crops (McDowell et al. 1984; Willis et al. 1992, 1994, 1996; Zhou et al. 1997). Thus, the information available for grape farmers about reapplication of insecticides after rainfall comes from either this limited research or "conventional wisdom."

Many of the newer reduced risk (USEPA 1997) insecticides have chemical properties different from the conventional organophosphate, carbamate, and pyrethroid compounds and have not been studied under rainfall conditions. Understanding the performance characteristics of old and newer insecticides under rainfall conditions could prevent unnecessary insecticide reapplication and the associated costs.

The objectives of this study were to 1) determine the effect of rainfall on the effectiveness against Japanese beetles of five different insecticides representing five major classes of insecticides, 2) determine the relative effect of aging in the field for these insecticides, and 3) compare the relative performance of these insecticides against each other as they age and receive rainfall.

Materials and Methods

Insects. Japanese beetle adults were collected from grass fields at the Michigan State University Trevor Nichols Research Center (TNRC) in Fennville, MI (42.5951° N, −86.1561° W), during July 2008 and August 2009. Beetles were captured using yellow and green canister traps with a floral lure (Great Lakes IPM, Vestaburg, MI) during the 24-h period preceding each study. After collection, beetles were held in cages with nonsprayed Concord grape (*Vitis labrusca* L.) foliage at ≈25°C and a photoperiod of 16:8 (L:D) h. Healthy beetles exhibiting mobility on the foliage were used in the experiments.

Field Plots and Treatment Applications. In 2008, each field plot consisted of one row of seven mature *V. labrusca* 'Concord' grape vines, with five replicate plots for each of the five insecticide treatments and one control (Table 1). We avoided the addition of any spray adjuvants so as to attain baseline data that represent the rainfastness characteristics of representative insecticides alone. A minimum of two buffer rows separated each treatment row. Insecticide treatments were applied at labeled rates by using an FMC 1029 airblast sprayer calibrated to deliver 467.5 liters water/ha (50 gal/acre) (Table 1). Insecticide applications were made on 22 July 2008 and 5 August 2009 at timings that are representative offspring sprays for Japanese beetles in Michigan vineyards (Wise et al. 2010b). These plots served as the source of foliage for use in bioassays and residue analysis. Untreated control (UTC) plots were not sprayed. Daily high and low temperatures, and precipitation volumes were recorded with an automated weather station (Michigan Automated Weather Network 2011) located within 1 km of the field plots.

Bioassays. In 2008 bioassays were used to compare the toxicity of the five insecticides and to determine the temporal progression of these effects as the residues aged in the field and received rainfall. Grape shoots of four to five leaves were collected from the field plot 24 h and 7 d after application.

Shoots were then randomly selected for exposure to different simulated rainfall regimes. Shoots were placed in water-soaked floral foam bricks (Smithers-Oasis Co., Kent, OH) that were placed in the rain booth, a Generation three Research Track Sprayer (DeVries Manufacturing, Hollandale, MN). Shoots received either 0, 12.7, or 25.4 mm of simulated rain. Three rain gauges were placed around the inside of the rain booth to accurately assess the amount and uniformity of simulated rain treatments. Shoots not assigned to receive rainfall were not placed in the rain booth.

From each shoot the most recent fully expanded leaf from the distal end was removed and placed in water-soaked floral foam in a clear polypropylene 950-ml container (Fabri-Kal, Kalamazoo, MI), with a lid added to complete the bioassay chamber. The foam was covered with sealing wax (Gulf Wax, distributed by Royal Oak Sales, Inc., Roswell, GA) to preserve the integrity of the foliage by reducing evaporation. Holes were punched in the lid to reduce condensation of water vapor inside the container and minimize risk of fumigation effects. Each of these containers was considered an experimental unit in the bioassays. As soon as bioassay arenas were prepared, five randomly selected Japanese beetle adults were placed in the bottom of each arena and the containers were held in the laboratory at 21°C and a photoperiod of 16:8 (L:D) h. There were five replicates for each treatment at each post application time interval and rainfall amount

