to the whole trees, either the spring flush leaves were enlarged or summer growth flush sprouts were induced to grow earlier. BA prevented postbloom drop only when it was applied directly to the surface of fruit.

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Levels of Dichlorvos on Calimyrna Figs[1]

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Abstract. **Residues of 2,2-dichlorovinyl dimethyl phosphate (dichlorvos) on Calimyrna figs (*Ficus carica* L.) declined to <5 ppb by day 6 after trees were pressure sprayed with 2,805 liters/ha at a rate of 2.24 kg Vaponite 2 a.i./ha for control of dried fruit beetle (*Carpophilus hemipterus* L.) and *Drosophila* spp. and fruit were sampled at 0, 1, 2, 4, 6 and 10 days. Very little residue (<5 to 33 ppb) was detected on fresh figs after multiple applications of 2.24 and 4.48 kg a.i./ha. All of the ground-dried figs had significant residues. About 90.9% of the residues were removed after dehydration. Dichlorvos residues were on the surface of the figs but were not easily removed by surface wash only. Residues were absorbed in the surface cuticle materials of the figs and surface waxes must be dissolved to successfully remove the residues from the plant material.**

Dichlorvos (DDVP, Vapona) is an organic insecticide-acaricide effective as a fumigant, stomach, and contact poison. Some of the pests controlled by this chemical are ants, aphids, mites, mealybugs, ticks, drosophila, centipedes, flying moths, other small flying insects, flies, fleas, gnats, spiders, wasps, and roaches. It is also utilized in sprays on animals, animal shelters and greenhouses (2). Use of dichlorvos on figs is one of the few applications on raw agricultural commodities.

Dichlorvos is registered for use on processed figs, but it has not been registered for control of insects on fresh or dried figs. The purpose of these experiments was to determine the residues of dichlorvos after multiple applications to Calimyrna fig trees for the control of dried fruit beetles and *Drosophila spp.*

An experiment to ascertain the disappearance of dichlorvos residues on the figs over a period of time after a single spray application consisted of 3 replications of single tree plots centrally located in a commercially producing fig orchard located in central California. Trees were sprayed with 2,805 liters/ha at a rate of 2.24 kg a.i./ha with Vaponite 2 Emulsifiable 22.8% (0.242 kg dichlorvos a.i./liter) applied with an air-blast pressure sprayer at the beginning of fruit harvest in August 1979. One kg of residue samples and untreated controls were collected 0, 1, 2, 4, 6, and 10 days after treatment, frozen and stored for analysis at −10°.

Two rates, 2.24 kg a.i./ha and 4.48 a.i. kg/ha were used in a second experiment. The lower dosage is the effective rate of application for pest control. Spray was applied to single-tree plots with 3 replicates, including untreated controls, at the beginning of harvest, August 15, and subsequently at 5-day intervals for a total of 5 applications per treatment of 2.24 and 4.48 kg a.i./ha. Five samplings of both fresh fruit and ground-dried fruit were collected and analyzed for dichlorvos residues. Fresh figs were collected from the trees just prior to each spray application and the ground dried figs were collected just prior to multiple dichlorvos applications. Samples were frozen immediately after collection and stored for analysis at −10°.

Frozen ground-dried samples were thawed, rinsed with running tap water for about 5 min, and placed in a dehydrator at 43° to 49° for 24 hr or until the moisture content was 15 to 17% as determined by drying in a vacuum oven. Samples were repackaged and stored frozen at −10° for residue analysis.

Partially thawed figs were chopped, 25 or 50 g weighed and blended with 1 ml of 12N hydrochloric acid, 250 g anhydrous sodium sulfate and 200 ml mixed pentanes (b.p. = 30–60°C). The solvent was decanted into a round-bottomed boiling flask; the remaining solid material was rinsed 3 times with 50 ml pentanes and combined. One hundred ml water was added to the pooled solvent and the mixture evaporated *in vacuo* at 25–30° to remove the pentanes. The water bath temperature should not exceed 32° to prevent loss of dichlorvos by evaporation.

The aqueous layer was filtered through Whatman #41 filter paper into a 1 liter separatory funnel, 50 g sodium chloride added, and partitioned three times with 50 ml pentanes which were combined. One ml of a polyethylene glycol-acetone solution (1:100 v/v) was added to the pooled pentanes to prevent dichlorvos evaporation losses and the mixture was evaporated *in vacuo* at 25–30° to 1 ml. The sample was quantitatively transferred to a 6.5 ml sedimentation tube with pentanes and the final volume was adjusted by slow evaporation of the solvent under nitrogen gas while in a thermostatted water bath at 25–30° so that 1 µl would contain 25 to 500 mg fig extractives for GLC analyses, depending upon ppb dichlorvos present.

Gas-liquid chromatography and an alkali flame ionization detector were used to determine dichlorvos residue levels (1). The method, as modified in this laboratory is applicable for the quantitative analysis of dichlorvos in or on fig fruit down to 5 ppb. The gas chromatograph was an Aerograph Model 600B equipped with an alkali flame ionization detector and containing a 76 cm x 31 mm (2.5 ft x 1/8 inch) glass coiled column packed with 5% OV-101 on Chromosorb G, 110/120 mesh, DMCS. Operating parameters were injector temperature, 160°C, column temperature, 115°, detector temperature, 115°, hydrogen flow 30 ml/min., air flow 180 ml/min., carrier gas N_2 flow 30 ml/min, and attenuation 4. The recorder was a poten-

