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Lindane and Methylparathion Residue Degradation in Carnation Byproduct (*Dianthus caryophyllus*, L.) under Different Environmental Conditions

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Carnation plant (*Dianthus caryophyllus, L.*) is an important ornamental cultivar in Southern Spain. A byproduct is obtained from this crop consisting mostly in leaves and stems that has a good nutritive value for animals. But pesticide contamination resulting from agriculture practices for pest control limits the safe use of this byproduct as animal feed (Cerón, 1993).

Although insecticide residues in food is causing great concern to international health authorities, most reports and research are related to products used for human consumption. A limited number of reports address residues and their degradation in vegetables destined for animal feed (Waldron and Goleman, 1969; Johnson et al., 1972; Shivankar and Ram, 1988).

Lindane and methylparathion are pesticides heavily used in carnation and can produce toxic effects in animals due to the consumption of aldulterated carnation byproducts (Cerón, 1993). The purpose of this work is to study the degradation of lindane and methylparathion in carnation plant and in the carnation byproduct under different environmental conditions of storage prior to its usage as an animal feed. A knowledge of these events may provide a basis to avoid contamination of animal foods and to safely feed the carnation byproduct to animals.

MATERIAL AND METHODS

The carnation plants were grown at an experimental greenhouse in Los Urrutias (45 km south of Murcia, Spain), and were collected during the second year of growth. Commercial formulations of lindane (90% dust) and methylparathion (35% emulsifiable concentrate) were sprayed March 10, 1992 onto a plot measuring 10 m^2 at the recommended field application rates of 0.270 kg/Ha (300 l/Ha) and 0.105 kg/Ha (300 l/Ha) respectively (Cerón, 1993). A control plot was included for blank analysis.

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One sample of 100 g was collected two hours after spraying (day 0). Twenty four hours after the application, 5 kg of byproduct was obtained from the plot, 100 g was used for 24 hours analysis and rest of the byproduct was divided in three subsample groups of approximately 1.6 kg each:

- Group A was exposed to the open air. Mean temperature during experimental period was 15.3°C, with mean maximum of 24.7°C and minimum of 7.6°C (n=48 days). Average relative humidity was of 57% and average sunshine hours were 8.77. Rainfall took place between 23-27 March and 2-9 April with a total rainfall of 8.7 mm.
- Group B was washed with tap water, one sample was taken following washing to determine the decrease of pesticide residues and the rest of the subsample was exposed to the open air.
- Group C was placed in an enclosed container to simulate storage of the byproduct within a confined area. The mean inside temperature with the enclosure was 26°C.

Representative samples (100 g) of the 3 groups and of greenhouse plots were collected the days 7, 14, 21, 28, 35 and 49 following the application. The mean greenhouse temperature during the experimental period was 22°C, with a mean maximum of 30°C and a minimum of 15°C. Samples were brought to the laboratory in plastic bags, minced in a food chopper for homogenization and kept frozen (-20°C) until analysis. Sample dry matter was determined by drying a separate 50 g subsample to constant weight at 105°C.

Extraction of lindane and methylparathion were carried out according to the method of Andersson (1986). Vegetable samples were homogenized with acetone, filtered through anhydrous Na_2SO_4 and the homogenate was partitioned into n-hexane-dichloromethane using liquid-liquid extraction, followed by cleaned up on florisil microcolumn prior to gas chromatographic analysis.

An Autosystem Perkin Elmer GLC, fitted with ^{63}Ni source electron capture detector and silica column (30 m x 0.25 mm i.d.) packed with 0.25 µm of SPB-5 (Supelco^R) was used for lindane quantification and identification. The operating temperatures were: column oven 250°C, injection port 250°C and detector 300°C. The carrier gas (nitrogen) flow rate was 1 ml/min (make up 90 ml/min). A Sigma 4B Perkin Elmer GLC was employed to determine methylparathion residues under these conditions:

- Column: 30 m x 0.75 mm i.d. glass column packed with 1 µm of SPB-5 (Supelco^R).
- Detector: termoionic nitrogen-phosphorus specific detector (NPD).
- Carrier gas: nitrogen at a flow rate of 15 ml/min.
- Operating temperatures: injector, 250°C; detector, 250°C and column 200°C.

The recoveries obtained with the above mentioned procedure for carnation byproduct samples fortified with lindane at different levels between 0.02-1 mg/kg were of 98.38%±0.43, and with methylparathion at the same levels was of

97.33%±0.16. The theoretical limit of sensitivity obtained were 0.001 mg/kg in case of lindane and 0.0008 mg/kg for methylparathion. Standards were obtained from Agricultural Chemistry Department of Murcia University.

