



**HAL**  
open science

## Modelling non-systemic pesticides residues in fruits with initial deposit variability and weather effects

Ruifen Huo, Domingo Salazar, Kieran Hyder, Xiangming Xu

### ► To cite this version:

Ruifen Huo, Domingo Salazar, Kieran Hyder, Xiangming Xu. Modelling non-systemic pesticides residues in fruits with initial deposit variability and weather effects. *Food Additives and Contaminants*, 2007, 24 (11), pp.1257-1267. 10.1080/02652030701329926 . hal-00577455

**HAL Id: hal-00577455**

**<https://hal.science/hal-00577455>**

Submitted on 17 Mar 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Modelling non-systemic pesticides residues in fruits with initial deposit variability and weather effects**

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2006-297.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	10-Mar-2007
Complete List of Authors:	Huo, Ruifen; East Malling Research Salazar, Domingo; Syngenta Hyder, Kieran; Syngenta Xu, Xiangming; East Malling Research
Methods/Techniques:	deterministic modelling, Risk assessment - modelling
Additives/Contaminants:	Pesticide residues
Food Types:	Fruit

SCHOLARONE™  
Manuscripts

## Modelling non-systemic pesticides residues in fruits with initial deposit variability and weather effects

R. Huo<sup>1</sup>, J. D. Salazar<sup>2</sup>, K. Hyder<sup>2\*</sup> and X.-M. Xu<sup>1†</sup>

<sup>1</sup> East Malling Research, New Road, East Malling, Kent, ME19 6BJ, UK

<sup>2</sup> Dietary Safety, Syngenta, Jealott's Hill International Research Centre, Bracknell, RG42 6EY, UK

\* Current address: Centre for Epidemiology & Risk Assessment, Veterinary Laboratories Agency, New Haw, Addlestone, Surrey KT15 3NB, UK

† Correspondence: Xiangming Xu. E-mail: [Xiangming.Xu@emr.ac.uk](mailto:Xiangming.Xu@emr.ac.uk).

**Abstract**

A flexible and generic model was developed to predict the decline of residues of a non-systemic pesticide for both single and multi-spray situations as well as for different tree canopy zones. The model predicts not only the average residue levels but also the confidence interval of the residues through either a deterministic or stochastic approach. This generic model includes several key aspects of residue fates in the environment: initial deposit, physical loss and growth dilution. The model considers tree canopy into three distinct zones for which initial deposition of pesticides may differ. In addition to predicting the average residue within each zone, it also estimates the 95% and 99% confidence intervals of residues on individual fruit within each zone. For the purpose of evaluation, this model was parameterised specifically for captan, one of the most important non-systemic fungicides used to control diseases in horticultural crops. The observed average initial deposit for each zone was used in the evaluation. The overall correlation between predicted average residues and those observed on apple fruit in two applications was 0.93. Confidence intervals were also predicted accurately.

**Keywords:** *Deterministic models, predicting, contact pesticides, residue dissipation*

## Introduction

Pesticides are widely used to control pests and diseases of many plant species. Their residues in food crops are strictly regulated and monitored (Hamilton et al. 2004, Hyder et al. 2003). For this purpose, mathematical models have been developed to optimise pesticide input and monitor residues on fruit, e.g. Timme & Frehse (1980), Quest et al. (1993) and Holland et al. (1996).

Many research studies have revealed that the non-systemic pesticide residues per fruit weight unit are dependent on three processes, i.e. variation in initial deposit (Walklate et al. 2003, Xu et al. 2006), physical decay due to weather factors (Smith & MacHardy 1984) and growth dilution (Lakso et al. 1995). The degradation of pesticide residues concentration due to the three processes has been approximately described by a first-order reaction model (Holland et al. 1996, Timme & Frehse 1980). This first-order reaction model, however, can not provide the confidence limit of their predictions as the variation in initial deposit is unknown. Moreover, because three processes in tandem drive the degradation of pesticides, the predictions by first-order reaction models can be very poor when the initial deposit variation is big and the weather effect is large. One of the most important factors influencing pesticide residues is the canopy structure (Franz et al. 1998, Xu et al. 2006), however, this factor is often not explicitly incorporated into residue models.

In this paper, we describe a flexible model developed to predict the decline of residues of a contact (i.e., non-systemic) pesticide, primarily for tree crops. First, the general model structure is described. Then, we present model parameters calibrated specifically for captan, a widely used contact fungicide (Elzemaity 1988, Gilvydis et al. 1986, Northover et al. 1986). Finally we evaluate the model predictions against field data of captan residues on apple.

## Description of the model

### *Model overview*

This model estimates residues for both single and multi-spray situations. Furthermore, it predicts not only the average residues but also the confidence interval of the residues through either a deterministic or stochastic approach. It consists of three main components: (1) initial deposits, (2) physical decay due to weather variables, and (3) host growth model. The model estimates true pesticide loss by removing the growth dilution effect. It is coded in Delphi (version 5) for Windows.

### *Model for Initial deposits*

Accurate estimation of initial deposits is critically important for any model. Holland et al. (1996) assumed that the amounts of initial deposit on fruit were linearly related to the application rate and the surface area of fruits at the time of application. However, in many practical situations, the initial deposit is strongly influenced by variability in canopy structure, weather conditions and spray technology (Franz et al. 1998, Walklate et al. 2002, Walklate et al. 2000, Xu et al. 2006) but less dependent on the fruit area. Further, plant tissue surface structure can also greatly affect the initial deposit concentration (Hall et al. 1997, Smith & MacHardy 1984). Thus, the initial deposit concentration varies greatly with crop growth stages. For example, due to the increasing wax deposition on apple surface with increasing fruit maturity, the deposits do not cover the surface evenly. Instead, most of them accumulate on the stalk and/or the calyx ends depending on the fruit orientation. Thus, it is unlikely that the amount of deposit is proportional to the area of fruit surface. Furthermore, many studies showed the importance of canopy structure in affecting initial deposit concentration; usually fruits

1  
2  
3 in the top and outside regions of the canopy are likely to receive more deposits than  
4  
5 those inside the canopy.  
6  
7

8  
9  
10  
11 *Estimating average initial deposits.* The model considers the canopy effect by dividing  
12 it into three distinct zones: top, outside and inside. Then, it estimates the initial deposit  
13 within each zone via two methods: constant retention factor ( $R$ ) per unit of area/weight  
14 or per fruit.  
15  
16  
17  
18

