Phototransformation of Bifenthrin and Methoxyfenozide Residues on Pistachio (*Pistacia vera*) Hulls and Model Surfaces

A Thesis submitted in partial fulfillment of the Requirements for the degree of Master of Science in Civil and Environmental Engineering

by

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May, 2015
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Phototransformation of Bifenthrin and Methoxyfenozide Residues on Pistachio (Pistacia vera) Hulls and Model Surfaces

be accepted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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ABSTRACT

Phototransformation of two pesticides, bifenthrin and methoxyfenozide, were studied on the surfaces of pistachio nut hulls and other model surfaces after application using a laboratory spray chamber. The experiments were carried out using pistachio nut hulls, glass microscope slides, glass pistachios, glass microfiber filters, and cellulose filter papers. The pure compounds were investigated under simulated sunlight using a xenon arc lamp (λ > 300 nm). At the recommended agricultural application rates, both pesticides transformed more rapidly on all of the surfaces tested than previous studies using natural sunlight have shown on soil or in solution. The primary factors influencing transformation rates were shown to be macroscale surface geometry. Expected field half-lives obtained on pistachio surfaces for bifenthrin and methoxyfenozide were 18 and 30 days, respectively, and were shown to be in agreement with previous studies demonstrating residual activity for navel orangeworm control. This work highlights the importance of evaluating the photoreactivity of pesticides under conditions that are most similar to the environment of their application.
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Introduction

The benefits of pesticide use such as increased food production and reliability come with the inherent risk of the intentional, widespread distribution of these compounds in the environment. With annual pesticide use in the United States consistently approaching 500 million kg of active ingredient (AI), the necessity of understanding the degradation processes of these compounds is clear [1]. Despite an abundance of pesticide degradation data from regulatory testing and decades of pesticide research, it still remains difficult to accurately predict the level of pesticide degradation under specific field conditions such as plant surfaces [2, 3]. As plant surfaces are an important degradation environment of pesticides after application, understanding the transformation rates and pathways of pesticides on these surfaces is critical to understanding the environmental fate of these compounds [2]. This knowledge is vital to managing both application rates and understanding potential environmental risks. Furthermore, understanding pesticide phototransformation rates on specific crop surfaces is key to predicting pesticide residue concentrations on crops and identifying optimum timing of applications.

Pistachios (*Pistacia vera*) are an important crop, particularly in California. In 2012, 250,000 metric tons of pistachios were produced, with an estimated $1.1 billion in value to pistachio growers [1]. California produces 98% of United States’ pistachios, comprising 24% of the world total production [1]. The dietary importance of pistachios has increased in recent years due to increasing popularity of a so-called “Mediterranean” diet that favors more nutrient-dense foods such as nuts. Pistachios are a good source of unsaturated fatty acids and numerous antioxidants [4, 5]. Relative to other commonly
consumed nuts and legumes, pistachios are the richest source of vitamin B-6 (1.3 mg/100 g), potassium (1042 mg/100 g), β-carotene (157 µg/100 g), and lutein + zeaxanthin (1205 µg/100 g) and are one of the richest sources of protein (21.4 g/100 g), fiber (10.3 g/100 g), selenium (9.3 µg/100 g), and γ-tocopherol (22.5 mg/100 g) [4]. Pistachios grow in grape-like clusters, and consist of a soft outer hull, a hard shell, and the inner kernel, which is the edible portion. Pistachios are most commonly harvested after the hull and shell have split, as pistachios with the shell on are the most frequently consumed product. However, after hull split, the fruit becomes more vulnerable to infestation by damaging insects and fungi, and is thus a key life stage for crop loss [6].

Navel orangeworm (NOW) (*Amyelois transitella*) is the primary pest associated with pistachios in California, having the potential to cause crop damage exceeding 30% in a given growing season, which implies potential crop damage in excess of $300 million annually [6]. NOW is best controlled by Integrative Pest Management (IPM) programs, and the first steps in pest control are better cultivation techniques, where unharvested and withered fruit (called “mummies”) are removed to reduce the likelihood of fungal and insect infestations [7]. After this, biological control measures are usually undertaken, such as the use of several parasitoid wasp species to reduce the damage caused by NOW larvae [7]. The last measure in IPM is chemical control, using a formulated pesticide [7].

In California alone, 17 million kg of insecticide were applied in agricultural applications in 2012 [1]. Bifenthrin (Fig. 1-A) is a broad-spectrum synthetic pyrethroid insecticide, with high efficacy for a wide range of pests afflicting tree-nut crops in California [1]. Bifenthrin is the active ingredient (AI) in product formulations such as:
Brigade™, Bifenture™, and BaseLine™. Its relatively high adsorption coefficient $K_{oc}$ (237,000) and low Henry’s Law coefficient ($1.0 \times 10^{-6}$ atm m$^2$/mole), make it an effective choice for pest control as it partitions effectively to plant surfaces with minimal leaching during rain or appreciable volatilization [3]. Pyrethroids are synthetic analogs of pyrethrin, a natural product isolated from *Chrysanthemum* flowers demonstrating insecticidal qualities that have been utilized in agriculture for centuries [8]. Pyrethroids bind to sodium and potassium ion-channels in neurons, forcing them to remain open, which rapidly produces paralysis via ion channel depletion [3]. Pyrethrin is an effective insecticide, however, its short half-life in sunlight (10-48 hrs) makes it too costly to use in most modern agricultural operations because of high application rates.

Synthetic pyrethroids were developed to have the same insecticidal mode of action as pyrethrum, with reduced rates of photolysis allowing better efficiency and insecticidal activity at lower application rates [3]. As concern over the use of organophosphate insecticides has increased, their use has been getting phased out and often replaced with pyrethroids in most cases [8]. Bifenthrin is the second-most applied insecticide on pistachios, with the use of bifenthrin on pistachios increasing over 5-fold from 2008 to 2012, with 15,000 kg applied to 70,300 hectares in California [1]. While the risk associated with pyrethroids is expected to be lower than organophosphate insecticides, there is growing evidence of their adverse ecological impact, especially on aquatic invertebrates and fish, arising from their environmental persistence [1, 3, 7]. One study by Weston et al. (2004) examined the concentrations of pyrethroids in sediment samples from 70 locations around California’s Central Valley and evaluated these sediment samples toxicity on *Hyalella azteca* [9]. This study found that 42% of the
samples collected demonstrated significant mortality, and 14% of these samples demonstrated extreme (>80%) mortality, and pyrethroids were detected at concentrations high enough to be responsible for this mortality [9].

