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Organophosphate Insecticide Activity Reduced when Mixed with Copper(II) Hydroxide in Peach Dormant Sprays[1]

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Abstract Dormant-season applications of copper-containing fungicides and organophosphate insecticides are common in *Prunus* spp. orchards, and these compounds are often mixed into a single application. However, copper(II) catalyzes the hydrolytic breakdown of many organophosphate insecticides. We measured the impact of tank-mixing these products using field efficacy data collected from 2002 to 2004 coupled with active ingredient degradation studies in the laboratory. Formulations of the organophosphate insecticides chlorpyrifos and diazinon were applied with and without the fungicide $Cu(OH)_2$ in peach orchards, and the resulting peach twig borer (*Anarsia lineatella* Zeller) damage was measured. Laboratory experiments to quantify the degradation of the active organophosphate ingredient in various dry deposits from treatment solutions showed that addition of $Cu(OH)_2$ to laboratory organophosphate solutions resulted in more rapid degradation of the active organophosphate ingredient in dry deposits stored at 100% relative humidity at room temperature. Unsurprisingly, there was significantly more peach twig borer field damage in chlorpyrifos treatments containing copper than those that excluded copper. However, this was not observed with diazinon. Because copper(II) catalyzes the breakdown of various organophosphate insecticides across a range of pH values, caution should be used with the simultaneous application of copper(II)-containing fungicides/bactericides and organophosphate insecticides.

Key Words chlorpyrifos, diazinon, peach twig borer, *Anarsia lineatella*, hydrolysis

Pesticide applications timed during the orchard dormant season have been commonly recommended to control various insect and pathogen pests of *Prunus* spp. trees. Copper compounds are often applied to *Prunus* spp. trees during the dormant season to control peach leaf curl disease (*Taphrina deformans* (Berkeley) Tulasne and shot hole disease (*Wilsonomyces carpophilus* (Léveillé) Adaskaveg, Ogawa, and Butler (Adaskaveg et al. 2013). Peach leaf curl disease can be a serious problem affecting leaves, shoots, and fruits of *Prunus* spp. trees globally (Giosuè et al. 2000). Shot hole disease is a serious disease of *Prunus* spp. infecting

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leaves and fruit, with disease severity increasing with longer wet periods (Grove 2002, Shaw et al. 1990).

Organophosphate insecticides have been widely used to control peach twig borer, *Anarsia lineatella* Zeller (Lepidoptera: Gelechiidae), in *Prunus* spp. since the late 1950s (Summers et al. 1959, Zalom et al. 2002). The recommended application timing was during the dormant season when simultaneous control of San Jose scale, *Quadraspidiotus perniciosus* (Comstock) (Hempitera: Diaspididae), could be achieved (Daane et al. 1993, Rice and Jones 1988, Zalom et al. 2002). Peach twig borer is an important insect pest of California stone fruits and almonds (Daane et al. 1993, Jones 1935, Price and Summers 1961, Weakley et al. 1990). Peach twig borer larvae bore into shoots, killing the shoot meristem and causing deformation of small trees (Jones 1935, Weakley et al. 1990). More significantly, the larvae cause direct feeding damage on the fruit (Jones 1935, Weakley et al. 1990, Zalom et al. 2002). Though organophosphates are no longer the dominant class of insecticides applied to peaches, almonds, and other tree crops in California during the dormant season due to concerns about pesticides in waterways (Epstein et al. 2001), thousands of hectares still receive these treatments (California Department of Pesticide Regulation 2012).