19  
20 Assuming a constant retention factor per unit of area or weight ( $\mu\text{g}/\text{cm}^2$  or  $\mu\text{g}/\text{g}$ ), the  
21 average initial deposit ( $L$ ) per fruit (here we called it 'load') for each spray application  
22 at the full manufacturer's recommended rate is estimated as,  
23  
24  
25  
26

$$27 \quad L = RX \quad (1)$$

28  
29 where  $X$  is the average surface area ( $\text{cm}^2$ ) or fruit weight (g) at the time of the  
30 application. Another option to estimate average initial deposit per fruit is to assume a  
31 constant retention factor per fruit ( $\mu\text{g}/\text{fruit}$ ), i.e.  $L=IR$  ('1' indicates one fruit).  
32  
33  
34  
35  
36  
37

38 In both methods, the model assumes that the input parameter of the retention factor  
39 ( $R$ ) for each zone is for cases when the pesticide is applied at the full manufacturer's  
40 recommended rate. Then  $R$  is assumed to vary linearly with the rate of application as the  
41 percentage ( $F$ ) of the full recommended rate. The mean of initial deposits due to the  $i$ th  
42 application in each single zone is then given by  
43  
44  
45  
46  
47  
48

$$49 \quad L_{0,i} = LF_i \quad (2)$$

50  
51 where  $F_i$  is the rate of the  $i$ th application rate as percentage of the full recommended  
52 rate.  
53  
54  
55  
56  
57  
58  
59  
60

*Estimating variability in initial deposits.* To model the variability in initial deposit, the model needs a further parameter ( $V$ ) describing the variation in the initial deposit. This can be either variability factors (FAO/WHO 1997) at 5% ( $V_5$ ) and 95% ( $V_{95}$ ) percentiles or standard deviation of the initial deposit. The model also assumes that  $V$  is not dependent on the application rate. For each zone, the model uses parameter  $V$  to estimate the 95% confidence interval for initial deposits:

$$\begin{cases} L_{0,i95} = V_{95}L_{0,i} \\ L_{0,i5} = V_5L_{0,i} \end{cases} \quad (3)$$

where we have taken  $L_{0,i}$  as a proxy for the mean of the initial distribution for a specific zone.

Alternatively, we estimate the 95% confidence interval of the initial deposit by assuming that it follows a lognormal distribution as shown by many researchers (Cross et al. 2001, Hamey 2000, Hill 2000). The mean ( $m$ ) and variance ( $S^2$ ) of a lognormal distribution for a random variable  $X$  are related to the original mean ( $\mu$ ) and variance  $\sigma^2$  of the  $X$  (Evans et al. 2000):

$$\begin{cases} m = \ln\left(\frac{\mu^2}{\sqrt{\mu^2 + \sigma^2}}\right) \\ S = \sqrt{\ln\left[\left(\frac{\sigma}{\mu}\right)^2 + 1\right]} \end{cases} \quad (4).$$

In the present context,  $\mu$  is equivalent to  $L_{0,i}$ . Thus the 95% confidence interval for initial deposits can be estimated as

$$\begin{cases} L_{0,i95} = \exp(m + 1.96S) \\ L_{0,i5} = \exp(m - 1.96S) \end{cases} \quad (5).$$

In order to take into account the growth dilution effect and hence estimate the true pesticide loss, only the total pesticide residues ( $\mu\text{g}$ ) per fruit are used in the subsequent decay model, instead of the concentration ( $\mu\text{g}/\text{cm}^2$  or  $\mu\text{g}/\text{g}$ ).

#### *Physical decay model with the weather effects*

The model considers two situations for pesticide loss from fruit surface: loss under dry and under rainy conditions. All studies indicated that rain can wash a large proportion of pesticides off the plant tissue surface although the precise relationship between the amount of rainfall and the extent of pesticide wash-off varies greatly even for same pesticides between studies or between fields in the same studies (Frank et al. 1987, Frank et al. 1985, Smith & MacHardy 1984). The daily loss of pesticides under dry conditions is generally much less than that due to rain wash-off. Similarly, the loss under dry conditions varies greatly between studies and to a large extent this variability is due to growth dilution effects.

The model assumes a constant daily loss ( $k_1 < 1.0$ ) of pesticide residues on fruits. Several factors, such as temperature and relative humidity, may affect  $k_1$  although we have insufficient information to implement such relationships in the model. However, the model is so structured that these relationships can be incorporated easily into the model in future.

Rain wash-off is modelled by several alternative models where the rate of loss ( $k_2 < 1$ ) due to rain is either linearly or exponentially related to the amount of rainfall (Bruhn & Fry 1983, Smith & MacHardy 1984):

$$k_2 = \begin{cases} a + bY & \text{(linear relationship)} \\ 1 - \exp(a + bY) & \text{(exponential relationship)} \end{cases} \quad (6)$$

where  $Y$  is the daily total amount of rainfall ( $mm$ ), and  $a$  and  $b$  are parameters. The linear relationship must be bound by 1 for the interval of acceptable rainfalls. Another model is also implemented to estimate the effect of rainfall on residue wash-off. The rationale for this model is that the first rainfall after an application may result in the largest losses in residues but subsequent rainfalls are likely to result in far less loss due to the tenacity of remaining residues on the surface. We used a step function to model this kind of rain wash-off:

$$k_2 = \begin{cases} \text{as equation 7} & \text{for the first rain after an application} \\ (Y/Y_{\max})k_3 & \text{for other rainfalls if } Y \leq Y_{\max} \\ k_3 & \text{for other rainfalls if } Y > Y_{\max} \end{cases} \quad (7)$$

where  $Y_{\max}$  is the threshold of rainfall such that further increase over this threshold will not lead to increased wash-off of residues, and  $k_3$  ( $< 1$ ) is the maximum loss due to the rain other than the first after an application.

Thus, if the residue on day  $t$  is  $L_t$ , then the residue on day  $t+1$  ( $L_{t+1}$ ,  $\mu\text{g}/\text{fruit}$ ) is given by

$$L_{t+1} = L_t \cdot (1 - k_1 - k_2) \quad (8)$$

where  $k_2$  is zero on dry days or calculated as in equations [7-8] in rainy days depending on the user's choice. If day  $t+1$  is an application day, the estimated initial deposits for the three points (mean and 95% confidence intervals) for each zone from the application are then added to  $L_{t+1}$ .

#### *Host growth*

This model assumes that host tissue (fruit or leave) growth does not result in actual loss or degradation of pesticide residues but only affects residue concentrations over time due to host expansion. Hence the growth model does not affect residue losses as

modelled in the physical decay component but only the presentation of predicted residues to the end users. This may be important since the dietary risk assessment is often expressed on the basis of residue concentrations.