Furthermore, growing concerns over the use of pyrethroid insecticides has driven the development of more target-specific insecticides. Methoxyfenozide (Fig. 1-B) is an insect growth regulator (IGR) and belongs to a newer class of compounds called diacylhydrazines that represent a direction of future development in insecticides [10]. Methoxyfenozide is an ecdyson agonist, which binds to ecdysone receptors inducing a premature and incomplete molt in Lepidopteran pests such as NOW [10]. Methoxyfenozide has been characterized by the USEPA as having reduced environmental risk for aquatic invertebrates and fish, and very low mammalian toxicity. Methoxyfenozide is available in the product formulation Intrepid-2F™. Use of methoxyfenozide is increasing as growers seek more environmentally benign pesticides; in 2012, 6,100 kg of methoxyfenozide were applied to 15,100 hectares of pistachios in California [1]. Several integrated pest management programs rate methoxyfenozide as the highest valued insecticide for control of NOW and other Lepidopteran pests because it is the least toxic to natural enemies, honeybees, and the environment [7].

Pesticide use is managed by standards mandating a delay in re-entry of personnel into areas after application to prevent exposure, “Re-Entry Intervals” (REI), as well as required time elapsed post-application until the crop is harvested called “Pre-Harvest Intervals” (PHI). The PHI is designed to allow sufficient time for a pesticide to dissipate from crop surfaces in the field, to achieve a residue concentration that is low enough to pose a minimal risk to human consumers as determined by human-risk exposure models.
Maximum Residue Limits (MRL) are mandated by the Environmental Protection Agency, and are usually determined by repeated field studies where a pesticide is applied according to good agricultural practices (GAP), and after the appropriate PHI has elapsed, residue concentrations are measured [1]. For many pesticides the MRL is set at the limit of detection (LOD) for a given measurement method [1]. On pistachios, the MRLs for bifenthrin and methoxyfenozide are 0.05 mg/kg and 0.1 mg/kg, respectively. Pistachio residues are measured for MRL compliance using the kernel only, and do not supply information about residues present on the hull, although these are the primary application environment.

The primary route of dissipation for most pesticides on plant surfaces is photolysis [2, 3, 8]. When a target compound absorbs light, is elevated to an excited energy state, and subsequently undergoes a chemical reaction, the process is termed direct photolysis [11]. Indirect photolysis occurs if light is absorbed by a nearby chemical that is excited to form a reactive species that then induces a chemical change in the target compound [11]. In the presence of water and atmospheric oxygen, sunlight induces the generation of reactive species (e.g., HO\(^{-}\), O\(_3\), NO\(_3\)\(^{-}\)) that act as powerful oxidants [11]. Direct photolysis can only occur if a given compound’s absorbance spectrum overlaps with that of the incident light source [11]. Because sunlight at the earth’s surface drops off at wavelengths <290 nm, only compounds with absorbance at wavelengths >290 nm are expected to undergo direct photolysis [11]. Although neither bifenthrin nor methoxyfenozide have substantial absorbance at wavelengths >290 nm, however, there is still a small amount of absorbance for these two compounds within these wavelengths that will allow some direct photolysis to occur. Therefore, a surface
such as a silica plate is often used as a non-reactive surface to exclude indirect pathways and only allow direct photolysis to occur [2, 12, 13]. This rate can be quantified and used to determine the indirect pathway’s contribution to pesticide degradation on more complex surfaces, such as pistachio hulls.

The USEPA pesticide registration process requires study of phototransformation of compounds in aqueous and soil environments, and these are therefore well studied [12-18]. The observed aqueous photolysis half-life of bifenthrin from pesticide registration studies, where direct pathways were explored was 413 days in pH 7.0 buffered water [19]. In similar direct photolysis experiments, methoxyfenozide demonstrated an aqueous half-life of 7 to 10 days when natural lake water was used, however, no phototransformation was observed in experiments with pH-buffered deionized water [20]. Soil photolysis half-lives are also required for registration and these experiments allow for both direct and indirect pathways to occur. The constrained half-life for bifenthrin and methoxyfenozide on loamy sand soil surfaces are 97 and 363 days respectively [20, 21].

While aqueous and soil phototransformation processes are well studied, there is no requirement for analysis of phototransformation on plant surfaces, despite their critical and controlling role in environmental fate. Plant surfaces have many unique characteristics that can impact phototransformation processes of pesticides applied to them [2]. Both surface chemical composition and surface geometry can contribute significantly to observed degradation of pesticides [2]. The unique chemical composition of pistachio hulls is a possible contributor to the photoreactivity of sorbed compounds, especially with respect to governing indirect photolysis [2]. Pistachio hulls have a high
concentration of phenolic compounds, such as β-carotene, that can act as reducing agents, and singlet oxygen quenchers [22]. This could contribute by retarding phototransformation rates, as reactive oxygen species generated on these surfaces could be subsequently quenched by phenolic groups present in hull material. Furthermore, light attenuation effects from a curved and geometrically complex surface can also moderate photolysis rates. Studies by Herbert and Miller demonstrate that the depth dependence of photolysis rates observed for soil samples may imply similar relationships for pesticide sorption within plant material to dark, non-reactive areas [23]. These soil studies found that direct photolysis was restricted at depths <0.4 mm, and that indirect photolysis mechanisms only applied to slightly deeper distances. Pistachio hulls are at least several millimeters thick, providing ample opportunity for light attenuation for compounds that have migrated beyond the surface photic zone.

While several studies have investigated plant surface photolysis, most studies have been focused on photochemical processes occurring on the leaf surface [24-26]. Leaf surfaces are covered with a protective cuticle, comprised of a waxy layer on the surface of a layer of pectin. Pistachio hulls have a very different chemical composition relative to the leaves of the plant as they do not contain stomata, and typically have a thinner cuticle. While the cuticle is often mimicked in laboratory studies by using a control surface composed of epicuticular wax [24], this approach was not utilized in the current study in-lieu of surfaces that allow more rapid sample throughput. Furthermore, plant-surface anatomy and chemistry vary widely between plant species [27, 28], and species-specific studies would therefore prove instructive.
We therefore report a series of comparative experiments designed to quantify photolysis on the surface of nut hulls relative to model surfaces typically used to estimate environmental half-lives. In order to perform these experiments at a field-relevant surface concentration, the first step was to measure the surface concentration of bifenthrin and methoxyfenozide on pistachio hulls in-situ following field applications of commercial formulations. After the field-relevant concentration was determined, developing a reliable and reproducible method of active ingredient application to pistachio hulls and other surfaces is essential to obtaining uniform surface concentrations across the series of experiments. The next step was to determine the rates of photodegradation of bifenthrin and methoxyfenozide on pistachios, glass pistachios, glass slides, glass fiber filters, and filter paper at field-relevant surface concentrations. These kinetic data will allow the determination of relative contributions of surface characteristics to photolysis rates and, finally, estimate half-lives of bifenthrin and methoxyfenozide under pistachio orchard field conditions.

