Bull. Environ. Contam. Toxicol. (1997) 58:976-984

Bulletin of Environmental Contamination and Toxicology

Half-Lives of Pesticides on Greenhouse Crops

D. H, Brouwer, M. de Haan, L, H. Leenheers, S. A, F. de Vreede, J. J, van Hemmen

Department of Occupational Toxicology, TNO Nutrition and Food Research Institute. P.O. Box 360. 3700 AJ Zeist, The Netherlands

Received: 6 November 1996/Accepted: 5 February 1997

Re-entry exposure to pesticide residues have been reported to result in potential health risk (Van Hemmen et al., 1992). For risk assessment purposes it is therefore essential to characterize the exposure processes. Since especially dermal exposure is important in this context, this requires special attention.

Models for re-entry exposure estimates have been developed over the past 10 years (Popendorf and Leffingwell 1982. Nigg et al. 1984; Zweig et al. 1985). Recent reviews have considered these issues for greenhouse crops in more detail (Van Hemmen, 1993, Van Hemmen et al., 1995). The basic assumption of the developed models is that exposure results from the transfer of pesticide residue present at the crop during worker activities. More specifically, it was stated that dermal exposure (DE [g/day]) is determined by the amount of transferable residue (expressed as dislodgeable foliar residue DFR [g/m^2], a crop and work activity specific-transfer factor (TF [m^2/hr) and duration of re-entry (T, [hr/day]), which can be expressed in the most genera1 form as:

$$D\ E_i = DFR_{it} * T\ F_m * T_m \quad (1)$$

where:

i = i-th pesticide
m = m-th task
t = t-th day after application.

The transfer factor (TF) is an empirical factor which is assumed to be crop and activity specific but pesticide independent. TF's have been derived from exposure data and data on dislodgeable foliar residue established for a variety of crop activities, and are accepted to be relevant for risk assessment. However, within crop and activities variances of the TF may be substantial (Krieger et al. 1991).

The actual dislodgeable foliar residue at time of re-entry is considered to be an important source strength for dermal exposure. The level of actual pesticide residue may differ from the initial amount of DFR depending on the decay rate and the elapsed time since application. The dissipation of the foliar pesticide deposit is considered to be a complex process of environmental factors, metabolism and translocation (foliar penetration and plant growth), and pesticide formulation (Bentson 1990). Willis and McDowell (1987) assumed that the process of decay may in many cases be described by a first order process. Thus, the relationship between initial and actual DFR can be described as:

Correspondence to: D.H. Brouwer

$$ln\ DFR_{t} = ln\ DFR_{0} + kt \quad (2)$$

where:

DFR_0 = initial DFR (day 0 after application)
k = first-order reaction constant

and

$$k = -ln\ 2\ (t_{1/2})^{-1} \quad (3)$$

where

$t_{1/2}$= half-life [days].

Dissipation curves of pesticides have been used as a risk assessment tool to establish re-entry intervals. *i.e.* the calculated expectation that pesticide residues would reduce to the safe re-entry levels within this interval (Dong et al. 1992). Foliar residues fates and dissipation have been reported for many pesticides and many crops, however very limited data are published on greenhouse crops. As a part of several tield studies on re-entry exposure, dissipation curves for various pesticides have been established.

MATERIALS AND METHODS

Residue dissipation studies were part of field studies on the assessment of exposure during re-entry in ornamental flower crops (Brouwer et al, 1992[a,b,c], 1993, 1994). Pesticides selected for dissipation studies were amongst the most extensively used pesticides in the cultivations under study. Details on pesticides, crops and number of greenhouses involved are listed in table 1.

Prior to application and at stratified time intervals after re-entry four samples of 12 leaves were taken from randomly selected flowers in the sector of the greenhouse where pesticides were applied, in the harvesting zone or from two zones of height (high and low). Sampling intervals ranged from two or four hours after application up to 24 hours (for dichlorvos) and from 12 hours after application up to 28 days (methiocarb and thiophanate-methyl).The leaves were cut from the foliage and stored in a polyethylene bottle in the dark at 4-7°C awaiting further processing.
After the collection of leaves, dislodgeable residues were subjected to a procedure based on the method described by Iwata et al. (1977). Briefly, approximately 100 cm^2 leaf area of leaves were extracted twice by shaking for 30 minutes with about 100 ml deionised water containing 4 drops of a Triton X-100 solution (Triton X-100-water 1:5O v/v). Then the bottle containing the leaves was rinsed with another 100 ml water and after removal of the leaves it was rinsed with 2 x 10 ml methanol. All extract liquids were combined and the solution was shaken for 30 minutes. This solution containing the dislodgeable residue was analyzed for the specific pesticide. Projected leaf surface area (one-sided) was measured with an area meter (LI-COR, 3100, Lincoln, Nebraska, USA).

