Behavior of Some Pesticide Residues on Greenhouse Tomatoes. 2. Fungicides, Acaricides, and Insecticides

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Experiments were carried out on greenhouse tomatoes for studying the degradation kinetics of two insecticides (Deltamethrin and Permethrin), one acaricide (Dicofol), and four fungicides (Fenarimol, Triadimefon, Chinomethionat, and Pyrazophos) and for estimating the residues left by repeated applications on fruits harvested at commercial ripening. Fenarimol, Triadimefon, and Chinomethionat completely degraded in three weeks while all the others a.i. showed considerable persistence. Except for Chinomethionat and Pyrazophos, an accumulation of residues left by repeated applications was observed, as already noted by several authors with other a.i. Remarks on residue values and limits fixed by Italian Food Safety Regulations are made with suggestions for avoiding toxic hazards.

Greenhouse tomatoes are grown in Sardinia between Nov and May. During this season the most frequent diseases are due to *Botrytis cinerea* and *Phytophthora infestans*. The behavior of some families of fungicides used against these pests has been described by several authors (Vanachter et al., 1979; Van Wambeke et al., 1980; Cabras et al., 1982, 1985).

Owing to market demand there has recently been a trend toward a growing season from July to Feb. In this case the diseases most commonly found are due to a fungus (*Erysiphe taurica* Lev.), a mite (*Tetranycus urticae* Koch.), and insects (*Trialeurodes vaporariorum* Westw. and *Myzus persicae* Sulz.). The pesticides most used in Sardinia for their control are the pyrethroid insecticides (i) Deltamethrin and Permethrin, the acaricide (a) Dicofol, and the fungicides (f) Fenarimol, Triadimfeon, Pyrazophos, and Chinomethionat. The latter is sometimes used even as an acaricide.

Data on the behavior of the resdiues of these a.i. are scarce (Balayannis, 1974; Harris et al., 1977; Balinov and Balinova, 1982; Grounds, 1983). As part of a project involving the study of the behavior of the main pesticides applied to greenhouse tomatoes, we carried out a trial according to the aims and criteria already described in a previous paper (Cabras et al., 1985).

MATERIALS AND METHODS

The trial was carried out in a 500-m^2 air-warmed glasshouse with galvanized iron framework. The tomato variety employed was Vemone F1 (SLUGRO), seeded on July 29, 1983, and transplanted on Sept 5, 1983. A completely randomized block design was adopted with four replications. Each single plot had 8 plants spaced 30 × 80 cm, and plant density of 36 plants/m^2. Samples weighing 500 g were gathered starting on Jan 9, 1983 (at the beginning of commercial ripening) and carried on thereafter at weekly intervals. Pesticide sprayings were performed according to manufacturers specifications (Table I) and to the schemes reported in Table II by using combinations of (1f + 1a + 1i) or (1f + 1f) or turning to a different fungicide after each application.

Pesticides were sprayed every 10 or 20 days, up to the beginning of sampling. The degradation kinetics of each a.i. was studied following the doses suggested by the manufacturers (single dose experiment, SDE) and/or doubling them (double dose experiment, DDE). Harvesting was performed 0, 1, 2, 4, 7, 14, and 21 days after the application (Table IV) and weekly after the preharvest time (Table V).

Table I. Application Rates and Legal Limits of Pesticides on Tomatoes Fixed in Italy

pesticide	application rate, g a.i./hl[a]	tolerance levels, ppm	preharvest interval/timing, days
Fenarimol	3.00	0.10	21[b]
Triadimefon	4.00	1.00	2
Chinomethionat	10.00	0.30	7
Pyrazophos	24.0	0.10	7[b]
Dicofol	27.75	0.50	15
Daltamethrin	1.40	0.50	3
Permethrin	7.89	1.00	2

[a] The spray volume ranged between 45 and 60 hl/ha according to the vegetative growth. [b] At the present time approved only on cucurbitaceae.

Table II. Application Scheme[a]

scheme	sprayed a.i.	date of treatment: Nov			Dec		
I	D + E + F	9		29		19	
II	B + E + G	9		29		19	
III	C + G	9	18	29	9	19	29
IV	A + E + F	9		29		19	
V	B + D	9	18	29	9	19	29
VI	A + C	9		29		19	
VII	D, B, C, A turning	9, D	19, B	29, C	9, A		29, D

[a] A = Fenarimol: B = Triadimefon; C = Chinomethionat; D = Pyrazophos; E = Dicolfol; F = Deltamethrin; G = Permethrin.