Table 1. Formulated compounds, field rates, and concentrations used for bioassay experiments and residue analysis

Formulated name	Chemical class	AI	Rate/acre	g (AI)/a	ppm	Company
Imidan 70 WP	Organophosphate	Phosmet	2 lb	1,569	3,355	Gowan Company Yuma, AZ
Sevin XLR 4L	Carbamate	Carbaryl	2 qt	4,481	9,586	Bayer CropScience, Pittsburgh, PA
Capture 2EC	Pyrethroid	Bifenthrin	6.4 fl oz	112	240	FMC Corp., Princeton, NJ
Actara 25 WG	Neonicotinoid	Thiamethoxam	3.5 oz	61	131	Syngenta Crop Protection, Greensboro, NC
Avaunt 30WG	Oxadiazine	Indoxacarb	6 oz	126	269	DuPont Crop Protection, Wilmington, DE

All preparations were based on 468 liter/ha spray volume (50 gall/acre).

combination. The number of beetles that were alive, immobile, or in a knockdown condition was recorded after 0, 4, 24, and 48 h of exposure. The knockdown condition was defined as beetles that were twitching in a nonupright position at the bottom of the container. Beetles were counted as alive if they seemed to behave normally.

The proportion of the leaf defoliated by Japanese beetles was determined for each leaf used in the bioassay. This was done by using Photoshop Elements, version 8.0 (Adobe Systems, San Jose, CA). Images of the leaves were scanned into a computer using a Canon Image Runner c2880/c3380. Different layers of the image were created for damaged and undamaged areas of leaf tissue using the Magic Wand Tool in Photoshop (Adobe Systems). The numbers of pixels comprising the two layers of the image were determined using the Histogram window in Photoshop, and the proportion of the leaves defoliated was calculated. These data were arcsine square-root transformed before being analyzed by a two-way analysis of variance (ANOVA) in which there were two levels of the field aging factor (24 h and 7d) and three levels in the rainfall simulation factor (0, 12.7, or 25.4 mm).

The mean proportions of beetles in a particular condition were compared across insecticide treatment by an ANOVA on arcsine square-root–transformed values. Mean separation was done using Tukey's honestly significant difference (HSD) test. These data also were analyzed by logistic regression to determine the time at which half of the organisms were in the immobile condition (LT_{50}) (Robertson et al. 2007). Logistic regressions analyses were performed at every insecticide, rainfall, and aging combination. These analyses were conducted in R, version 2.12.1 (R Development Core Team 2010) using the MASS library (Venables and Ripley 2002), the lmtest library (Zeileis and Hothorn 2002), and the doBy library (Højsgaard et al. 2011).

In 2009, a similar spray and rainfall regimen was repeated during the summer, but with a focus on fruit cluster residues. After 24-h aging time in the field, clusters of grapes were collected form field plots of Concord grapes. These clusters were subjected to the same rainfall regimen as the shoots were in 2008. The clusters were pruned to 10 berries and placed in bioassay chambers constructed as they were in 2008. Beetles were evaluated in the same manner as in 2008, and data were analyzed the same as in 2008. A 7-d harvest, rainfall simulation, and bioassay setup were planned for the 2009 experiment, but a natural rainfall event occurred on 10 August 2009, so the 7-d part of the experiment was eliminated.

Insecticide Residue Analysis. In 2008, a parallel series of foliage samples were taken from field plots after 24 h postapplication time and received the same rainfall regimen as the shoots used in the bioassays (0, 12.7, or 25.4 mm). There were three replicates for each treatment at both of the postapplication time intervals.

To determine the amount of residue on the leaf surfaces, 10-g samples of grape leaves 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 sample was dried via rotary evaporation and brought up in acetonitrile for HPLC analysis. The remaining leaf 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).

Samples were analyzed for insecticide residue with a 2690 Separator Module HPLC equipped with a 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 AG 1998). The mobile phase was water/acetonitrile (80:20) at 55°C. The HPLC level of quantification was 0.457 μg/g (ppm) active ingredient, and level of detection was 0.138 ppm.

