RESIDUAL LIFE OF PESTICIDES ON KIWIFRUIT

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SUMMARY

The decay of a number of pesticides was studied on kiwifruit (*Actinidia chinensis*) at several sites in the Waikato/Bay of Plenty. Residues on the fruit generally followed bimodal first order decay patterns. Initial half lives in days were: dichlorvos 0.6-1, pirimiphosmethyl 1-2, etrimfos 7, captan 12-21, permethrin 14-15, chlorpyrifos 8-15, carbaryl 17, triazophos 22, folpet 17-30, vinclozolin 30, chlorfenvinphos (Z + E) 35, phosmet 40, captafol 20-48. After 1-3 half lives a marked reduction in decay rate occurred and low level residues of most pesticides were very persistent. Residues from applications made close to fruit set were generally less persistent initially than those from main season sprays. Low levels of captan were detectable at harvest, 5 months following application.

INTRODUCTION

An important feature of the New Zealand kiwifruit industry is the use of relatively intense insecticide spray programmes through the growing season. These are required to ensure high fruit quality and to reduce pest species to extremely low levels so that quarantine regulations of importing countries can be met. Fungicides are also included at key dates to reduce fruit rots. Any resulting pesticide residues on the fruit are subject to regulation at destination (Holland and Watts 1980). The design of spray programmes must take into account the residual properties of pesticides to ensure effectiveness and to keep within maximum residue limits (MRL's) set by importing countries.

Sprays programmes were formerly based on azinphos-methyl, carbaryl, and captan but the high residues at harvest and lack of tolerance in some export markets has restricted their use to early season. Main season insecticide programmes are currently based on phosmet and diazinon, with chlorpyrifos also recently gaining registration. Main season fungicides are currently limited to the dicarboximides, iprodione and vinclozolin.

The residual properties of azinphos-methyl, diazinon, omethoate (Love and Ferguson 1977), and phosmet (Love *et al* 1978) have been studied in detail. There is need for residue data on further pesticides that cover a wider range of activities. Pests such as mites could affect kiwifruit production in the future, problems of resistance may arise, and the choice of fungicides is very limited, particularly for control of leaf disorders.

This paper summarises several seasons work on the residual properties of a number of pesticides on the fruit when applied either immediately post blossom or through the main growing season.

METHODS

Sprayer calibration

To check the suitability of a smaller sprayer for predicting residues in a grower situation, a trial was set up in a mature pergola kiwifruit block at Te Puke. Two separate blocks were treated (20.2.81) with diazinon (37.5 g ai/100 litres) with either a motorised knapsack mistblower or a conventional tractor towed airblast orchard sprayer. Knapsack applications were made at the widest jet setting (2.3 litres/min), motor medium-high speed, and a volume rate of 2080 litres/ha. the airblast sprayer was calibrated for dilute spraying (2280) litres/ha) and operated with 16 nozzles at 2000 kPa.

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When the spray had dried 10 representative leaf samples were taken from the canopy, at the inner region directly exposed to the spray, in the middle, and from upper regions. Fruit samples (10) were also taken. Each leaf and fruit sample was individually washed in acetone for 10 minutes and the extracts analysed for diazinon by gas chromatography.

Treatments

Residue trials were carried out on orchards in the Waikato and Bay of Plenty districts (locations in Table 2). Hayward vines at least 3 years old from grafting were used under both pergola and T-bar training. Single vine replicates with guard vines were used, with two or three replicates for each treatment. Treatments were applied with a knapsack sprayer at volume rates of 1500-2500 litres/ha, depending on foliage density. Wetting agent (Citowett, 10ml/100 litres) was used with wettable powder formulations. In some trials the treatments were applied shortly following fruit set to study long term residues remaining at harvest. In other trials treatments were applied during the main season to study the residues remaining at short withholding periods. The treatment dates are noted in the results and tables.

Samples (10-20 fruit) were taken at intervals following the last spray and were stored at -18 °C in polythene bags prior to analysis.

Analysis

Fruit samples were generally analysed using skins only following the multiresidue procedure of Holland and McGhie (1983). This method uses methanol extraction, toluene partition, carbon/Florisil cleanup prior to determination by gas chromatography using electron capture or alkali flame detection. Propargite was detected with a flame photometric detector (S mode). Dichlorvos was analysed by the procedure of Luke *et al* (1975). Selected flesh samples were also tested for residues. The residues are all expressed on a whole fruit basis and are uncorrected for recoveries which were in the range 80-100%.

To determine half lives the residues in $\mu\text{g}/\text{fruit}$ were plotted versus time of sampling on semilog paper. This eliminates growth dilution which affects residues expressed in mg/kg. Where a simple linear relationship was apparent a log-linear regression was carried out. For data exhibiting pronounced curvature hand fitting was used to estimate bimodal half lives and intercepts by extrapolation to day 0 (Popendorf and Leffingwell 1978)

RESULTS

Sprayer calibration

The residues from the two sprayers (Table 1) were similar. On a rate adjusted basis the airblast sprayer deposits are slightly higher than the knapsack sprayer, but are also rather more variable. The results give confidence that careful high volume applications using a portable sprayer are appropriate for residue trials.