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**Tables and Figures**

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Phototransformation of Bifenthrin and Methoxyfenozide Residues on
Pistachio (*Pistacia vera*) Hulls and Model Surfaces

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For submission to *Journal of Agriculture and Food Chemistry*

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ABSTRACT

Phototransformation of two pesticides, bifenthrin and methoxyfenozide, were studied on the surfaces of pistachio nut hulls and other model surfaces after application using a laboratory spray chamber. The experiments were carried out using pistachio nut hulls, glass microscope slides, glass pistachios, glass microfiber filters, and cellulose filter papers. The pure compounds were investigated under simulated sunlight using a xenon arc lamp ($\lambda > 300$ nm). At the recommended agricultural application rates, both pesticides transformed more rapidly on all of the surfaces tested than previous studies using natural sunlight have shown on soil or in solution. The primary factors influencing transformation rates were shown to be macroscale surface geometry. Expected field half-lives obtained on pistachio surfaces for bifenthrin and methoxyfenozide were 18 and 30 days, respectively, and were shown to be in agreement with previous studies demonstrating residual activity for navel orangeworm control. This work highlights the importance of evaluating the photoreactivity of pesticides under conditions that are most similar to the environment of their application.

INTRODUCTION

Characterizing transformation rates and pathways of pesticides is a critical aspect of optimizing agricultural application practices as well as defining their environmental fate and subsequent ecological risk. For many pesticides, surface photochemistry is a critical fate process as this is the primary reaction environment for many agricultural applications. Relative to surface-mediated reactions, the photochemistry of pyrethroids and other insecticides in the aqueous phase are well characterized [1-4], although
agricultural surfaces are the key environmental compartment for these compounds. Plant surfaces affect photochemistry by providing a medium for either photo-sensitization or stabilization. The phototransformation of pesticides on surfaces is poorly characterized due to both the heterogeneity of plant surface material and uncertainty regarding specific irradiation rates at these surfaces, as well as their possible contributions to reactivity. While pesticide photolysis studies on soils are required for the registration of many chemicals, and are thus partially explored, the photolysis rates on the surfaces of fruits remain especially uncertain [2-8]. Photolysis rates of some pesticides have been explored on leaf surfaces, and model cuticular wax surfaces are frequently used as representative models for leaves [9-12]. However, reactions on soil and leaf surfaces still fail to accurately match the most important surface with respect to pesticide fate, namely the nut hull surface and primary point of application. Nut hull chemistry varies significantly from leaves and other plant parts, as they contain higher concentrations of phenolic compounds to deter infestation of the undeveloped fruit. Knowledge of nut hull surface transformation pathways can lead to improved understanding of the environmental fate of these compounds and allow for more accurate prediction of pesticide residues and biocidal activity *in-situ*.

When a target compound’s absorption spectrum overlaps with the solar spectrum, that compound can absorb sunlight directly and may subsequently be subjected to reactions, a process known as direct photolysis [1-4]. In contrast, if the localized surface environment adjacent to the target compound absorbs sunlight and results in an excited species that then reacts with the compound, this process is known as indirect or surface-mediated photolysis [1-4]. Both reaction pathways can be significant for pesticides on
plant surfaces [2]. Respective reaction contributions are often elucidated using a control surface, such as a glass slide, to isolate indirect contributions by comparing rates observed for plant surface rates with rates on glass slides. Control surfaces can also help distinguish the different contributions to observed photolysis rates from factors such as surface geometry, partitioning, or absorption into dark, non-reactive compartments.

Bifenthrin is a broad-spectrum, non-systemic, pyrethroid insecticide that is the active ingredient in a wide variety of formulations (product name: Brigade, FMC 54800, Talstar, Bifenthrine, and Capture). Bifenthrin’s hydrolytic stability, hydrophobicity (log $K_{ow} = 6.5$), low water solubility ($1.4 \times 10^{-5}$ ppm), and broad-spectrum efficacy make it a very reliable choice of pest control for many agricultural commodities [6, 9]. For example, in 2012, 130,000 kg of bifenthrin were used in agricultural applications in California [15]. Methoxyfenozide, belonging to the diacylhydrazine class of chemicals, is an ecdysone agonist with high selectivity toward lepidopteran larvae, inducing a premature and incomplete molt upon ingestion [Dhadialla et al., 1998]. Methoxyfenozide, available in the product formulation “Intrepid 2F”, exhibits high target specificity reducing ecological risk with lower non-target organism toxicity compared to many predecessor insecticides and is thus used in many integrated pest management programs [15]. Use of methoxyfenozide has increased 27% in 4 years, with 84,000 kg applied in California in 2012, compared to 61,000 kg applied in 2008 [15].

In the present study, the surface environment of interest is the hull of Pistacia vera fruit, pre-hull split and pre-harvest. Our research objective was to investigate the phototransformation rates and mechanisms of the insecticides bifenthrin and methoxyfenozide on both the pistachio hulls and several control surfaces in order to
determine the contribution of different surface properties to photolysis rates. While the main phototransformation pathways and major photoproducts of bifenthrin and methoxyfenozide are characterized in aqueous systems [2, 13, 14, 17], comparable studies are limited with regard to surface photochemistry. Therefore, the aim of the present study is to determine the relative phototransformation rates of these two insecticides on pistachio hulls, filter paper, glass slides, glass filter paper, and custom-made glass pistachios utilizing simulated sun light in a laboratory photoreactor.

MATERIALS AND METHODS

Chemicals and Reagents. Analytical standards of bifenthrin [2-methylbiphenyl-3-methyl(Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropanecarboxylate] (99.0 % purity, LOT: 1593700) and methoxyfenozide [N-tert-butyl-N9-(3-methoxy-o-toluoyl)-3,5-xylohydrazide] (98.9 % purity, LOT: 032303) were supplied by Chem Service (West Chester, PA, USA). Stock solutions (1,000 mg/L) were prepared by dissolving 10 mg of bifenthrin or methoxyfenozide in acetonitrile and isopropyl alcohol (7:3 v/v, 10 mL). Acetonitrile, isopropyl alcohol, and hexane were HPLC grade and obtained from Fisher Scientific (Pittsburg, PA).