In 2009, the fruit residues were analyzed using the same methods as in 2008, except that 10 g of grape fruit were used for insecticide analysis.

Results

Inherent Toxicity. In 2008, Japanese beetles exposed to grape leaves with 24-h field-aged insecticide residues exhibited significantly higher numbers in the immobile condition after 48 h than those exposed to untreated grape leaves ($F = 90.55$; df = 5, 24; $P < 0.001$) (Fig. 1). Japanese beetles exposed to grape leaves with 24-h field-aged insecticide residues exhibited significantly lower numbers of beetles in the alive condition after 48 h than when exposed to untreated grape leaves after 48 h ($F = 33.93$; df = 5, 24; $P < 0.001$) (Fig. 1). Beetles exposed to grape leaves with 24-h field-aged residues of thiamethoxam, indoxacarb, and bifenthrin exhibited significantly higher numbers in the knockdown condition after 48 h than those exposed to residues of phosmet, carbaryl, and untreated grape leaves ($F = 11.75$; df = 5, 24; $P < 0.001$) (Fig. 1).

In 2009, Japanese beetles exposed to grape berries with carbaryl and bifenthrin 24-h field-aged residues exhibited significantly higher numbers in the immobile condition after 48 h than those exposed to untreated grape clusters ($F = 6.09$; df = 5, 24; $P < 0.001$) (Fig. 2). Japanese beetles exposed to grape berries with thiamethoxam 24-h field-aged residues exhibited significantly higher numbers in the knockdown condition than those exposed to untreated grape fruit ($F = 3.53$; df = 5, 24; $P = 0.016$) (Fig. 2). Japanese beetles exposed to grape fruit with phosmet, carbaryl, bifenthrin, or thiamethoxam 24-h field-aged residues exhibited significantly lower numbers of beetles displaying the alive condition than those exposed to untreated grape fruit ($F = 17.73$; df = 5, 24; $P < 0.001$) (Fig. 2).

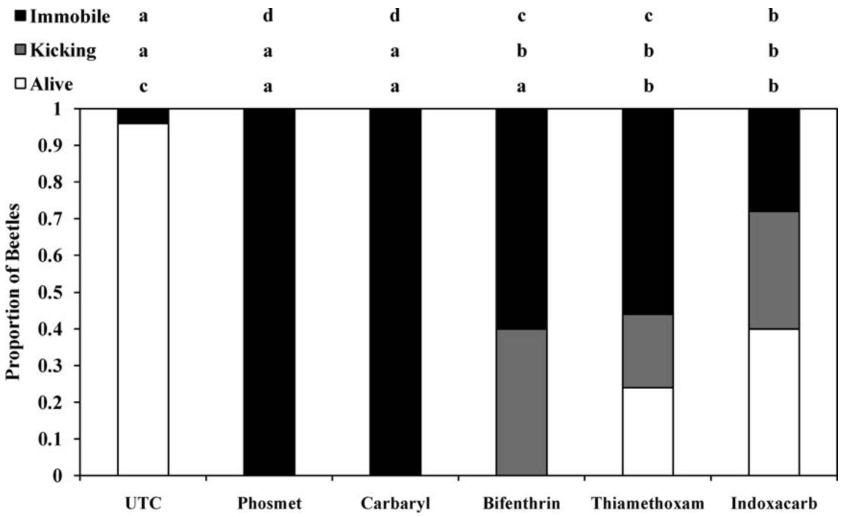

Fig. 1. Mean proportion of beetles observed in different conditions after 48 h of exposure to grape foliage with 24-h field-aged residues from 2008. Letters above the bars within a row show significant differences among insecticides within each condition, and bars with the same letter are not significantly different ($P < 0.05$). Data were arcsine square-root transformed before ANOVA. Mean separation calculated using the Tukey's HSD test. Data shown are nontransformed means.