RESULTS AND DISCUSSION

Results of lindane and methylparathion residues evolution in the greenhouse and in the three groups are shown in tables 1, 2 and 3. Results were analyzed and kinetic studies were done based on data expressed on 100% dry matter, (real dry matter percents appear in table 4), because values calculated on a dry basis are more useful when related to animal feeding according to Beck et al. (1966). Initial deposits of lindane and methylparathion were of 66.15 and 27.36 mg/kg respectively.

Methylparathion had a faster decrease (with no detectable residues at 21 days) compared with lindane. This fast degradation is typical of organophosphorous compounds with high vapour pressure (Barbera, 1989). Waldron and Goleman (1969) reported a rapid decline in methyparathion residues on green alfalfa after the application of this compound at the rates of 0.54 kg/Ha and 1.08 kg/Ha. Similarly to our results, a long persistence of lindane residues have been found after the treatment of a pasture, mixture of perennial ryegrass (Lolium perenne, L.) and white clover (Trifolium repens, L.), with this organochlorine at a rate of 2.23 kg/Ha (Collet and Harrison, 1968).

Residues of the byproduct following washing with tap water were decreased by 22.91% of original levels in case of lindane and by 47.92% for methylparathion (table 5). The minor reduction of lindane is probably due to the low solubility of this compound in water versus that of other pesticides such as organophosphates (methylparathion) which are removed in bigger amounts (Contreras and Aguera, 1991). But there are other factors (not only water solubility) that have an important influence in the disappearance of pesticides following washing such as the interaction with plant constituents or the different emulsifiers and coadjuvants that can be included in the formulation (Talekar et al., 1977; Ong et al., 1988).

Kinetic studies of lindane and methylparathion are shown in tables 6 and 7, and in figures 1, 2 and 3 are represented the disippation kinetics of lindane and methylparathion under different conditions ajusted to an exponential equation. According to the pesticide degradation curves based on experimental data, evolution of lindane and methylparathion in all groups studied fits pseudo-first order kinetics. Thus, linear regression analysis was used to calculate the kinetic constants for each pesticide on the different groups according to the equation $\ln R = \ln R_0 - kt$, where "R" is the pesticide residue level (mg/kg); "R_0" is the theoric initial residue level; "k" is the degradative constant (day^{-1}), and "t" the time after spraying (days).

Methylparathion had bigger k absolute values and smaller half lives compared with lindane. There was a faster decrease of lindane and methylparathion in open air exposed groups (Groups A and B) compared with group C that had lower k absolute values and higher half lives, possible due to the lack of exposure to environmental factors such as high temperatures, solar radiation, or wind movement, which enhance pesticide residue degradation (Edwards, 1974; Navarro, 1985).

If the data were expressed on green-weight basis, there would be an increase on residue levels in Groups A, B and C in relation with residues in byproduct from the greenhouse compared with the results on dry weight (specially after 21 days in case of lindane and 14 with methylparathion) because the residue content in the drying process virtually increases to the same extent that the water content decreases. So special provision must be made in advance to provide safety to livestock that will consume the harvested product destined for the preparation of hay, according to Maier-Bode (1968).

Values of lindane residues 49 days after spraying were below 1 ppm in greenhouse and Groups A and B, but only byproduct from greenhouse were found to be below the maximum residue levels in feeds for animals (0.2 mg/Kg on green weight basis) recommended by Noble (1990), that are the same as, or bigger than the levels set in U.S.A. (0.1 mg/kg), Germany (0.1-0.2 mg/Kg) or the Netherlands (0.1 mg/Kg) for lindane in stockfeed (Noble, 1990). According to the equation $\ln R = \ln R_0 - kt$, values of lindane residues would be below the levels in feeds recomended by Noble (1990) 53, 52 and 146 days after spraying in Groups A, B and C respectively. Methylparathion residues after 14 days were below 0.17 ppm (green weight) in the greenhouse and groups A, B and C. These ammounts are below the maximum residue levels established in vegetables in the European Union (0.2 mg/kg green weight) and U.S.A. (1 mg/kg green weight) (Contreras and Aguera, 1991).

Table 1. Lindane and methylparathion residues (mg/kg) in carnation byproduct from greenhouse.

Days after treatment	Lindane		Methylparathion	
	Dry weight	Green weight	Dry weight	Green weight
0	66.15	12.10	27.36	5.00
1	64.28	11.24	18.37	3.21
7	60.05	10.38	7.91	1.36
14	21.53	3.97	0.34	0.06
21	6.50	1.28	N.d.	N.d.
28	5.50	1.01	-	-
35	4.14	0.79	-	-
49	0.74	0.13	-	-

Table 2. Lindane residues (mg/kg) in carnation byproduct under different conditions.