Fruit growth pattern can be represented by a number of functions such as the expolinear (Lakso et al. 1995), and Gompertz and logistic (Thornley & Johnson 1990) equations. We have implemented these functions in the model. For example, a logistic model for fruit expansion is given as

$$W_t = \frac{W_{\max}}{1 + A \cdot \exp(-B \cdot t)} \quad (9)$$

where  $W_t$  is the fruit weight (g) on day  $t$  ( $t = 0$  on the day of full bloom),  $W_{\max}$  is the maximum weight (g) to which fruit can reach,  $A$  and  $B$  are parameters. Once the fruit weight is obtained, residue concentration ( $\mu\text{g/g}$ ) on day  $t$  can then be estimated.

#### *Stochastic effects*

To evaluate the uncertainty propagation in the deterministic model, we have incorporate sub-models dealing with two specific aspects of stochastic variation. First, the model can sample an initial deposit within each zone from a lognormal distribution. Second, on any given day, parameters  $k_1$ ,  $k_2$  and  $k_3$  for the physical decay sub-model are sampled from normal distributions. These two aspects of stochasticity can be invoked simultaneously or separately to investigate their joint effects on the dynamics of residues over time. Details on the implementation are not presented here since this paper deals with validation of the deterministic model.

*Execution of the deterministic model*

Figure 1 presents the model flow diagram. The model executes by first looping through spray applications. For each application, the initial deposit sub-model estimates the average initial deposit and its 95% confidence limits for each zone using equations [1-5]. Then, the model loops through days between applications at a daily step. Depending on weather conditions, the model uses equations [6-8] to estimate daily loss of residues and hence to calculate residues for the three points within each zone. On the day of an application other than the first, the estimated initial deposits for the three points (mean and 95% confidence intervals) for each zone are added to the respective predicted residues on the day as a result of previous application(s). At the same time, daily average fruit weight is estimated using the fruit growth model. Finally the model presents predicted residues in the form of both total residues per fruit and residue concentrations ( $\mu\text{g/g}$ ).

In addition to the model parameters described in section 2.1-2.3, the model also needs the following input: date and rate (as a percentage of the full recommended rate) of each application and daily average temperature and humidity as well as daily total rainfall (mm).

**Model evaluation**

We evaluate the model predictions against a specific contact fungicide, Captan (N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide). Captan is one of the most important fungicides used to control apple scab, particularly when apple mildew is not severe, and is also widely used to control diseases in many other crops (Elzemaity 1988, Gilvydis et al. 1986, Northover et al. 1986). Many studies have been conducted to investigate captan residues on various crops in relation to physiological and physical

factors in laboratory, storage and field conditions (Elzemaity 1988, Frank et al. 1987, Frank et al. 1985, Kiigemagi et al. 1991, Smith & MacHardy 1984).

#### *Model parameters for captan*

Model parameters were obtained from previously published as well as from unpublished studies at East Malling Research. The most difficult parameters to obtain are those related to initial deposition of captan. Spray retention of captan on leaves varies greatly within a growing season due to the change in canopy leaf density (Smith & MacHardy 1984). Retention of a Zn tracer on apple fruit also varied greatly between years and between orchards (Xu et al. 2006). Because of these uncertainties, we decided to use the actual average captan deposit for the inner zone from the orchard experiments as an input, which is 10 µg per fruit (i.e. the retention rate -  $R$ ). Then, based on previous work on a Zn tracer (Xu et al. 2006), we assumed that the average captan deposit in the top and outside zones is 25% more than the inner zone, i.e. 12.5 µg per fruit. Furthermore, the variability factors ( $V_5$  and  $V_{95}$ ) are assumed to be equal among the three zones ( $V_5 = 0.42$  and  $V_{95} = 2.2$ ) based on the same Zn data though these values were not given in the previous paper (Xu et al. 2006); this is equivalent to a 45% coefficient of variation.

Several previous studies reported that there was no appreciable loss of captan on tomato fruit (Frank et al. 1987), apple and grape (Frank et al. 1985), and cherry and peach (Northover et al. 1986) under dry conditions. However, large loss of captan was shown under dry conditions in another field study (Smith & MacHardy 1984), which may have resulted from heavy dew. Several papers have stated that the half-life of captan on vegetation is between 3-17 days, but no detailed data were provided (de Cock et al. 1998, Decision 1999). Without rainfall, such a short half-life time is most unlikely and may result from not taking growth dilution effects into consideration. We recently

1  
2  
3 conducted several experiments to investigate the loss of captan under dry conditions on  
4  
5 both leaves and fruit (Xu, unpublished), and showed that daily loss of captan on fruit  
6  
7 and leaves was very small. From these data,  $k_1$  was estimated to be 0.01 irrespective of  
8  
9 temperature and humidity, and hence that value is used in the model.  
10  
11

12  
13 As reported previously (Frank et al. 1987, Frank et al. 1985, Northover et al. 1986,  
14  
15 Smith & MacHardy 1984), there was significant loss of captan due to wash-off by rain.  
16  
17 The relationships between the loss and the amount of rainfall varied greatly between  
18  
19 experiments and fields. In two recent experiments conducted at East Malling Research  
20  
21 (Xu, unpublished), we demonstrated that even rainfall as little as 1 mm after an  
22  
23 application led to about 50% loss of captan on leaves of rootstock plants independently  
24  
25 of the amount of rainfall. However, the loss due to subsequent rainfall was very small.  
26  
27 Thus, we have used a step function to estimate the rain wash-off of captan. The first  
28  
29 rainfall less than or equal to 1 mm is not treated as a rainfall event for the following  
30  
31 reason. More rain is needed to penetrate tree canopy than rootstock plants to wash  
32  
33 captan from leaves and fruit inside the canopy. This is supported by field observations  
34  
35 that 1 mm rainfall resulted in negligible loss of captan even on leaves (Smith &  
36  
37 MacHardy 1984).  
38  
39  
40  
41  
42

43  
44 The loss of captan on the upper surface of leaves due to the first rainfall after an  
45  
46 application is estimated to be 65% (Xu, unpublished) although the average loss is circa  
47  
48 50% over the upper and lower surface. Because of the nature of fruit shape (round) and  
49  
50 surface (waxier than leaves), we set  $k_2$  to 0.65 instead of 0.50. From the same  
51  
52 experiment, we estimated  $k_3$  to be 0.15 and  $Y_{max}$  to be 12 mm (since the maximum  
53  
54 rainfall in the experiment was 12 mm).  
55  
56

57  
58 In this evaluation, we did not activate the fruit growth sub-model. As explained  
59  
60 earlier, the growth model does not affect the prediction of captan residues. Therefore,