Effect of Rainfall and Field Aging. Using the 2008 data, the time at which half of the Japanese beetles were killed (LT_{50}) by insecticides was calculated as a measure of toxicity for each insecticide on grape leaves at different rainfall and aging combinations. The LT_{50} values for phosmet were higher on leaves receiving rainfall, but no increase in LT_{50} values was seen after 7-d field aging of leaves treated with phosmet (Table 2). The LT_{50} values for carbaryl increased as rainfall increased but did not increase with field aging time (Table 2). The LT_{50} values for bifenthrin on grape leaves did not increase with rainfall, but they did increase after 7-d field aging (Table 2). The LT_{50} values for thiamethoxam did not increase on leaves after rainfall occurred and did not increase after the residues had been aged for 7 d in the field (Table 2). The LT_{50} values for indoxacarb did not increase on leaves after rainfall occurred and did not increase after the residues had been aged for 7 d in the field (Table 2).

Rainfall amount and field aging time affected defoliation by depending on which insecticide was sprayed. Defoliation of leaves sprayed with phosmet was significantly affected by rainfall on the leaves ($F = 8.45$; df = 1, 26; $P = 0.007$) but not aging ($F = 1.58$; df =

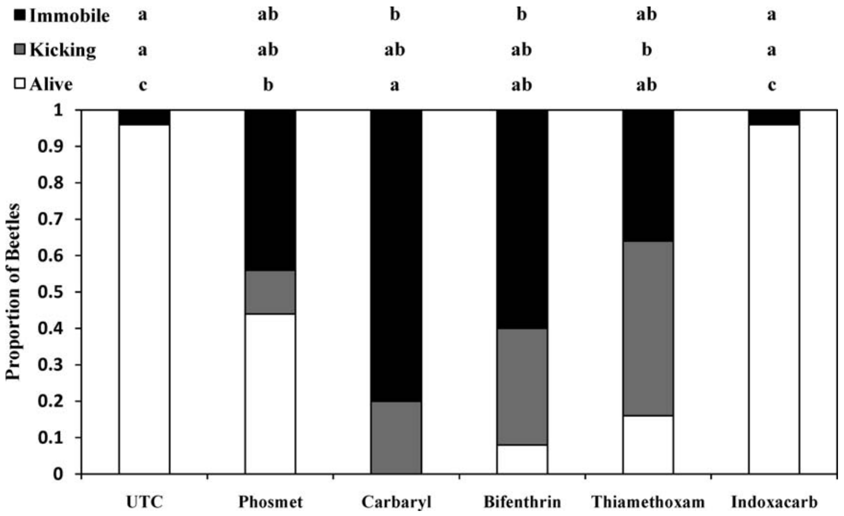

Fig. 2. Mean proportion of beetles observed in different conditions after 48 h of exposure to grape fruit with 24-h field-aged residues from 2009. Letters above the bars within a row show significant differences among insecticides within each condition, and bars with the same letter are not significantly different ($P < 0.05$). Data were arcsine square-root transformed before ANOVA. Mean separation calculated using the Tukey's HSD test. Data shown are nontransformed means.

Table 2. LT_{50} values for the insecticides sprayed on grape leaves at all rainfall and field aging combinations for Japanese beetle adults from the 2008 experiment

