JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

The Persistence and Degradation of Chlorothalonil and Chlorpyrifos in a Cranberry Bog

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The effect of a spray-tank adjuvant on the persistence, distribution, and degradation of two pesticides, chlorothalonil and chlorpyrifos, was studied in a commercial cranberry bog. Pesticides were applied according to label instructions to cranberry plants in paired plot studies. Dislodgeable foliar and whole fruit residues of both pesticides and several degradation products were assessed over a growing season. Residues were also assessed in soil samples collected at fruit harvest. Adjuvant increased both fruit and foliar residues but did not significantly alter the dissipation rate or metabolism of either pesticide. The dissipation of dislodgeable foliar chlorothalonil and chlorpyrifos residues followed first-order kinetics, with estimated half-lives of 12.7 and 3.5 d, respectively. All residue levels on harvested fruit were well below the current U.S. EPA tolerances for fresh cranberries. Chlorothalonil (58%) was the major residue in fruit at harvest (76 d post-chlorothalonil application), with 4-hydroxy-2,5,6-trichloroisophthalonitrile and 1,3-dicarbamoyl-2,4,5,6-tetrachlorobenzene accounting for 26% and 6% of the total residues, respectively. Degradation products accounted for 88% of the total chlorothalonil residues in soil at fruit harvest. The products 1,3-dicarbamoyl-2,4,5,6-tetrachlorobenzene, 1-carbamoyl-3-cyano-4-hydroxy-2,5,6-trichlorobenzene, 2,5,6-trichloro-4-methylthioisophthalonitrile, and 2,4,5-trichloroisophthalonitrile have not been previously identified in cranberry bog environments. Chlorpyrifos was detected in fruit at harvest (62 d post-chlorpyrifos application), but no metabolites were found. Chlorpyrifos-oxon and 3,5,6-trichloro-2-pyridinol, however, were detected in earlier fruit samples and in foliage and soil samples.

KEYWORDS: Chlorothalonil; chlorpyrifos; degradation; cranberry cultivation; *Vaccinium* spp.

INTRODUCTION

Cranberry (*Vaccinium* spp.) is a low-growing, woody broadleaf, nondeciduous vine. Most cranberry cultivation in Massachusetts occurs on constructed bogs that are surrounded and traversed with drainage ditches to maintain a constant water level 30−40 cm below the soil surface. The bogs are sanded every 3−5 years to encourage new growth as well as to manage some pests. This practice results in layered soils of medium coarse sand, 3−4 cm thick, with approximately 5% organic matter separated by peat layers of variable thickness. At about 40 cm, well-decomposed peat is formed. The pH of the sediments and water in the irrigation ditches is relatively acidic, with pH values of 4.4−6.0 for sediment and 5.1−6.6 for irrigation water (*1*, *2*).

Chlorothalonil (CHT, 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile, **Figure 1**) is a nonsystemic, broad-spectrum fungicide that is currently registered in Massachusetts to control several fruit rots of cranberry. Several studies investigating CHT metabolism in soil (*3*−*5*) and sediment (*6*) suggest that there are several degradation pathways. Metabolites involving substitution reactions of Cl atoms on the aromatic ring with methyl sulfide, methoxy, and hydroxyl groups or with hydrogen atoms, and conversion of the CN groups to amides, thiazole, and acidic groups, have been identified. Degradation in soil is primarily microbial, and the major metabolite reported in soil and plants is 4-hydroxy-2,5,6-trichloroisophthalonitrile (compound **II**, **Figure 1**).

Chlorpyrifos (CHP, *O*,*O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate, **Figure 2**) is a broad-spectrum insecticide registered in Massachusetts to control insect pests on cranberry, including cranberry weevil, fireworms, spanworms, *Sparganothis* fruitworm, and cranberry fruitworms. CHP is degraded by both biotic and abiotic processes, with 3,5,6-trichloro-2-pyridinol (TCP) being the major metabolite (*7*, *8*). There is presently little information on the degradation of CHT or CHP in cranberry bog environments.

There have been several studies aimed at extending pesticide activity on cranberry fruit, including the use of spray adjuvants (*9*−*11*). The addition of spray adjuvants that increase pesticide residues during peak infestation periods may permit the reduc-

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10.1021/jf020744r CCC: $25.00
Published on Web 11/19/2002

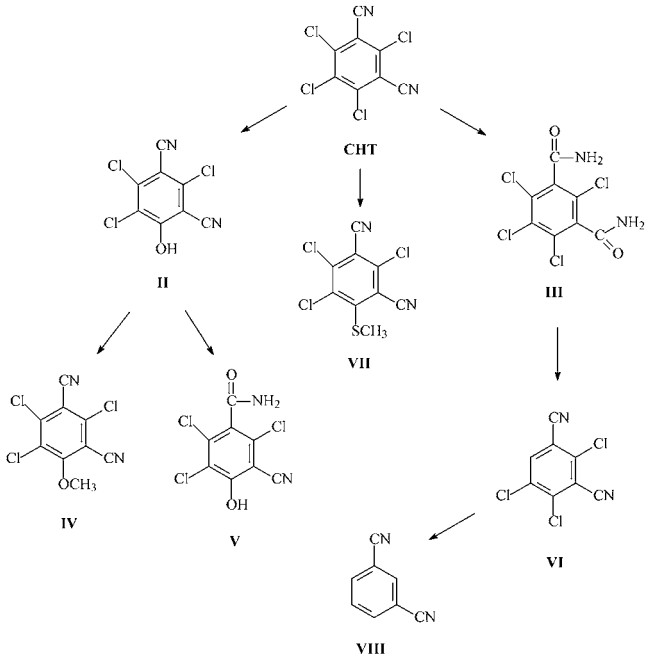

Figure 1. Chlorothalonil and target degradation. Arrows represent possible environmental degradation pathways. Chlorothalonil (CHT); 4-hydroxy-2,5,6-trichlororisopthalonitrile (**II**), 1,3-dicarbamoyl-2,4,5,6-tetrachlorobenzene (**III**); 2,5,6-trichloro-4-methoxyisophthalonitrile (**IV**); 1-carbamoyl-3-cyano-4-hydroxy-2,5,6-trichlorobenzene (**V**); 2,4,5-trichloroisophthalonitrile (**VI**); 2,5,6-trichloro-4-methylisophthalonitrile (**VII**); and isophthalonitrile (**VIII**).

