MODELLING OF PESTICIDE RESIDUES ON FRUIT II : PERSIMMON

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ABSTRACT

A deterministic model for prediction of pesticide residues originally developed for kiwifruit has been applied to persimmon. The model accommodates: varying spray programmes (rates, number of applications); separation of physical decay from dilution by crop growth; predictions for both short and long preharvest intervals. Decay rate parameters for carbaryl, chlorpyrifos, diazinon, dimethoate, permethrin and pirimiphos-methyl on persimmon have been estimated from residue data collected from a range of field trials. Fruit growth data (diameter, weight) were used to formulate a growth curve. The model has been implemented as a Microsoft ACCESS database application for personal computer which provides flexible input of spray diary information and reports summarising predicted residues. The model has been tested by comparison of predicted versus measured (laboratory analysis) residues from three field trials and a survey of fruit from 68 growers in the 1995 harvest season. The model was found to provide reasonable predictions of diazinon, pirimiphos-methyl and permethrin residues at both short and long preharvest intervals.

Keywords: pesticide residues, persimmon, prediction, modelling

INTRODUCTION

The development of persimmon as an export crop has required particular attention to the quarantine and pesticide residue regulations of overseas markets. Some residue decay data has been reported for persimmon and related to pest control and maximum residue limits (MRLs) in Japan (Prestidge *et al*. 1989). The diversification of markets has increasingly restricted the scope of acceptable spray programmes due to differences in MRLs for persimmon between countries. The industry is adopting a ‘nil’ or low residue strategy which not only addresses these varying MRL requirements but also contributes to a more sound environmental image for the crop. Spray schedules and pre-harvest intervals (PHIs) have been adjusted to maintain adequate pest control while minimising residues. A residue model for prediction of residues on kiwifruit (Stevens *et al*. 1993; Holland and Malcolm 1996) has been adapted to persimmon to assist this optimisation.

The model calculates initial spray deposits from chemical rate and fruit surface area factors. This initial deposit (micrograms per fruit) is then decayed to the given harvest date using a biphasic exponential decay equation where initial rapid losses (volatilisation) are followed by slower degradation of pesticide retained in the cuticle (Popendorf and Leffingwell 1978). The final predicted residue at harvest is calculated from the sum of decayed deposits (multiple pesticide applications) divided by the estimated fruit weight. This study has derived parameters for the model from field trial data on persimmon covering fruit growth and residue decay for several key insecticides. The model has been validated through further field trials and the use of industry residue monitoring data.

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METHODS

Residue Model

For *Deposition*, the model assumes orchard sprayers giving good coverage without excessive runoff generate initial deposits of 2.0 mg pesticide per cm^2 area of crop for each 1 kg ai/ha ingredient applied (Holland and Malcolm 1996). Thus the initial deposit for a pesticide application is given by:

$$D(t_1) = 2 \,.\, W \,.\, A(t_1)\ \mu g \qquad 1.$$

where t_1 = date of spray application
W = rate of application in kg a.i./ha
$A(t_1)$ = surface area of fruit in cm^2

Detailed field trials have shown that *pesticide decay* of many pesticides on many crops can be described by a 2 stage first order model where a fast initial decline in residues is followed by a slower second phase. Thus the breakdown of the initial deposit can be calculated to provide the deposit at harvest date t_2:

$$D(t_2) = \frac{D(t_1)}{(1+R)} \,.\, (R\, e^{-k_1 (t_2 - t_1)} + e^{-k_2 (t_2 - t_1)})\ \mu g \qquad 2.$$

where k_1, k_2 and R are emperical decay constants for the pesticide which must be established from field trials with each pesticide and crop.

Exponential rate constants k are related to first-order half lives: $k = 0.693 / T_{0.5}$

For low volatility pesticides, e.g. synthetic pyrethroids, the first term is negligible and a simple first order rate equation applies.

i.e., $R \quad O \quad \text{and} \quad D(t_2) \quad D(t_1)\, e^{-k_2 (t_2 - t_1)}$ 3.