Insecticide	Field aging (d)	Rainfall (mm)	n	Slope (+SE)	LT_{50} (h)	95% CI	χ^2
Phosmet	1	0	20	−0.27 (+0.06)	11.56	(7.54, 15.57)	<0.0001
		12.7	20	−0.07 (+0.01)	33.54	(25.45, 41.62)	<0.0001
		25.4	20	−0.08 (+0.02)	40.30	(32.24, 48.36)	<0.0001
	7	0	20	−0.19 (+0.04)	19.70	(15.85, 23.56)	<0.0001
		12.7	20	−0.06 (+0.02)	59.39	(41.45, 77.34)	0.0014
		25.4	20	−0.09 (+0.02)	43.35	(35.80, 50.90)	<0.0001
Carbaryl	1	0	20	−0.20 (+0.04)	18.95	(15.14, 22.76)	<0.0001
		12.7	20	−0.13 (+0.03)	25.64	(20.70, 30.58)	<0.0001
		25.4	20	−0.10 (+0.02)	38.49	(32.08, 44.90)	<0.0001
	7	0	20	−0.18 (+0.03)	17.49	(13.51, 21.47)	<0.0001
		12.7	20	−0.09 (+0.02)	29.92	(23.48, 36.36)	<0.0001
		25.4	20	−0.09 (+0.02)	47.18	(38.48, 55.88)	<0.0001
Bifenthrin	1	0	20	−0.07 (+0.01)	34.07	(26.24, 41.90)	<0.0001
		12.7	20	−0.11 (+0.02)	30.60	(24.87, 36.33)	<0.0001
		25.4	20	−0.10 (+0.02)	31.30	(25.04, 37.56)	<0.0001
	7	0	20	−0.05 (+0.02)	57.74	(39.11, 76.37)	0.0010
		12.7	20	−0.06 (+0.01)	44.60	(33.29, 55.91)	<0.0001
		25.4	20	−0.82 (+256.76)	50.43	(−1,440.96, 1,541.82)	0.9975
Thiamethoxam	1	0	20	−0.06 (+0.01)	35.83	(26.43, 45.24)	<0.0001
		12.7	20	−0.08 (+0.02)	53.62	(41.56, 65.67)	0.0003
		25.4	20	−0.05 (+0.02)	67.54	(40.52, 94.55)	0.0066
	7	0	20	−0.07 (+0.03)	65.38	(42.98, 87.78)	0.0105
		12.7	20	−0.06 (+0.02)	55.84	(40.39, 71.29)	0.0005
		25.4	20	−0.80 (+153.43)	49.73	(−597.96, 697.41)	0.9958
Indoxacarb	1	0	20	−0.11 (+0.04)	56.53	(44.70, 68.35)	0.0077
		12.7	20	−0.77 (+260.11)	52.12	(−2,669.06, 2,773.30)	0.9976
		25.4	20	−0.08 (+0.04)	73.19	(37.90, 108.47)	0.0556
	7	0	20	−0.84 (+252.54)	49.64	(−914.03, 1,013.32)	0.9973
		12.7	20	−0.07 (+0.03)	66.19	(43.15, 89.23)	0.0110
		25.4	20	−0.84 (+252.68)	49.64	(−914.47, 1,013.76)	0.9973

1, 26; P = 0.220) (Fig. 3B). Defoliation of leaves sprayed with carbaryl was significantly affected by rainfall (F = 39.122; df = 1, 26; P < 0.001) and aging (F = 38.335; df = 1, 26; P < 0.001) (Fig. 3C). In contrast defoliation of leaves sprayed with bifenthrin was not significantly affected by rainfall (F = 0.849; df = 1, 26; P = 0.365) but was significantly affected by aging (F = 15.729; df = 1, 26; P < 0.001) (Fig. 3D). Defoliation of leaves sprayed with thiamethoxam was not significantly affected by rainfall (F = 0.016; df = 1, 26; P = 0.900) but was significantly affected by aging (F = 7.640; df = 1, 26; P = 0.010) (Fig. 3E). Defoliation of leaves sprayed with indoxacarb was not significantly affected by rainfall (F = 1.789; df = 1, 26; P = 0.193) and was not significantly affected by aging (F = 0.176; df = 1, 26; P = 0.678) (Fig. 3F).

In 2009 experiments, the LT_{50} values of the Japanese beetles that were killed by insecticides were calculated as a measure of toxicity for each insecticide on grape fruit at different rainfall levels. The LT_{50} values for phosmet, carbaryl, thiamethoxam, and indoxacarb on grape fruit did not increase after rainfall (Table 3).

Residue Analysis. In 2008, the residue analysis of grape leaves treated with insecticides showed evidence of wash off because of rain for some compounds. Of the 24-h aged residues, phosmet and bifenthrin showed ≈50% wash-off from 12.7 mm of simulated rain, whereas thiamethoxam, indoxacarb, and carbaryl residues were minimally affected (Table 4). Of the 24-h aged residues, phosmet, carbaryl, bifenthrin, and indoxacarb showed 50% or more wash-off from 25.4 mm of simulated rain, whereas thiamethoxam residues remained stable.