Technical grade bifenthrin was purified from commercial powder product (10% Active ingredient by wt.), Brigade WSB (FMC, Philadelphia, PA). Briefly, a 500-g batch of commercial product was rapidly stirred in a 1-L Erlenmeyer flask containing 750 mL of hexane. For purification, the supernatant was decanted onto a 30-cm diameter glass column packed with 150 g of silica gel 60 (70-230 mesh ASTM) (EMD, Billerica, MA). A pressure of 13.8 kPa was applied at the inlet and the flow was adjusted to ~15 mL/min with the column stopcock and this flow was kept consistent via the addition of hexane
eluent. Ten sequential 250-mL fractions of eluent hexane were collected in 250 mL beakers to ensure that all of the bifenthrin had eluted from the column. The 2nd through 5th fractions eluted all of the bifenthrin (verified via thin layer chromatography) and these fractions were combined and concentrated using a rotary evaporator. This process yielded 13.2 g of product that was determined to be 91% pure bifenthrin based on HPLC comparison to analytical standards, and any subsequent calculations of dose accounted for this measured purity.

**Surface Characterization.** Kerman variety pistachios (*Pistacia vera*) were harvested from UC Kearny Agricultural Research Extension (Parlier, CA) orchards that did not receive field applications of bifenthrin or methoxyfenozide. Individual pistachios were manually stemmed and had a mass of 2.4 ± 0.2 g (\( \bar{x} \pm SD, n = 50 \)) and estimated surface area of 10.4 ± 1.3 cm² based on caliper measurements (n = 50) of the 3 major axes (a, b, c) of the nut hull ellipsoid surface area (S) approximations

\[
S \approx 4\pi \left( \frac{ab^{1.6} + (ac)^{1.6} + (bc)^{1.6}}{3} \right)^{\frac{1}{1.6}}.
\]

As geometric controls, a set of custom glass pistachios were crafted (Fresno Scientific Inc., Fresno, CA) with surface areas of 10.9 ± 1.7 cm² (n=25). No.1 glass microscope cover slides (EMS, Ft. Washington, PA) were used as standard glass surface controls, with a calculated surface area of 3.24 cm². Whatman GF/A glass microfiber filters (GE Healthcare Bio-Sciences, Pittsburgh, PA) were used as model abiotic surfaces and have a surface area (A=d²π/4) of 17.3 cm². Finally, for comparison to an organic surface environment, 55mm diameter Whatman No. 1 cellulose fiber filter papers were used which have an estimated surface area of 23.8 cm².
Analytical Procedure, Calibration Standards, and Recoveries. Surfaces were prepared for residue analysis via modification to the extraction method of Walse and Karaka [21]. Briefly, surfaces, which included pistachios, glass pistachios, glass slides, glass microfiber filters, and cellulose filter papers were transferred to 50-mL plastic centrifuge tubes (Fisher Scientific, Pittsburgh, PA) containing 5 mL acetonitrile and isopropyl alcohol (7:3 v/v). Each sample was sonicated (B3510, Branson Ultrasonics, Danbury, CT) for 15 min at ambient laboratory temperature (20°C). Aliquots (1.5 mL) of each extract were transferred to a 2-mL glass screw-top vial for HPLC analysis.

In general, pesticide residues, defined as the mass of pesticide per unit area (µg/cm²), were identified based on chromatographic and spectroscopic agreement with pure analytical standards. HPLC retention time and UV-Vis spectra were used for analyte identification and quantification based upon absorption at λ = 254 nm, referenced relative to linear least-squares analysis of a 9-point plot of concentration versus detector response, to determine concentration over the range of 0.1 to 50 ng•µL⁻¹. Detector response and retention indices were determined each day in calibration studies involving serial dilutions of analytical stock solutions in known volumes of acetonitrile and isopropyl alcohol (7:3 v/v) (i.e., calibration standards). Calibrations for the quantification of residue levels were derived from the detector response to spiked blanks, in which the 5 mL extract from non-treated surfaces was spiked with 50, 40, 30, 20, 10, 8, 4, 2, 1 µL of insecticide stock. Extraction recoveries were calculated as the fractional percentage, relative to results from spiked blanks, of residues quantified following application of insecticide stocks (30 µL) to a surface of non-treated nut hull prior to extraction (i.e.,
surface-spiked). Extraction recoveries for each surface type and compound were assessed using multiple (n= 15) replicates (Table 1).

Analyses were performed with a Shimadzu HPLC system consisting of dual Shimadzu LC-10AD pumps, a Shimadzu SC-10A photodiode array (PDA) detector, and an Agilent Zorbax ODS C18 Column (250 mm × 4.6 mm) at 20 °C. Column flow (1 mL/min) was isocratic with an eluent composition of 10 mM ammonium formate in a 10%/90% deionized water/acetonitrile mixture for 25 minutes. The injection volume was 30 µL. The method limit of detection (LOD) based on absorbance at 254 nm was 0.2 and 0.1 µg/L for bifenthrin and methoxyfenozide, respectively [22, 23]. All instrument runs included sample blanks, with 20 ng/ µL check standard injections at 5-sample intervals. Instrument precision was maintained throughout all sample analysis as the measurement of check standards were below 3% RSD.

**Field Residues.** Kerman pistachios (n = 50) were harvested after the label specified reentry period following either aerial application of Brigade (FMC, Philadelphia, PA) or Intrepid 2F (Dow AgroSciences, Indianapolis, IN) at the maximum label recommended application rates for pistachios (224.1 g Active Ingredient (AI) per hectare) for Brigade WSB formulation and 425.0 g AI per hectare for Intrepid 2F. Each field pistachio was transferred to 50-mL plastic centrifuge tubes (Fisher Scientific, Pittsburgh, PA) and processed as described above for HPLC analyses. The measured average residue from these commercial applications served as the target concentration in subsequent laboratory spray chamber applications of bifenthrin and methoxyfenozide (*vide infra*). The field surface residue concentrations were determined to be (± S, n =50) 1.2 ± 0.19 µg/cm² for bifenthrin, and 3.7 ± 0.33 µg/cm² for methoxyfenozide
(equivalent to nut hull residues of 8.1 mg/kg for bifenthrin and 14 mg/kg for methoxyfenozide).