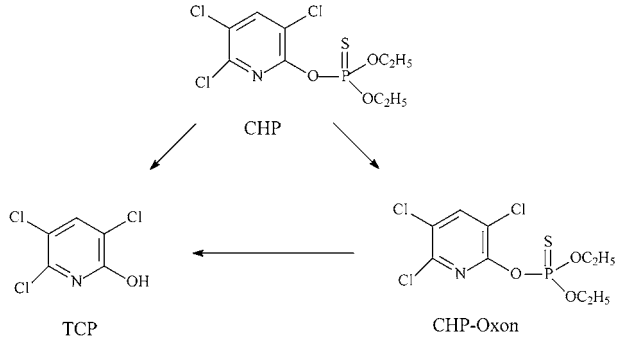

Figure 2. Chlorpyrifos and target degradation products. Chlorpyrifos (CHP); 3,5,6-trichloro-2-pyridinol (TCP); and diethyl 3,5,6-trichloro-2-pyridyl phosphate (CHP-Oxon).

tion in the number of applications or the rate of active ingredient applied per application. A balance must be maintained, however, between the extension of pesticide activity and the residues remaining in fruit at harvest.

The present investigation evaluates the persistence and degradation of fruit and dislodgeable foliar residues of CHT and CHP in the presence and in the absence of a spreader-sticker adjuvant previously shown to reduce off-site drift during pesticide applications to cranberry bogs (*12*). With this research, we will determine if the addition of the spray-tank adjuvant increases application efficacy by prolonging the period that protective residue levels remain on cranberry plants, alters pesticide degradation, or results in higher residues in fruit at harvest.

MATERIALS AND METHODS

Chemicals. Analytical grade standards of CHT, CHP, TCP, chlorpyrifos-oxon (*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphate), and compound **II** (4-hydroxy-2,5,6-trichloro-1,3-dicyanobenzene) were obtained from the U.S. EPA. Compounds **VI** (2,4,5-trichloro-1,3-dicyanobenzene, 99.9% pure), **VII** (4-methylthio-2,5,6-trichloro-1,3-dicyanobenzene, 98.8% pure), and **IV** (4-methoxy-2,5,6-trichloro-1,3-dicyanobenzene, 97.6% pure) were generously provided by Dr. Arata Katayama, Nagoya University, Japan. Compounds **III** (1,3-dicarbamoyl-2,4,5,6-tetrachlorobenzene) and **V** (1-carbamoyl-3-cyano-4-hydroxy-2,5,6-trichlorobenzene) were synthesized according to the method of Rouchaud et al. (*13*). Compound **VIII** (1,3-dicyanobenzene, 98.0% pure), iodoethane (99%), and the diazomethane precursor, 1-methyl-3-nitrosoguanidine (97%), were obtained from Aldrich (Milwaukee, WI). Solvents (pesticide grade) and 1 M tetrabutylammonium hydroxide (TBAH) solution in methanol were obtained from Fisher Scientific (Pittsburgh, PA). Pesticide formulations were provided by the University of Massachusetts Cranberry Experiment Station, Wareham, MA. CHT applications were made with Bravo 720, 54.0% CHT (ISK Biotech Corp., Mentor, OH; EPA Reg. No. 50534-188), and CHP applications were made with Lorsban 4E, 40.7% a.i. (Dow AgroSciences Indianapolis, IN; EPA Reg. No. 62719-23). Applications in the presence of a spreader-sticker adjuvant were made with Bivert, which was a gift from the Wilbur-Ellis Co. (Fresno, CA).

Field Treatments. Four experimental plots (5×5 m) or (5 m^2) on an established cranberry bog in Plymouth, MA, were used for backpack applications of Bravo with and without adjuvant, and Lorsban with and without adjuvant. At each paired plot, the application of pesticide without adjuvant was immediately followed by the application of pesticide with adjuvant. CHT applications were made at a rate of 6.4 L of Bravo 720/ha. Applications in the presence of adjuvant included Bivert at a rate of 1.8 L/ha. The first CHT applications were made at 20% cranberry blossom bloom. The second CHT applications were made 14 d later, at approximately 80% bloom. Each CHP test plot received a single treatment in the presence or in the absence of Bivert at 100% cranberry fruit development. CHP applications were made at a rate of 2.0 L/ha. CHP applications in the presence of adjuvant included Bivert at a rate of 0.5 L/ha.