In 2009, the residue analysis of grape fruit treated with insecticides showed evidence of wash off because of rain for some compounds and differences between patterns of wash-off between surface and subsurface residues. Phosmet readily washed off the surface of the fruit, but subsurface residues were less affected (Table 5). Carbaryl, bifenthrin, and thiamethoxam residues remained relatively stable under rainfall conditions, but declining subsurface values suggest cuticle partitioning as surface residues are exposed to water. For indoxacarb, the limited surface residues were susceptible to washed off, but subsurface residues were stable under rainfall conditions.

Discussion

This study provides new insights into the rainfastness of grape insecticides as well as the influence of inherent toxicity and field residual on the overall performance of a compound after precipitation. We found that the two most toxic insecticides to Japanese beetle were phosmet and carbaryl, followed by bifenthrin, thiamethoxam, and then indoxacarb. For the more toxic compounds, especially phosmet and bifenthrin, their inherent toxicity in effect masks their weakness in terms of wash-off susceptibility. This was most evident when comparing the high proportion of residue loss at 12.7 mm of simulated rainfall, but the minimal impact on performance in terms of Japanese

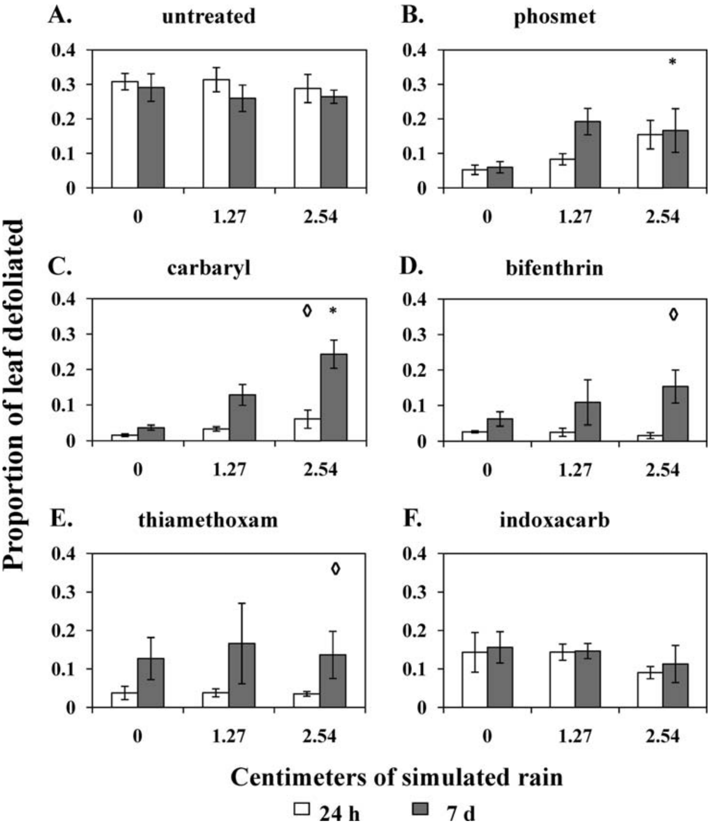

Fig. 3. Mean ± SE proportion of grape leaves defoliated alive after 48 h of beetle exposure to leaves treated with insecticides. Insecticide treated leaves were aged in the field for 24 h or 7 d before bioassay setup. A significant effect of rainfall is represented with an asterisk (*). A significant effect of field aging is represented with a diamond (◊). Data were arcsine square-root transformed before two-way ANOVA ($\alpha = 0.05$). Nontransformed means are shown.

beetle survival in the 24-h field-aged bioassays. Differing patterns were also found between insecticide toxicity on grape leaves versus fruit.

A compound's field residual also influences the observed performance under rainfall conditions. As with inherent toxicity, the negative effects of residue wash-off for phosmet is minimized by its relatively high environmental persistence. Conversely for carbaryl and bifenthrin, the negative effects of residue wash-off are compounded by their weaker residual activity.

Even though thiamethoxam and indoxacarb were the weakest in terms of inherent toxicity, based on both residue and bioassay results, they were shown to be the most resistant to wash-off from precipitation.