1  
2  
3 fruit expansion over the experimental period is not estimated because our emphasis is  
4 on evaluating the model for its accuracy of predicting captan losses.  
5  
6  
7  
8  
9

### 10 *Field experiments*

11  
12 Only a brief summary of experiments is given here. Experiments were conducted in  
13 2005 in two orchards at East Malling Research. A suspension of Captan 80 WG (1.2 g/L,  
14 the full recommended rate) was applied on two occasions (May and August) in the same  
15 orchards but to different blocks of trees using the same spray machine (Hardi Ilemo  
16 with 8 nozzles at each side) at a spray volume of 200 l/ha and a speed of 5.8 km/hour.  
17 An electronic data logger (Skye, Wales) was installed in each of the three zones in a  
18 selected tree in each orchard.  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29

30 For each application, a number of fruit were sampled from each of the three canopy  
31 zones on six occasions: 0 (the same day), 5, 8, 13, 19 and 26 days after the May  
32 application, and 0, 5, 9, 15, 21 and 28 days after the August application. For the day 0  
33 (initial deposit) and the last sampling day, there were 26 samples (either single-fruit  
34 samples or two-fruit composite samples) from five trees for each zone. For all other  
35 sampling days, there were 16 samples (either single-fruit samples or two-fruit  
36 composite samples) from four trees for each zone. Throughout the sampling periods, the  
37 same four trees were sampled for each application and the same fifth tree was used for  
38 the day 0 and the last day sampling as well. The total weight of the fruit in each sample  
39 was determined before captan extraction.  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53

54 Each sample (one or more fruit) was transferred to a 150 mm x 25 mm test tube and  
55 5 ml ethyl acetate (containing 50 mg kg<sup>-1</sup> captafol as internal standard) was then added.  
56 The tube was then whirl-mixed for 15 sec, ensuring that all surfaces of the fruit were  
57 completely wetted by the solvent. When fruit was too large for the tube, each sample  
58  
59  
60

was transferred to a small polythene bag and then 5 ml extraction solvent was added to the bag. The mouth of the bag was closed by twisting, and the bag was then shaken manually for about 15 sec. A portion of the extract was transferred to a 2 ml GC vial; the vial was then capped with a Teflon-lined crimp-cap lid and stored at  $-18^{\circ}\text{C}$  until analysed. Preliminary studies showed that the recovery rate of captan by this method was  $> 80\%$ .

Analysis of captan and captafol was performed on a Hewlett-Packard HP6890 gas chromatograph equipped with an HP-5 capillary column (30 m x 0.32 mm, film thickness 0.25 mm), and an ECD detector. The carrier gas was helium ( $3\text{ ml min}^{-1}$ ) and the make-up gas was nitrogen ( $60\text{ ml min}^{-1}$ ). Injector temperature was  $200^{\circ}\text{C}$ , and detector temperature was  $300^{\circ}\text{C}$ . Following sample injection, the initial temperature of the oven was maintained at  $100^{\circ}\text{C}$  for 1 min, then increased at a rate of  $50^{\circ}\text{C min}^{-1}$  to  $275^{\circ}\text{C}$ , and maintained at  $275^{\circ}\text{C}$  for 5 min. Retention times for captan and captafol were ca 6.5 min and 8.0 min, respectively. For each batch of samples, four standards (200, 100, 50 and  $25\text{ mg kg}^{-1}$  captan in the extraction solvent with  $50\text{ mg kg}^{-1}$  captafol) were quantified first to obtain a calibration curve. The instrument was programmed first to quantify the  $200\text{ mg kg}^{-1}$  captan standards twice before the four standards to condition the instrument. In addition, the instrument was instructed to quantify the  $50\text{ mg kg}^{-1}$  captan standard after every 10th experimental sample to adjust for the potential drift in the detector.

### Validation results

Figures 2 and 3 show the predicted levels of residues against the observed for each zone over the two orchards. The predicted average residues and 95% confidence interval for each zone are shown in Fig. 2. Overall, the predicted residues were close to those

1  
2  
3 observed for both sprays. For the May application, the level of residues actually  
4  
5 increased for the last two sampling days, especially for the outer and inside zones (Fig.  
6  
7 2bc). For the August application, there appeared to be no systematic prediction errors in  
8  
9 the average residues. The Pearson's correlation coefficients between predicted zone  
10  
11 averages and the observed were 0.92 and 0.94 for the May and August application,  
12  
13 respectively; the overall correlation was 0.93.  
14  
15

16  
17  
18 Similarly, the model predicted the residue variability reasonably well and the  
19  
20 prediction error in the variability shows no systematic trend. Table 1 shows the  
21  
22 observed coefficient of variation (CV) of total captan per fruit for each zone on any  
23  
24 sampling day. The average CV over all sampling days for the May application was  
25  
26 greater than the model parameter (45%), but was close to that value for the August  
27  
28 application. CVs fluctuated greatly between sampling days but with no obvious pattern.  
29  
30

31  
32  
33 When the predicted zone averages were regressed on to the corresponding observed  
34  
35 values, the fitted linear model did not differ significantly between the May and August  
36  
37 applications, but it did differ between the three zones. However, this zone difference  
38  
39 only accounted for about 2.5% of the total variation, with coefficients of determination  
40  
41  $R^2$  increasing from 0.851 to 0.876. The constant term (i.e., the intercept) was not  
42  
43 significantly different from 0 but the regression slope ( $0.82 \pm 0.03$ ) was significantly  
44  
45 less than 1.0, thus indicating that the captan model systematically underestimated  
46  
47 residues by 18%.  
48  
49  
50  
51  
52  
53

## 54 Discussion

55  
56  
57 We have developed a generic model to predict the dissipation of contact pesticides over  
58  
59 time. This generic model included several key aspects of residue fates in the  
60  
environment including the initial deposit, physical loss and growth dilution. This

1  
2  
3 generic model is parameterised specifically for captan of evaluation purposes and is  
4 shown to be able to predict average residues together with the confidence intervals  
5 accurately. The overall correlation between predicted average residues and the observed  
6 in two applications was as high as 0.93, which is surprisingly accurate given the fact  
7 that the model was developed from independent data from published or unpublished  
8 sources.  
9