Average monthly temperatures in the greenhouse were as follows. Nov: max 24.1 °C and and min 13.5 °C. Dec: max 22.1 °C and min 13.0 °C. Jan: max 21.7 °C and min 12.2 °C.

Apparatus and Chromatography. A Varian 5020 solvent delivery system (Palo Alto, CA) equipped with a UV/vis variable wavelength UV 50 detector, Valco AH 20 injector (loop 50 μL), and a Hewlett-Packard 3390 A reporting integrator was employed. Columns, chromatographic conditions, Minimal Detectable Values (MDV), and recoveries are reported in Table III. MDV are calculated as previously reported (Cabras et al., 1982). The standard curve of each pesticide was constructed by plotting peaks areas vs. concentrations by using the external standard method. A good linearity was achieved in the range 0–1 ppm.

Chemicals. Water was distilled twice and filtered through a MilliQ. apparatus. Acetonitrile was HPLC grade

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Table III. Chromatographic Conditions and Recovery

pesticide	column	flow, mL/min	mobile phase H_2O–CH_3CN	t_R, min	λ, nm	M.D.V., ppm	fortification level, ppm	% recovery[a] ± RDS
Fenarimol	RP 8	1.5	50:50	5.41	200	0.01	0.1	93.6 ± 4.9
							0.5	103.4 ± 2.9
Triadimefon	RP 8	1.5	50:50	6.22	200	0.02	0.1	97.6 ± 5.5
							1.0	96.4 + 2.6
Chinomethionat	RP 8	1.5	50:50	9.91	215	0.02	0.1	94.1 ± 3.8
							0.5	92.6 ± 1.7
Pyrazophos	RP 8	1.5	50:50	11.00	240	0.02	0.1	92.5 ± 4.7
							0.5	89.5 ± 3.6
Dicofol	RP 8	1.5	30:70	5.41	200	0.02	0.1	81.4 ± 2.3
							0.5	77.8 ± 4.4
Deltamethrin	RP 8	1.5	30:70	8.77	200	0.02	0.1	88.3 ± 7.8
							0.5	90.9 ± 8.5
Permethrin	RP 8	1.5	30:70	9.31 (cis) 10.39 (trans)	200	0.02	0.1	91.1 ± 6.3
							1.0	94.2 ± 9.0

[a] The reported values are the means of duplicated analyses from four replicates.

Table IV. Residues (ppm ±SD) at Intervals (Days) after Application[a]

pesticide	rate	day 0	1	2	4	7	14	21
Fenarimol	SDE	0.05 ∓ 0.01	0.03 ∓ 0.00	0.03 ∓ 0.02	0.01 ∓ 0.00	*b*	*b*	*b*
	DDE	0.12 ∓ 0.03	0.09 ∓ 0.02	0.09 ∓ 0.02	0.12 ∓ 0.02	0.07 ∓ 0.04	0.05 ∓ 0.01	*b*
Triadimefon	SDE	0.07 ∓ 0.01	0.08 ∓ 0.03	0.04 ∓ 0.01	0.03 ∓ 0.01	*b*	*b*	*b*
	DDE	0.12 ∓ 0.03	0.17 ∓ 0.02	0.15 ∓ 0.01	0.20 ∓ 0.07	0.17 ∓ 0.08	0.08 ∓ 0.03	0.03 ∓ 0.01
Chinomethionat	SDE	0.10 ∓ 0.04	0.14 ∓ 0.04	0.07 ∓ 0.01	0.06 ∓ 0.01	0.07 ∓ 0.01	0.04 ∓ 0.00	*b*
	DDE	0.26 ∓ 0.08	0.23 ∓ 0.03	0.16 ∓ 0.03	0.19 ∓ 0.07	0.13 ∓ 0.04	0.11 ∓ 0.04	0.06 ∓ 0.03
Pyrazophos	SDE	0.15 ∓ 0.05	0.18 ∓ 0.05	0.26 ∓ 0.06	0.14 ∓ 0.05	0.19 ∓ 0.03	0.14 ∓ 0.03	0.12 ∓ 0.07
	DDE	0.23 ∓ 0.04	0.20 ∓ 0.05	0.38 ∓ 0.10	0.23 ∓ 0.07	0.34 ∓ 0.09	0.31 ∓ 0.13	0.19 ∓ 0.04
Dicofol	SDE	0.27 ∓ 0.07	0.33 ∓ 0.11	0.38 ∓ 0.04	0.53 ∓ 0.20	0.59 ∓ 0.18	0.40 ∓ 0.09	0.52 ∓ 0.19
	DDE	0.68 ∓ 0.10	0.59 ∓ 0.14	0.78 ∓ 0.16	0.80 ∓ 0.23	0.83 ∓ 0.15	0.78 ∓ 0.17	0.71 ∓ 0.13
Deltamethrin	SDE	0.08 ∓ 0.04	0.06 ∓ 0.03	0.06 ∓ 0.02	0.08 ∓ 0.01	0.13 ∓ 0.04	0.07 ∓ 0.01	0.06 ∓ 0.02
	DDE	0.16 ∓ 0.05	0.16 ∓ 0.04	0.18 ∓ 0.07	0.14 ∓ 0.04	0.16 ∓ 0.02	0.08 ∓ 0.01	0.11 ∓ 0.05
Permethrin	SDE	0.10 ∓ 0.01	0.07 ∓ 0.01	0.12 ∓ 0.04	0.15 ∓ 0.01	0.15 ∓ 0.09	0.10 ∓ 0.01	0.05 ∓ 0.03
	DDE	0.14 ∓ 0.07	0.12 ∓ 0.04	0.20 ∓ 0.09	0.26 ∓ 0.11	0.20 ∓ 0.10	0.12 ∓ 0.09	0.09 ∓ 0.06