Where a number of spray applications, n, of the same pesticide are made, each initial deposit is decayed to the harvest date and then summed to give the total decayed deposit. Dividing by the fruit weight $M(t_2)$ at the harvest date gives the *terminal residue* P:

$$P(t_2) = \underset{\text{all } t_1}{\acute{Y}} D(t_2) / M(t_2)\ \text{mg/kg} \qquad 4.$$

$A(t_1)$ and $M(t_2)$ are estimated from crop growth curves.

This model has been implemented as a Microsoft ACCESS database application for personal computer. Data are stored on pesticide products, pesticide decay rates and crop growth. Database entry routines then allow facile entry of orchard and spray diary information along with any laboratory residue data. Predicted residues for each spray programme are then reported using the Query facility to carry out the model calculations.

Crop growth

Persimmon cv ‘Fuju’ fruit growth data was recorded for the 1993 harvest seasons on an orchard in each of the Auckland, Gisborne, Hawkes Bay and Waikato districts. Eight typical fruit per tree were sampled from four trees per orchard at four weekly intervals following full bloom. Maximal diameters were measured with calipers and fruit weights taken.

Pesticide decay parameters

The decay rate parameters for each pesticide were derived from residue data generated by field trials on persimmon cv ‘Fuju’ in Gisborne and Waikato districts. Mature crops were sprayed to run-off (*ca* 2000 L/ha) using a hand-gun (small plots of 3-4 trees with 2-4 replicates) with one to three applications in the March-April period. Calm fine conditions (18°-24°C) were chosen and no rain fell with 24 hours of spray application. Samples for residue analysis were taken at intervals after the last application (generally 1, 3, 7, 14, 28, 56 days). Five-ten fruit per plot were collected directly into polythene bags and stored at -20°C prior to residue analysis. The samples were analysed for residues using standard multi-residue procedures with gas chromatographic determination (Holland and Malcolm 1992). Detection limits were 0.01 mg/kg.

Residue data were plotted as microgram per fruit against time on a semi-logarithmic scale. The slope of the regression line generated for the data points at 7-56 days provided the rate constant k_2. Data for carbaryl, dimethoate, permethrin and taufluvalinate was well fitted over the complete 0-56 day period i.e. the simplified decay equation 3 was appropriate.

In the case of the more volatile pesticides chlorpyrifos, diazinon and pirimiphos-methyl, residues declined rapidly in the 0-7 day period and required the biphasic decay equation 2. Graphical interpolation to best fit the 0-7 day data provided the exponential decay constant k_1 and the ratio of intercepts at day 0 for the two first order plots, R.

Model validation

Model predictions for particular pesticides, spray timings and preharvest intervals were compared to laboratory residue data for: an adjuvant plus insecticide trial in the Waikato (Gaskin *et al*. 1996); two grower trials in the Waikato and Bay of Plenty using standard spray programmes (air blast application) and a persimmon industry quality assurance programme for the 1995 harvest covering 68 orchards. Fruit samples taken within 21 days of main harvest were tested for pesticide residues by multi-residue procedures (National Chemical Residue Laboratory, MAF Qual, Wallaceville) and grower spray diaries were also made available.

RESULTS

Fruit growth parameters

Fruit growth through the season was characterised by a rapid initial increase in fruit diameter with time followed by slower expansion . The mean fruit diameters, d, over the 4 orchards were modelled by 3 linear segments:

$d = 1.0 + 0.061 * t$ cm $0 < t < 69$ days after full bloom
$d = 3.7 + 0.025 * t$ cm $70 < t < 155$ days
$d = 7.7 + 0.002 * t$ cm $t > 155$ days

The surface area of the fruit at a given time of application was then calculated assuming spherical geometry. The weight of the fruit at a given diameter (2r) was better fitted to the formula 1.22 Þr^3 rather than the spherical volume assumption with unit density, 1.33 Þr^3. The fruit growth as measured by mean fruit weights from this limited data set for 1992/93 closely matched that from a larger set of industry data covering several seasons (A. Mowat pers. comm.).

Pesticide decay parameters

Table 2 summarises the field trials used to provide residue data for modelling purposes and gives the derived pesticide decay parameters.