Rather than entering an orchard multiple times during the dormant season, many applicators mix their insecticide and fungicide compounds into one application. Glotfelty et al. (1990) exemplify this in their dormant application drift study by applying a solution of diazinon mixed with $Cu(OH)_2$ and oil. However, copper(II) catalyzes the breakdown of many organophosphate insecticides in the laboratory (Blanchet and St. George 1982, Mortland and Raman 1967, Smolen and Stone 1997), and industrial research where copper fungicides and organophosphate insecticides were codeposited on seeds indicated that copper compounds accelerated the decomposition of the organophosphate (H.B. Sher, Univ. California - Davis, Unpubl. data). Therefore, we hypothesized that tank-mixing copper containing fungicides with organophosphate insecticides may decrease the activity of these insecticides. To generate biological activity data, we performed field experiments using peach twig borer damage in peach orchards (2002–2004) examining the impact of tank-mixing $Cu(OH)_2$ with emulsifiable concentrate (EC) and microcapsule formulations of the organophosphate insecticides chlorpyrifos and diazinon. Laboratory experiments were also included to quantify the amount of active ingredient remaining over time for various treatment solutions. Because pH may also impact degradation of organophosphate insecticides, the effect of pH on chlorpyrifos was included in the 2004 field efficacy and laboratory degradation experiments.

This study was additionally prompted by a larger research focus on developing best management practices to help mitigate the negative impact organophosphate dormant sprays were having on water quality at the time of the study (Sacramento and San Joaquin rivers were not in compliance with the Clean Water Act due to organophosphate contamination following winter rainfall events). Therefore, California pesticide use records were also examined to determine the prevalence of copper and organophosphate applications (these data are not available in other geographic regions where dormant-season sprays are applied).

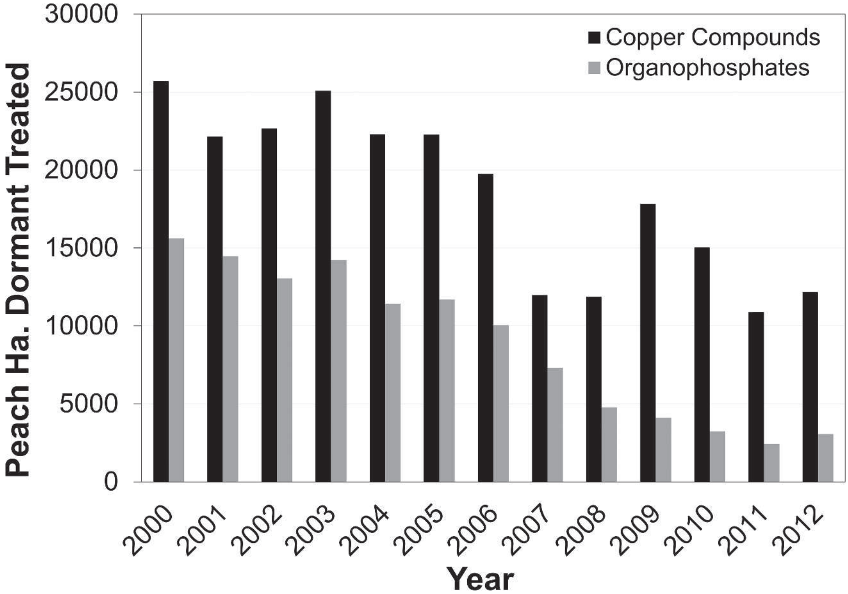

Fig. 1. Hectares of California peaches dormant (Dec., Jan., Feb.)-treated with organophosphate insecticides and copper-containing fungicides from 2000 to 2012.

Materials and Methods

Dormant-season pesticide usage records in peach for 2000–2012. California Department of Pesticide Regulation (CDPR) pesticide usage data from 2000 to 2012 were downloaded using the California Pesticide Information Portal (http://calpip.cdpr.ca.gov/main.cfm). The dormant season of each year was defined as December of the year prior, January, and February because most dormant pesticide applications occur in these months after the leaves abscise in the fall and before trees bloom in the spring. Data for applications of chlorpyrifos, diazinon, methidathion, and naled (the most commonly used organophosphates in peach orchards) were downloaded. Dormant usage data for all copper compounds (copper, copper ammonium carbonate, copper ammonium complex, copper diammonium diacetate complex, copper hydroxide, copper octanoate, copper oxide [ous], copper oxychloride, copper oxychloride sulfate, copper salts of fatty and rosin acids, copper sulfate [basic], and copper sulfate [pentahydrate]) were also downloaded and the total hectares treated with organophosphates or copper compounds were graphed for each dormant season from 2000 to 2012 (Fig. 1).