TABLE 1: Leaf and fruit residues of diazinon following knapsack or airblast high volume applications to kiwifruit.

	Diazinon rate kg ai/ha	Leaf residue g/m ²			Fruit residue mg/kg
		inner	middle	outer	
Knapsack mistblower	0.78	1.3 ± 0.3	0.5 ± 0.4	0.6 ± 0.3	1.5 ± 0.5
Tractor airblast	0.86	1.9 ± 0.7	0.8 ± 0.7	0.5 ± 0.2	1.8 ± 0.5

Decay rates — main season

The residue data did not always follow simple first order decay. For some pesticides there appeared to be two separate linear regions with a slower rate of breakdown taking place after an initial period of residue decay. Figure 1 presents data for five organophosphates which exhibited this behaviour. This bimodal pattern has been reported for several pesticides on citrus (Gunther 1969), and other crops. It may be rationalised as initial volatilisation and breakdown on the fruit surface, followed by a slower, mainly photochemical degradation, of a proportion of the pesticide that has penetrated further into the cuticle. The decay patterns and the initial deposition for several pesticides are summarised in Table 2 using the half lives for the linear regions. The intercepts at day 0 are expressed in mg/kg giving initial residue deposits. The estimates for second half lives have a greater uncertainty than for the first due to limitations of sampling record. Only single decay rates were apparent for the fungicides captafol, folpet, and carbaryl and for the miticide propargite (Table 2).

By comparison the data of Love and Ferguson (1977) show single half lives for azinphos-methyl and omethoate on kiwifruit of 28 and 8 days respectively. Their diazinon data be split into a bimodal pattern with first and second half lives of 5 and 14 days respectively. Chlorpyrifos residues on Californian citrus showed first half lives of 2-7 days and second half lives of about 45 days (Iwata *et al* 1983). In the two trials here, chlorpyrifos had initial half lives of 7-15 days (Table 2).

TABLE 2: Decay of pesticide residues applied to kiwifruit during the main growing season.

Site and spray dates	Training ¹	Pesticide	Rate ² kg ai/ha	Half life ³ days		Intercept (mg/kg)	
				1	2	1	2
Te Puke 13.4, 24.4.80	P	vinclozolin	1.1	30	>70	3.8	1.8
Te Aroha 11.2, 16.3, 16.4.81	T	folpet	1.6	30	-	5.4	-
Te Puke 11.2, 16.3, 16.4.81	T	captafol	1.6	48	-	4.8	-
Katikati 25.1, 25.2, 25.3.83	T	folpet	1.6	31	-	5.3	-
Te Aroha 1.5.80	T	captafol	1.6	30	-	6.8	-
		folpet	2.0	30	-	8.7	-
		captafol	2.0	63	-	7.7	-
	T	dichlorvos	5.8	1	>17	3.8	0.38
		chlorpyrifos	1.5	15	28	3.1	2.1
		chlorfenvinphos	2.9	35	>70	4.7	2.5
		propargite	3.5	50	-	6.8	-
Tauranga 22.4.80	T	carbaryl	3.6	17	-	6.2	-
		dichlorvos	3.0	0.6	4.6	2.5	0.25
		etrimfos	1.5	7	40	4.0	0.55
Te Puke 8.4.80	T	phosmet	3.3	40	>70	4.4	2.1
Gordonton 18.12.83, 25.2.84	P	captan	2.2	12	33	4.9	1.5
		captafol	2.2	14	45	5.4	2.0
		chlorpyrifos	0.55	8	36	1.3	0.05
		pirimiphos-methyl	1.1	2	20	2.4	0.10
		permethrin	0.055	14	36	0.09	0.027

¹ T-Bar or pergola

² Per application

³ Following final application, 1 = initial half life, 2 = second, if observed

⁴ 6 prior applications 3 weekly from 12.11.79

Fig. 1: Degradation patterns for chlorfenvinphos (Z+E) and chlorpyrifos (Te Aroha), dichlorvos and etrimfos (Tauranga), and pirimiphosmethyl (Gordonton) on kiwifruit. See Table 2 for application details.

The data for chlorfenvinphos (Table 2, Fig. 1) is based on the sum of the Z and E isomers. There was evidence that residues of the predominant Z isomer (85:15 ratio in the EC formulation) rearrange to the E isomer. Residues for the E isomer doubled over the first 10 days and then declined at a somewhat slower rate than for the Z isomer. This effect, probably photochemical, has been reported by Beynon *et al* (1973).

Climatic and cultural differences between the sites were not large. At a number of sites folpet gave the same half life of 30 days whereas captafol ranged from 14 to 42 days (Table 2). Persistence was less earlier in the season and the fewer the number of sprays. This effect may also be operating for chlorpyrifos where the half life of 8 days at Gordonton was doubled at Te Aroha where the application was made 9 weeks later in the season.