Solutions of dislodgeable foliar residue (DFR) containing abamectin were extracted with n-hexane. Extraction efticiency of abamectin from dislodgeable foliar residue solutions into n-hexane was set at 100%. because abamectin was not detectable in the aqueous phase after extraction. Abamectin was converted into a fluorescent compound by derivatization with trifluoroacetic anhydride and subsequent hydrolysis of the unstable trifluoroacethyl derivative at position 4" with methanolic ammonium hydroxide. The residue was analyzed with reversed phase High Performance Liquid Chromatography (HPLC) and fluorescence detection. The between day coefficients of variation of three field samples with abamectine concentrations of

5,7, and 10 µg/L were 5 %, (n=12), 4 % (n=14), and 5% (n=9), respectively. The method was described by Jongen et al. (1991[6]).

Table 1. Summary of data on dislodgeable foliar residue sampling

Pesticide	Type	Formulation	Crop	Application		N
				technique	rate (g AI/ 1000 m²)	
abamectin	acaricide/ insecticide	EC 18 g/l	chrysanthemums (seedling production)	LV HV	0.9	1 1
bitertanol	fungicide	SC 300g/l	chrysanthemums (seedling production)	HV	45	1
chlorothalonil	fungicide	SC 500g/l	chrysanthemums (seedling production)	LV	100-150	2
dichlorvos	insecticide	EC 550 g/l	chrysanthemums (seedling production)	LV	50	2
mancozeb	fungicide	WP 75% SC 450 g/l	chrysanthemums (seedling production)	HV	137 254	4
methiocarb	insecticide /acaricide	SC 500g/l	carnations production	HV	50	3
methomyl	insecticide	EC 200g/l	carnations production	HV	35	2
propoxur	insecticide	EC 200g/l FSD 2%	carnations production	LF D	30	2 3
thiophanate-methyl	fungicide	WP 70% SC 500 g/l	carnations production	HV	325 150	6

N number of trials
EC Emulsifiable Concentrate
FSD Field Strength Dust
LV Low-volume spraying
HV High-volume spraying
SC Suspension Concentrate
WP Wettable Powder
LF Low-volume fogging
D Dusting

Solutions of dislodgeable foliar residue containing bitertanol were without further clean-up directly analyzed with reversed phase HPLC and UV detection at 254 run. The between day coefficients of variation were less than 5% within a concentration range from 180 up to 1126 µg/L (n=4) (Brouwer et al. 199[6]).

Solutions of dislodgeable foliar residues containing chlorothalonil were extracted with hexane. Recovery was 100 % ± 1% (n=6). Chlorothalonil was quantified by means of normal phase liquid chromatography with UV detection at 254 nm. The between day coefficients of variation of field samples were less than 7% within a concentration range from 174 up to 2220 µg/L (n=7) (Jongen et al. l991[b]).

Solutions of dislodgeable foliar residue containing dichlorvos were extracted with n-hexane. Samples of the extract were analyzed with gas chromatography and nitrogen phosphorus detection using a cold on-column injection technique. Coefficient of variation was less than 5 % within a concentration range 10 to 500 µg/L (Brouwer et al. 1992[d]).

In the DFR procedure for mancozeb the methanol step was replaced by an 0.1 M EDTA-solution in deionised water. Depending on the concentration of mancozeb a part this DFR solution was put into a head space vial containing 2.5 ml of a $SnCl_2$/HCl-solution. The vial was kept at constant temperature and the liberated carbon disulphide was measured with gas chromatography and electron capture detection. Between day coefficients of variation were less than 10 % within a concentration range from 125 upto 1250 ng/L (n=2) (Ravensberg and Langenhuizen 1993).

Extracts of DFR-samples containing methiocarb were adjusted to pH 4.5 with acetic acid directly after DFR procedure, in order to avoid the hydrolysis of methiocarb caused by the Triton in the extract. Extracts were analyzed by reversed phase HPLC and UV detection at a wavelength of 266 nm. Between day coefficients of variation were less than 10% with concentrations of 411 and 719 µg/L, repectively (n=6) (Soekhoe and Kerstens 1995).

Solutions of dislodgeable foliar residue containing methomyl were directly injected onto a reversed phase HPLC system with UV detection at 238 nm. The between day coefficients of variation were less than 5% with concentrations of 96 and 528 µg/L, repectively (n=4) (De Vreede et al. 1994).