Efficacy of dormant-season pesticide mixtures against peach twig borer. A second- or third-leaf peach orchard that had peach twig borer shoot strikes in the previous year was selected each year in Sutter or Butte counties for dormant-season copper and insecticide applications. Peach twig borer shoot strike damage is more easily observed on younger trees, therefore each year a new planting was used so that young trees were present. Treatments were applied at field rate

Table 1. Pesticide formulations and rates used for laboratory and field experiments.

Product	Formulation	Active Ingredient	Amount/Ha (935.3 L carrier)
Lorsban- 4E*	Emulsifiable concentrate	44.9% chlorpyrifos	1.06 L
Empire 20*	Microencapsulated	20.0% chlorpyrifos	2.32 L
Drexel diazinon**	Emulsifiable concentrate	48.2% diazinon	4.67 L
KnoxOUT 2FM†	Microencapsulated	23.0% diazinon	9.37 L
Champ Formula 2‡	Flowable	37.5% $Cu(OH)_2$	6.18 L

* Dow AgroSciences LLC, Indianapolis, IN.
** Drexel Chemical Co., Memphis, TN.
† Cerexagri Inc., King of Prussia, PA.
‡ Nufarm Americas Inc., Burr Ridge, IL.

(adjusted so that the different formulations of a compound would have the same quantity of active ingredient) with the equivalent of 378.5 L of carrier water per 0.40 ha with 1.5% oil (Volck® Supreme [emulsifiable],Valent USA Co., Walnut Creek, CA) by volume using an Echo Duster-Mister Air Assist sprayer (Echo, Inc., Lake Zurich, IL) (Table 1). In 2002 and 2003, two formulations of chlorpyrifos and diazinon were applied and in 2004 only the EC formulations were used. These were the two most commonly used organophosphates according to CDPR Pesticide Use Reports. For all years all insecticide formulations were applied both with and without the fungicide/bactericide $Cu(OH)_2$ to determine the impact of tank-mixing on insecticide efficacy. We chose $Cu(OH)_2$ as our copper compound because it is one of the most commonly used dormant-season compounds in peaches. In 2004 an additional treatment was included for the chlorpyrifos formulation, a phosphate buffer (laboratory-grade KH_2PO_4) treatment to adjust pH. Ten to twelve replicate peach trees were sprayed during the winter for each treatment every year in a randomized complete design, with an unsprayed buffer tree between each sprayed tree (including the untreated control). Peach twig borer shoot strike damage (the number of dead shoot tips resulting from larval feeding) was assessed the following spring (April) for each replicate to determine insecticide efficacy.

To confirm that pest pressure was consistent across years (2002–2004) in each orchard, the number of peach twig borer shoot strikes in the untreated control trees were compared for each year using a one-way analysis of variance in the Fit Y by X platform of JMP 10.0.0 (SAS Institute Inc., Cary, NC). Data met the assumption of normality of residual errors as determined by a Shapiro–Wilke test and the assumption of homogeneity of variance as determined by a Levene's test. Because no significant difference was found in pest pressure, year was not included as an effect in subsequent models. Data were sliced by insecticide active ingredient for treatment comparisons, so chlorpyrifos treatments were analyzed separately from diazinon treatments. Due to the low numbers of shoot strikes in the insecticide treatments, shoot strikes were converted to a presence/absence binomial response, and a logistic generalized linear model was constructed to analyze fixed effects in the Fit Model platform of JMP 10.0.0 (SAS Institute Inc.). For 2002–2003 the fixed effects "formulation" and "copper" were included in the model. For the 2002–2004 analysis, only copper was included in the model, as 2004 data did not include a microencapsulated formulation. An additional analysis was performed using data collected in 2004 to determine the impact of pH and $Cu(OH)_2$ on the efficacy of chlorpyrifos. A logistic generalized linear model was constructed to analyze fixed effects in the Fit Model platform of JMP 10.0.0 (SAS Institute Inc.) with "buffer" and "copper" as the fixed effects.