Sample Collection. Three random foliage and fruit samples were collected at each sampling period, and their location was marked with a flag to prevent resampling. Foliage samples were initially collected 1 h postapplication, followed by collections at 3, 7, 13, and 28 d postapplication. To minimize disruption of the dislodgeable residues, foliage samples were handled using a preweighed 2.5-g piece of cotton cheesecloth. The vine was grabbed using the cheesecloth and cut approximately 12 cm from the tip (15−20 leaf sets). The vines (approximately 15 g per sample) and cheesecloth were placed into a glass jar, which was placed into a cooler containing ice-packs. To preserve the compartmentalization of the dislodgeable residues, foliage samples were stored at 4 °C (never frozen) and were analyzed within 24 h of collecting. Fruit collections started during late fruit development and continued until cranberry harvest. Fruit was harvested using an acetone-cleaned cranberry scoop and placed into amber glass bottles. A 750-g composite soil sample (1−6 cm deep) was taken from the center of each experimental plot during the last sampling period using a stainless steel spatula. Soils were essentially uniform to 10 cm (95% sand, 4% OC, 1% silt, and 0% clay; pH 5.1, with a cation-exchange capacity of 3.6 mequiv/100 g) as a result of cultivation practices.

Apparatus. (*a*) *Gas Chromatography with Mass-Selective Detector* (*GC/MSD*). CHT, CHP, CHP-oxon, and ethylated degradation products were analyzed using a Hewlett-Packard GC (model 5890, Series II) equipped with an automatic sampler (model 7673) and a MSD (model 5971). The capillary column was a fused silica DB-5 liquid phase, 30 m $\times$ 0.25 mm i.d., 0.25 μm film thickness (J&W Scientific, Folsom, CA). The helium carrier gas had a linear velocity of approximately 30 cm/s. The injector temperature was 250 °C, and the transfer line temperature was 300 °C. The oven was temperature programmed from 80 °C (held for 3.0 min) to 250 °C (held for 5.0 min) at 20 °C/min. Depending on the analyte concentration, the GC/MSD was operated using electron impact ionization (70 eV) mode in either full-scan mode (35−450 amu) or selected ion-monitoring mode (SIM). The ions monitored for each analyte are listed in **Table 1**.

(*b*) *Gas Chromatography with Electrolytic Conductivity Detector* (*GC/ELCD*). Compound **III** was analyzed using a Hewlett-Packard GC (model 5890, Series II) equipped with a model 4420 ELCD operating

Table 1. GC-SIM-MS (70 eV) Data for Target Pesticides

pesticide	t_R[a] (min)	target ions, *m/z* (relative intensity)
VIII	7.2	101 (21), 128 (100)
TCP (methyl ester)	10.92	182 (100), 211 (70), 213 (68)
VI	12.51	195 (10), 230 (100), 232 (96), 234 (31)
CHT	14.17	231 (11), 264 (85), 266 (100), 268 (52)
II (ethyl ester)	14.38	246 (100), 248 (95), 274 (13), 276 (11)
IV	14.43	232 (100), 260 (97), 262 (94), 264 (29)
CHP-oxon	15.57	197 (100), 199 (96), 270 (80), 298 (61)
CHP	15.67	197 (96), 199 (100), 314 (54)
VII	16.73	243 (100), 276 (79), 278 (79), 280 (28)
V (ethyl ester)	18.48	248 (100), 266 (34), 292 (11), 294 (11)

[a] See Apparatus (Materials and Methods) for experimental conditions.

in halogen mode (O.I. Corp., College Station, TX). The capillary column was a fused silica HP-50 + liquid phase, 0.53 mm i.d. × 15 m, 1.0 μm film thickness (Hewlett-Packard). Operating conditions were as follow: injection volumem 1.0 μL; injector temperature, 250 °C; detector temperature, 850 °C; septum purge on at 1 min; column oven temperature, 80 °C for 2 min, ramped at 15 °C/min to 275 °C, and held for 10 min. The ELCD was vented for 15 min. The carrier gas was helium at a rate of 10 mL/min^{-1}. The detector was supplied with hydrogen at a flow rate of 100 mL/min^{-1}.

(c) High-Pressure Liquid Chromatograph with Ion-Trap Mass Spectrometer. The presence of compound **III** was qualitatively confirmed in representative fruit and soil samples using a Finnigan LCQ HPLC/ion-trap MS system (Finnigan MAT Corp., San Jose, CA) in positive-ion mode via direct infusion. The ion source was APCI at 450 °C, and the infusion pump was at 3.0 μL/min. The MS parameters were set as follows: discharge current, 5.0 μA; capillary temperature, 200 °C; and sheath gas, N_2.

Analytical Procedures. *Dislodgeable Foliar Residues*. Foliage samples were analyzed for dislodgeable residues of CHT, CHP, chlorpyrifos-oxon, and compound **II** using a modified methanol surface extraction (*14*). After the collecting jar and contents were weighed, methanol (200 mL) was added, and the jar was shaken for 45 s. The methanol was decanted through Whatman No. 1 filter paper into a boiling flask, reduced to ~20 mL under vacuum at 50 °C, and transferred to a separatory funnel. The boiling flask was rinsed with 100 mL of a 0.3% H_2SO_4 solution (pH approximately 1.3), combined in a separatory funnel with the sample extract plus 5 g of NaCl, and extracted two times with 100 mL of petroleum ether:diethyl ether (50:50). The ether layers were decanted through anhydrous Na_2SO_4 contained on Whatman No. 1 filter paper into a second boiling flask, and the combined extracts were evaporated under vacuum at 40 °C to less than 10 mL and quantitatively transferred with acetone to a centrifuge tube. The final volume of the reduced extract was adjusted and analyzed for CHT, CHP, and chlorpyrifos-oxon by GC/MSD.