**Spray Chamber Residues.** Experiments utilized a 30.5-cm diameter platform rotated at 36 rpm within an enclosed cylindrical spray chamber. The 50-mL reservoir was loaded with 10 mL of acetonitrile and isopropanol (7:3 v/v) mixture containing either technical bifenthrin (40 mg/L) or analytical grade methoxyfenozide (70 mg/L) to match field residue levels (Grand mean of all surfaces ± Spooled: bifenthrin, 1.66 ± 0.082 µg/cm²; methoxyfenozide, 3.51 ± 0.12 µg/cm²). Spray solutions were delivered with 30 psig of nitrogen gas through a full cone fog nozzle (Spraying Systems, TG 0.4) positioned 61 cm above the center of the platform. For uniform spray coverage, as determined in preliminary experiments, surfaces were localized radially 13 cm from center on the platform. Surfaces were dried in air for 1 hour, and transferred to the photoreactor. Measured concentrations for each individual surface and compound are summarized in Table 2.

**Photolysis.** A Q-Sun Xenon Test Chamber, Model Xe-1-BC (Q-Lab Corporation, Columbus OH), Xenon Arc Lamp, 1800W (p/n X-1800, Q-Lab Corporation, Columbus OH) equipped with a spectral output, \( \lambda \), of 290 to 800 nm and temperature control was used. The test chamber was fitted with a Daylight-Q filter to match the spectral output of the xenon arc lamp with the solar spectrum (Figure 1). Surfaces were exposed at 30 °C for 24 hrs to 1 W/m² at 340 nm (2.84 µmol photons/ m² s). The irradiance in the solar simulator is estimated to be 13.5-fold higher than that observed in a pistachio tree canopy in Parlier, CA (36.6° N, 119.53° W) based on measurements obtained over the 2011 and 2012 growing season of daily
photosynthetically active radiation (150 µmol photons/m² s). Dark controls were covered with aluminum foil to prevent exposure to incident light. Samples were removed from the photoreactor at 0, 2, 8, 16, and 24 hr intervals and immediately processed for HPLC analysis as described above. Five replicate samples were prepared and analyzed for each irradiation time, with 3 replicate experiments performed for each surface and insecticide combination.

**Statistics.** All analyses have been carried out using JMP software (Version 11.2.0, SAS Institute, 2013). An analysis of variance (ANOVA) produced p values <0.001 for all fits. An analysis of covariance (ANCOVA) was used to determine that all the fits for each surface were significantly different from each other for each compound.

**RESULTS AND DISCUSSION**

The insecticide surface concentration on pistachios and control surfaces after spray chamber application was consistent with residues measured on pistachio hulls harvested 24 hours after application at maximum label recommended rates. Average surface concentrations of spray chamber-applied bifenthrin of 1.8 ± 0.12 µg/cm² or methoxyfenozide of 3.8 ± 0.18 µg/cm² compared to field measured residues of 1.2 ± 0.19 µg/cm² and 3.7 ± 0.33 µg/cm², respectively. Extraction efficiencies for these compounds on each surface (n=15) were determined in independent studies as described above, and ranged from 92-104 % (listed in Table 1).

In dark control studies at 30 ± 1°C, insecticide concentration remained nearly constant (>87%) on pistachios, glass slides, glass filter paper, glass pistachios, and filter paper over the 24 hour experimental time period. The controls were used to assess the
combined contribution to insecticide loss by volatilization, hydrolysis, poor extraction efficiencies, matrix-derived analytical interferences, or microbial transformation over the experiment. Negligible losses in controls (<13%) over 24 hours indicate that the observed attenuation of residual insecticide over time in irradiated samples is primarily due to photo-induced transformation (Fig. 3A, 4A).

Insecticide loss in irradiated samples was dominated by phototransformation, and over the 24 hours, we observe up to 97% loss in surface concentration for bifenthrin (Figure 2). Transformation was assessed as the difference between initial concentration ($C_0$), and the concentration at time of analysis ($C$). Rates are expressed by the pseudo-first-order differential rate equation:

$$\frac{-d[\text{insecticide}]}{dt} = -k_{\text{photolysis}}[\text{insecticide}]$$

Plots of $\ln([\text{insecticide}]_t/[\text{insecticide}]_0)$ versus time ($t-t_0$) were linear when constrained to first-order kinetics over experimental time scales (Fig. 3B, 4B). The rate of photolysis, $k_{\text{photolysis}}$ (hours$^{-1}$), the negative slope obtained from a least-squares analysis of regression featuring replicate analyses are summarized in Table 3. Experimental data support this kinetic model; distinct variation in rates of transformation is observed between the different surfaces and indicates that surface effects play a substantial role in the transformation of these compounds.

Phototransformation rates are influenced by both the intensity and spectral distribution of the radiation source. While the experimental apparatus used in the current study utilizes a xenon arc lamp with a filter that can closely approximate the spectral distribution of light in the regions >290 nm (Fig. 1), there is still a great deal of
uncertainty with regard to solar radiation in the UV-B region (280-320 nm). This region of radiation is responsible for the direct photolysis of many organic pollutants in the environment, and would likely have a large impact on the transformation rates of bifenthrin and methoxyfenozide in the field. The intensity of UV-B radiation on a given plant surface in the field is controlled by numerous factors such as: time of day, time of year, and average ozone amounts at a given latitude. These factors make approximations of data produced using laboratory photoreactors to expected field rates challenging.

Furthermore, the timescale used in these experiments (24 hours) was not sufficient to produce >50% loss of initial surface concentration of bifenthrin or methoxyfenozide. Therefore, the half-lives presented herein are representative of fits that are constrained to first order kinetics.

Synthetic pyrethroids were designed to have enhanced photostability over natural pyrethrum, however, they still transform in sunlight. Previously reported photolysis half-lives for bifenthrin in aqueous systems range as high as 416 days, and on soil surfaces a half-life of 96.9 days was observed [3, 24, 26]. By comparison, the constrained half-life observed in this study, normalized to typical irradiation rates expected in field environments, on pistachio nut hulls was 18 days. Consistent with trends observed for other pyrethroids, this may indicate that photosensitization occurs on some soil surfaces and implies the existence of substantial surface mediated effects on the phototransformation of bifenthrin [3].