Laboratory reactions and quantitative analysis. Solutions of formulated (either EC or microencapsulated) chlorpyrifos and diazinon insecticides mixed with and without $Cu(OH)_2$ (same formulations and rates as the field experiment [Table 1]) were introduced to concave glass microscope well slides and allowed to dry in a fume hood before storage in a 100% relative humidity chamber at room temperature. Two replicate slides were withdrawn after 0, 2, 6, and 13 d to determine the rate of breakdown of the active ingredient under these conditions. Because $Cu(OH)_2$ changes the pH of the solution, additional experiments were performed using the EC formulation of chlorpyrifos with 1.5% oil (Volck® Supreme [emulsifiable], Valent USA Co.) by volume in solutions with and without $Cu(OH)_2$, and with and without a phosphate buffer (laboratory grade KH_2PO_4). The pH was recorded for each solution, and slides were withdrawn from the humidity chamber after 0, 3, 8, and 15 d. The organophosphate insecticides were extracted from the glass slides after removal from the chamber by placement in an individual 50-ml jar with 45 ml of ethyl acetate. The jar was then placed in a bath sonicator for 5 min, and subsequently shaken for 1 h at 400 rpm and room temperature (~25°C). The sample jar was then placed in a −20°C freezer and stored for up to 4 mo before chemical analysis.

Jars were removed from the freezer and allowed to warm to room temperature before quantifying the amount of insecticide remaining. The ethyl acetate solution from the jar was transferred to a volumetric flask, and the jar and slide were rinsed twice with 2 ml of ethyl acetate, after which the rinse fluid was added to the flask. Diazinon (for chlorpyrifos samples) or parathion (for diazinon samples) was added to the flask at 100 parts per billion as an internal standard, and then the flask was brought to the standard volume with more ethyl acetate and shaken to mix. The homogenized samples were analyzed by a gas chromatography (Hewlett Packard 5890 Series II Plus, Agilent Technologies, Santa Clara, CA) using a J&W Scientific DB-35 MS column (Agilent Technologies) and a nitrogen phosphorus detector. Concentrations of the organophosphate insecticide in the solution were determined by comparison to the standard curves generated with the internal analytical standards that were run concurrently with the samples.

Results

Dormant-season pesticide usage records in peach 2000–2012. Copper compounds and organophosphate insecticides are regularly applied to peach orchards during the dormant season, though organophosphate usage has been

Table 2. Mean ± SE peach twig borer (*Anarsia lineatella*) shoot strike damage in the insecticide treatments from 2002 to 2003.

Insecticide	Formulation	Copper	*n*	Damage (Mean ± SE)
Chlorpyrifos*	EC†	Yes	22	0.23 ± 0.09
	EC†	No	22	0.09 ± 0.06
	Microcapsules	Yes	22	0.41 ± 0.13
	Microcapsules	No	22	0.09 ± 0.06
Diazinon**	EC†	Yes	22	0.45 ± 0.27
	EC†	No	22	0.23 ± 0.11
	Microcapsules	Yes	22	0.36 ± 0.12
	Microcapsules	No	22	0.32 ± 0.14

* Logistic Generalized Linear Model $\chi^2 = 6.87$, df = 2, $n = 88$, $P = 0.0323$; Encapsulation $\chi^2 = 0.71$, df = 1, $n = 44$, NS; Copper $\chi^2 = 6.21$, df = 1, $n = 44$, $P = 0.0127$.
** Logistic Generalized Linear Model $\chi^2 = 1.76$, df = 2, $n = 88$, NS; Encapsulation $\chi^2 = 1.69$, df = 1, $n = 44$, NS; Copper $\chi^2 = 0.07$, df = 1, $n = 44$, NS.
† EC, emulsifiable concentrate.

declining in recent years (Fig. 1). In most cases, the copper and insecticide are mixed in the applicator tank and applied simultaneously to the orchard (CDPR data, not shown here).