10  
11  
12  
13  
14  
15  
16  
17  
18 When parameterising the model for captan, we encountered difficulties in estimating  
19 average initial deposits for each canopy zone. In the end, we resorted to the observed  
20 average residues for the inside zone to initiate the model; this is the only model  
21 parameter that was obtained from the evaluation data. Spray retention of captan on  
22 leaves varies greatly within a growing season due to the change in canopy leaf density  
23 (Smith & MacHardy 1984) and surface structure (Hall et al. 1997). Retention of a Zn  
24 tracer on apple fruit also varied greatly between years and between orchards (Xu et al.  
25 2006). Variability in initial deposit has been observed for many other pesticides in  
26 relation to plant architecture (Bennett et al. 1994, Bruhn & Fry 1982, Cross et al. 1997)  
27 and to spray technology (Ade et al. 2000, Brenneman et al. 1990, Cross et al. 2001). In  
28 modelling initial deposit on kiwi fruit, a constant retention factor per unit of surface  
29 fruit area was assumed (Holland et al. 1996) and the resulting model generated  
30 reasonable predictions for several chemicals. We believe that the accurate prediction of  
31 initial spray deposits is one of the bottlenecks for accurate prediction of residues on  
32 food stuff. Accurate prediction of residues depends on many factors as aforementioned,  
33 including canopy structure, tissue surface structure and spray technology.  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54

55  
56 The large differences in the average observed residues between different zones  
57 indicated the importance of including the canopy in the captan model. The overall  
58 consistent correlation between predicted and observed average residues for each zone  
59  
60

1  
2  
3 further supported our assumption on the effect of canopy. Namely, the canopy mainly  
4 affects the residues by influencing the initial deposition process but it does not exert any  
5 significant differential effect on the loss of captan. It reinforces the previous point that  
6 estimating initial deposits is critically important, whereas predicting subsequent  
7 declines is relatively straightforward, at least for captan on apple.  
8  
9

10  
11  
12  
13  
14  
15  
16 The model generally predicted the overall trend in residue decline over time for  
17 each canopy zone. However, there was an apparent and statistically significant increase  
18 in captan residues from June 8<sup>th</sup> to 14<sup>th</sup> fruit samples. The most likely explanation is the  
19 phenomenon of June-drop. That normally takes place from mid-June to early July, but  
20 may have occurred earlier in 2005 as the trees blossomed earlier than usual that year.  
21 Therefore, most fruit retained on the tree and sampled on the last two dates for the May  
22 application may have been from cohorts bigger than the average at the time of  
23 application. Hence the stalk and calyx end of these fruit would also have been bigger at  
24 the time of application. The average size of fruits was small at the time of application  
25 (about 1 g in weight) and the smallest of these may be most susceptible to June-drop.  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38

39  
40 Our model differed from several previous models in several aspects. The model  
41 developed by Holland et al. (1996) did not consider the spatial variability of initial  
42 deposits due to canopy structure. To take into account some reports that decline of  
43 residues sometimes was much faster shortly after spray applications than the later stage,  
44 they used decay constants to describe the two decay phases. However, it is difficult to  
45 decide which of the two decay constants should be adopted in which circumstance. The  
46 two different decay rates may be due to the variation in wash-off between first rain and  
47 the subsequent rains, where the former causes considerably more loss of residues than  
48 the latter. Thus, our model explicitly assigned a decay constant depending on weather  
49 conditions. Timme and his co-workers (Timme & Frehse 1980, Timme et al. 1986) did  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

not consider initial deposits in their model and used a series of reaction kinetics, labelled as 1<sup>st</sup>, 1.5th, etc., order equations to model the degradation behaviour. Later, they (Quest et al. 1993) proposed a two-zone model where the degradation of residues in the outer zone and the degradations in the inner zone are assumed to follow different rules, which was used to accommodate dramatic losses of residues observed occasionally soon after applications. This two-zone model, however, does not consider weather effects explicitly. In addition, our model assumed that the canopy structure affects the initial deposition process only.

It is well known that variability in pesticide residues whether in field or shelf samples is very large (Ambrus 2000, Harris 2000, Harris & Davis 1998, Hill 2000, Hill & Reynolds 2002). Accurate prediction of acute dietary risks of pesticide residues in food also depends critically on our understanding of this variability. Our current model assumed a CV for residues within each canopy zone. This is an over-simplification but a necessary one since as yet we do not understand residue variability sufficiently to predict it. This is illustrated by the large yet erratic variability in captan residues observed in the present field trials. There are many factors that may have contributed to the observed variability by influencing the dissipation process, including canopy structure, spray technology, sampling and weather condition (Dubus et al. 2003). In addition, instrumentation used in quantifying residues can also contribute substantially to the observed variability (Ambrus 2004). It remains a challenge to predict this variability accurately. One way forward is to implement a stochastic version of the current deterministic model. There are two stochastic processes that should be investigated: initial deposition and weathering effects (i.e., uncertainty in the model parameters  $k_1$ ,  $k_2$ ,  $k_3$ ). This is our current research focus. In addition, there is another

factor that can affect residue variability, though not residue loss, i.e. plant growth. This growth process can also be studied stochastically.

In summary, we have developed a generic framework for predicting dissipation of contact pesticides. We did not conduct sensitivity analyses for the captan model because it is obvious that the model would be most sensitive to the two parameters ( $k_2$  and  $k_3$ ), describing rain wash-off effects, once an accurate estimation of initial deposit is given. Evaluation of the generic model specifically parameterised for captan against independent field data has showed promising results. The model not only predicted very accurately the average residues but also estimated the residue variability reasonably well. However, one of the remaining key challenges for the prediction of residues is the accurate estimation of initial deposit concentrations.

### Acknowledgements

This research was funded jointly by the Biotechnology and Biological Sciences Research Council and Syngenta.

### References

- Ade, G., Pezzi, F., Cooper, S. E., and Taylor, W. A. 2000. The influence of some application variables on spray deposition in field-grown tomatoes. *Aspects of Applied Biology* 57:225-233.
- Ambrus, A. 2000. Within and between field variability of residue data and sampling implications. *Food Additives and Contaminants* 17:519-537.
- Ambrus, A. 2004. Reliability of measurements of pesticide residues in food. *Accreditation and Quality Assurance* 9:288-304.