In general, methoxyfenozide was shown to be more photostable on all surfaces used in this experiment. Previous studies on the phototransformation of radiolabeled methoxyfenozide in pH 7 buffer solution irradiated with a xenon arc lamp at 25°C
showed no observed photolysis [17]. Soil surface phototransformation of radiolabeled methoxyfenozide on loamy sand was also investigated utilizing a xenon arc lamp, yielding an observed half-life of 363 days [17]. This study, by contrast, reports a constrained half-life of 30 days for methoxyfenozide on pistachio surfaces (Table 3).

These results indicate that both bifenthrin and methoxyfenozide show increased reactivity in the solid phase compared to studies performed in solution. When considering soil photolytic processes, steric constraint of solid-phase pesticide molecules likely plays a substantial role in the increase of observed rates relative to rates observed in water. This limited mobility can sometimes alter degradation mechanisms, and it is likely that bifenthrin and methoxyfenozide are subject to a greater degree of steric hindrance on nut hulls [2]. Chen et al. (1984) attribute the increased reactivity of 36 pesticide thin-films applied to glass slides to the more sterically hindered state of molecules, with an increase in reactivity observed up to a thin-film thickness of \( \sim 100 \, \text{Å} \), corresponding to concentrations of 33 µg/cm\(^2\), above which a decrease in photolytic rate is observed due to light shielding [28]. In addition to the effects of steric hindrance, the different profiles of UV absorption in the solid state compared to that in solution may account in part for some of the discrepancy between aqueous and solid phototransformation rates [29, 30]. A study by Weber et al. (2009) attributed the nearly three-fold increase in quantum yield for methyl-parathion and two-fold increase for fenitrothion in solid ice compared to liquid water to the enriched local concentrations of pesticides in ice crystals to account for this difference, where the specific concentration effect [32, 33] increases the likelihood of intermolecular reactions [31-33]. Furthermore, diffusion of pesticides in soil systems results in a heterogeneous distribution of pesticide molecules at these
interfaces. This may be similar to what occurs on nut hulls, however, soils typically have diffusion coefficients 5 or 6 orders of magnitude higher than those on cuticular wax [2]. This could be responsible for the larger degree of light attenuation in soil systems as a larger fraction of pesticide mass is transported from the surface and down into dark, unreactive layers.

**Insecticide Transformation on Model Surfaces.**

Historically, silica surfaces have been used as an ordered, two-dimensional environment to assess the role that direct photolysis pathways play in pesticide transformation [26-28]. Silica surfaces are considered incapable of generating reactive oxygen species in the presence of sunlight, and exclude indirect pathways from occurring [28]. Therefore, direct photolysis is the most likely pathway of transformation of bifenthrin and methoxyfenozide on glass surfaces.

Insecticide transformation rates on glass surfaces were the fastest observed in this experiment with half-lives ranging from 3.0 to 5.3 days for bifenthrin and from 3.4 to 6.2 days for methoxyfenozide (Table 3). The most rapid transformations observed were on glass slides, which suggests that these surfaces are not ideal models of pistachio hulls or other agriculturally relevant surfaces, substantially overestimating surface photolysis rates, and generally indicating that interfacial environments strongly influence transformation. Given the extensive number of studies utilizing glass slides as representative surfaces [2, 3, 7, 26-28], we conclude that such efforts are likely to overestimate actual transformation rates expected in agricultural environments.

Glass pistachios were utilized to help elucidate the role that surface geometry might play, as the surface is nearly identical to those of glass slides, with the exception
that the curved surface geometry of the pistachio hull is mimicked without the potential for absorption into the surface and partitioning into dark compartments. The approximately two-fold reduction in the rate of phototransformation observed on glass pistachios suggests that the ellipsoidal geometry of pistachios certainly affects photolysis rates by partial shielding of incident light, with half-lives increased from 3.0 to 5.3 days for bifenthrin (56%) and from 3.4 to 6.2 days for methoxyfenozide (55%).

Glass microfiber filters provide an alternative model surface, defined by a fibrous, non-reactive surface with negligible absorption and partitioning into the interior of these fibers. The observed half-lives for bifenthrin and methoxyfenozide on glass microfiber filters were 3.9 and 5.3 days, respectively, which are very similar to transformation rates observed on glass pistachios. Thus, both the glass pistachios and glass microfiber filters seem to induce similar levels of light shielding, and might be considered equivalent model surfaces for photochemical processes. As these rates are faster than their respective rates on cellulose filter paper, an organic surface, it can be inferred that sorption to the interior and subsequent shielding of insecticide from incident light plays the most significant role in phototransformation rates on matrices like the cellulose filters.

Relative to the glass surfaces, the observed phototransformation half-lives of bifenthrin and methoxyfenozide on cellulose filter paper slowed further to 6.1 and 6.7 days, respectively. These results suggest that cellulose filter paper were closer matches to actual pistachio hulls in photolysis rates for this experiment, although observed rates on cellulose fiber filters were still much faster than on actual nut hulls. While filter paper does not share any macro-scale surface geometry with pistachio hulls, the porous
cellulose fiber is more similar to the hulls of pistachios in terms of chemical composition, surface partitioning potential, and potential for light shielding. The contribution of absorption into the fibers or adsorption into dark microenvironments on these organic surfaces probably plays the most significant role governing the phototransformation rates of both insecticides by allowing a substantial fraction of the applied mass to be shielded from incident light. Previous studies have demonstrated this “inner filter effect” on retardation of photolysis rates of pyrene sorbed to fly ash particulate, as well as 15 other polyaromatic hydrocarbons that demonstrated 20-fold lower photoreactivity when sorbed to fly ash when compared to their unsorbed form [36]. However, when considering field applications of these compounds, which employ adjuvant and water-based carriers that differ in chemical composition and effect from the 70% acetonitrile 30% isopropyl alcohol carrier used in this study, it is possible that some differences in the spatial distribution of pesticide residues exist on these nut hulls. However, adjuvant and water-based carrier mixtures representative of field applications could not be tested successfully with our experimental apparatus and likely require direct sampling in field conditions.

**Insecticide Transformation on Pistachio Hulls.**

The unique chemical composition of pistachio hulls also is an important contributor to the photoreactivity of sorbed compounds. Pistachio hulls have a high concentration of phenolic compounds, such as β-carotene, that can act as reducing agents and singlet oxygen quenchers [36]. While some nut hull constituents are reactive oxygen species (ROS) generators and can also be expected to induce indirect phototransformation, the balance between ROS sources and sinks will play a critical role in governing the magnitudes of indirect phototransformation processes. This could
contribute by retarding phototransformation rates, as reactive oxygen species could be quenched by phenolics present in hull material. However, the largest factor in the observed reduction of photolysis rates observed on pistachios is most likely a larger degree of light attenuation due to curved surface geometry and inner-filter effects. Out of the surfaces tested, both bifenthrin and methoxyfenozide were most stable on pistachio hulls. The respective field-correlated constrained half-lives for bifenthrin and methoxyfenozide were 18 and 30 days, 600 and 880% longer than rates observed on glass slides (Table 3).

