Reduced ultraviolet light transmission increases insecticide longevity in protected culture raspberry production

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High tunnels are large protective structures used for season extension of many crops, including raspberries. These structures are often covered in plastic films to reduce and diffuse ultraviolet light transmission for pest and disease control, but this may also affect the photodegradation and efficacy of pesticides applied under these tunnels. We compared the residue levels of ten insecticides under three tunnel plastics with varying levels of UV transmission and open field conditions. Raspberry plants placed in research-scale tunnels were treated with insecticides and residues on fruit and foliage were monitored for one or two weeks in early 2015 and early and late 2016. Plastics that reduce UV transmission resulted in 50% greater residues of some insecticides compared to transparent plastics, and 60% compared to uncovered tunnels. This increased persistence of residues was evident within 1 day and remained consistently higher for up to 14 days. This pattern was demonstrated for multiple insecticides, including bifenthrin, esfenvalerate, imidacloprid, thiamethoxam, and spinosad. In contrast, the insecticide malathion degraded rapidly regardless of the plastic treatment, indicating less sensitivity to photodegradation. Bioassays using insecticide-treated leaves that were under UV-blocking plastic revealed higher mortality of the invasive fruit pest, Drosophila suzukii, compared to leaves that were uncovered. This indicates that the activity of pesticides under high tunnels covered in UV-reducing plastics may be prolonged, allowing for fewer insecticide applications and longer intervals between sprays. This information can be used to help optimize pest control in protected culture berry production.

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1. Introduction

Raspberries are an economically important crop that enhance human diets throughout the world (Manganaris et al., 2014; Yang and Kortesniemi, 2015). Raspberry growers are increasingly implementing high tunnels to better control their climatic variability and expand the regions where berry production can be profitable (Kadir et al., 2006; Thompson et al., 2009; Lamont, 2009; Demchak, 2009; Neri et al., 2012). High tunnels are steel structures covered with plastic which enable modification and greater control of the crop environment, extending the growing season into both the spring and the fall (Lamont, 2009; Giacomelli, 2009; Hanson et al., 2011). This approach also protects the plants from rain, which is a frequent concern for producers in many temperate production regions, thereby reducing disease incidence and preventing wash-off of pesticide residues (Demchak, 2009; Hanson et al., 2011; Neri et al., 2012).

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Increasingly, production under these tunnels is being optimized through the manipulation of the plastic covering type. Various plastics can be selected for their specialized features, based on the needs of the crop and region, including light diffusion, manipulation of infrared radiation, and decreased condensation (Esplin et al., 2006; Heidenreich et al., 2008; Lamont, 2009). Plastics manufacturers are also developing ways to reduce the transmission of ultraviolet (UV) light. This began primarily for improved plant growth and yield (Kataoka et al., 2003; Dufaut and Ward, 2009), but blocking UV light has also been found to reduce disease and pest incidence in tunnel-grown crops (Esplin et al., 2006; Heidenreich et al., 2008). Ultraviolet light that reaches the earth’s surface has a wavelength from 280 to 400 nm, slightly shorter than the visible light spectrum for humans. The visible spectrum of light for insects, however, includes UV light, and disrupting this has been shown to have behavioral effects on dispersion, feeding, and mating of whiteflies, aphids, and some other pests (Antignus et al., 2001; Costa et al., 2002; Diaz and Fereres, 2007; Doukas and Payne, 2007; Johansen et al., 2011; Ben-Yakir and Fereres, 2016). Blocking UV light transmission also reduces disease incidence, since it is required for sporulation by many common fungal pathogens (Reuveni et al., 1989; Nicot and Baille, 1996; Raviv and Antignus, 2004; Paul et al., 2005; Ben-Yakir and Fereres, 2016).

While these plastics may be promising for reducing disease and insect pest pressure in raspberry production, occasional pesticide applications are still required for controlling pest outbreaks, and these plastics have the potential to affect pesticide degradation. This is especially important for managing the invasive insect, spotted wing Drosophila (Drosophila suzukii), a devastating new pest of this and other berry crops (Asplin et al., 2015). Management of this insect can include cultural (Leach et al., 2016, 2017) and biological (Daane et al., 2016; Woltz and Lee, 2017) approaches, but in larger commercial production settings, frequent insecticide applications are commonly used to protect berries from infestation by its larvae (VanTimmeren and Isaacs, 2013; Diepenbrock et al., 2016). It is important to maintain control of D. suzukii through the long ripening period of raspberries, and high tunnel coverings that reduce pesticide degradation may allow for less frequent applications and/or improved control.