- 1  
2  
3  
4 Bennett, R. S., Edge, W. D., Griffis, W. L., A.C.Matz, Wolff, J. O., and Ganio, L. M.  
5 1994. Temporal and spatial distribution of azinphos-methyl applied to alfalfa.  
6 Archives of Environmental Contamination 27:534-540.  
7  
8  
9  
10  
11 Brenneman, T. B., Summer, H. R., and Harrison, G. W. 1990. Deposition and retention  
12 of chlorothalonil applied to peanut foliage: effects of application methods,  
13 fungicide formulations and oil additives. Peanut Science 17:80-84.  
14  
15  
16  
17  
18 Bruhn, J. A., and Fry, W. E. 1982. A mathematical model of the spatial and temporal  
19 dynamics of chlorothalonil residues on potato foliage. Phytopathology 72:1306-  
20 1312.  
21  
22  
23  
24  
25  
26 Bruhn, J. A., and Fry, W. E. 1983. Weathering of chlorothalonil residues in a potato  
27 canopy. Phytopathology 71:205.  
28  
29  
30  
31  
32 Cross, J., Walklate, P., Murray, R., and Richardson, G. 2001. Spray deposits and losses  
33 in different sized apple trees from an axial fan orchard sprayer: 1. Effects of  
34 spray liquid flow rate. Crop Protection 20:13-30.  
35  
36  
37  
38  
39  
40 Cross, J. V., Murray, R. A., Ridout, M. S., and Walklate, P. J. 1997. Quantification of  
41 spray deposits and their variability on apple trees. Aspects of Applied Biology  
42 48:217-224.  
43  
44  
45  
46  
47  
48 de Cock, J., Heederik, D., Kromhout, H., Boleij, J., Hoek, F., Wegh, H., and Ny, E.  
49 1998. Determinants of exposure to captan in fruit growing. American Industrial  
50 Hygiene Association Journal 59:166-172.  
51  
52  
53  
54  
55 Decision, R. E. 1999. Reregistration Eligibility Decision (RED): Captan; EPA-738-R-  
56 99-015; U.S. Environmental Protection Agency, Office of Pesticide Programs,  
57 U.S. Government Printing Office: Washington, DC, Nov 1999; 2-49.  
58  
59  
60

- 1  
2  
3  
4 Dubus, I. G., Brown, C. D., and Beulke, S. 2003. Sources of uncertainty in pesticide  
5 fate modelling. *The Science of the Total Environment* 317:53-72.  
6  
7  
8  
9  
10 Elzemaity, M. S. 1988. Degradation behavior of captan and folpet on greenhouse  
11 tomatoes. *Bulletin of Environmental Contamination and Toxicology* 40:80-85.  
12  
13  
14  
15 Evans, M., Hastings, N., and Peacock, B. 2000. *Statistical Distributions*. (New York:  
16 Wiley).  
17  
18  
19  
20  
21 FAO/WHO. 1997. Food consumption and exposure assessment of chemicals. World  
22 Health Organization in collaboration with the Food and Agriculture  
23 Organization of the United Nations, Geneva, Switzerland, pp 1-70.  
24  
25  
26  
27  
28  
29 Frank, R., Braun, H. E., and Ritcey, G. 1987. Disappearance of captan from field-grown  
30 and greenhouse-grown tomato fruit in relationship to time of harvest and amount  
31 of rainfall. *Canadian Journal of Plant Science* 67:355-357.  
32  
33  
34  
35  
36 Frank, R., Northover, J., and Braun, H. E. 1985. Persistence of captan on apples, grapes,  
37 and pears in Ontario, Canada 1981-1983. *Journal of Agriculture, Food and*  
38 *Chemistry* 33:514-518.  
39  
40  
41  
42  
43  
44 Franz, E., Bouse, L. F., Carlton, J. B., Kirk, I. W., and Latheef, M. A. 1998. Aerial  
45 spray deposit relations with plant canopy and weather parameters. *Transactions*  
46 *of the American Society of Agricultural Engineers* 41:959-966.  
47  
48  
49  
50  
51  
52 Gilvydis, D. M., Walters, S. M., Spivak, E. S., and Hedblad, R. K. 1986. Residues of  
53 captan and folpet in strawberries and grapes. *Journal of the Association of*  
54 *Official Analytical Chemists* 69:803-806.  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 Hall, F. R., Downer, R. A., Cooper, J. A., Ebert, T. A., and Ferree, D. 1997. Changes in  
5 spray retention by apple leaves during a growing season. *HortScience* 32:858-  
6 860.  
7  
8  
9  
10  
11 Hamey, P. Y. 2000. A practical application of probabilistic modelling in assessment of  
12 dietary exposure of fruit consumers to pesticide residues. *Food Additives and*  
13 *Contaminants* 17:601-610.  
14  
15  
16  
17  
18 Hamilton, D., Ambrus, A., Dieterle, R., Felsot, A., Harris, C., Petersen, B., Racke, K.,  
19 Wong, S., Gonzalez, R., Tanaka, K., Earl, M., Roberts, G., Bhula, R., and Wong,  
20 S. S. 2004. Pesticide residues in food - acute dietary exposure. *Pest Management*  
21 *Science* 60:311-339.  
22  
23  
24  
25  
26  
27  
28 Harris, C. A. 2000. How the variability issue was uncovered: the history of the UK  
29 residue variability findings. *Food Additives and Contaminants* 17:491-495.  
30  
31  
32 Harris, C. A., and Davis, T. J. 1998. Unit to unit variation of pesticide residues in celery,  
33 plums and kiwi fruit. Pesticide Safety Directorate, pp 1-62.  
34  
35  
36  
37  
38 Hill, A. R. C. 2000. Residue variability and sampling - practical problems and  
39 consequences for residues monitoring. *Food Additives and Contaminants*  
40 17:539-546.  
41  
42  
43  
44  
45 Hill, A. R. C., and Reynolds, S. L. 2002. Unit-to-unit variability of pesticide residues in  
46 fruit and vegetables. *Food Additives and Contaminants* 19:733-747.  
47  
48  
49  
50  
51 Holland, P. T., Malcolm, C. P., Mowat, A. D., Rohitha, B. H., and Gaskin, R. E., 1996,  
52 Modelling of pesticide Residues on Fruit II: Persimmon. *Proceedings of the*  
53 *Proceedings of the 49th New Zealand Plant Protection Conference*, pp 192-197.  
54  
55  
56  
57  
58  
59 Hyder, K., Travis, K. Z., Welsh, Z. K., and Pate, I. 2003. Maximum residue levels: Fact  
60 or fiction? *Human and Ecological Risk Assessment* 9:721-740.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60
- Kiigemagi, U., Inman, R. D., Mellenthin, W. M., and Deinzer, M. L. 1991. Residues of benomyl (determined as carbendazim) and captan in postharvest-treated pears in cold-storage. *Journal of Agricultural and Food Chemistry* 39:400-403.
- Lakso, A. N., Grappadelli, L. C., Barnard, J., and Goffiet, M. C. 1995. An exponential model of the growth pattern of the apple fruit. *Journal of Horticultural Science* 70:389-394.
- Northover, J., Frank, R., and Braun, H. E. 1986. Dissipation of captan residues from cherry and peach fruits. *Journal of Agriculture, Food and Chemistry* 34:525-529.
- Quest, S., Walter, H.-F., Frehse, H., and Timme, G. 1993. Statistical interpretation and graphical representation of the degradational behaviour of pesticide residues. IV. Physically based models. *Pflanzenschutz-Nachrichten Bayer* 46:289-314.
- Smith, F. D., and MacHardy, W. E. 1984. The retention and redistribution of captan on apple foliage. *Phytopathology* 74:884-899.
- Thornley, J. H. M., and Johnson, I. R. 1990. *Plant and crop modelling*. (Oxford: Clarendon).
- Timme, G., and Frehse, H. 1980. Statistical interpretation and graphic representation of the degradational behaviour of pesticide residues I. *Pflanzenchutz-Nachrichten Bayer* 33:47-60.
- Timme, G., Frehse, H., and Laska, V. 1986. Statistical interpretation and graphical representation of the degradational behaviour of pesticide residues. II. *Pflanzenschutz-Nachrichten Bayer* 39:187-203.