Each of the remaining extracts was treated with iodoethane and analyzed for ethylated compound **II** by GC/MSD. Extracts were reduced to 2.5 mL under N_2 and filtered through a 0.45-μm nylon filter, and then an aliquot of this extract was transferred to a centrifuge tube, reduced to dryness under N_2, and reconstituted into acetone (400 μL). Iodoethane (400 μL) and K_2CO_3 (~0.3 g) were added, and the extract was incubated at 65 °C for 30 min. After cooling, the extract was reduced just to dryness under N_2, reconstituted into 10 mL of hexane, and partitioned with 2.5 mL of H_2O and Na_2SO_4 (~1.0 g) by vortexing for 1 min. The hexane layer was decanted into a centrifuge tube, and the remaining aqueous phase was re-extracted with 10 mL of diethyl ether. The combined extracts were solvent-exchanged to ethyl acetate and reduced to 1.0 mL under N_2.

Fruit and Soil Residues: *Method 1*. CHT, CHP, chlorpyrifos-oxon, and compounds **IV**, **VI**, **VII**, and **VIII** were extracted as follows. A 50-g aliquot of fruit or soil was weighed into an amber glass bottle. Cranberries were transferred to a blender jar with 200 mL of hexane:acetone solution (60:40), blended for 2 min, and decanted back into the bottle. The jar was rinsed with 100 mL of hexane:acetone solution, and the rinse solution was combined in the bottle. The sample was shaken in the bottle on a rotary shaker at low speed for 30 min and decanted through glass wool into a separatory funnel containing 200 mL of distilled water plus 12 g of NaCl. The bottle and glass wool were washed with 50 mL of hexane, combined in the separatory funnel, and shaken for 2 min, and the aqueous layer was collected in a beaker. The organic layer was decanted through anhydrous Na_2SO_4 into a boiling flask. The aqueous layer was re-extracted with two 100-mL hexane aliquots, which were combined in the flask. The extract was reduced under vacuum at 50 °C to ~5 mL, quantitatively transferred with acetone to a centrifuge tube, reduced to ~2 mL under N_2, and adjusted to a final volume of 4.0 mL with the hexane:acetone solution.

Soil samples were extracted in amber glass bottles for 90 min on a rotary shaker with hexane:acetone (60:40). The extract was filtered through Na_2SO_4 into a flask, and the bottle was rinsed with 50 mL hexane, which was combined with the extract. The extract was decanted into a separatory funnel containing 200 mL of distilled water plus 12 g of NaCl and extracted as described for fruit.

A 1.0-mL aliquot of the fruit or soil extract was transferred to a centrifuge tube and solvent-exchanged by reducing the aliquot to 0.5 mL under N_2, adding 4 mL of hexane, and reducing under nitrogen to 1 mL. The 1-mL extract was transferred to a Florisil SPE cartridge (6 mL × 1 g of Florisil, J&W Scientific) that had been pretreated with 3 mL of hexane and topped with 1 g of anhydrous Na_2SO_4. The tube was rinsed with 4 mL of hexane, which was pulled through the SPE cartridge in a dropwise manner under vacuum. A clean tube was placed in the SPE manifold, analytes were eluted with 5 mL of hexane:acetone (20:80) under vacuum, and the eluant was reduced to 1.0 mL under N_2 and filtered through a 0.45-μm nylon filter.

Fruit and Soil Residues: *Method 2*. Compounds **II**, **V**, and TCP were extracted as follows. Fruit and soil (25 g) were weighed into individual amber glass bottles. Each sample was transferred to a blender jar with 110 mL of an acetone:sulfuric acid solution (99:1), blended (2 min), and decanted back into the bottle. The jar was rinsed with two 50-mL aliquots of acetone, which were combined with the solution in the bottle. The sample was shaken in the bottle on a rotary shaker for 30 min, gravity-filtered through Whatman No. 1 filter paper, and rinsed with 50 mL of acetone into a boiling flask. The sample was reduced to <20 mL under vacuum at 40 °C and decanted into a separatory funnel. The flask was rinsed with 100 mL of a 0.5 N NaOH solution and combined in the funnel. The pH of the extract was adjusted to pH 12 with 5 N NaOH, the solution was extracted three times with 100-mL hexane aliquots, and the organic phase was discarded. The aqueous extract was decanted into the original flask, adjusted to pH 1.5 with 10% H_2SO_4, and decanted into a separatory funnel containing 15 g of NaCl. The flask was rinsed with 100 mL of ethyl acetate, which was combined in the separatory funnel. After 2 min of shaking, the ethyl acetate layer was decanted into an Erlenmeyer flask containing 20 g of anhydrous Na_2SO_4. After 15 min, the ethyl acetate was decanted through anhydrous Na_2SO_4 into a boiling flask. The remaining aqueous phase was decanted back into the separatory funnel with an additional 10 g of NaCl and re-extracted × twice for 2 min with 100 mL and 50 mL of ethyl acetate. The combined ethyl acetate extract was reduced to <5 mL under vacuum at 40 °C and quantitatively transferred to a centrifuge tube.

Compounds **II** and **V** were derivatized with iodoethane as described above. However, the presence of co-extractives made it necessary to add 200 μL of TBAH prior to derivitization to improve reaction efficiency. TCP was methylated with diazomethane. One-milliliter extract aliquots were transferred to individual tubes and reduced to 0.5 mL under N_2. Four milliliters of diethyl ether was added to the sample, and the mixure was reduced to 0.5 mL under N_2 and brought to 2 mL with diethyl ether. Two milliliters of freshly prepared diazomethane in diethyl ether (approximately 15 mg/mL) was added, the tube capped, and the sample incubated for 30 min at room temperature. Hexane (2 mL) was added, and the sample was reduced to 1 mL under N_2. This solvent transfer was repeated two more times, resulting in a final extract of 1 mL of hexane.