Residues in the flesh of fruit were low for all pesticides studied, none of which are known to have marked systemic behaviour. The flesh residues were generally about 3% of the total residues. Surface hair introduced in cutting is likely to explain most of the flesh residue (Love and Ferguson 1977).

TABLE 3: Decay of pesticide residues applied to kiwifruit close to fruit set

Site and spray dates	Training ¹	Pesticide	Rate ² kg ai/ha	Half life (days)		Intercept (μ g / - fruit)	
				1	2	1	2
Te Aroha 10.12.81	T	captan	1.6	16	-	135	-
		folpet	1.6	19	-	145	-
		captafol	1.6	20	-	130	-
Te Puke 10.12.81	T	captan	1.6	13	-	100	-
		folpet	1.6	19	-	65	-
		captafol	1.6	20	-	90	-
Katikati 24.12.82	T	captan	2.0	21	-	145	-
		folpet	2.0	17	-	150	-
		captafol	4.0	22	-	460	-
		azinphos-methyl	1.0	31	-	80	-
		triazophos	0.8	22	-	90	-
Gordonton 18.12.83	P	captan	2.2	12	36	240	130
		pirimiphos-methyl	1.1	2	15	100	4
		permethrin	0.055	15	35	5.7	2.7

¹ T-Bar or pergola**Decay rates — early season**

Table 3 presents the residues on fruit for a number of pesticides applied shortly following fruit set. The data again exhibited bimodal behaviour for several of the less persistent pesticides. The lack of two half lives in some trials is probably due to limited sampling periods (28 days in many cases). The half lives for folpet and captafol were shorter than those observed for the same pesticides from main season sprays (Table 2). Longer daylight hours, higher temperatures, and less leaf cover in the early season crop may enhance dissipation. The residues at harvest (20.5.82) for captan from the Te Aroha and Te Puke applications on 10.12.81 (Table 3) were 8 and 3 μ g/fruit (0.08 and 0.03 mg/kg) respectively. These are higher than would be predicted from the half lives in Table 3 and confirm that decay slows later in the season.

The first intercept values, giving estimated day 0 deposits, are broadly related to the size of the fruitlets at spraying. The treatments were applied closer to fruit set at Te Puke than at the other sites.

DISCUSSION

The decay rates of the various pesticides cover a very wide range. For efficacy the first half life is likely to be the most important. The very rapid initial decay of the highly volatile dichlorvos is as expected. The short residual life of pirimiphos-methyl indicates this relatively new material will need careful timing of application. However permethrin, a common co-ingredient, is quite persistent. The longer residual lives of chlorfenvinphos, and propargite, and, to a lesser extent, carbaryl and etrimfos should give them useful periods of field activity. However MRL's will be required before registration can proceed.

The fungicides studied all have long residual lives which again makes MRL's essential and these are being sought for folpet and captafol.

The general residue characteristics of the pesticides on kiwifruit have important implications for spray recommendations. Firstly, the initial residues following spray application are high relative to many other fruit crops. This appears to be largely due to the extra surface area provided by the fruit hairs (Love and Ferguson 1977). Secondly, several pesticides showed greater persistence in these trials than on other crops such as tamarillos (Holland *et al* 1982), passionfruit and avocado (Holland, P.T., unpublished data). These factors mean that residues can reach very high levels on the kiwifruit if applied in a multiple spray programme. For example Love *et al* (1978) showed that phosmet was extremely persistent on kiwifruit and residues could exceed 20 mg/kg

following seven applications. If intensive use of a pesticide is contemplated, MRL's need to be relatively high. This has proved possible with the USA, although the registration procedures are very lengthy. However for Japan and European countries obtaining generous MRL's is often difficult. These problems could be overcome if regulatory authorities would accept edible portion only residues.

The importance of early season sprays for good insect and disease control has led in practise to limited use of pesticides with no MRL's set in some markets. The persistence of low level residues leads to the risk of detectable residues at harvest, even if only one or two applications are made close to fruit set.

The data presented here will be of value in refining spray recommendations and in obtaining residue tolerances for new materials. It can also form the basis for a comprehensive model for pesticide behaviour on kiwifruit.

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Chemical Appendix:

azinphos-methyl (Gusathion M 50), captan (Difolatan 80 WP), captan (Orthocide 80 WP), carbaryl (Septan 80 WP), chlorfenvinphos (Birlane 24 EC), chlorpyrifos (Lorsban 40 EC), dichlorvos (Vapona 100 EC), etrimfos (Ekamet 52 EC), folpet (Phaltan 80 WP), phosmet (Imidan 75 WP), pirimiphos-methyl and permethrin (Attack 50 EC), propargite (Omite 30 WP), triazophos (Hostathion 40 EC), vinclozolin (Ronilan 50 WP).