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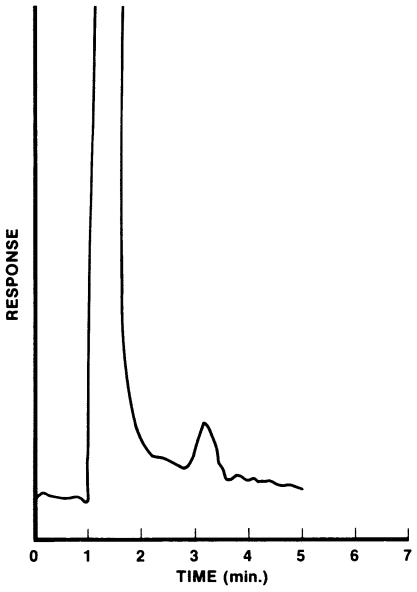

Fig. 1. Dichlorvos analytical standard (2.5 ng) using GLC and an alkali flame ionization detector with a chart speed of 1 cm/min. and an attenuation of 4.

tiometric strip chart, 1 millivolt full-scale with a chart speed of 1 cm/min. A 1 µl aliquot of the cleaned-up sample was injected into the gas chromatograph (1). The amount of dichlorvos was determined by area comparison of peaks relative to a known amount of dichlorvos analyzed. A chromatogram of 2.5 ng of dichlorvos analytical standard is shown in Fig. 1.

Dichlorvos residues from fresh figs sprayed on the trees with 2.24 kg a.i./ha applied with a pressure sprayer in 2,805 liters/ha declined from 720 ppb at day 0 to 190 ppb (day 1), 80 ppb (day 2), 70 ppb (day 4), and <5 ppb (day 6, day 10) which was below the limit of detection for the method. Residue levels of dichlorvos on the fresh Calimyrna figs after multiple applications of 2.24 kg a.i./ha and 4.48 kg a.i./ha were very low, <5 to 33 ppb, and this was mainly on the 3- and 4-application samples (Table 1). All of the ground-dried samples analyzed had significant dichlorvos residues. Average chemical residue levels of dehydrated figs on the 3-, 4-, and 5-application samples were 19, 12, and 36 ppb, respectively, which represented 90.5, 93.8, and 88.5% removal of residues on ground-dried figs previously sprayed at the 4.48 kg a.i./ha rate.

Two laboratory experiments were performed: 1) to determine the site of the dichlorvos residues on the ground-dried figs and 2) determine if these residues could easily be washed from the fruit with several solvents

Table 1. Dichlorvos residues[z] on fresh, ground-dried, and dehydrated[y] figs, 1979.

Date			Fresh (ppb)[w]			Ground-dried (ppb)[x]		
Treated	Sampled	Dichlorvos Concn (kg a.i./ha)	High	Low	Avg	High	Low	Avg
Aug. 10	Aug. 15	2.24	<5	<5	<5	88	21	55
		4.48	<5	<5	<5	--	--	--
10;15	20	2.24	<5	<5	<5	33	25	29
		4.48	<5	<5	<5	--	--	--
10;15;20	25	2.24	<5	<5	<5	97	48	65
		4.48	10	8	9	297	144	200
10;15;20;25	30	2.24	20	8	13	59	20	36
		4.48	50	13	33	353	116	195
10;15;20;25;30	Sept. 4	2.24	<5	<5	<5	244	37	112
		4.48	<5	<5	<5	527	197	313

[z]All control samples had <5 ppb residue; duplicate samples fortified at the time of extraction with 5, 25, and 250 ppb dichlorvos gave recoveries averaging 85% (80–88%). Duplicate samples fortified with 5, 25, and 50 ppb dichlorvos and stored at −10° for 1.5 months gave recoveries averaging 93% (80–100%); this was the interval between sampling and analysis.

[x]Method sensitivity 5 ppb by GLC analysis.

[y]Dehydrated figs; high, low, average; sampled August 25, 1979, 25, 12, 19 ppb; sampled August 30, 1979, 27, <5, 12 ppb; sampled September 4, 1979, 54, 21, 36 ppb. Application rate 4.48 kg a.i./ha.

Table 2. Dichlorvos residues[z] in washes and figs after a surface rinse and a reflux wash of the figs.

Dichlorvos residue (ppb)				
On fruit before wash	After wash: Wash	After wash: Fig	Solvent	Temp (°C)
		Surface wash		
105	22	105	Water	(24°)
110	16	140	Water	(24°)
200	32	161	Water	(24°)
313	35	280	Water	(24°)
318	18	298	Water	(24°)
110	21	146	Hexane	(46°)
200	15	155	Absolute ethanol	(24°)
318	98	230	Benzene	(70°)
		Reflux wash		
130	20	7	Water	(100°)
127	56	38	Benzene	(81°)
159	90	18	Absolute ethanol	(78.5°)
159	70	129	Mixed pentanes	(40°)

[z]Method sensitivity 5 ppb.

(Table 2). The first experiment included washing whole figs with the solvents at the temperatures shown in Table 2 by swirling the solvents over the figs for 3 min with 3 washes which were combined. Washes and the washed figs were then analyzed separately. Washed figs contained most of the original residues indicating dichlorvos residues were not easily removed and were absorbed in or on the figs. The second experiment included refluxing whole figs for 30 min with the solvents and at temperatures shown in Table 2, followed by separate analysis of the reflux solvent and figs. Figs were refluxed with water, benzene, absolute ethanol and mixed pentanes and dichlorvos removed was 94.6, 70.0, 88.7, and 18.8%, respectively. Refluxing the figs at 100° with water removed most of the residue. This might serve as a partial way to remove the dichlorvos residues from the figs. The conclusion was the residues are absorbed in surface cuticular waxes on the fruit and these must be dissolved to remove them successfully from the fruit surface. Dehydrated ground-dried figs, however, had very little of the dichlorvos residues remaining after water washing and dehydration (Table 1). The dichlorvos residues apparently volatilized aong with the moisture during drying at 43 to 49° for 24 hr.

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