Fruit and Soil Residues: Method 3. Compound **III** was extracted as follows. Approximately 25 g of fruit or soil was weighed into a blender jar with 100 mL of acetone, blended for 2 min, and decanted into an amber glass sample bottle with × two 50-mL acetone rinses.

Table 2. Method Recoveries and Limits of Detection in Cranberry Fruit and Bog Soil

	fruit[a]			soil[b]		
compound	recovery (%) ± SD	*n*	LOD[c]	recovery (%) ± SD	*n*	LOD[c]
CHT	88.1 ± 15.0	5	25	98.2 ± 13.3	5	5
II	78.9 ± 19.4	10	20	97.8 ± 8.8	5	20
III	96.1 ± 9.9	6	2.5	97.6 ± 4.9	5	2.5
IV	105.6 ± 13.6	5	5	78.2 ± 5.1	5	1
V	31.6 ± 21.4	10	5	94.3 ± 10.3	5	25
VI	89.1 ± 14.0	5	5	78.1 ± 5.7	5	1
VII	101.1 ± 9.2	5	5	88.9 ± 16.0	5	1
VIII	51.8 ± 12.7	5	10	63.2 ± 20.4	5	5
CHP	92.7 ± 13.3	6	25	96.1 ± 16.9	5	10
TCP	98.0 ± 14.4	5	20	101.9 ± 17.4	5	10
CHP-oxon	92.0 ± 14.0	5	10	93.0 ± 5.1	5	20

[a] Fortification range, 50–200 μg/kg. [b] Fortification range, 25–2000 μg/kg. [c] Limit of detection (μg/kg).

The bottle was capped and shaken on a rotary shaker for 60 min, the sample filtered through Whatman No. 1 filter paper into a boiling flask, the bottle rinsed with 50 mL of acetone, which was combined with the extracts. The extract was reduced to <30 mL under vacuum at 45 °C and decanted into a separatory funnel, and the flask was rinsed with 250 mL of alkaline H_2O (pH 12 with NaOH), which was combined in the separatory funnel with 20 g of NaCl. The flask was rinsed with 100 mL of hexane, which was added to the separatory funnel, and then the funnel was shaken for 2 min and the hexane layer discarded. The aqueous phase was decanted back into the separatory funnel and extracted for 2 min with 100 mL of ethyl acetate. The ethyl acetate was decanted into an Erlenmeyer flask containing 20 g of anhydrous Na_2SO_4, equilibrated 10 min, and decanted into a flask. The aqueous phase was re-extracted sequentially with 100-mL portions of ethyl acetate and ethyl ether, and the organic phases were combined as above. The extract was reduced to <5 mL under vacuum at 50 °C, quantitatively transferred with ethyl acetate to a centrifuge tube, reduced to a final volume of 2 mL under N_2, and filtered through a 0.45-μm nylon filter. This extract was saved for GC/ELCD analysis.

Quality Control Samples. Pesticide recoveries were determined from fortified foliage, fruit, and soil. Each analytical set included a matrix blank and a fortified matrix spike amended with the pesticide(s) of interest. Untreated foliage, fruit, and soil were collected from an unused cranberry bog. For cranberry and soil, a 1−2-mL aliquot of an analytical standard solution was added to 50 g of fruit or soil in an amber glass bottle. After being shaken briefly by hand, the bottle was uncapped and the solvent evaporated. For foliage, 1-mL aliquots of analytical standards were added to the 200-mL methanol extracting solution. Matrix and reagent blanks fortified with both CHT and CHP were analyzed for breakdown products to ensure that the analytical methods were not converting the parent pesticides to targeted metabolites.

Pesticide Quantitation. Pesticide quantitation was performed using external calibration techniques, and linear regression was used to estimate pesticide concentrations. Poor linearity (linear regression < 0.995) was typical on the GC/MSD at or near the limit of detection (LOD). In these cases, single-point quantitation was used to estimate pesticide concentrations.

The LOD was established as the amount of analyte that produced a signal greater than 5 times the background signal of the matrix blank. Additionally, the qualitative identification of a compound was based on its GC retention time and comparison of its sample mass spectrum, after background correction, with the characteristic ions in the reference standard mass spectrum. The relative intensities of the target ions (**Table 1**) were required to agree within 20% of the relative intensities of the ions in the reference spectrum for positive identifications. The LOD for dislodgeable foliar residues of CHT, compound **II**, CHP, and TCP was 50 μg/kg. The LOD values for fruit and soil residues are presented in **Table 2**.

Statistical Analysis. Dissipation curves for foliar and fruit residues were analyzed using simple linear regression statistics. The decline of residues over time was modeled as an exponential decay function:

$$\text{residue}_t = \text{residue}_{t_o} \times \exp^{kt}$$

where k is the decay rate in micrograms per gram of foliage per day and t is the number of days postapplication. The decay rate (k), intercept, and correlation coefficient (r^2) were estimated with regression analysis on the log-transformed pesticide residue concentrations [ln(residues$_t$)] versus time, with the slope parameter used as the least-squares estimate of k.

The half-life of dislodgeable foliar residues in days was calculated as

$$\text{half-life} = [\ln(0.5)]/k$$

Analysis of covariance (ANCOVA) was used to compare decay rates and intercepts (STATISTIX software package, Analytical Software, Chicago, IL).

RESULTS AND DISCUSSION

Structural Confirmation. Synthesized compounds **III** and **V** had individual physiochemical characteristics (IR and mass spectrum) identical to those reported by Rouchaud et al. (*13*). Purity was >97% for both, as determined by TLC and GC/MS (data not shown).