The rates of degradation of pesticides are influenced by light, plant metabolism, temperature, and microorganisms (Baskaran et al., 1999; Burrows et al., 2002; Sinderhauf and Schwack, 2003). Photodegradation by sunlight is a major abiotic degradation pathway of chemicals largely caused by light in the ultraviolet spectrum (Schwarzenbach et al., 2003). Photodegradation of pesticides tends to happen within the first few hours after the application, so reducing UV light is expected to change the initial degradation curve of these chemicals (Burrows et al., 2002; de Urzeda et al., 2007; Weber et al., 2009). Reduced degradation of pesticides has previously been reported on crops grown under protective structures compared to open fields (Garaux et al., 2002; Weber et al., 2009; Allen et al., 2015; Sun et al., 2015). Van Emden and Hadley (2011) found that the insecticide cypermethrin can provide sustained control on the confused flour beetle (Tribolium confusum) for up to 6 months longer in bioassays when exposed to a UV reducing plastic compared to a UV transparent plastic. However, the dissipation of commonly used insecticides under protected culture with UV reducing plastics has not been studied in raspberries or other berry crops, despite the widespread use of these plastics across this industry. This may be increasingly important in many berry production regions due to the widespread use of these plastics across this industry. This may be increasingly important in many berry production regions due to the widespread use of these plastics across this industry. This may be increasingly important in many berry production regions due to the widespread use of these plastics across this industry. This may be increasingly important in many berry production regions due to the widespread use of these plastics across this industry. This may be increasingly important in many berry production regions due to the widespread use of these plastics across this industry.

Understanding how insecticides may degrade differently under specialty plastics will be important for developing appropriate intervals between applications, and for exploring potential prolonged efficacy on pests and also longer periods of risk to beneficial arthropods.

The objectives of this study were (1) to determine how different agricultural plastics alter UV transmittance under small-scale tunnels compared to field conditions, (2) to determine how ten different insecticides degrade on raspberry foliage across these treatments in early and late summer, (3) to determine how these insecticides degrade differently on raspberry fruit under these treatments in late summer, (4) to observe the degradation of these chemicals over time across the different plastic treatments, compared to uncovered tunnels, and finally (5) to compare the efficacy of insecticides under UV-blocking plastics in comparison to open conditions.

2. Materials and methods

2.1. Experimental setup

This research was conducted in small research-scale tunnels covered with different plastic types at the Horticultural Teaching and Research Center in East Lansing, Michigan, USA. The tunnels were 1.2 m × 3 m and each tunnel covered eight potted raspberry plants (cv. “Polka”). The same plants were used in each of the leaf sample trials described below. Plants were irrigated daily using 3.2 GPH Netafim spray stakes (Trickl-Eez Irrigation Inc., St. Joseph, MI) inserted into the base of each 11.4 L pot. Each tunnel was constructed from five hoops of 1.9 cm diameter metal conduit, shaped using a hoop bender (QuickKHoops™, Johnny’s Selected Seeds, Fairfield, ME) (Fig. 1). The hoops were anchored by sliding them over 1.3 cm diameter conduit stakes that were pounded into the ground, 0.75 m apart and leaving 0.6 m above the ground. Plastic was secured on the sides of the tunnel using 3.8 cm × 8.9 cm × 3 m wood on each side, raised 0.3 m above the ground to allow for airflow (Fig. 1). In 2015, we constructed 12 tunnels, with two plastic types covering each of four replicates and uncovered controls arranged in a randomized complete block design. Tunnels were 2 m apart from each other. The following plastic types were compared: diffuse Luminance® plastic (Visqueen, Stevenston, UK) and diffuse Lumisol® plastic (Visqueen, Stevenston, UK). In 2016, we constructed 16 tunnels with 4 replicates covered in three plastic types and uncovered controls arranged in a randomized complete block design. The three plastic types were Luminance®, research-grade clear UV-blocking (Visqueen, Stevenston, UK), and research-grade clear UV-transparent (Visqueen, Stevenston, UK). The uncovered control was left uncovered unless rain was predicted, in which case...
they were then temporarily covered in plastic to keep the plants dry. Plants in this treatment were covered for no more than 12 h, once in the first trial, three times in the second trial, four times in the third trial, once in the final leaf residue trial, and once in the efficacy trial, and all rain events occurred overnight so there was little effect on UV exposure.

During each trial in 2016, the UV light under each tunnel was measured at canopy height using a UV sensor sensitive from 250 to 400 nm (MU-200, Apogee Instruments Inc, Logan, UT) and compared to the UV light conditions immediately outside of the tunnel between 12 and 2pm. Additionally, four samples of each plastic were tested in a UV-Vis spectrophotometer (NanoDrop, 2000/2000c, Thermo Fisher Scientific Inc., Waltham, MA) to determine their transmittance at the full spectral wavelength (190—480 nm). UV light data for the periods of the experiments were also gathered from the USDA’s (Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, www.uvm.net. colostate.edu/UVB/index.jsf) UV-B monitoring research program at the closest recording station with a similar latitude in Geneva, NY. One temperature probe (HoboWare Data Logger, Onset Computer Corp., Bourne, MA) was hung in the center of each tunnel at canopy height to record temperature once every hour for June—October from 2016. Additional temperature and humidity values were taken from a MSU Enviroweather weather station 3.9 km from the site for dew point information (www.enviroweather. msu.edu).