	Group A		Group B		Group C	
Days*	D. w.	G. w.	D. w.	G. w.	D. w.	G. w.
0	64.28	11.24	64.28	11.24	64.28	11.24
6	20.25	10.88	19.90	9.75	61.95	10.47
13	14.74	10.69	14.38	10.09	38.03	11.40
20	6.45	5.28	2.92	2.42	24.07	10.17
27	1.14	0.98	2.00	1.74	18.48	9.54
34	1.06	0.92	0.91	0.79	14.65	11.79
48	0.72	0.63	0.62	0.55	12.81	10.67

Table 3. Methylparathion residues (mg/kg) in carnation byproduct under different conditions.

	Group A		Group B		Group C	
Days*	D. w.	G. w.	D. w.	G. w.	D. w.	G. w.
0	18.37	3.21	18.37	3.21	18.37	3.21
6	0.91	0.48	0.65	0.31	1.85	0.31
13	0.12	0.08	0.06	0.04	0.58	0.17
20	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.

* Days after groups were made.

D.w. (dry weight); G.w. (green weight)

Table 4. Dry matter percent of carnation byproduct.

Days	Greenhouse	Group A	Group B	Group C
0	18.30	-	-	-
1	17.50	-	-	-
7	17.30	53.77	49.00	16.91
14	18.46	72.57	70.20	30.00
21	19.82	81.93	83.21	42.29
28	18.43	86.71	87.00	51.66
35	19.21	87.32	87.50	80.50
49	18.72	87.85	88.76	83.31

Table 5.Disappearance of lindane and methylparathion residues following washing with tap water.

	Lindane	Methylparathion
Initial levels (mg/kg)	64.28	18.37
Levels after washing (mg/kg)	49.55	9.56
% of reduction	22.91	47.92

Table 6. Kinetic study of lindane.

Parameters	Greenhouse	Group A	Group B	Group C
R_0 (ppm)	75.2563	42.5040	39.8172	62.2774
Stand. error	1.3645	1.7939	1.6736	1.2245
k (days)	-0.0926	-0.0990	-0.0998	-0.0380
Stand. error	0.0067	0.0143	0.0126	0.0049
Half life (days)	7.48	7.00	6.94	18.21
r^2	0.9687	0.9053	0.9259	0.9222
r	0.9842	0.9541	0.9622	0.9603

Table 7. Kinetic study of methylparathion.

Parameters	Greenhouse	Group A	Group B	Group C
R_0 (ppm)	31.3840	14.3823	14.2962	14.2905
Stand. error	1.8074	1.7456	1.7693	1.7709
k (days)	-0.2989	-0.3843	-0.4375	-0.2630
Stand. error	0.0529	0.0605	0.0620	0.0621
Half life (days)	2.31	1.80	1.58	2.63
r^2	0.9409	0.9757	0.9803	0.9471
r	0.9700	0.9877	0.9901	0.9731

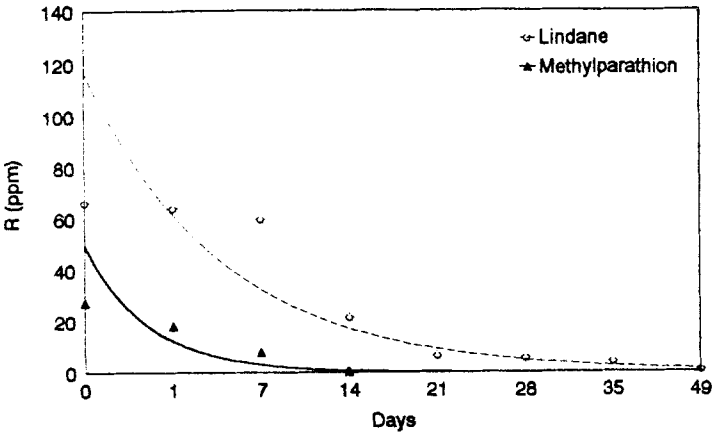

Figure 1. Dissipation curves of lindane and methylparathion in greenhouse.