[a] The reported values are the means of duplicated analyses from four replicates. [b] Not detectable.

Table V. Residues (ppm ±SD) on Tomato at Commercial Ripening

pesticide	treatment scheme	no. of applicatns	preharvest interval, days	days after preharvest interval[a] 0	7	14	21	28	35
Fenarimol	IV	3	20	0.11 ∓ 0.02	0.05 ∓ 0.01				
	VI	3	20	0.08 ∓ 0.01	0.03 ∓ 0.02				
	VII	1	30	*b*					
Triadimefon	II	3	20	0.03 ∓ 0.01	0.07 ∓ 0.03				
	V	6	10	0.06 ∓ 0.03	0.08 ∓ 0.02				
	VII	1	50	*b*					
Chinomethionat	VI	3	20	*b*	*b*				
	III	6	10	0.05 ∓ 0.01	0.03 ∓ 0.00				
	VII	1	40	*b*					
Pyrazophos	VII	2	10	0.11 ∓ 0.03	0.04 ∓ 0.01				
	I	3	20	0.15 ∓ 0.02	0.14 ∓ 0.03				
	V	6	10	0.27 ∓ 0.09	0.14 ∓ 0.03				
Dicofol	I	3	20	0.90 ∓ 0.16	0.74 ∓ 0.09	0.41 ∓ 0.07	0.21 ∓ 0.07	0.21 ∓ 0.07	0.19 ∓ 0.06
	II	3	20	1.14 ∓ 0.31	0.83 ∓ 0.01	0.41 ∓ 0.29	0.21 ∓ 0.03	0.25 ∓ 0.07	0.24 ∓ 0.03
	IV	3	20	0.68 ∓ 0.19	0.51 ∓ 0.15	0.37 ∓ 0.01	0.21 ∓ 0.09	0.19 ∓ 0.03	0.15 ∓ 0.05
Deltamethrin	I	3	20	0.16 ∓ 0.06	0.15 ∓ 0.03	0.08 ∓ 0.01	0.06 ∓ 0.03	0.03 ∓ 0.01	
	IV	3	20	0.11 ∓ 0.04	0.10 ∓ 0.03	0.06 ∓ 0.02	0.03 ∓ 0.01	0.03 ∓ 0.01	
Permethrin	II	3	20	0.31 ∓ 0.04	0.26 ∓ 0.04	0.11 ∓ 0.07	0.05 ∓ 0.02	0.03 ∓ 0.01	
	III	6	10	0.39 ∓ 0.03	0.24 ∓ 0.06	0.13 ∓ 0.04	0.06 ∓ 0.03	0.03 ∓ 0.02	

[a] The reported values are the means of duplicate analyses from four replicates. [b] Not detectable.

solvent, while cyclohexane and benzene were pesticide grade solvents (all from Carlo Erba, Milan, Italy). Fenarimol (>99.0%), Triadimefon (>99.0%), Chinomethionat (>99.0%), Pyrazophos (>99.0%), Dicofol (>99.0%), Deltamethrin (>99.0%), and Permethrin (>91.0%) were kindly supplied by Siapa (Milan, Italy), Bayer (Milan), Hoechst (Milan), and ICI Solplant (Milan).