2.2. Insecticide applications and plant samples

In 2015, one application of insecticides was made to the raspberry plants on 9 September. The insecticides were combined as a tank mix and were applied to the plants at the equivalent of 468 L of water per hectare using a CO2 powered backpack sprayer operating at 50 psi with a single head boom and TeeJet 8003VS spray nozzle. Insecticides were applied at their maximum labeled rate for raspberries: thiamethoxam (Actara 25WG, 70.61 g Ai ha⁻¹), Syngenta Crop Protection, LLC, Greensboro, NC, CAS No. 153719-23-4; imidacloprid (Admire Pro 2 F, 347.5 g Ai ha⁻¹), Bayer Crop Science LP, Research Triangle Park, NC, CAS No. 138261-41-3; esfenvalerate (Asana XL 0.66 EC, 56.04 g Ai ha⁻¹), DuPont de Nemours and Company, Wilmington, DE, CAS No. 66230-04-4; acetamiprid (Assail 30SG, 112.09 g Ai ha⁻¹), United Phosphorus, Inc., King of Prussia, PA, CAS No. 66230-40-4; bifenthrin (Brigade 2 EC, 112.09 g Ai ha⁻¹), FMC Corp., Philadelphia, PA, CAS No. 82657-04-3; spinetoram (Delegate 25WG, 105.1 g Ai ha⁻¹), AgroSciences LLC, Indianapolis, IN, CAS No. 187166-40-1; spinosad (Entrust 2SC, 94.6 g Ai ha⁻¹), AgroSciences LLC, Indianapolis, IN, CAS No. 131929-60-7; cytraniliprole (Exirel 10SE, 149.07 g Ai ha⁻¹), E. I. du Pont de Nemours and Company, Wilmington, DE, CAS No. 736994-63-1; malathion (Malathion 8 F, 1782.17 g AI ha⁻¹), Gowan Company LLC, Yuma, AZ, CAS No. 121-75-5; and cypermethrin (Mustang Maxx 0.8 EC, 28.0 g Ai ha⁻¹), FMC Corp., Philadelphia, PA, CAS No. 52315-07-8). No adjuvants were included in the tank mix. The structural formula and UV-Vis absorbance of each compound are included in the supplemental material (Figure S1).

Twenty-five leaves (approx. 12 g) were sampled from one replicate of each treatment before the application (0 days after treatment (DAT)) to make sure no insecticides were found on the leaves prior to the application. Immediately after the application dried (0.5 DAT), and at 1, 3, 5, and 7 DAT, twenty-five leaves were sampled from under each tunnel. The leaves sampled were fully expanded leaves on the upper part of the canopy, so that they were exposed to the light conditions within each tunnel. Samples were placed immediately in 0 °C conditions in a cooler with ice and then shipped overnight in a freezer box for residue analysis.

In 2016, the same insecticides were studied, and all except thiamethoxam, spinetoram, and spinosad were applied at a reduced rate of 50% from the previous year. Thiamethoxam, spinetoram, and spinosad were applied at 100% of the suggested field rate as described above. These three materials degraded more quickly than the others in our 2015 results, and this reduced rate allowed all chemicals to be brought to a similar scale for the residue analyses. Applications were made on the raspberry plants on 8 July (early summer) and 6 September (late summer), and leaf samples were subsequently taken after each application at 1, 3, 5, 7, and 14 DAT. A longer sampling period of 14 days was added to better quantify the end of the residue decline. Sampling was also done at 0 DAT as described above.

In 2016, an additional application was made on 7 October to measure residues on raspberry fruit. Plants grown under the small tunnels did not produce enough fruit for this, so unsprayed canes producing raspberries from the MSU Clarksville Research Center in Clarksville, MI were cut and placed in buckets with water and floral foam. The fruits and stems were then sprayed with the tank mixture as described above. Fifty ripe fruits (approx. 100 g) from each tunnel were harvested on 1, 3, and 5 DAT. Fruits located in the upper part of the canopy were selected so they were exposed to the light conditions of each tunnel. Sampling was done at 0 DAT for the described above with fifty fruit for each sample. They were frozen immediately after collection and sent overnight for residue analysis.