Dislodgeable foliar residue solutions containing propoxur were after appropriate dilution with water extracted with n-hexane and determined with liquid chromatography using fluorescence detection. Excitation and emission wavelengths were 275 and 300 nm, respectively. Coefficients of variation were less than 10% with concentrations of 39 and 317 µg/L, respectively (n=6) (Brouwer et al. 1993).

Solutions of dislodgeable foliar residue containing thiophanate-methyl were analyzed with reversed phase liquid chromatography and UV detection at 254 nm. Coefficients of variation were less than 5% with concentrations of 864 and 2963 µg/L, respectively (n=6) (Brouwer et al. 1992[a]).

The quantity of pesticide residues for each sample were divided by the surface area (one-sided) of the sampled leaves. The results were presented as DFR in the units of $\mu g/cm^2$. Half-lives were determined using log-normal transformed values of DFR as a function of time since time of application. The results were analysed using a linear regression model: $\ln DFR = a + b\,T$. Lineair regression results with probability levels $p>0.05$ were excluded from half-life estimates.

RESULTS AND DISCUSSION

The results of the half-life estimates are listed in table 2. Estimated half-lives range from 0.2 (dichlorvos) to 41 days (thiophanate-methyl). For all pesticides a large between-trial variation was observed. Lowest and highest estimates may differ a factor two. Within-crop-between-trial variation of dislodgeable residues in field crops summarized by Willis and McDowell (1987) show similar ranges.

Table 2. Half-life estimates

Pesticide	Application	Regression coefficient	R^2	p-Value	Half-life estimate [days]
abamectin	LV	-0.025	0.91	<0.0001	1.1
	HV	-0.012	0.96	<0.001	2.4
bitertanol	HV	-0.012	0.93	<0.001	2.5
chlorothalonil	LV	-0.006	0.88	<0.001	5.3
	LV	-0.009	0.98	0.02	3.2
dichlorvos	LV	-0.142	0.96	0.02	0.2
	LV	-0.132	0.94	0.01	0.2
mancozeb	HV	-0.007	0.49	0.19	*
	HV	-0.011	0.95	<0.0001	3
methiocarb	HV	-0.048	0.89	<0.001	15
	HV	-0.049	0.72	0.002	14
	HV	-0.084	0.89	0.001	8
methomyl	HV	-0.147	0.85	0.002	4.7
propoxur	LV	-1.504	0.93	0.03	0.5
	LV	-0.682	0.59	0.23	*
	D	-0.840	0.92	0.001	0.8
	D	-1.442	0.75	0.33	*
	D	-1.090	0.68	0.08	0.6
thiophanate-methyl	HV	0.004	0.09	0.43	*
	HV	-0.017	0.52	0.02	41
	HV	-0.003	0.49	0.04	22
	HV	-0.022	0.85	<0.001	32
	HV	-0.019	0.85	<0.001	36
	HV	-0.041	0.89	<0.001	17

* Since p>0.05 no half-life was estimated
HV High-volume application
LV Low-volume application
D Dust application

In part, these differences may be due to different environmental conditions in the greenhouses, i.e. temperature, relative humidity and UV irradition. The influence of rainfall (except wash off by watering) and wind speed are considered to be negligible on the dissipation of pesticide residues in greenhouse (indoors) conditions. In part, the observed differences may be related to the application technique (low-volume versus high-volume technique (abamactin) or the liquid formulation (emulsifiable concentrate or wettable powder) versus field strenght dust (propoxur)). In addition, the location of the crop where the leaf samples were taken may determine the estimates of half-life. Calculated half-lives from leaf samples taken from the low zone of the crop tendend to be larger than half-lives based on the upper zone samples. (additional data are shown in Table 3). Resulting different dilution by diferent growth rates of the foliage in both zones may be another determining factor for the observed differences, especially for pesticides with a large half life. Moreover, physiological and chemical processess which affect the dissipation of the residue may be different at different locations of the foliage. Saiz et al. (1993) demonstrated in a study into captan residues on strawberry foliage, that the residue levels on outer leaves were significantly higher than on inner leaves.