Table 3. LT$_{50}$ values for insecticides sprayed on grape berries after 0, 12.7, or 24.5 mm of rainfall, for Japanese beetle adults from the 2009 experiment

Insecticide	Rainfall (mm)	*n*	Slope (+SE)	LT$_{50}$ (h)	95% CI	χ^2
Phosmet	0	20	−0.06 (+0.06)	49.80	(36.59, 63.01)	0.0001
	12.7	20	−0.06 (+0.02)	55.84	(40.39, 71.29)	0.0005
	25.4	20	−0.02 (+0.016)	153.41	(−90.31, 397.13)	0.2948
Carbaryl	0	20	−0.07 (+0.01)	23.40	(16.50, 30.30)	<0.0001
	12.7	20	−0.03 (+0.01)	57.53	(25.71, 89.35)	0.0161
	25.4	20	−0.07 (+0.01)	33.63	(25.46, 41.81)	<0.0001
Bifenthrin	0	20	−0.06 (+0.01)	34.71	(25.57, 43.86)	<0.0001
	12.7	20	−0.06 (+0.01)	19.05	(11.14, 26.95)	<0.0001
	25.4	20	−0.02 (+0.01)	103.08	(−1.23, 207.39)	0.1300
Thiamethoxam	0	20	−0.01 (+0.01)	90.55	(−68.09, 249.19)	0.3672
	12.7	20	−0.05 (+0.01)	46.25	(32.34, 60.16)	0.0002
	25.4	20	−0.06 (+0.01)	44.09	(32.44, 55.74)	<0.0001
Indoxacarb	0	20	−0.05 (+0.04)	109.62	(−20.79, 240.02)	0.2536
	12.7	20	−0.02 (+0.02)	177.63	(−186.99, 542.24)	0.4077
	25.4	20	−0.03 (+0.02)	88.07	(21.51, 154.64)	0.0589

Table 4. Insecticide residues recovered on grape leaves after 24-h field aging after 0, 12.7, or 25.5 mm of rain

Insecticide	Simulated rainfall		
	0 mm	12.7 mm	25.4 mm
Phosmet	220.7	146	157.6
Carbaryl	40.9	39.8	2.7
Bifenthrin	588.9	249.8	130.4
Thiamethoxam	2.9	2.8	3.9
Indoxacarb	0.6	0.4	0.2

Residue values are presented as in micrograms per gram (ppm) of active ingredient per 10 g of leaves.

The contact toxicity of thiamethoxam on beetles is known to be short lived, but as residues move into plant tissue antifeedant effects become more prominent (Hoffmann et al. 2010). The antifeedant effects of thiamethoxam on Japanese beetle protect grape leaves from defoliation (Fig. 3E), but as measured in this study would not be credited as direct toxicity. One possible reason indoxacarb was shown to be the least toxic to Japanese beetles in this experiment is that ingestion is an important mode of entry for the bioactivation of formulated DPX-JW062 to its decarbo methoxylated metabolite (Wing et al. 1998, Tillman et al. 2002). If the time duration used in our bioassays was longer, higher levels of mortality may have been observed.

Insecticides were less toxic to Japanese beetles when applied to grape fruit than to grape leaves, and the toxicity of the insecticides on grape fruit was not affected by rainfall. There are a couple of reasons why this may have occurred. In the bioassay experiments, Japanese beetles consumed more leaf material than fruit material. It is expected that ingestion of the insecticides causes higher toxicity than physical contact. Indoxacarb, for example, must be ingested for the insecticide to become activated (Wing et al. 1998, Tillman et al. 2002). The decreased exposure to insecticide residues from ingestion of fruit would mask the effects of rainfall on toxicity to Japanese beetles. There are probably cuticular and wax composition differences between the grape leaves and fruit that also could account for differences in an insecticide's performance.