Efficacy of dormant-season pesticide mixtures against peach twig borer. Peach twig borer pest pressure was present in all years, with untreated control trees exhibiting 6.00 ± 0.94 (values are mean ± SE) ($n = 10$), 3.50 ± 0.56 ($n = 12$), and 5.17 ± 0.74 ($n = 12$) damaged shoots per tree on average in 2002, 2003, and 2004, respectively. The untreated control trees did not experience significantly different damage across years ($F = 2.92$; df = 2, 33; $P = 0.0690$); therefore overall pest pressure was similar each year. Trees treated with different formulations of chlorpyrifos mixed with and without $Cu(OH)_2$ experienced between 0.09 ± 0.06 (n = 22) and 0.41 ± 0.13 ($n = 22$) damaged shoots per tree (mean across 2002 and 2003) (Table 2). The logistic generalized linear model was significant ($\chi^2 = 6.87$; df = 2; $n = 88$; $P = 0.0323$), and applications that included $Cu(OH)_2$ exhibited significantly more damage ($\chi^2 = 6.21$; df = 1; $n = 44$; $P = 0.0127$) than applications without $Cu(OH)_2$. The formulation of chlorpyrifos did not have a significant impact on peach twig borer damage ($\chi^2 = 0.71$; df = 1; $n = 44$; $P = 0.4006$) (Table 2). Applications of different formulations of diazinon resulted in between 0.23 ± 0.11 ($n = 22$) and 0.45 ± 0.27 ($n = 22$) shoot strikes per tree across 2002 and 2003 (Table 2). The overall logistic generalized linear model was not significant (Logistic Generalized Linear Model $\chi^2 = 1.76$; df = 2; $n = 88$; $P = 0.4143$) for the diazinon treatments, which did not show an effect of encapsulation or addition of copper (Table 2). Comparing the addition of copper to the insecticide mixtures across 3 yr (2002–2004), there was significantly ($\chi^2 = 5.49$; df = 1; $n = 112$; $P = 0.0191$) more damage 0.70 ± 0.26 shoot strikes ($n = 56$) in the chlorpyrifos applications with copper than damage 0.23 ± 0.07 shoot strikes ($n = 56$) without copper. This trend

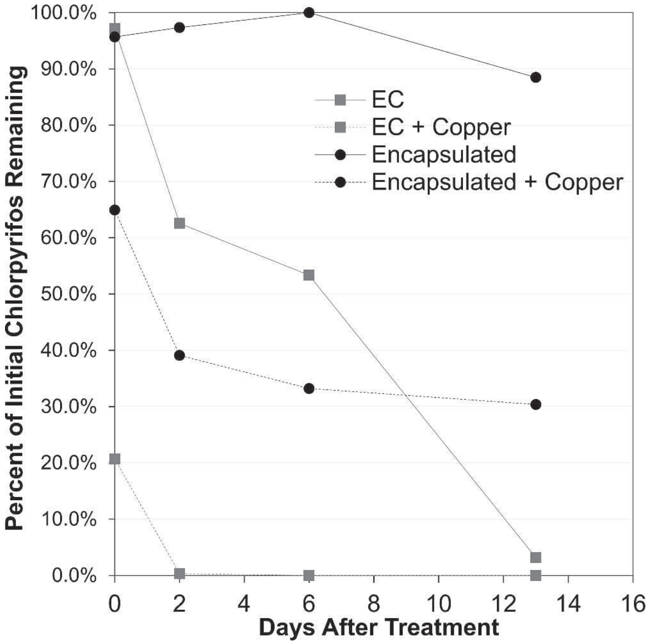

Fig. 2. Mean percentage of initial chlorpyrifos remaining after treatment for emulsifiable concentrate (EC) and microencapsulated formulations with and without $Cu(OH)_2$ in laboratory quantification studies.