TABLE 1: Pesticide residue trials on persimmon and associated residue decay rate parameters.

District	Year	Formulation	Pesticide	Sprays/ rate g ai/100L	k_1 day $^{-1}$	k_2 day $^{-1}$	R
Waikato	1989	Carbaryl 80 WP	carbaryl	1 x 120	0.70	0.05	5
Gisborne	1991	Carbaryl 50F	carbaryl	3 x 120	0	0.07	0
Pukekohe	1992	Carbaryl 80W	carbaryl	1 x 80	0	0.06	0
Gisborne	1995	Carbaryl 50F	carbaryl	3 x 120	0	0.06	0
Waikato	1989	Lorsban 50W	chlorpyrifos	1 x 36	0.90	0.038	3.5
Gisborne	1993	Lorsban 40EC	chlorpyrifos	1 x 36	0.80	0.054	2.5
Waikato	1989	Basudin 50W	diazinon	1 x 50	0.60	0.10	3.4
Pukekohe	1992	Diazinon 50W	diazinon	4 x 50	0.70	0.10	2.6
Gisborne	1991	Attack 50EC	pirimiphos-methyl	2 x 47.5	0.25	0.05	3
			permethrin	2 x 2.5	0	0.010	0
Waikato	1989	Rogor 20W	dimethoate	1 x 20	0	0.069	0
Gisborne	1993	Rogor 20W	dimethoate	1 x 64	0	0.085	0
Gisborne	1993	Mavrik Aquaflow	taufluvalinate	1 x 7.2	0	0.008	0

The k_2 rate constants (0.008-0.10) were consistent between trials for a given pesticide and the errors in the fit of the regression lines for this parameter were about ±20%. The errors in the estimates for the initial rapid decay parameters k_1 and R are higher due to the few data points in the 0-7 day period. However this will only affect predictions at short PHIs because these parameters work together to set the effective starting residue for the slower and better estimated decay governed by k_2. The 1989 Waikato trial was affected by heavy rain in the period 1-5 days after spray application. This reduced initial carbaryl residues leading to apparent k_1 and R values which were not required in fitting the data for the other trials with this relatively persistent pesticide.

Model validation - field trials

Tables 2-4 present comparisons of laboratory measured versus predicted residue for three field trials covering different spray programmes. Mean values of the decay constants for diazinon in Table 1 were used in the model for predicting residues in the validation trials.

TABLE 2: Measured and predicted residues (mg/kg) of diazinon and permethrin on persimmon (trial Gaskin *et al*. 1996). Sprayed 18.4.95 and 2.5.95 (50 + 2.5 g ai/100L diazinon/permethrin).

Sample Date	Residue mg/kg			
	Diazinon		Permethrin	
	Found	Predicted	Found	Predicted
9.5.95	0.40	0.28	0.13	0.14
16.5.95	0.14	0.12	0.11	0.13
23.5.95	0.10	0.06	0.11	0.11
30.5.95	0.04	0.03	0.17	0.11

TABLE 3: Measured and predicted residues (mg/kg) of pirimiphosmethyl, permethrin and diazinon on persimmon - Grower trial, Waikato[1].

Sample	Pirimiphos-methyl		Permethrin		Diazinon	
date	Found	Predicted	Found	Predicted	Found	Predicted
20.4.95	0.08	0.088	0.11	0.114	0.11	0.180
27.4.95	0.09	0.057	0.11	0.099	0.72	0.500
9.5.95	0.02	0.028	0.07	0.077	0.13	0.104
16.5.95	0.02	0.018	0.05	0.067	0.09	0.048
23.5.96	n.d.	0.012	0.06	0.060	0.03	0.023
30.5.95	n.d.	0.009	0.05	0.056	0.03	0.011

[1] Spray Programme: Attack 50EC 10.1, 27.1, 5.2, 19.2, 5.3, 19.3.95 (70 mL/100L);
Diazinon 50EC 30.3, 11.4, 23.4.95 (75, 75, 100 mL/100L).