2.3. Residue analysis

To analyze the residues of the active ingredients of the insecticides on the leaves, 1 g of frozen homogenized leaves were combined with 10 mL of acetonitrile and 5 mL of deionized water. A packet of QuEChERS extracting salts (Sulp QuE Citrate, Sigma-Aldrich Corporation, St. Louis, MO) (Official Method EN 15662; Anastassiades et al., 2003) were added, and the sample was centrifuged. Numbers for method validation are provided in the supplemental material (Table S1). Extracts were then put into the dispersive Solid Phase Extraction (dsPE, EN 15662 dsPE Tubes, United Science Corp., Forest Lake, MN) and centrifuged again. Samples were then analyzed using gas chromatography-triple-quadrupole mass spectrometry (GC-MS/MS) and liquid chromatography-triple-quadrupole mass spectrometry (LC-MS/MS). GC-MS/MS analysis was performed using a Varian 4000 GC/MS Ion Trap (Varian Medical Systems Inc, Palo Alto, CA) for bifenthrin, cypermethrin and esfenvalerate. Injections were made in splitless mode at 250 °C onto a VF-XMS column (30 m × 0.25 mm ID). The column started at 50 °C and increased to 260 °C at a rate of 45 °C/min, then increased to 310 °C at a rate of 15 °C/min for a total run time of 12 min.

LC-MS/MS analysis was performed using a Thermo TSQ Endura MS and Vanquish HPLC for all other analytes (Thermo Fisher Scientific Inc., Waltham, MA). An Accucore Phenyl-X column (2.6mm, 100 × 2.1 mm, Thermo Fisher Scientific Inc., Waltham, MA) was used with a flow rate of 0.3 mL/min. The gradient program began with 100% of an aqueous solution containing 0.05% acetic acid, 10 mM ammonium acetate, and 2% ACN. This mobile-phase A composition was held for 0.5 min and ramped to 100% of a mobile-phase B ACN solution containing 0.05% acetic acid, 10 mM ammonium acetate, 5% H₂O and held from 5.5 to 9.0 min. The column was then re-equilibrated at the initial mobile-phase conditions for a minute resulting in a 10 min run time. A separate method was run for cytraniliprole using the same mobile-phases with a different gradient profile. This gradient program began with 50% of aqueous solution and 50% of ACN solution, ramped to 100% at 3.5 min and held until 5.5 min. The column was re-equilibrated at the initial
mobile-phase condition for a 0.5 min resulting in a 6 min run time. Both LC methods used Atmospheric Pressure Chemical Ionization (APCI) as the mass spectrometer ion source type.

To analyze the residues of the active ingredients of the insecticides on the fruit, 10 g of frozen homogenized fruit were combined with 10 mL of acetonitrile and 1.5 mL of deionized water. A packet of extracting salts QuEChERS (Supel QuE Citrate, Sigma-Aldrich Corporation, St. Louis, MO) (AOAC Official Method, 2007.01, Table S1; Anastassiades et al., 2003) was added. The sample was shaken for 15 min in a mixer (MIX-003-001), then centrifuged for 5 min. The supernatant was added to a tube containing the dispersive Solid Phase salts (dSPE, Supel QuE PS, Sigma-Aldrich Corporation, St. Louis, MO), shaken, and centrifuged for 2 min. The extract was then analyzed using gas and liquid chromatography coupled with mass spectrometry detectors triple-quadrupole (GC-MS/MS) and (LC-MS/MS). The GC-MS/MS analysis was performed using a 436-GC and EVOQ-TQ (Bruker Corp., Billerica, MA) for the following analytes: bifenthrin, cypermethrin and esfenvalerate. Injections were made in split mode at a temperature of 280 °C at 200 °C/c min onto a 5% Phenyl-Methyl Siloxano column (20 m × 0.18 mm ID and 0.18 μm of film). The column temperature ramp started at 60 °C and increased to 180 °C at a rate of 45 °C/min, then increased to 300 °C at a rate of 25 °C/min, then to 330 °C at a rate of 50 °C/minute for a total run time of 16.07 min.

LC/MS/MS analysis was performed using a UHPLC-Advance and EVOQ-Elite-TQ (Bruker Corp., Billerica, MA) for all other analytes. A built-in oven and a HPLC column (Intensity Solo 2 C18, 2 μm, 100 × 2.1 mm, Bruker Corp., Billerica, MA) was used with a flow rate of 0.4 mL/min. The gradient program began with 98% of mobile phase A containing 0.05% formic acid and 2 mM ammonium formate in water and 2% mobile phase B containing 0.05% formic acid in methanol. This mobile-phase composition was held for 10 min and ramped to 65% mobile phase A and held for 7 min then 2% mobile phase A and held for 3 min. The column was reequilibrated at the initial mobile-phase conditions for 3 min resulting in a 13 min run time. For the LC-MS/MS technique, an Electrospray Ionization (ESI) source was used. For the GC-MS/MS analysis an Electron Ionization (EI) source was used.