was not seen across 3 yr of data in the diazinon applications ($\chi^2 = 0.05$; df = 1; $n =$ 112; $P = 0.8251$), with 0.41 ± 0.12 ($n = 56$) shoot strikes in the copper treatment, and 0.32 ± 0.09 ($n = 56$) in the without-copper treatment. When using carrier water at a pH of 7.30 in 2004, chlorpyrifos (EC formulation) alone resulted in a solution with pH 7.63 and treated trees experienced 0.75 ± 0.25 ($n = 12$) shoot strikes; however, the addition of $Cu(OH)_2$ to the chlorpyrifos solution raised the pH to 8.48 and treated trees experienced 2.08 ± 1.12 ($n = 12$) shoot strikes. A phosphate buffer added to the $Cu(OH)_2$ and chlorpyrifos solution brought the pH to 7.13 and treated trees experienced 1.00 ± 0.30 ($n = 12$) shoot strikes. There were no significant differences in peach twig borer damage between these treatments in 2004 (overall model: $\chi^2 = 0.69$; df = 2; $n = 36$; $P = 0.7084$).

Laboratory reactions and quantitative analysis. After 2 wk, the microencapsulated formulation retained more active chlorpyrifos relative to the EC, with the EC degrading almost completely as shown in Fig. 2. For both formulations, the addition of $Cu(OH)_2$ to the insecticide solution resulted in faster degradation of chlorpyrifos and less active ingredient remaining than without $Cu(OH)_2$ (Fig. 2). A similar trend was found for diazinon, with the microencapsulated formulation showing longer persistence than the EC, and the addition of $Cu(OH)_2$ decreasing persistence of the active ingredient (Fig. 3). However, for diazinon, the microencapsulated formulation showed more resistance to the effects of $Cu(OH)_2$, with a smaller decline in active ingredient over time relative to the EC (Fig. 3).

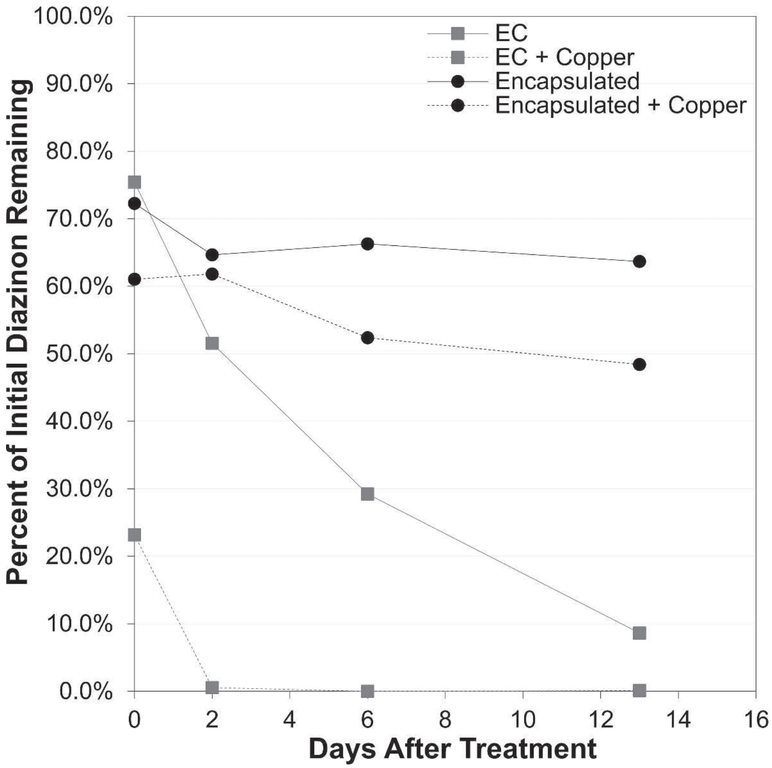

Fig. 3. Mean percentage of initial diazinon remaining after treatment for emulsifiable concentrate (EC) and microencapsulated formulations with and without $Cu(OH)_2$ in laboratory quantification studies.