Table 3. Comparison of half-life estimates based on leaf samples from different crop zones

Pesticide	half-life estimate (days) low zone	half-life estimate (days) high zone
thiophanate-methyl	36.8	36.1
thiophanate methyl	23.8	16.9
methiocarb	14.5	11.1

The dissipation of the pesticides on greenhouse crops may differ very much from the dissipation of the same pesticides on field crops.The observed half-life of methomyl (EC formulation) observed on carnations (4.7 days) fits into the rage of half-lives of methomyl on grape crop (1.0 to 7.7 days) reported by Reeve et al. (1992), but is very different from half-life estimates given by Willis and McDowell (1987), *i.e.* a half-life of 0.5 -0.7 days. In contrast, the observed half-lives of abamectin (1.1 and 2.4) and chlorothalonil are very similar to half-life estimates given by Willis and McDowell (1987) for cotton and apple (foliage), respectively

Dong et al. (1992) demonstrated clearly the relevance of appropriate half-life estimates for risk assessment of re-entry workers. For particular crops which are being harvested on a daily basis throughout several months, *e.g.* roses and carnations, lack of data on half-lives of pesticides may be less relevant for risk assessment, because re-entry intervals will be 24 hours or less. Since for other crops the elapsed time between application and re-entry may be substantial, for registration purposes a default for half-life may be used. To enlarge the data set half-lives of other pesticides on greenhouse crops as reported by Goedicke (1988.1989) and listed inTable 4 are included. The median of insecticide half-lives from the half-lives presented in Table 2 and 4 was 3.4 days (n=12,confidence interval (CI): 0.7-5) and the median of half-lives for fungicides was 6.6 days (n=10, CI: 1.9-10.2). Since no significant difference was observed between fungicides and insecticides (Mann- Whittney, p=0.18), the median of all considered pesticides (4.2 days, n=22,:CI 1 .9-9) can be used as default. In a more conservative approach the upper limit of the confidence interval (9 days) would be more appropriate.

Table 4. Half -lives of pesticides on greenhouse crops as reported by Goedicke

Pesticide	Type	Crop	Half-life [days]	Reference
benomyl	fungicide	lettuce	1.6[a]	Goedicke, 1988
carbendazim	fungicide	lettuce/ tomatoes	9[b]	Goedicke, 1988,1989
diazinon	insecticide	tomatoes/ cucumbers	6.5[a]	Goedicke, 1988
dicofol	insecticide	cucumbers/ tomatoes	5[a]	Goedicke, 1988
dimethoate	insecticide	cucumbers	2.7[b]	Goedicke, 1988, 1989
lindane	insecticide	cucumbers	2.5[a]	Goedicke, 1988
fenazox	fungicide	cucumbers	1,2[a]	Goedicke, 1988
iprodione	fungicide	tomatoes	10.2[a]	Goedicke, 1988
malathion	insecticide	tomatoes	4.4[b]	Goedicke, 1989
metalaxyl	fungicide	tomatoes	9[a]	Goedicke, 1988
metamidophos	insecticide	roses	4.1[b]	Goedicke, 1989
pirimiphos-methyl	insecticide	tomatoes	0.7[b]	Goedicke, 1989
vinclozolin	fungicide	tomatoes	9.8[a]	Goedicke, 1988

a) dislodgeable or total residue b) dislodgeable residue

Acknowledgment. This study was financially supported by the Dutch Ministery of Social Affairs and Employment. The contribution of Mr. S. Monté to the preparation of the manuscript is acknowleged.

REFERENCES

Bentson KF (1990) Fate of xenobiotics in foliar pesticides deposits Rev Environ Contam Toxicol 114:125-161.

Brouwer DH, Brouwer R, De Mik G, Maas CL, Van Hemmen JJ. (1992[a]) Pesticides in the cultivation of carnations in greenhouses. Part I: Exposure and concomitant health risks. Am ind Hyg Assoc J 53:575-581.

Brouwer R, Brouwer DH, Tijssen SCHA, Van Hemmen JJ. (1992[b]) Pesticides in the

cultivation of carnations in greenhouses. Part II: Relationship between between foliar residues and exposure. Am Ind Hyg Assoc J 53:582-587.

Brouwer R, Marquart H, De Mik G, Van Hemmen J. (1992[c]) Risk assesment of dermal exposure to greenhouse workers to pesticides after re-entry. Arch Environ Contam Toxicol 23:273-280.

Brouwer DH, De Vreede JAF, Ravensberg JC, Engel R, Van Hemmen JJ. (1992[d])Dissipation of aerosols from greenhouse air after application of pesticides using a low volume technique. Implications for safe re-entry. Chemosphere 28:1135-1146.

Brouwer R, Van Maarleveld K, De Kort WLAM, Van Hemmen, JJ (1993) Skin contamination, airborne concentrations, and urinary metabolite excretion of propoxur during harvesting of flowers in greenhouses. Am J Ind Med 24:593-603.