Bioassays, such as contact mortality testing, can provide a critical link to a pesticide’s performance in the field. Eggs are placed in containers of treated nuts that are collected at regular intervals post-application of a commercial insecticide, and mortality is assessed after an incubation period of 17 days, producing a correlation between mortality and time, post-application. In one series of contact mortality experiments, Siegel et al. notes a significant reduction in navel orangeworm (NOW) contact mortality at 21 and 30 days post-application for bifenthrin and methoxyfenozide, respectively, suggesting that biologically active concentrations can be maintained for substantial time periods post-application. Threshold effects are observed at 50% of the initial concentration. Therefore, using kinetic data from glass slides, the predicted surface concentrations would be 0.009 and 0.008 µg/cm² for bifenthrin and methoxyfenozide, well below biologically active residuals, at 21 and 30 days, respectively. In comparison, the model generated using data from pistachios would predict surface concentrations of 0.55 and 1.85 µg/cm² for bifenthrin and methoxyfenozide at the same respective time intervals. Thus, the predicted surface concentrations would be 1.5 and 2.5 orders of
magnitude lower using the glass slide data to model environmental fate and persistence, assuming that phototransformation remains the dominant attenuation process. A comparison of glass slide and pistachio surface transformation models to the NOW contact mortality data for bifenthrin reveals that the model generated using glass slides to predict surface concentrations is poorly aligned with observed reduction in NOW control (Fig. 5). In contrast, the model generated utilizing kinetic data from studies performed on pistachio surfaces demonstrates the best agreement between the transformation half-life and the observed reduction in NOW control.

The University of California’s Statewide Integrative Pest Management program suggests spraying one month prior to harvest for effective control of NOW during periods of moderate to high pest pressure. The manufacturer label for the formulation Brigade WSB recommends a Pre-Harvest Interval (PHI) of 7 days for bifenthrin and also suggests timing sprays with the onset of hull-split. Application intervals are to be based upon pest intensity but are to remain a minimum of 15 days apart. Our findings, as well as those by previous work [41] suggest that the optimal spraying interval for bifenthrin applications could be increased to ~20 days while still maintaining maximum NOW control in late-season pistachio orchards. Methoxyfenozide applications typically begin earlier in the growing season to have more impact on curtailing larval development. The manufacturer label for Intrepid 2F states that in addition to earlier applications, spraying with the onset of hull-split followed by one additional spray 10 to 14 days later for moderate infestations, and one additional application 10 to 14 days after that for severe infestations, with total annual applications not to exceed 450 g AI/ha. The expected constrained half-life determined in the present study (30 days) suggests that the manufacturer
recommended application interval of 10 days may be more aggressive than necessary to maintain efficient NOW control in pistachio orchards, although more field studies measuring residual concentrations would be necessary to validate the optimal interval for methoxyfenozide as suggested above for bifenthrin.

While bifenthrin and methoxyfenozide are expected to be microbially degraded on the surface of postharvest produce with representative half-lives of 33-129 days [38-40], results suggest that the contribution from microbial transformation on pistachio hulls was negligible over the irradiation (24 hour) time period as microbial transformation typically occurs on much longer time scales. Also, the measured concentrations for insecticide on dark controls were within the relative standard deviations established in the recovery/extraction studies, suggesting negligible biological attenuation processes. Furthermore, fungal transformation studies (data not shown) of bifenthrin were attempted using two strains of fungi: *Alternaria alternata* and *Botryosphaeria dothidea*. These strains cause the two most common forms of pistachio blight, and are therefore expected to be common on pistachio surfaces. These studies involved the addition of bifenthrin to cultures grown in liquid media broth. Loss of bifenthrin was found to be negligible over time periods up to 8 weeks, again suggesting that abiotic photolysis processes were the critical attenuation mechanism for these pesticides in these systems.

**Conclusions**

Comparison of the two surface transformation models for bifenthrin in relation to NOW control on pistachios makes it clear that glass slides can be expected to greatly overestimate phototransformation rates for pistachio hulls. Observed constrained field half-lives were 600 and 880% longer on actual pistachio nut hulls compared to glass
slides for bifenthrin and methoxyfenozide, respectively. Comparison of the pistachio surface degradation models to studies demonstrating the persistence of NOW control in pistachio orchards demonstrates that half-lives determined in this manner could facilitate the more efficient timing of applications of pesticides in the field. Furthermore, the constrained half-lives observed on actual crop surfaces provide a more relevant set of experimental conditions for determining kinetic data for input into pesticide fate and transport models than other plant surface models such as glass slides.

Despite the reduced absorbance in both bifenthrin and methoxyfenozide in wavelengths >290 nm, direct photolysis was observed to be the predominant transformation pathway of both compounds suggesting much more efficient phototransformation rates at environmental interfaces relative to rates observed in water. However, in this system we observe that the negative effects of light shielding, or inner-filter effects, on complex heterogeneous surfaces outweigh the positive contribution of enhanced phototransformation via indirect pathways.

Overall, these results demonstrate the role that different surface environments play in the phototransformation of insecticides. The use of more plant surface-specific transformation rates would provide a better source of input into risk assessment models, as well as give growers a valuable tool in more efficient control of key pests such as NOW.

ACKNOWLEDGEMENTS
This research project was made possible by a grant from the California Pistachio Research Board. Research was performed at the San Jaoquin Valley Agricultural Research Science Center.

REFERENCES


[15] California’s Pesticide Use Reporting database; [www.cdpr.ca.gov](http://www.cdpr.ca.gov)


Tables

Table 1. Extraction efficiencies for bifenthrin and methoxyfenozide on pistachios and control surfaces.