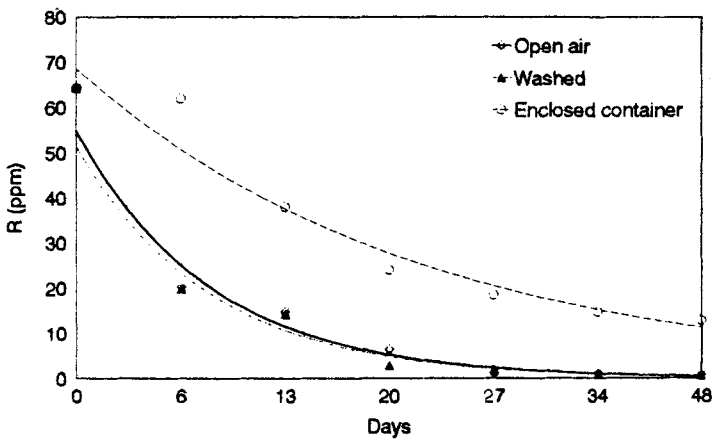

Figure 2. Dissipation curves of lindane under different environmental conditions.

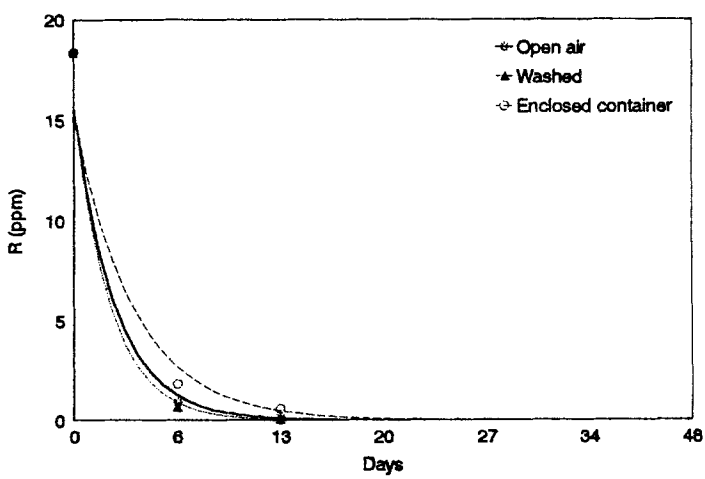

Figure 3. Dissipation curves of methylparathion under different environmental conditions.

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REFERENCES

Andersson A (1986) A capillary gas chromatographic multirresidue method for determination of pesticides in fruits and vegetables. Var Foda 38:79-109.

Barbera C (1989) Pesticidas agrícolas, 4th ed. Omega, Barcelona.

Beck EW, Johnson JC, Woodham D, Leuck D, Dawsey H, Robbins J, Bowman M (1966) Residues of endosulfan in meat and milk of cattle fed treated forages. J Econ Entomol 59:1444-1450.

Cerón JJ (1993) El subproducto de clavel (Dianthus caryophillus) en la alimentación animal: problemática de los residuos de plaguicidas. Thesis, Murcia University.

Collet JN, Harrison DL (1968) Lindane residues on pasture and in the fat of sheep grazing pasture treated with lindane prills. NZ J Agr Res 11:589-600.

Contreras M, Aguera A (1991) Plaguicidas agrícolas. Recopilación de propiedades y LMRs. Coexphal, Almeria.

Edwards CA (1974) Factors that affect the persistence of pesticides in plants and soils. Pesticide Chemistry 3. I.U.P.A., 39. Butterworths, London.

Johnson JC, Bowman MC, Leuck DB, Knox FE (1972) Persistence of dasanit in corn silage and effects of feeding dairy cows the treated silage. J Dairy Sci 56:775-781.

Maier-Bode H (1968) Properties, effect, residues and analytics of the insecticide endosulfan. Res. Rev., 22:1-39.

Navarro S (1985) Residuos de plaguicidas en productos agrícolas. II Jornadas sobre la Química Agrícola en el País Vasco, Alava.

Noble A (1990) The relation between organochlorine residues in animal feeds and residues in tissues, milk and eggs: a review. Aust J Exp Agr 30:145-154.

Ong KH, Ch`ng AL, Chua GC, Chua SB, NG BB, Luck SC (1988) Dissipation of pesticide residues from leafy vegetable, Cai Xin (Brassica Chinensis). Sing J Pri Ind 16:41-59.

Shivankar VJ, Ram S (1988) Estimation of insecticidal residues on lucerne. J Entomol Res 12:4-8.

Talekar NS, Sun LT, Lee EM, Chen JJ, Lee TM, Lu S (1977) Residual behaviour of several insecticides on chinese cabbage. J Econ Entomol 70:689-692.

Waldron AC, Goleman DL (1969) Ethyl and methylparathion residues in green and cured alfalfa. J Agr Food Chem 17:1066-1069.