Analysis of Pesticide Formulations. Several of the targeted environmental degradation products were detected in the Bravo formulation in addition to CHT. The average concentration (grams per 100 g of formulation, $N = 2$) of each component detected was as follows: CHT, 53.3; compound **II**, 2.1; compound **VIII**, 0.10; compound **V**, 0.02; and compound **VI**, 0.008. Compounds **III**, **IV**, and **VII** were not detected at a detection limit of 0.0005% (5 μg/g of formulation). Partially chlorinated (**VI**) and unchlorinated (**VIII**) dicyanobenzene isomers are known to be present in chlorothalonil formulations as production impurities (*15*). In a similar analysis of duplicate Lorsban samples, the average concentration (grams per 100 g of formulation, $N = 2$) of each compound detected was as follows: CHP, 40.9; TCP, 1.7; and CHP-oxon, 0.71. Previous studies have reported varying amounts of TCP in CHP formulations, depending on age and storage conditions. CHP-oxon is rarely detected, however, and constitutes only 1% of parent CHP (*16*−*19*).

Dislodgeable Foliar Residues. The maximum levels of dislodgeable foliar CHT residues occurred in the 1-h postapplication samples in the presence of the adjuvant Bivert and were 385 ± 51.6 and 407 ± 43.6 mg/kg ($N = 3$) after the first and second Bravo applications, respectively. In the absence of adjuvant, the 1-h postapplication CHT residues were 204 ± 28.3 and 236 ± 104 mg/kg ($N = 3$) after the first and second Bravo applications, respectively. Thus, dislodgeable foliar residues of CHT were significantly increased (t-test, $p \leq 0.05$) in the presence of this adjuvant. CHT residues dissipated from cranberry foliage at similar rates after the first Bravo application in the presence and in the absence of adjuvant (ANCOVA, $p \leq 0.05$), and 7 d postapplication, 53.4 and 56.1% of the initial chlorothalonil residues remained in the presence and in the absence of adjuvant, respectively (data not shown). There were no additional foliage samples collected prior to the second Bravo application at 14 d, and the half-life and decay rates for CHT were estimated after the second application of Bravo. The dissipation of dislodgeable foliar residues of CHT followed first-order kinetics ($r^2 = 0.915$ and 0.875), and the estimated half-life of CHT on cranberry foliage was 12 and 13 d following the second applications in the presence and in the absence of adjuvant, respectively (**Table 3**).

Table 3. Linear Decay Model Parameters of Dislodgeable Foliar CHT and CHP after Application in the Presence and in the Absence of the Spreader-Sticker Adjuvant, Bivert

trial	initial residue (μg/g)	SD of intial residue	k^b (μg g^{-1} day^{-1})	SE of k	r^2	half-life[c] (days)
CHT	236.1	104	-0.057	0.011	0.872	12.1
CHT + adj.	400.7	43.6	-0.053	0.008	0.915	13.2
CHP	52.5	29.7	-0.183	0.0214	0.913	3.8
CHP + adj	125.4	31.0	-0.213	0.0278	0.893	3.3

[a] Regression analysis was performed on the second chlorothalonil application, initiated 14 d after the first application. [b] Decay rate, slope of the regression of ln residues versus days after application. [c] Calculated as [ln(0.5)]/k.

Due to the slow foliar growth rate of cranberry vines, there should be very little growth dilution of foliar pesticide residues. Nonetheless, the observed CHT half-lives on cranberry leaves in the current study are similar to previous findings. Foliar half-lives for CHT have been reported as 3.8 d on tomato foliage (*20*), 10−15 d on grape leaves (*21*), and 6.6 d on potato foliage (*22*). CHT half-life on peanut foliage was estimated as 4.4 d after high-volume chemigation application (*23*) and 6.5 d after boom sprayer application (*24*).

Applications of Lorsban 4E in the presence and in the absence of Bivert adjuvant resulted in initial (2 h) dislodgeable foliar CHP residues of 125.4 ± 31.0 and 52.5 ± 29.7 mg/kg, respectively (**Table 3**). The dissipation of dislodgeable foliar CHP residues also followed first-order kinetics ($r^2 = 0.893$ and 0.913) and displayed a more rapid dissipation from cranberry leaves, with estimated half-lives of 3.3 and 3.8 d in the presence and in the absence of adjuvant, respectively. After 3 d, 33.5 and 19.1% of the initial residues remained, and after 15 d, 3.0 and 4.9% of the initial residues remained, in the presence and absence of adjuvant, respectively. Small amounts of CHP-oxon were initially detected (<7 μg/kg), but residues did not accumulate.

Dislodgeable foliar residues of CHP were significantly higher (t-test, $p \leq 0.05$) in the presence versus the absence of adjuvant at the initial sampling period, but there was no significant difference between the two applications at later sampling times. Wauchope et al. (*25*) evaluated the deposition and persistence of chemigated CHP on corn foliage and found similar patterns. Chemigation of technical CHP dissolved in soybean oil resulted in 3-fold more CHP on the foliage than when an emulsion formulation of CHP was applied by chemigation, indicating a greater adhesion of the oil droplets to the foliar surface. CHP dissipation from the corn foliage was the same for both the soybean oil mixture and the formulation.

Fruit Residues. The concentrations of CHT and its degradation products in cranberries are presented in **Table 4**. The majority of CHT residues associated with fruit at harvest (76 d postapplication) were determined to be unaltered CHT, as expected. Residues of CHT were significantly higher (t-test, $p \leq 0.05$) in the presence of adjuvant compared to its absence during each sampling date.