In the laboratory, the EC formulation of chlorpyrifos exhibited a pH of 6.5 in solution, and a pH of 6.6 if a phosphate buffer (KH_2PO_4) was added to the solution. When $Cu(OH)_2$ was included the solution had a basic pH of 8.4, which decreased to 6.9 after adding a phosphate buffer (Fig. 4). Solutions with more neutral pH values showed fairly similar chlorpyrifos degradation, though the solution containing copper and buffer (at pH 6.9) exhibited a slightly quicker degradation, with less chlorpyrifos remaining 8 d after treatment relative to the chlorpyrifos alone and chlorpyrifos with buffer treatments (Fig. 4). The basic chlorpyrifos solution containing copper and no buffer (at pH 8.4) exhibited the fastest degradation of the active ingredient (Fig. 4).

Discussion

Copper(II) is known to catalyze the hydrolytic breakdown of organophosphate insecticides including chlorpyrifos and diazinon (Blanchet and St. George 1982, Mortland and Raman 1967, Smolen and Stone 1997). The rate of organophosphate breakdown by hydrolysis is also pH dependent for many of the compounds (Ku and

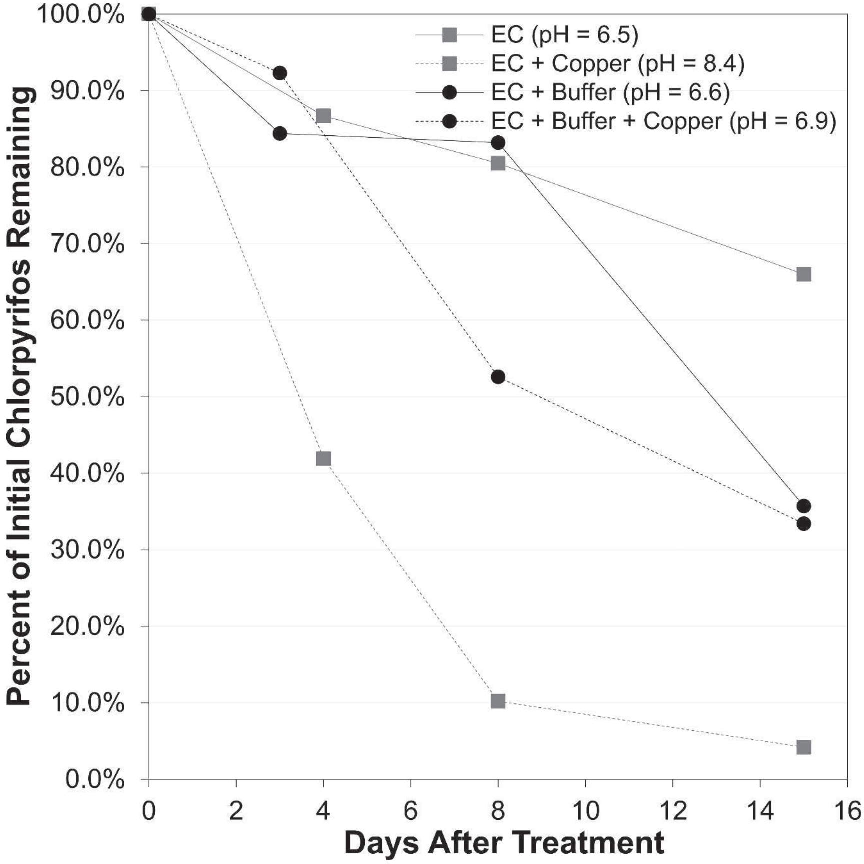

Fig. 4. Mean percentage of initial chlorpyrifos remaining for the emulsifiable concentrate (EC) formulation mixed with and without $Cu(OH)_2$ and with and without KH_2PO_4 buffer in laboratory quantification studies.

