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Residues of Dimethoate and Omethoate in Peaches and Apples following Repeated Applications of Dimethoate

Júlia R. Ferreira,* Manuela M. Falcão,[1] and Antônio Tainha

Repeated applications of dimethoate were carried out on peaches and apple trees in order to establish the maximum number of dimethoate sprays that will give rise to residues complying with international maximum residue limits. Samples were analyzed by gas chromatography for the determination of dimethoate and its oxygen analogue, omethoate, over a period of 3–4 weeks after last spray. Only in the case of apples with seven applications, mean residues of dimethoate exceeded 1 ppm at the end of the preharvest interval (14 days); residue levels of omethoate were always below 0.2 ppm. Considering the eventual need of a preharvest interval not longer than 14 days, restrictions on the number of applications during apples growth cycle should be enforced.

The insecticide dimethoate, *O,O*-dimethyl *S*-[(methylcarbamoyl)methyl] phosphorodithioate, is officially approved in Portugal for use on peach trees with a preharvest interval of 2 weeks and restricted to two applications at 40 g a.i./hl (a.i. = active ingredient), mainly to control the Mediterranean fly, and for most peach varieties no more than two applications will be necessary. Considering the control of other pests on peach trees, namely aphids, we assume that up to three applications of dimethoate during peach growth cycle might be made.

As far as apple trees are concerned, the dimethoate preharvest interval is 2 weeks and its wider use is, by far, against *Carpocapsa pomonella*. Although efforts are being made at national level in order to decrease the number of treatments, the use of dimethoate about every 2 weeks is still current, especially among traditional farmers. This practice can lead to a total of about seven applications during apple growth cycle.

During 1960–1970 considerable work on the disappearance of dimethoate, namely on peaches and apples, was carried out and reviewed by Pietri-Tonelli (1965) and by the Joint Meetings of the WHO/FAO (1968, 1971, 1978). Studies on peaches and oranges were carried out in Portugal by Silva Fernandes (1972, 1973) using the method of analysis of the Joint Dimethoate Residues Panel (1968). In these latter studies residues were determined as the sum of dimethoate and its oxygen analogue metabolite omethoate [*O,O*-dimethyl *S*-[(methylcarbamoyl)methyl] phosphorothioate]. For this reason, no information is given on the levels of this compound, also used as an insecticide and for which different countries have established separate and lower maximum residue limits.

Considering the insufficient information on residues of dimethoate to be expected in the case of some severe agricultural practices still used, together with the interest of determining omethoate residues resulting from the above-mentioned use of dimethoate, residue disappearance studies were carried out in order to assess whether the preharvest interval established in Portugal complies with international maximum residue limits.

MATERIALS AND METHODS

Field Treatments and Sampling. The trial on peach trees was set up at Pegões Experimental Field. One set of nine trees was selected from one row of the orchard for the execution of two applications; a second set of nine trees was selected from a different row for the execution of three applications. In both cases each set of three contiguous trees was considered as a field replicate for sampling. Details of the experiment are described in Table I. Sprays were carried out at high volume to the point of runoff with a wheelbarrow sprayer provided with a two-stroke engine-driven diaphragm pump operated at 20 kg/cm^2.

Average maximum daily air temperatures recorded at Pegões climatological station were 24.4 °C from 23 May up to the end of the month, 26.4 °C in June, and 26.9 °C from then to final sampling. For the same periods total rainfalls were 4.0, 6.6, and 6.8 mm.

Samples of 18 peaches were randomly collected from each field replicate on days 1, 4, 7, 11, 14, and 21 after the last application. Fruits used as controls were picked from trees separated from the treated plots by an unsprayed row. Samples were transported to the laboratory in plastic bags, the stones were removed, and the pulp was chopped in a Hobart food cutter. Three 100-g subsamples of pulp were taken for analysis.

The trial on apple trees was set up at Quinta de São João, Caldas da Rainha. Two sets of nine cordon-grown apple trees (palmette form) were used for the execution

Centro Nacional de Protecção da Produção Agrícola (INIAER), Quinta do Marquês, 2780 Oeiras, Portugal.
[1]Present address: Instituto Nacional de Investigação das Pescas, Centro de Investigação Pesqueira, 8000 Faro, Portugal.