Brouwer DH., De Vreede JAF., De Haan M, Van De Vijver L., Veerman M, Stevenson H, Van Hemmen JJ (1994). Exposure to pesticides during and after application in the cultivation of chrysanthemums in greenhouses. Health risk and risk management. Med. Fac. Landbouww Univ Gent 59/3b:1393-1401.

Dong MH, Krieger RI, Ross JH (1992) Calculated Reentry interval for table grape harvesters working in California vineyards treated with methomyl Bull Environ Contam Toxicol 49:708-714.

Goedicke HJ (1988) Rückstandstoxicologische Bewertungen des Einsetzes von Pflanzenschutzmittelen und Mitteln zur Steurung Biologische Prozesse in Gemüse unter Glas und Plasten [Residue based toxicological considerations for the use of pesticides in greenhouse crops] Die Nahrung 32:565-570.

Goedicke HJ (1989) Exposition durch Rückstände auf Planzenoberflächen nach Anwendung von Pflanzenschutsmittelen im Gewächshaus. [Exposure from foliar residues after use of pesticides in greenhouses] Z Gesamte Hyg 35:531-533.

Van Hemmen JJ, Brouwer R, Brouwer DH (1992) worker exposure to pesticides in greenhouses. Health risks during harvesting of flowers. Med Fac Landbouww Univ Gent 57/3b:l269-1283.

Van Hemmen JJ (1993) Re-entry exposure and product development. Pesticides and greenhouse crops: an example. In: Agrochemical Occupational Risk Assessment. The Future. Seminar, Brussels, Belgium, Jelllinek, Schwartz and Connolly, Washington DC, USA.

Van Hemmen JJ, Van Golstein Brouwers YGC, Brouwer DH (1995) Pesticide exposure and re-entry in agriculture. In: Curry PB, Iyengar S, Maroni M (eds) Methods of Pesticide Exposure Assessment, Plenum Press, New York, pp 9-19.

lwata Y, Knaak JB, Spear RC, Foster RJ (1977) Worker re-entry into pesticide- treated crops: I Procedure for the determination of dislodgeable residues on foliage. Bull Environ Contam Toxicol 10:649-655

Jongen MJM, Engel R, Leenheers L (1991[a]) High performance liquid chromatography method for the determination of occupational to the pesticide abamectin. Am Ind Hyg Assoc J 52:433-437.

Jongen MJM, Engel R, Leenheers L (1991[b]) Determination of the pesticide chlorothalonil by HPLC and UV detection for occupational exposure in the production of ornamentals. J Anal Toxicol 15:30-34.

Krieger RI, Blewitt C, Edmiston S, Fong HR, Meinders DD, O'Connell LP, Schneider F, Spencer J., Thongsinthusak T, Ross JH. (1991) Gauging pesticide exposure of handlers and harvesters in California agriculture. La Medicina del Lavora 8 1:474-479

Nigg HN, Stamper JH, Queen RM, (1984) The developement and use of a universal model to predict tree crop harvester pesticide exposure. Am lnd Hyg Assoc J 45: 182-186.

Popendorf WJ, Leffingwell JT (1992) Regulating OP pesticide residues for farmwork protection. Residue Rev 82:125-199.

Ravensberg JC, Langenhuizen N (1993) Gas chromatografic determination of mancozeb by headspace and electron capture detection (in Dutch). TNO Medical Biological Laboratory. Report BT-053, Rijswijk, The Netherlands.

Reeve MW, O'Connell, Bissell S, Ross J (1992) Characterization of methomyl dissipation on grape foliage Bull Environ Contam Toxicol 49:105-111.

Saiz, SG (1993) Dislodgeable and penetreted captan residues on strawberry foliage: Spatial diffferences in deposition and decay. California Department of Food and Agriculture. Report HS 1663.

Soekhoe U, Kerstens HJ (1995) Determination of propoxur, methiocarb and tinopal on gloves, filters, and leaves by high performance liquid chromatography. TN0 Nutrition and Food Institute, Department of Occupational Toxicology, Rijswijk, The Netherlands, Report BT-076 (in Dutch).

Willis GH, McDowell LL (1987) Pesticide persistence on foliage. Rev Environ Contam Tox 100:23-62.

Zweig G. Leffingwell JT, Popendorf W (1985) The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues. J Environ Sci Health B20:27-59.

De Vreede JAF, De Haan M, Brouwer DH, Van Hemmen JJ, De Kort WLAM (!994) Exposure to pesticides. Part III Application of methomyl to chrysanthemums in greenhouses. S 131-4. Ministery of Social Affairs and Employement, The Hague, The Netherlands.