For leaf and fruit analysis, one quantitative transition and at least one qualifier transition were monitored for each analyte. The SRM/MRM transitions of each analyte can be found in the supplemental material (Table S2). Retention times and ion ratios of quantitative and qualitative ions were determined from analytical standards. All analyses were calibrated with a minimum of a 5 point curve and samples were bracketed with Continuing Calibration Verifications (CCVs). The limit of detection (LOD) for leaf and fruit residues was 0.03 mg/kg and the limit of quantification (LOQ) was 0.01 mg/kg except for cypermethrin that was 0.05 mg/kg.

### 2.4. Effects of UV blocking on insecticide efficacy

To determine whether plastic type affected pest control efficacy, two raspberry plants in each tunnel were sprayed with cypermethrin or spinosad on 31 July 2017 (using the same methodology as described above). These were selected for their ability to cause contact mortality in *D. suzukii*. Within each tunnel, 4 untreated potted plants were placed in between the treated plants as a guard. At 0.5, 1, 3, 5, 7, 10, and 14 days after the applications, one fully expanded compound raspberry leaf was cut from each treated plant and the bottom two leaflets were removed so only the terminal leaflet remained. This allowed for a longer stem that was placed into a water pick (AquaPic, Syndicate Sales, Inc., Kokomo, IN) filled with distilled water. The two terminal leaflets from each plant were placed with the ventral surfaces facing each other. The water picks with the leaves were placed into the bottoms of 0.95 L clear plastic containers (Gordon Food Service, Wyoming, MI) so that the top of the water pick was just above the bottom of the cup (Van Timmeren and Isaacs, 2013). Leaves were returned to laboratory conditions (25 °C, 75% RH, 16:8 L:D) where ten adult 3–7 day old *D. suzukii* (5 male, 5 female) from a colony were anesthetized with CO2 and added to the cups. In each cup, we provided diet and water to decrease fly mortality. Water was added by using 4 cm long dental wicks moistened with distilled water. A small dish (0.1 L soffle cup lid, Gordon Food Service, Wyoming, MI) was filled with *Drosophila* diet (cornmeal recipe, Drosophila Species Stock Center, San Diego, CA). To prevent excess moisture, each container lid had a 5 cm diameter hole covered in fine mesh. Leaves from unsprayed plants were also sampled on each date to provide a control. After 48 h, the number of dead and moribund male and female *D. suzukii* were counted.

#### 2.5. Statistical analyses

Residue samples from each of the four experiments and from the efficacy experiment were analyzed using a linear mixed-effect model with repeated measures. Data were tested for normality using the Levene’s and Shapiro-Wilks tests. Residues from plants under the different plastic treatments were compared along with the uncovered control plants using analysis of variance with block as a random factor using the “nlme” package in R (Pinheiro et al., 2017). For the efficacy experiment, the number of dead and moribund flies were combined for each container before analysis. Tukey's Honestly Significant Difference test was used to conduct post-hoc comparisons among treatments using the “lsmeans” package in R (Lenth, 2016). All data were analyzed using R (3.3.3., R Core Team, R Foundation for Statistical Computing, Vienna, Austria).

### 3. Results

#### 3.1. Residue assessments

The amount of UV light allowed through the plastic treatments was significantly reduced compared to the uncovered tunnel, with the greatest reduction occurring from the complete UV blocking plastic, which allowed only 0.6% of UV light through, followed by 33.1% of UV light penetration under the partial blocking treatment, 74.2% of UV light penetration under the transparent plastic treatment, while the open treatment allowed an average of 99.4% of the UV light through (Fig. 2) ($F_{[3,12]} = 571.3; p < 0.001$). The
transparent plastic had greater transmittance of light in the UV spectrum (<400 nm) compared to the blocking or partial blocking plastics (Fig. 3). Additionally, the partial blocking plastic had greater UV transmission in the UVA wavelengths compared to the full blocking, which allowed almost no UV light through. The plastics also allowed a variable amount of visible light through, with the partial blocking allowing the least amount through (400–480 nm, Fig. 3).

Average temperature in the plant canopy during the daytime was 24.3 ± 0.3 °C in the open treatment, 25.3 ± 0.2 °C in the transparent treatment, 25.2 ± 0.4 °C in the partial blocking treatment, and 25.4 ± 0.2 °C in the blocking treatment. The temperature within the tunnels was not significantly different between any of the treatments in July (F [3,12] = 1.2; p = 0.3) or throughout the entire season (F [3,12] = 2.9; p = 0.1). In September, temperatures recorded in the uncovered tunnels were significantly lower than those in all other treatments (F [3,12] = 8.7; p = 0.005). However, the control treatments were within 1.1 ± 0.1 °C of the other treatments on average in September. Across all treatments, temperatures were 26.9 ± 2.9 °C in July and 21.8 ± 3.5 °C in September. Readings for UV light in Geneva, NY in September 2015 on average were 18.3 ± 12.2 kJ/m². In July 2016, total UV light was 31.1 ± 1.3 kJ/m², 21.7 ± 1.1 kJ/m² in September, and 9.6 ± 1.0 kJ/m² in October.