Extraction Procedure. Tomatoes (0.5 kg), sampled as previously described, were homogenized for 5 min at 3000 rpm with a Waring apparatus (Tecnochimica, Rome). Homogenate (50 g) was shaken by hand for 5 min in a 250-mL screw-capped flask (Sovirel, France) with 50 mL of a cyclohexane–benzene (8:2, v/v) mixture. Thereafter we carried on by centrifuging for 5 min at 3000 rpm, drawing off 5 mL of clear organic extract in a 25-mL beacker, and evaporating to dryness under reduced pressure (600 mmHg) at 45 °C. The residue was recovered with 5.0 mL of mobile phase, by scraping with a glass stick

equipped with a Teflon spout. This procedure enabled us to obtain the recovery percentages expected (Table III) from blank tomatoes treated with known amounts of pesticides.

RESULTS AND DISCUSSION.

Tables IV and V show respectively the data of the evolution of pesticide residues after a single spraying experiment and the residues found on tomatoes after repeated spraying, according to the schemes shown in Table II.

Fenarimol. This a.i. showed low levels of residue even just after spraying (0.05 ppm); the residue disappeared so rapidly that after a week it was no longer detectable. Following repeated spraying, that amount of residue was even higher than that left by single spraying with double doses. In the latter case the residue became indetectable after three weeks while on tomatoes sprayed three times there was still a residue of about 0.1 ppm.

Triadimefon. The behavior of this fungicide was very similar to that of Fenarimol, with a very low residue following single spraying and a very fast degradation kinetic. The residues left by repeated spraying were always less than 0.1 ppm, much lower than the maximum (1 ppm) fixed by Italian regulations.

Chinomethionat. This a.i. also showed low levels of residues (0.10 ppm) after spraying; it required a longer degradation time and did not show residual accumulation after repeated spraying; 20 days after the last of a series of three sprayings there was no detectable residue, and ten days following the last of six sprayings there was a residue of only 0.05 ppm.

Pyrazophos. This fungicide showed a low level residue after single spraying but with considerable persistence; after 21 days, only slight degradation occurred. However, residue data for repeated sprayings did not reveal differences varying with the number of sprayings; at the 20th and 14th day after the last of 3 and 6 sprayings, respectively, we found the same residue value.

Dicofol. The degradation curves of this acaricide showed an odd trend marked by an increase in content during the first week after spraying followed by a slight decrease during the next two weeks. The amount of residues after repeated sprayings (3) is higher than the amount left by a single spraying, being twice as much at the 20th day. These values decreased progressively thereafter, but only at the 34th day reached the figure of 0.5 ppm fixed as a maximum by the Italian regulations.

Pyrethroids. Both Deltamethrin and Permethrin show a very slow degradation with very little decrease during the first three weeks after spraying. However, they differ in the amounts of residues left on the fruits after repeated sprayings; at three weeks both left more residue than after a single spraying, but with a 2-fold increase for Deltamethrin and a 6-fold increase for Permethrin.

CONCLUSIONS

After spraying shows Fenarimol and Triadimefon completely desappeared in a very short time (1 week in SDE) while Chinomethionat took longer (3 weeks in SDE). The others a.i. studied showed instead a notable persistence; only in the case of Dicofol, the residue trend was characterized by an increase during the first week and a slight decrease in the following two weeks. Up to the present we are unable to explain satisfactorily this behavior even if it could be supposed that the molecules of the a.i. undergo initially a slight modification that gives a higher adsorbance at the wavelength used, this modified product then degrading and forming other compounds which do not interfere further with the signal of the a.i. In this way, there could be an increase in the detector signal, indicating a higher a.i. concentration.

The accumulation effect, formerly noted by several researchers on other pesticides after repeated sprayings (Cabras et al., 1985), was not confirmed for all the a.i. studied. The residue values of Chinomethionat and Pyrazofos were not positively correlated to the number of treatments. On the other hand, the lack of synergic and/or antagonist effects on the amount of residues left by multiple sprayings was confirmed.

Triadimefon, Chinomethionat, Deltamethrin, and Permethrin showed quite safe residue values on commercial fruits. Fenarimol too, owing to its very rapid degradation and to the very low amounts of a.i. sprayed, should not create problems even if the maximum amounts allowed in Italy for other crops are quite low (0.1 ppm).

Dicofol and Pyrazophos, on the other hand, have a high persistence and should be used with more care, avoiding routine sprayings and, in any case, making sure that a sufficiently long time elapses before harvesting.

Registry No. Deltamethrin, 52918-63-5; permethrin, 52645-53-1; dicofol, 115-32-2; fenarimol, 60168-88-9; triadimefon, 43121-43-3; chinomethionat, 2439-01-2; pyrazophos, 13457-18-6.

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