- 1  
2  
3  
4 Walklate, P. J., Cross, J. V., Richardson, G. M., Baker, D. E., and Murray, R. A. 2003.  
5 A generic method of pesticide dose expression: application to broadcast  
6 spraying of apple trees. *Annals of Applied Biology* 143:11-23.  
7  
8  
9  
10  
11 Walklate, P. J., Cross, J. V., Richardson, G. M., Murray, R. A., and Baker, D. E. 2002.  
12 Comparison of different spray volume deposition models using LIDAR  
13 measurements of apple orchards. *Biosystems Engineering* 82:253-267.  
14  
15  
16  
17  
18  
19 Walklate, P. J., Richardson, G. M., Cross, J. V., and Murray, R. A. 2000. Relationship  
20 between orchard tree crop structure and performance characteristics of an axial  
21 fan sprayer. *Aspects of Applied Biology* 57:285-292.  
22  
23  
24  
25  
26  
27 Xu, X.-M., Wu, P.-H., Thorbek, P., and Hyder, K. 2006. Variability of initial spray  
28 deposit in apple trees in space and time. *Pesticide Management Sciences* 62:947-  
29 956.  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 **Figure 1.** A flow diagram of the model. Initial deposits are for the top, outer and inner  
5 zone, respectively. Degradation of pesticides is always dependent on the daily loss rate.  
6  
7  
8 Extra loss occurs due to weather effects, i.e., rain events.  
9

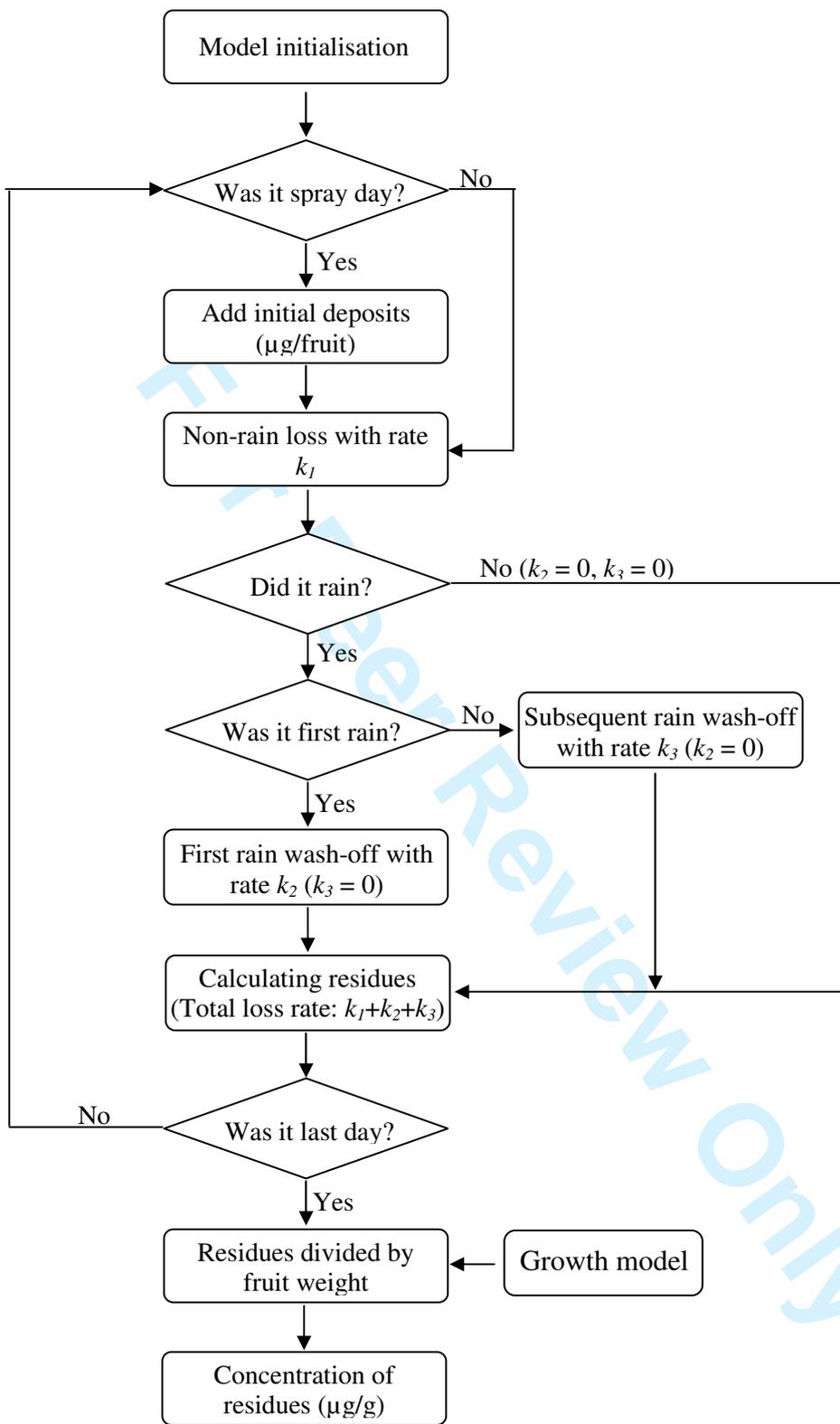
10  
11  
12 **Figure 2.** Predicted captan residues on apple plotted against the observed values  
13 following application of captan on 26 May and 3 August 2005. Bars are the minimum  
14 and maximum of the observed values (solid dot – average residues) and three lines are  
15 the average and the 95<sup>th</sup> percentiles of the predicted residues on each day. Residues  
16 were reported in  $\mu\text{g}$  per fruit rather than  $\mu\text{g g}^{-1}$  because the former reflects the amount of  
17 actual losses in captan residues but the latter may also include additional errors from  
18 variability in fruit growth among individual fruit (i.e. growth dilution due to fruit  
19 expansion). The average fruit weight on each sampling day of the May application was  
20 0.5, 0.7, 1.0, 1.4, 4.4 and 10.2 g, respectively; the corresponding value for the August  
21 application was 60.5, 75.2, 74.1, 84.7, 88.1 and 88.7 g.  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38