In 2015, the partial blocking treatment had significantly greater insecticide residues than the open uncovered treatment for nine of the ten insecticides tested over the entire experiment (Fig. 4). The leaf samples taken at 0 DAT were all found to be below detectable levels for the insecticides evaluated. Spinosad was the only insecticide found to not degrade differently among the treatments (F [2,53] = 2.74; p = 0.07), and the levels of this insecticide detected were very low by 1 DAT across all treatments (Fig. 8). For most insecticides, the amount of residue on leaves of raspberry plants growing under the partial transparent treatment did not differ from those on plants growing under the two other plastics. In some cases, as with acetamiprid, the partial transparent plastic was similar to partial blocking plastic, and had 26% and 35.5% higher residues, respectively, compared to the open control (F [2,53] = 8.74; p < 0.001). For imidacloprid, the blocking treatment had 30% and 49% greater residues compared to the partial transparent and open treatment, respectively (F [2,53] = 19.09; p < 0.001).

In the July 2016 trial with leaf samples, the fully or partially blocking plastics resulted in significantly higher insecticide residues compared to the transparent plastic or open control treatments for nine out of the ten insecticides tested (Fig. 5A). In contrast, malathion residues did not differ among any of the treatments (F [3,71] = 0.25; p = 0.8), partly because it degraded very quickly (Fig. 5A). The leaf samples taken at 0 DAT in this trial were all found to be below detectable levels for the insecticides evaluated. For all other insecticides except imidacloprid, the blocking plastic treatment was statistically similar to the partial blocking plastic treatment. For imidacloprid, residues under the blocking treatment were 11.5% higher than the partially blocking treatment (F [3,75] = 221.51; p < 0.001). For all insecticides except acetamiprid, the transparent treatment resulted in similar residue levels to the uncovered control. Acetamiprid residues were 22.5% higher under the transparent treatment compared to the uncovered tunnels (F [3,75] = 65.46; p < 0.001).

The pattern of insecticide residues measured from the September 2016 trial were similar to those of the July 2016 trial (Fig. 5B). Leaf samples taken at 0 DAT in this trial had variable levels of residues for each of the chemicals except malathion. All values were below 10 mg/kg with 72.5% of the samples below 4 mg/kg. Malathion again degraded quickly across the treatments and had high variability with no significant differences among the treatments (F [3,75] = 1.20; p = 0.3). For all other insecticides tested, the complete and partial UV blocking materials had significantly higher residues averaged across all sample dates compared to the transparent plastic or the uncovered control (Fig. 5B). In some cases, the complete UV blocking material had higher residues than the partial UV blocking plastic, as with imidacloprid, spinetoram, and spinosad (Fig. 3A). For imidacloprid, residues under the blocking treatment had an average of 481.6% higher residue levels compared to the uncovered tunnel, and 30.8% higher residues than the partial blocking treatment.

For the residues on raspberry fruit sampled in 2016, there were fewer differences among the plastic treatments than for the leaf analyses (Fig. 6). The fruit samples taken at 0 DAT in this trial were all found to be below detectable levels for the insecticides evaluated. Most insecticides had higher residues under plastic treatments compared to the uncovered controls. Some insecticides, such as acetamiprid and malathion, had no significant differences among the plastic treatments (F [3,39] = 1.95; p = 0.1, and F [3,39] = 1.06; p = 0.4, respectively). In some cases, residues from the blocking treatments were lower than the residues from the transparent plastics, as seen for bifenthrin which had an average of 33.7% higher residues under the transparent treatment compared to the blocking treatment (F [3,39] = 6.28; p = 0.001).

For most chemicals under the transparent and open treatments, residues declined rapidly within 1 d after the application, as seen with imidacloprid and cyrantraniliprole (Fig. 7). This was also true with cypermethrin and spinosad (Fig. 8). The blocking or partially blocking plastics, however, resulted in greater retention of the chemicals, and this increased retention remained consistent through time in most trials. In some cases, residues returned to statistically equivalent levels near the end of the trial, as seen with both imidacloprid and cyrantraniliprole in the September 2015 trial (7 DAT: F [2, 8] = 1.62; p = 0.2, and F [2, 8] = 0.32; p = 0.7, respectively). For many of the trials, both the partial blocking and the blocking treatment had similar residues through time, as seen with the July 2016 trial. In the fruit residue trial, these treatment differences were less evident, except that the open treatment had overall reduced residues compared to the covered treatments on 1 and 3 DAT.