One physical property of insecticides which affects its behavior in the environment, including rainfastness, is the octanol-water partition coefficient, K_{ow}, defined as the ratio of a chemical's concentration in an octanol solution ($[C_i]_{octanol}$) over its concentration in aqueous solution ($[C_i]_{water}$) (Leo et al. 1971):

$$K_{ow} = \frac{[C_i]_{octanol}}{[C_i]_{water}}.$$

K_{ow} varies from $\approx 10^{-3}$ to 10^7 and is usually expressed as $\log(K_{ow}) = P_{ow}$. Chemicals with lower P_{ow} are polar and have high solubility in water. Chemicals with higher P_{ow} are nonpolar and have low water solubility (Ragnarsdottir 2000). Phosmet has a P_{ow} of 2.83 (Chiou et al. 1977), an indication that phosmet has a lower water solubility and is more lipophilic. This would allow phosmet molecules to bind to the waxy cuticle, but have very limited penetrative capacity further into plant tissues. Although resistant to aging, phosmet was susceptible to wash-off. Carbaryl has a log P_{ow} of 2.34 (Noble 1993), indicating some resistance to wash off by rainfall. The residue data in our study showed carbaryl to be relatively rainfast at 12.7 mm of rain, but at 25.4 mm dramatic loss of residues was observed. It is well documented that carbaryl degrades in aqueous environments when exposed to sun and sun-like light (Zepp and Cline 1977, Wolfe et al. 1978, Bertrand and Barceló 1991). In addition, carbaryl has been found to become more unstable at higher temperatures (Lartiges and Garrigues 1995) and have its shortest half-life, ≈1 wk, during June and July compared with the rest of the year (Wolfe et al. 1978). The P_{ow} of bifenthrin is >6 (Baskaran et al. 1999), indicating that bifenthrin is highly lipophilic. It is likely the lipophilic tendency of bifenthrin that made it highly rainfast in this study. Although pyrethroids are considered to be more stable than pyrethrins, this study demonstrated a dramatic loss of efficacy for bifenthrin after 7 d of field aging. Thiamethoxam has a P_{ow} of -0.13 and is a systemic insecticide. It is known that thiamethoxam degrades readily when exposed to UV light (de Urzedo et al. 2007); thus, the systemic nature of thiamethoxam is probably the reason for its rainfastness. The systemic property of this insecticide is noticeable by its relatively low toxicity to Japanese beetles (Table 2) but its relatively high level of protection of the foliage (Fig. 3). Thiamethoxam is also known to be converted to clothianidin in plants (Nauen et al. 2003), which may provide extended protection to plants sprayed with thiamethoxam in the field. Indoxacarb has a P_{ow} of 4.6, indicating that indoxacarb is highly lipophilic. Indoxacarb's rainfastness is probably a result of penetration

Table 5. Insecticide residue recovered on grape fruit after 24-h field aging time after 0, 12.7, or 25.4 mm of rain

Insecticide	Simulated rainfall					
	0 mm		12.7 mm		25.4 mm	
	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface
Phosmet	0.08	0.07	0.00	0.03	0.01	0.08
Carbaryl	0.05	0.02	0.09	0.19	0.08	0.15
Bifenthrin	0.24	0.70	0.22	0.54	0.20	0.38
Thiamethoxam	0.02	0.07	0.01	0.05	0.02	0.09
Indoxacarb	0.03	0.63	0.02	0.90	0.0	0.62

Residue values are presented in micrograms per gram (ppm) of active ingredient per 10 g of fruit.

into the plant cuticle by means of the lipophylic pathway, compared with the polar pathway preferentially used by systemic insecticides such as the neonicotinoids (Buchholz 2006, Schönherr 2006).

As a result of this research we emphasize that vineyard managers should consider the compound's rainfastness characteristics as well as the relative toxicity and field residual of the insecticide as a part of their integrated pest management (IPM) decision-making process. The decision of whether or not to reapply an insecticide after a rainfall event will depend on these parameters as well as the nature of the target insect, whether it is a direct or indirect pest, and the quality standards of the market for which the crop will be sold. We have developed a "rainfastness decision chart" as a practical research-based guide for grape growers to use in their IPM program, with the purpose of reducing unnecessary pesticide sprays, and to enhance the sustainability of domestic fruit production (Wise et al. 2010a).

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