A high degree of correspondence was found between the residues measured in these three trials and those predicted by the model for a range of PHIs. In many cases, the values differed by only 10-20%. In some instances larger discrepancies exist but the overall pattern of residue decline is well predicted out to long PHIs (up to 74 days for Attack). For diazinon and pirimiphos-methyl, which have relatively short persistence, the model is calculating residue declines down to small fractions of the initial deposits. In making these comparisons, the poor precision of low level residue measurements must also be taken into account due to sampling and determination errors. Our laboratory has commonly found CVs of greater than 30% for residues below 0.2 mg/kg, similar to other observations (Horwitz *et al*. 1980).

TABLE 4: Measured and predicted residues (mg/kg) of pirimiphosmethyl, permethrin and diazinon on persimmon - Grower trial, Bay of Plenty[1].

Sample	pirimiphos-methyl		permethrin		diazinon	
date	Found	Predicted	Found	Predicted	Found	Predicted
20.4.95	0.09	0.119	0.13	0.215	0.44	0.261
26.4.95	0.08	0.082	0.15	0.190	0.16	0.125
3.4.95	0.04	0.054	0.09	0.164	0.85	1.05
10.4.95	0.01	0.035	0.09	0.140	0.33	0.253
17.4.96	n.d.	0.023	0.06	0.120	0.11	0.115

[1] Spray Programme: Attack 50EC 9.2. 1.3, 22.3.95 (100 mL/100L); Averte 50W 13.4.95 (112 g/100L); Basudin 50EC 1.5.95 (80 mL/100L).

Model validation - 1995 monitoring data

The spray diaries of the 68 growers were varied in respect to number and timing of sprays but generally involved Attack or Averte applications early-mid season and diazinon late season. The laboratory samples were generally taken at PHIs of greater than 21 days and gave only low to non-detectable residues (0.1 to <0.01 mg/kg). The model predictions for residues of the three common pesticides (diazinon, pirimiphos-methyl and permethrin) were generally substantially higher than those found (measured) with mean ratios Predicted:Found in the range of 3-5. In the case of permethrin, there were four samples where predicted residues were substantially lower than found. However, there were significant correlations ($P>0.90$) showing that a measured residue was generally associated with a predicted residue of similar low magnitude. The model therefore was able to provide a semi-quantitative estimate of expected residues from a given spray diary despite the low residue levels and overall gave worst-case estimates for residues from a variety of spraying situations.

DISCUSSION

The validation data show that the model is capable of remarkably accurate prediction of diazinon, pirimiphos-methyl and permethrin residues on persimmons for various spray programmes in field trial situations. These three pesticides cover the persistence spectrum from low, medium to high respectively. Based on more limited data for carbaryl, chlorpyrifos and dimethoate residues, the model was shown to be applicable to a wide range of pesticides on persimmon. A similar conclusion was made about the related model for kiwifruit (Holland and Malcolm 1996). The quantitative performance of the model was not as high with persimmon industry monitoring data where measured residues were consistently lower than predicted. This will reflect not only the poor precision and accuracy for low level residues of the screening assay used in the monitoring but also grower factors including poor spray coverage and post-harvest fruit handling which will tend to result in lower residues than found for field trial situations.

The key feature of the model, which is central to estimation of residues on crops, is that decay parameters derived from limited field trial data can be extrapolated to a variety of other situations including multiple spray applications, varying rates and short or long PHIs. This flexibility arises from the standard deposit concept (a simplifying but worst-case assumption), the explicit accounting for growth dilution of residues and the use of biphasic decay equations for the more volatile pesticides.

The decay parameters reflect not only the pesticide properties but also the average climatic conditions for the decay rate field trials. However the model does not explicitly account for severe wash-off of residues. This effect will certainly occur where heavy rain falls shortly after spray application, particularly for water soluble materials such as carbaryl on smooth skinned fruit such as persimmon. A sub-model is being developed to estimate losses by this route.

The model has proved useful in simulating terminal residues from various spraying situations (pesticide, number/timing of sprays, PHI) because of the reliable estimation of upper limits to residues at long PHIs. This has assisted the persimmon industry to set spray recommendations with high confidence that treated crops will meet market requirements.

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