### 3.2. Effects of UV blocking on insecticide efficacy

The highest mortality of *D. suzukii* was found in containers with leaves sampled under the blocking plastics. This was consistent across all sampling dates for spinosad, and for all sampling dates except DAT 5 for cypermethrin (Fig. 9). Across all sampling dates,
mortality was 15% greater on average under the blocking tunnels compared to the uncovered tunnels for cypermethrin, though this was not a statistically significant difference ($F[1, 6] = 5.70; p = 0.05$). For cypermethrin, the control bioassays consistently had statistically lower mortality compared to both the blocking tunnels ($F[1, 6] = 15.8; p < 0.001$) and the open tunnels ($F[1, 6] = 11.8; p < 0.001$). Only at 7 days after treatment did we find significantly higher mortality from cypermethrin under the UV blocking treatment ($62.5 \pm 11.1\%$) compared to the uncovered treatment ($22.5 \pm 10.3\%$) ($F[1, 6] = 7.02; p = 0.01$). For spinosad, the controls also had statistically lower mortality compared to both the blocking tunnels ($F[1, 6] = 10.4; p < 0.001$) and the open tunnels ($F[1, 6] = 6.8; p = 0.001$) for spinosad. Average percent mortality was significantly higher, but by only 3.2% on average, under the blocking tunnels compared to the uncovered tunnels ($F[1, 6] = 15.07; p = 0.007$). However, no individual sampling dates had significant differences between the blocking or uncovered treatments for spinosad.

4. Discussion

This study highlights the influence of plastic coverings used in high tunnels on the degradation of insecticides after they are applied. We found that the persistence of most insecticides is influenced by the level of UV exposure, with imidacloprid, cyantraniliprole, cypermethrin, and spinosad frequently declining more slowly when UV light was blocked from interacting with residues on the plant canopy and on the fruit. We found up to 60% greater retention of these materials across all sampling dates when covered in the UV blocking plastics. This extension of the period of residue
In this study, we evaluated the impact of partial blocking and blocking plastics on insecticide residue decline under tunnels. We found that in most cases, the residues were not statistically different. Furthermore, we observed that in some cases, the residues increased on certain sampling dates, as with imidacloprid in the September 2015 trial. This could be due to factors such as microclimate and insect activity. For both imidacloprid and cypermethrin, residues were lower in September compared to July. For both imidacloprid and cypermethrin, residues under the transparent treatment were lower than those under the partial blocking plastic, compared to open field-grown settings. This could result in fewer insecticide applications needed for repeated spraying to protect fruit from this pest. Slowing the degradation of insecticides may also provide an opportunity for organic growers struggling to control problematic insect pests, including D. suzukii and Halyomorpha halys (Van Timmeren and Isaacs, 2013). Spinosad is an organically certified chemical that has good efficacy, but has a short period of residual activity and it needs to be rotated frequently to reduce the risk of resistance (Van Timmeren and Isaacs, 2013). In this study, the mortality of D. suzukii when exposed to leaves treated with spinosad or cypermethrin was higher when the plants were kept under the UV blocking tunnels compared to uncovered tunnels. This could result in fewer insecticide applications needing to be applied, which would be significant for berry producers that are rebuilding integrated pest management systems after the arrival of D. suzukii. It could also translate into longer spray intervals, giving growers some relief from the time and money needed for repeated spraying to protect fruit from this pest. Slowing the degradation of insecticides may also provide an opportunity to increase sustainability on farms using protected culture. This could be particularly beneficial for organic growers growing berries under tunnels.
up to 14 days after application under UV blocking plastics, unlike the transparent or uncovered treatments, which fall to undetectable levels at 1–3 days after the application (Fig. 6). This could offer greater initial control as well as a longer duration of control, allowing organic growers to be more successful and economical in their production of berry crops. We found that *D. suzukii* mortality was higher overall and remained higher up to 14 days after the application of both cypermethrin and spinosad under the UV

Fig. 7. Average residue levels (mg/kg) of imidacloprid (left) and cyantraniliprole (right) (±S.E.) found on raspberry foliage and fruit across the four residue decline trials conducted in 2015 and 2016.
Fig. 8. Average residue levels (mg/kg) of cypermethrin (left) and spinosad (right) (±S.E.) found on raspberry foliage and fruit across the four residue decline trials conducted in 2015 and 2016.
blocking tunnels. Further research on other insect pests and on *D. suzukii* with other insecticides are still needed to better understand the potential for improved control and/or reduced need for spray applications. These experiments should include assays using fruit and assessing infestation by larvae as well as adult insect mortality. Moreover, the potential for negative side effects on beneficial insects and pollinators should be considered if this line of research develops further.