Compound **II** was the major CHT degradation product identified in fruit. At harvest, compound **II** was detected at 62 and 69% of the CHT residue level in the presence and in the absence of adjuvant, respectively (**Table 4**). The tolerance for CHT plus compound **II** in cranberries adopted by the U.S. EPA is 5 mg/kg (*26*). The combined residue levels of CHT and compound **II** detected at harvest in the current study (0.0795 and 0.129 mg/kg in the presence and in the absence of adjuvant, respectively) are significantly below this tolerance level (<2.6% of tolerance).

Compound **II** has been identified as the major CHT degradation product in a variety of plants, but its reported percent of the total residues varies widely. El-Nabarawy and Carey (*27*) detected compound **II** in cranberries at a maximum of 7.8% of the parent compound 92 d postapplication after a worst-case application of 16 pints (40.4% a.i)/acre. In contrast, compound **II** was not detected in cranberries (LOD = 10 μg/kg), even when CHT itself was detected at concentrations as high as 4 mg/kg (*28*). CHT degradation has been investigated in other crops, and compound **II** has been determined to constitute 5% of the total residues in mature potato plants (*29*), 0.3−1.0% in grapes (*21*), 0.5−1.9% in onion foliage (*30*), and 0% in apples (*31*). Rouchaud and Roucourt (*3*) investigated the hydrolytic biodegradation of CHT in cabbage and broccoli crops. Two months after treatment, compound **II** was detected at >600% of CHT (20−80 μg/kg CHT and 500 μg/kg compound **II**) in broccoli and >200% of CHT (20−50 μg/kg CHT and 100−300 μg/kg compound **II**) in cabbage.

Compound **III** also was detected in the cranberries at harvest at 7.2 ± 2.2 and 4.9 ± 0.7 μg/kg ($N = 3$) in the presence and in the absence of adjuvant, respectively. These residue levels correspond to approximately 10% of the CHT detected at harvest. Previous investigations are limited to broccoli and cabbage crops, where Rouchaud and Roucourt (*3*) detected compound **III** at 35% of the CHT levels in both crops 2.5 months after application.

Compounds **V** and **VI**, likewise, were detected in cranberries but at relatively low concentrations. Neither compound persisted, and they were not detected in cranberries at harvest. Compounds **III**, **V**, and **VI** have not been previously identified in cranberries.

The concentrations of CHP and its degradation products in cranberries are presented in **Table 5**. Only CHP (340−415 μg/kg) was detected in fruit at harvest (62 d postapplication). Small amounts of CHP-oxon (<18 μg/kg) were detected in fruit at 14 and 31 d postapplication, but these residues did not persist at harvest. Although fruit was not analyzed at 14 and 31 d postapplication, TCP residues were not detected at harvest (62 d postapplication). Given the apparent lack of metabolites, it appears that CHP loss from cranberries proceeds primarily through mechanisms other than degradation, such as wash-off or volatilization. As discussed earlier, volatilization is thought to be the primary factor responsible for CHP disappearance from foliar surfaces. Bauriedel and Miller (*32*) studied the fate of CHP on apples and reported that the majority of recovered radioactivity (35%, or 50 μg/kg) was CHP, whereas conjugated and free TCP was present at concentrations of less than 10 μg/kg. The limited transformation of CHP in fruit may be due to the lack of CHP penetration into the fruit or the limited ability of the fruit to metabolize CHP (*7*).

The decay rates of CHP residues in cranberries in the presence and in the absence of adjuvant were not statistically different between 14 and 62 d postapplication [$y = -0.0298x + 0.946$ ($r^2 = 0.946$) with adjuvant and $y = -0.0269x - 0.523$ ($r^2 = 0.829$) without adjuvant]. Residues detected at each sampling date, however, were significantly higher (t-test, $p \leq 0.05$) in the presence of adjuvant compared to its absence. Terminal CHP residues at harvest (0.415 ± 0.0065 mg/kg with adjuvant and 0.340 ± 0.0135 mg/kg without adjuvant) were well below the U.S. EPA tolerance level of 1.0 mg/kg for CHP plus TCP on fresh cranberries (*26*).

Soil Residues. Residue levels of CHT and its degradation products in soil following application are presented in **Figure**

Table 4. Residues of CHT and Degradation Products in Cranberry Fruit after Application in the Presence and in the Absence of a Spreader-Sticker Adjuvant

		mean concentration (μg/kg ± SD)					
days post-application[a]	spray adjuvant	CHT	II	III	V	VI	VII
28	–	271.3 ± 15.0	na	13.5 ± 1.1	na	nd	nd
	+	461.3 ± 25.6	na	16.2 ± 2.9	na	5.1[b]	nd
45	–	131.7 ± 17.2	321.7 ± 26.2	13.4 ± 4.7	28.3[b]	8.6 ± 1.5	nd
	+	221.7 ± 14.6	205.0 ± 14.5	18.0 ± 5.7	31.4 ± 6.2	19.6 ± 5.0	nd
76[c]	–	49.1 ± 3.9	35.0 ± 11.8	4.9 ± 0.7	nd	nd	nd
	+	76.1 ± 5.0	46.3 ± 21.4	7.2 ± 2.2	nd	nd	nd

[a] Days after second chlorothalonil application. [b] $N = 1$; two of three samples were below LOD. All others are $N = 3$. [c] Terminal residues.

Table 5. Residues of CHP, CHP-Oxon, and TCP in Cranberry Fruit after Application in the Presence and in the Absence of a Spreader-Sticker Adjuvant

		mean concentration (μg/kg ± SD)		
days post-application	spray adjuvant	CHP	TCP	CHP-oxon
14	–	1660 ± 96.0	na	17.0[a]
	+	1940 ± 122	na	18.1[a]
31	–	557.7 ± 56.0	nd	nd
	+	830.6 ± 62.2	nd	10.4[a]
	–	340.5 ± 13.1	nd	nd
62[b]	+	415.7 ± 6.7	nd	nd

[a] $N = 1$; two of three samples were below LOD. All others are $N = 3$. [b] Corresponds to fruit harvest.