Chang 1998, Meikle and Youngson 1978, Ramesh and Balasubramanian 1999, Smolen and Stone 1997). The practice of mixing a copper fungicide with an organophosphate insecticide for dormant-season application remains relatively common, but the effect on pest control has not been previously reported.

The half-life for chlorpyrifos hydrolysis (without a catalyst) is 22.8, 35.3, and 62.7 d at pH 8.1, 6.9, and 4.7, respectively (Meikle and Youngson 1978). Despite its relative stability from pH 5 to 6, chlorpyrifos hydrolysis will occur in the presence of copper(II) (Mortland and Raman 1967). Indeed, the rate of hydrolysis of chlorpyrifos in the presence of copper(II) increases with pH (Blanchet and St. George 1982). Therefore, when copper(II)-containing fungicides/bactericides are tank-mixed with chlorpyrifos, the hydrolytic breakdown of chlorpyrifos is catalyzed. This is likely exacerbated if the copper product also raises the pH of the solution. Our field data (using carrier water of pH 7.3) support this because treatments containing both $Cu(OH)_2$ and chlorpyrifos (pH 8.4) showed greater peach twig borer damage than those without $Cu(OH)_2$ (pH 7.6), presumably due to the more rapid degradation of the insecticide active ingredient (Table 2). Quantifying this degradation in the laboratory, we saw more rapid degradation of chlorpyrifos in treatments with $Cu(OH)_2$ (pH 8.4) than treatments without $Cu(OH)_2$ (pH 6.5), though the microencapsulated formulation exhibited better persistence than the EC (Fig. 2).

Diazinon hydrolysis (without a catalyst) only occurs for protonated diazinon species (acidic solutions), and the rate of hydrolytic breakdown decreases as pH increases above 2.4 (Ku and Chang 1998), with breakdown of diazinon only occurring below pH 4.5 (Smolen and Stone 1997). When catalyzed by copper(II), diazinon hydrolysis occurs most rapidly at slightly acidic pH levels, and hydrolysis will occur at a range of pH values (Smolen and Stone 1997). There was no significant impact of adding $Cu(OH)_2$ to diazinon formulations in the field (Table 2). We postulate that this may be due to the slower catalyzed hydrolysis rate at neutral and basic pH (pH 7.9 with $Cu[OH]_2$ and pH 7.5 with $Cu[OH]_2$, when mixed in carrier water of pH 7.3, [data not shown]). Alternatively, diazinon may be equally efficacious for peach twig borer control regardless of speed of breakdown. In laboratory quantification studies, we were able to detect a difference in the breakdown rate of diazinon when catalyzed with $Cu(OH)_2$ (Fig. 3). However, we did not record the pH of these solutions because no laboratory buffer study was performed with diazinon.

Because copper(II) catalyzes the breakdown of various organophosphate insecticides across a range of pH values, we do not recommend simultaneous application of copper(II)-containing fungicides/bactericides and organophosphate insecticides. Copper-containing fungicides/bactericides may also change the pH of the pesticide mixture; therefore, it may be beneficial to buffer the solution to a neutral pH. Although the difference in organophosphate insecticide field efficacy against peach twig borer observed in our experiments was not numerically very large, this may well have an important economic impact in terms of peach twig borer damage.

Organophosphate insecticides are used to control a variety of insect pests and may be mixed with copper-containing fungicides/bactericides in other agricultural systems around the world. Without specific data regarding impacts of this mixture on control efficacy in these systems, caution should be used given the more rapid degradation exhibited by organophosphate insecticides when catalyzed by copper(II)-containing compounds.

Acknowledgments

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