Reduced degradation of pesticides has been observed for tomatoes and lettuce, which are commonly produced under protected culture (Garau et al., 2002; Cengiz et al., 2007; Chuanjiang et al., 2010; Allen et al., 2015). Allen et al. (2015) measured pesticide residues of multiple crop types grown under protected culture or in open field settings, and found significantly more types of pesticides and greater residues on the protected crops. Additionally, Garau et al. (2002) found that on greenhouse-grown tomatoes, some fungicides have slower degradation, particularly cyprodinil, and they discussed that this finding may have implications for the maximum residue limit or pre-harvest intervals (PHI) set for this pesticide. While the residual activity of fungicides, miticides, and other pesticides were not evaluated in our study, similar results are expected based on these and other chemical degradation studies (Burrows et al., 2002; Sun et al., 2015).

The time of year and corresponding sun intensity may change the degree of benefit provided by UV blocking plastics, which could explain the different results between our fruit and leaf residue trials. The fruit trial was conducted in early October, and based on light data from Geneva, NY, there is an average of 12.1 kJ/m² less UV light compared to September, and 21.5 kJ/m² less UV light compared to July. Raspberry production in high tunnels in northern temperate regions tends to begin in late June and can last through October, depending on the specific region and the cropping system used (Hanson et al., 2011). However, given that our results for both the early summer and late summer applications in 2016 are very similar, we do not expect time of year to have a profound impact on the effects of plastics on insecticide residues for the majority of the growing season.

While slowing insecticide residue declines has potential benefits for growers, it may also be a concern for meeting residue tolerances set for insecticides on harvested fruit, safety for the growers/harvesters, as well as affecting the risks to beneficial insects. Increased insecticide use has been shown to harm pollinators and natural enemies in multiple systems (Desneux et al., 2007; Biondi et al., 2012; Gill and Raine, 2014; Roubos et al., 2014; Chagnon et al., 2015), and the potential for increased longevity of insecticide residues affecting beneficial insects under tunnel production should be explored further. Decreased populations of natural enemies may result in surges of secondary pests (Beers et al., 2016; Yang et al., 2016), and prolonged insecticide residues may alter the dynamics of pest and beneficial insect populations.

Depending on the magnitude of the difference in residues in open and protected crop systems, labels for pesticides in protected production may require different PHI, retreatment interval, and reentry interval (REI) restrictions to manage the potential concerns about increased persistence of residues. However, the variation in types of plastics used on tunnels may make it challenging to...
provide a broadly applicable and enforceable approach. While plastic type and UV transmittance of agricultural plastics are not standardized among plastic producers, they could fit into generalized UV blocking categories, such as those presented in this study, that would help to clarify pesticide labeling. The US EPA currently sets pesticide restrictions based on Good Laboratory Practice field residue data from relevant production systems (U.S. EPA, 2011), thus standards for protected culture are different than open-field practices. However, if this industry moved predominantly to UV-blocking plastics, bridging data from one crop setting could potentially be used to amend labels for a broader range of crops.

Exported berries must pass below maximum residue limits (MRLs) when they are inspected for pesticide residues, yet these limits can vary widely among countries (Yeung et al., 2017). This is an increasingly important issue for food industries as international trade expands, and so there is greater interest in learning how typical pest management programs influence residue levels at harvest (Haviland and Beers, 2012). Since the magnitude of change seen in the insecticide residues on the leaves and fruit was generally rather small, this suggests that it is unlikely that the use of UV-blocking plastics would trigger a MRL concern. Still, a more comprehensive analysis is warranted once the implications of UV blocking plastic are better understood. This could then be integrated into a system such as that developed recently for tea by Shiga et al. (2017) that models the probability of exceeding MRLs.

The information presented in this study highlights that UV degradation is an important breakdown pathway for the active ingredients of most of the insecticides studied, particularly the pyrethroids, neonicotinoids, and spinosyns, where the blocking plastics consistently reduced residue decline compared to the transparent plastic and the open control. Interestingly, this pattern was not observed for the organophosphates studied, which could be used strategically before harvesting since its degradation is similar regardless of plastic covering. To our knowledge, this is the first time that the degradation of insecticides under protected culture plastics that modify UV transmittance has been studied on berry crops. Reducing UV exposure after insecticide applications through specialty plastics presents a new way to prolong the active ingredient and therefore increase efficacy of these compounds, in addition to the benefits of keeping the plants dry. Efficacy of two of the studied compounds was evaluated using D. suzukii, where the UV blocking plastic resulted in higher mortality than the open uncovered tunnel. This suggests the potential for manipulating efficacy of insecticides for pest control under tunnels covered in these UV blocking materials, and highlights the need to further explore implications for other pest control materials. These plastics should be considered as a component of integrated insect and disease management approaches for high tunnels, with potential for reducing the frequency of pesticide applications.

Conflict of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.09.086.

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