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Table I. Details of the Experiments

trial	location	year	crop	variety	type of formulation	active ingred content of formulation, g/L	concn in spray, g a.i./hl	no. of appl	dates of appl
1	Pegões	1982	peach	EA 68-50	ec[a]	400	40	2	8 June 24 June
								3	27 May 8 June 24 June
2	Caldas da Rainha	1982	apple	Golden Delicious	ec[a]	400	50	5	3 June 23 June 14 July 6 Aug 26 Aug
								7	3 June 17 June 30 June 14 July 29 July 12 Aug 26 Aug

[a] ec = emulsifiable concentrate.

Table II. Residues of Dimethoate and Omethoate on Peaches Resulting from Multiple Applications with Dimethoate

no. of appl	days between last appl and harvest	residues found,[a] ppm							
		field replicate 1		field replicate 2		field replicate 3		mean	
		dimethoate	omethoate	dimethoate	omethoate	dimethoate	omethoate	dimethoate	omethoate
2	1	1.8	0.09	2.2	0.09	1.7	0.07	1.9	0.08
	4	1.3	0.09	1.4	0.08	1.5	0.05	1.4	0.07
	7	0.89	0.08	1.0	0.09	0.98	0.09	0.95	0.09
	11	0.54	0.07	0.66	0.05	1.0	0.08	0.73	0.07
	14	0.54	0.08	0.64	0.08	0.73	0.06	0.64	0.07
	21	0.52	NA[b]	0.61	NA	0.57	NA	0.57	
3	1	2.4	0.19	2.5	0.20	2.0	0.18	2.3	0.19
	4	1.6	0.15	1.8	0.17	1.5	0.15	1.6	0.16
	7	1.3	0.16	1.5	0.17	1.4	0.15	1.4	0.16
	11	1.2	0.14	1.2	0.14	1.0	0.15	1.1	0.14
	14	1.1	NA	1.2	NA	0.83	NA	1.0	
	21	0.9	NA	0.7	NA	0.86	NA	0.82	

[a] Mean of three analyses. [b] NA = not analyzed.

Table III. Residues of Dimethoate and Omethoate on Apples Resulting from Multiple Applications with Dimethoate

no. of appl	days between last appl and harvest	residues found,[a] ppm							
		field replicate 1		field replicate 2		field replicate 3		mean	
		dimethoate	omethoate	dimethoate	omethoate	dimethoate	omethoate	dimethoate	omethoate
5	1	1.7	0.12	2.1	0.14	1.7	0.14	1.8	0.13
	4	1.7	0.10	1.7	0.11	1.2	0.11	1.5	0.11
	7	1.5	0.10	1.3	0.10	1.2	0.12	1.3	0.11
	12	1.0	0.09	1.2	0.12	1.1	0.11	1.1	0.11
	14	0.79	0.09	0.93	0.09	0.86	0.09	0.86	0.09
	21	0.80	0.11	0.92	0.12	0.79	0.14	0.84	0.12
	28	0.74	NA[b]	0.72	NA	0.68	NA	0.71	
7	1	2.7	0.16	2.5	0.14	2.6	0.16	2.6	0.15
	4	2.3	0.18	2.1	0.18	1.8	0.15	2.1	0.17
	7	2.1	0.15	1.9	0.16	1.9	0.16	1.9	0.16
	12	1.8	0.15	1.8	0.14	1.5	0.14	1.7	0.14
	14	1.7	0.16	1.5	0.14	1.4	0.12	1.5	0.14
	21	1.6	0.13	1.4	0.14	1.1	0.12	1.4	0.13
	28	1.3	0.12	1.4	0.11	1.3	0.11	1.3	0.11

[a] Mean of three analyses. [b] NA = not analyzed.

of five and seven applications, respectively. Each set of three contiguous trees formed, in both cases, a field replicate for sampling. Details of the experiment are described in Table I. Sprays were carried out at high volume to the point of runoff with the same type of sprayer used for peaches.

Average daily air temperatures recorded at Caldas da Rainha were 16.9 °C in June and 18.3 °C in July. Total rainfalls in June and July were 20.4 and 10.1 mm, respectively. Unfortunately, no climatological data were available for the period after July.