<table>
<thead>
<tr>
<th>Insecticide</th>
<th>Surface</th>
<th>% Recovery (n=15) ± (STDEV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>Pistachios</td>
<td>93 ± 4.3</td>
</tr>
<tr>
<td></td>
<td>Glass slides</td>
<td>96 ± 5.9</td>
</tr>
<tr>
<td></td>
<td>Glass fiber filter</td>
<td>104 ± 7.8</td>
</tr>
<tr>
<td></td>
<td>Glass pistachios</td>
<td>99 ± 9.1</td>
</tr>
<tr>
<td></td>
<td>Filter paper</td>
<td>94 ± 3.9</td>
</tr>
<tr>
<td>Methoxyfenozide</td>
<td>Pistachios</td>
<td>93 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>Glass slides</td>
<td>102 ± 6.9</td>
</tr>
<tr>
<td></td>
<td>Glass fiber filter</td>
<td>96 ± 3.4</td>
</tr>
<tr>
<td></td>
<td>Glass pistachios</td>
<td>96 ± 8.8</td>
</tr>
<tr>
<td></td>
<td>Filter paper</td>
<td>92 ± 5.0</td>
</tr>
</tbody>
</table>

Table 2. Measured surface concentrations after spray chamber and field applications of bifenthrin and methoxyfenozide.

<table>
<thead>
<tr>
<th>Insecticide</th>
<th>Surface</th>
<th>Spray Chamber Applications (n= 25)</th>
<th>Field Applications (n= 50)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{x}$ (µg/cm²) ± (STDEV)</td>
<td>$\bar{x}$ (µg/cm²) ± (STDEV)</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>Pistachios</td>
<td>1.8 ± 0.12</td>
<td>1.2 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>Glass pistachios</td>
<td>1.66 ± 0.082</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 3. Kinetic data for the phototransformation of bifenthrin and methoxyfenozide. Constrained half-lives are based upon field measurements of photon flux in the region of 300-800 nm in Parlier, CA.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Experiment</th>
<th>Replicate #</th>
<th>$k_{(obs)}$ (hours^{-1})</th>
<th>$r^2$</th>
<th>Constrained Half-Life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bifenthrin</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Pistachios</td>
<td>1</td>
<td>-0.022</td>
<td>0.75</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.021</td>
<td>0.84</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.021</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass Slides</td>
<td>1</td>
<td>-0.14</td>
<td>0.86</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.11</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.12</td>
<td>0.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass Microfiber</td>
<td>1</td>
<td>-0.096</td>
<td>0.83</td>
<td></td>
<td>3.9</td>
</tr>
<tr>
<td>Filter Paper</td>
<td>2</td>
<td>-0.11</td>
<td>0.81</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.094</td>
<td>0.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass Pistachios</td>
<td>1</td>
<td>-0.076</td>
<td>0.91</td>
<td></td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.072</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.072</td>
<td>0.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose Filter Paper</td>
<td>1</td>
<td>-0.063</td>
<td>0.89</td>
<td></td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.061</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.059</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Methoxyfenozide</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Pistachios</td>
<td>1</td>
<td>-0.014</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.013</td>
<td>0.88</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.012</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure 1.** Spectral output of Q-Sun photoreactor with Daylight filter, compared to natural sunlight.

<table>
<thead>
<tr>
<th>Material</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Slides</td>
<td>-0.12</td>
<td>-0.11</td>
<td>-0.11</td>
<td>0.79</td>
</tr>
<tr>
<td>Glass Microfiber Filters</td>
<td>-0.067</td>
<td>-0.065</td>
<td>-0.071</td>
<td>0.88</td>
</tr>
<tr>
<td>Glass Pistachios</td>
<td>-0.061</td>
<td>-0.058</td>
<td>-0.055</td>
<td>0.91</td>
</tr>
<tr>
<td>Cellulose Filter Paper</td>
<td>-0.058</td>
<td>-0.057</td>
<td>-0.059</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Figure 2. Surfaces used in comparative phototransformation study. (A) pistachios, (B) glass pistachios, (C) glass slide covers, (D) GF/A glass microfiber filters, (E) Whatman 55 mm No. 1 filter papers.
Figure 3A. Typical bifenthrin surface concentration over experimental time course. Error bars represent 95% confidence intervals.
Figure 3B. Typical bifenthrin surface phototransformation kinetic data. Error bars represent 95% confidence intervals.
Figure 4A. Typical methoxyfenozide surface concentration over experimental time course. Error bars represent 95% confidence intervals.
Figure 4B. Typical methoxyfenozide surface phototransformation kinetic data. Error bars represent 95% confidence intervals.
Figure 5. Lines represent % remaining vs. time model fits based upon experimental data from model surface phototransformation studies. Fits are extrapolated 20 days from constrained experiments. Data points represent % mortality (normalized to controls) in NOW larval contact mortality on pistachio hulls collected from the field at ~5 day intervals post-application of Brigade, from study by Siegel et al (2011).
**Summary and Conclusion**

Phototransformation is a critical fate process for pesticides in the natural environment. Determining the rates of transformation of pesticides in different environmental compartments is critical to generating accurate models of pesticides for both the timing of applications and understanding contaminant fate and transport. In the case of surface phototransformation, plant and fruit surfaces are the most important agricultural surfaces and remain relatively unexplored. Surfaces such as glass slides are often used that are poor models of actual fruits for the purposes of determining phototransformation rates. Nut hull surfaces in particular allow for a much greater degree of diffusion into subsurface environments, resulting in attenuation of incident light and a reduction in the observed rates of phototransformative processes. Furthermore, the curved nature of pistachio surfaces also allow for a greater degree of light shielding than a flat surface such as a glass slide or filter paper. The data obtained from experiments performed on nut hull surfaces allows for more accurate prediction of bifenthrin and methoxyfenozide residues in the field, and can be used to more efficiently time applications for control of key pests such as NOW. A comparison of the model created from data based upon nut hulls correlates well to observed duration of NOW mortality in field assays. Bioassays such as this can help bridge the gap between laboratory phototransformation studies, and environmental fate as it applies to more specific field conditions.
Recommendations for Future Research

The kinetic data obtained from glass microfiber filters and cellulose filter papers will be used in future NOW larval contact mortality studies that involve the field application of formulated pesticides to filter papers. NOW eggs are then placed in the center of a treated filter paper that is placed on top of larval diet. After an egg hatches, the larva must move across the treated surface to reach a food source. Mortality is assessed after 17 days, where eggs have had sufficient incubation time to hatch and larval mortality can be assessed.

Experiments such as these will demonstrate the correlation between irradiance time to observed reduction in NOW mortality, or more importantly, the correlation between time post-application of formulated pesticides and NOW mortality in the field. These studies can be used as a guide to conduct further research that will aid in the control of key pests. The more efficient use of pesticides will ultimately result in fewer applications, and therefore reduce the spread of contaminants into the environment.