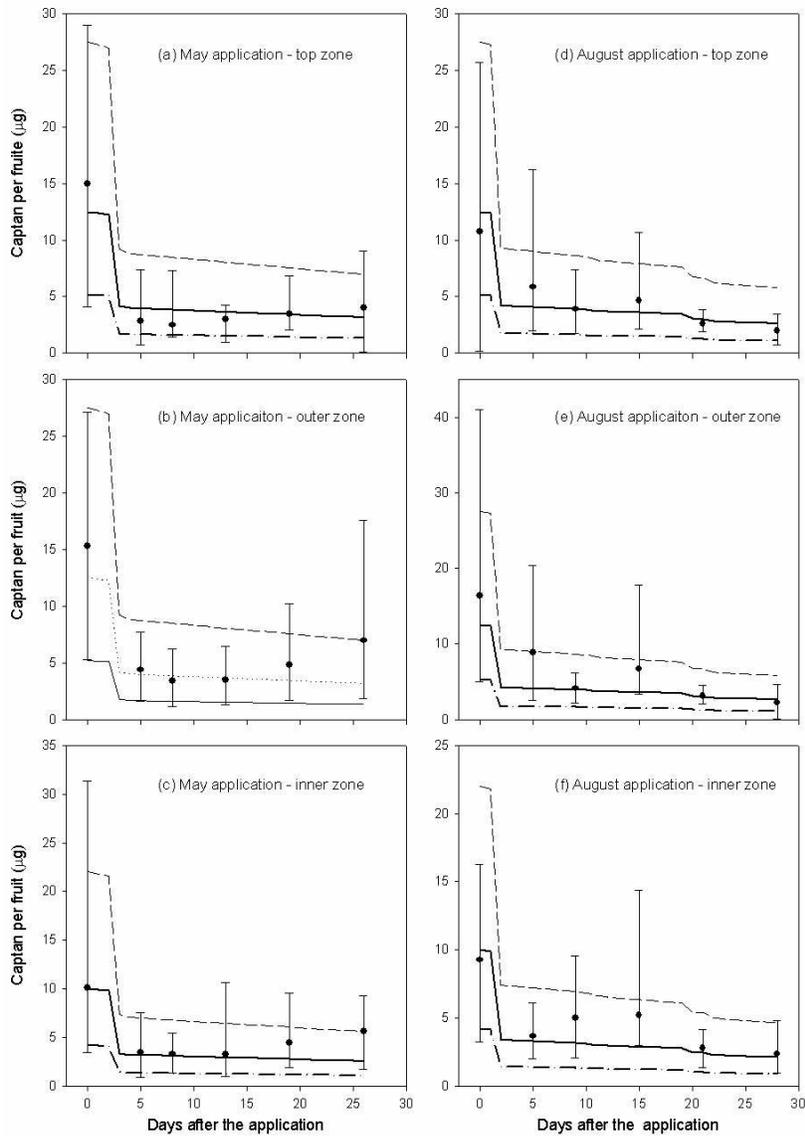
39 **Figure 3.** Predicted average captan residues on apple for each zone against the observed  
40 values.  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

Table I The observed coefficient of variation (CV, %) of total captan residues per apple fruit within each zone on each sampling date over two orchards. The model used a single CV value to estimate the 95% confidence intervals for the initial deposit for each zone.

Sampling day <sup>a</sup>	May application			Sampling day	August application		
	Inner	Outer	Top		Inner	Outer	Top
0	70.4	35.4	51.1	0	34.1	52.7	37.4
5	60.0	47.4	62.7	5	33.0	73.1	67.6
8	38.5	42.7	58.1	9	48.8	34.3	43.1
13	76.4	39.7	32.7	16	68.1	60.8	58.7
19	51.4	42.0	37.3	21	27.7	19.4	18.6
26	39.0	53.3	57.7	28	43.9	45.4	37.8
Average	56.0	43.4	49.9	Average	42.6	47.6	43.9

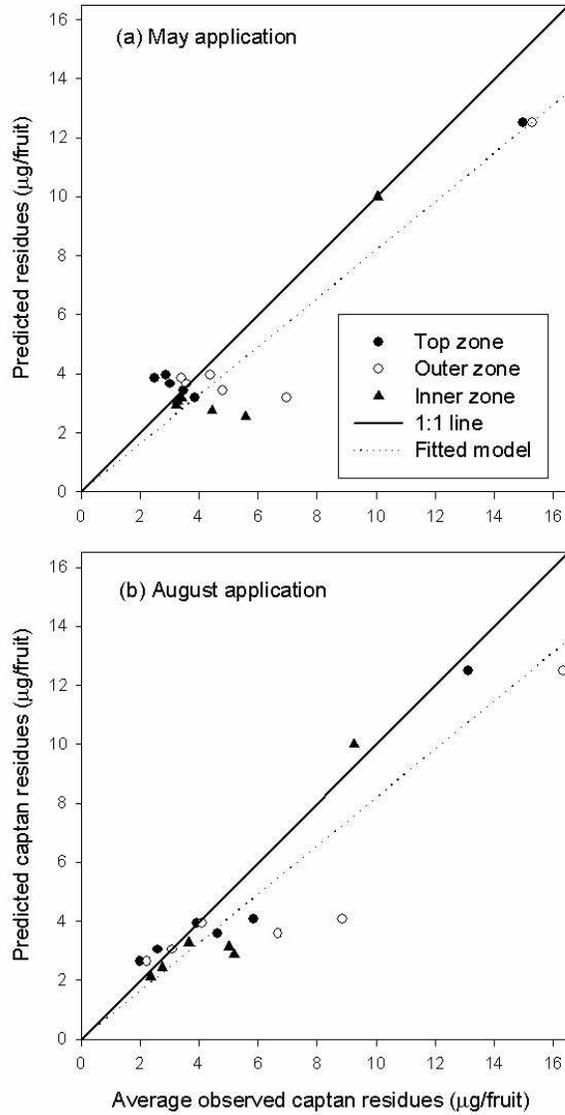
<sup>a</sup>: number of days since the spray (day 0 is the spray day)





158x227mm (150 x 150 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



100x196mm (150 x 150 DPI)