Samples of 18 apples were randomly collected from each field replicate on days 1, 4, 7, 12, 14, 21, and 28 after the last application. Fruits used as controls were picked from trees separated from the treated plots by an unsprayed row. Samples were transported to the laboratory in plastic bags and chopped in a Hobart food cutter after removal of the stems. Three 100-g subsamples were taken for analysis.

Residue Analysis. Both peach and apple samples were analyzed for the determination of dimethoate and omethoate. Extraction was carried out by blending at high

speed for 3 min with acetone, according to the general method of Ferreira and Silva Fernandes (1980) used in this laboratory for the determination of organophosphorus insecticides in fruits and vegetables, but the amount of samples and extracting solvent has been doubled.

An aliquot of the aqueous acetone, equivalent to a 50-g sample, was transferred into a separatory funnel, 75 mL of water added, and partition carried out with two 50-mL portions of hexane. The organic layers were discarded and dimethoate and omethoate extracted from the aqueous layer by partitioning with four portions of chloroform (200 + 100 + 100 + 100 mL). The chloroform phases were dried over anhydrous sodium sulfate and combined. The solvent was totally evaporated in a rotary vacuum evaporator at 40 °C and the residue taken in a suitable volume of acetone for GLC determination.

Chromatographic analysis was carried out with a Varian Aerograph 2700 gas chromatograph equipped with thermionic rubidium sulfate detector and glass column (1 m × 2 mm (i.d.)) packed with 4% Reoplex 400 on 80–100-mesh Gas Chrom Q. Operating conditions: injector temperature, 225 °C; oven temperature, 200 °C; detector temperature, 240 °C; carrier (nitrogen) flow, 40 mL/min; hydrogen flow, 40 mL/min; air flow, 150 mL/min. Under these conditions retention times of 3.9 and 5.6 min were observed, respectively, for omethoate and dimethoate.

It should be emphasized that satisfactory gas chromatographic conditions were only achieved after 3 days of continuous injections of microgram amounts of dimethoate and omethoate alternately with plant extracts.

Recovery experiments were carried out at fortification levels ranging from 0.1 to 1 ppm with untreated peaches and apples by adding appropriate aliquots of dimethoate and omethoate standard solutions prior to the addition of the extracting solvent. Mean recoveries were higher than 90% for dimethoate but not greater than 80% for omethoate. Results obtained at each fortification level showed satisfactory repeatability for both compounds. The detection limit of the method is 0.01 ppm for dimethoate and 0.05 ppm for omethoate.

RESULTS AND DISCUSSION

The results of the studies are shown in Tables II and III for peaches and apples, respectively. Those values are expressed on the whole commodity and have not been corrected for recovery efficiencies. Residues of the oxy analogue omethoate were found in both peaches and apples but rarely exceeded 10% of the parent compound. Besides, omethoate residues were relatively similar throughout sampling time, which is in accordance with studies on sweet cherries reported by Zwick et al. (1977).

In the case of peaches, the effect of remaining old residues from previous applications does not seem to have influenced significantly the rate of dimethoate disappearance, as the calculated half-lives for two and three applications did not differ statistically. The situation was however different for the treatments carried out on apples, in which case dimethoate apparent half-life with seven applications was higher than with five applications.

In the case of two applications on peach trees and five applications on apple trees a maximum residue limit of 1 ppm could be accepted on the basis of the existing 2 weeks of preharvest interval. However, if peaches are sprayed three times during the season, the same preharvest interval may not be sufficient to guarantee residue levels below 1 ppm at harvest time, especially when we consider the extent of possible variations of the residue levels due mainly to different climatic conditions or peach varieties. In the case of seven applications of dimethoate on apple trees, residue data show that the preharvest interval necessary to comply with the 1 ppm limit would be too high to be acceptable for an efficient control of the pest; for this reason, the practice of carrying out seven applications of dimethoate during the apple growth cycle should be discontinued, and a restriction on the maximum number of applications should be enforced.

Registry No. Dimethoate, 60-51-5; omethoate, 1113-02-6.

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