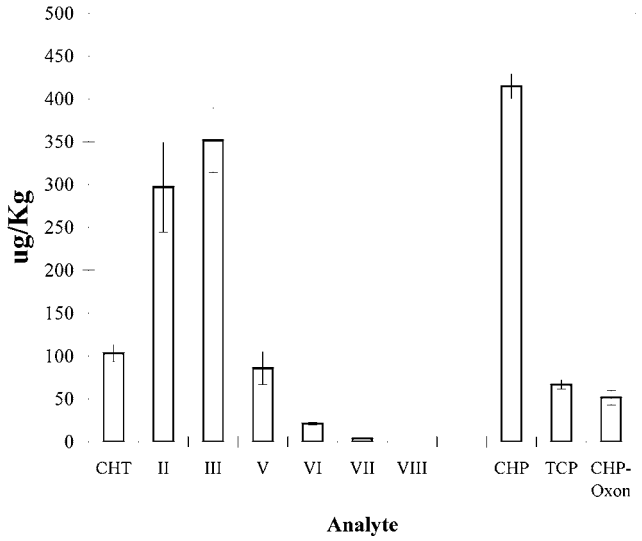

Figure 3. Distribution of chlorothalonil (CHT), chlorpyrifos (CHP), and their degradation products in the top 6 cm of cranberry bog soil at harvest time (76 d post-CHT application and 62 d post-CHP application). Chlorothalonil degradation products are compounds **II**, **III**, **V**, **VI**, **VII**, and **VIII**. Chloropyrifos degradation products are TCP and CHP-oxon. Each data point represents a single composite soil sample analyzed in triplicate.

3. Compound **III** was the major soil residue, accounting for 41% of the total detectable residues 76 d postapplication. Compound **II**, CHT, and compound **V** made up 34, 12, and 10% of the detectable residues, respectively. Small amounts of the methylthioated product (compound **VII**) and the dechlorinated product (compound **VI**) also were detected. Similar to fruit samples, compounds **IV** and **VIII** were not detected in any soil samples.

Although compound **VI** was detected at approximately 21.2 μg/kg, its presence in the formulation used for field applications makes its origin uncertain. Nevertheless, compound **VI** was previously reported in soil treated with chlorothalonil (*5*), but it was not quantitated. Our detection of compounds **III**, **V**, **VI**, and **VII** in cranberry bog soil is the first such report. Their high concentrations in soil and their low concentrations in cranberry fruit suggests that their formation requires stronger hydrolysis or microbial conditions for formation, and that they are not systemic to a significant level in cranberry plants.

The majority of CHP residues in soil were determined to be unaltered CHP (77.8%), with TCP and CHP-oxon accounting for the remaining 12.5 and 9.7%, respectively (**Figure 3**). The levels of TCP relative to CHP and CHP-oxon reported here are lower than those reported elsewhere (*7*, *33*). There are several characteristics of cranberry bog environments that may have contributed to the relatively low levels of TCP detected, including a high percentage of sand and a low soil pH (5.1). The former contributes to wide fluctuations in soil moisture, which may facilitate chlorpyrifos-oxon formation and the removal of TCP through leaching into the soil profile. TCP is weakly adsorbed to soil particles and is moderately mobile and persistent in soils. In the present study, only the top 6 cm of soil was analyzed, which may not have been deep enough to recover the majority of TCP residues. The other important factor may be decreased CHP degradation as a result of the low soil pH. The major routes of CHP loss from soil are volatilization, microbial degradation, and chemical hydrolysis (*34*). The major environmental factors that influence CHP loss in soil are moisture, organic matter, clay content, microbial activity, and pH (*35*−*38*). CHP is more persistent in soils with a pH < 7. The hydrolytic degradation of CHP involves the cleavage of the phosphate ester bond, most commonly forming TCP. This reaction is accelerated under alkaline conditions and attenuated under acidic conditions.

Approximately 3.2 g of CHP was applied to the (5 × 5 m) paired plots in the present study. Sixty-two days after application, CHP was detected at a level of 415 μg/kg in the top 6 cm of soil. Although there were no kinetic or mass balance studies performed, the high level of CHP and the relatively low level of TCP residues suggest decreased CHP degradation and/or leaching of TCP into the irrigation ditch water and/or groundwater. In either case, further study is warranted.

Conclusions. The addition of the spray-tank adjuvant Bivert increased both fruit and foliar residues, but it did not significantly alter the dissipation rate or metabolism of either CHT or CHP. If managed properly, the addition of adjuvant could increase pesticide residues during peak infestation periods and may permit the reduction in the number of applications or the rate of active ingredient applied per application. Several of the identified degradation products have the potential to move offsite via irrigation ditch water or with the discharge of harvest

floodwater. A more detailed investigation of the metabolite distribution and movement in cranberry bog soil is warranted, because only the top 6 cm of soil was monitored and metabolite distribution over the entire growing season was not monitored in the present study.

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Received for review July 9, 2002. Revised manuscript received October 8, 2002. Accepted October 10, 2002. This work was supported by a U.S. Department of Agriculture—Northeast Pesticide Impact Assessment Program grant (6-37426), Minimizing Pesticide Residues on Cranberry Fruit by Ground, Aerial, and Chemigation Application.

JF020744R