

Residues of Some Pesticides in Fresh and Dried Apricots

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The persistence of three pesticides (fenitrothion, dimethoate, and ziram) in apricots in field conditions and their fate during the drying process were studied. After the treatments, the pesticides showed fast decay rates with pseudo-first-order kinetics and half-lives ranging from 6.9 to 9.9 days. The drying process showed a different effect on residue concentrations in dried apricots: omethoate (metabolite of dimethoate) and ziram residues had almost doubled, while fenitrothion disappeared and dimethoate remained constant.

Keywords: Residues; pesticides; apricot; dried apricot

Apricot production is widely diffuse in the Mediterranean area. Italy is the major producer followed by Spain, Greece, and France (Scorza and Hui, 1996). Among fruit-bearing plants, apricot is considered a minor crop. Perhaps for this reason few studies (Patsakos et al., 1992; Miliadis et al., 1995; Liapis et al., 1995) on pesticide residues in fresh apricots and in the dried fruit have been carried out. From the point of view of pesticide residues, the production of dried fruits is remarkably interesting, since during the drying process the fruit is concentrated about 5 times. For this reason the residues in fruit should be increased by this factor. In this paper the persistence of three pesticides (fenitrothion, dimethoate, and ziram) in field conditions and their fate during the drying process were studied.

MATERIALS AND METHODS

Field Trials. The trial was carried out in an apricot orchard (cv. Boccuccia) of Agricola Mediterranea SpA, located at San Giovanni di Uta, near Cagliari, Italy. The grove was planted in 1988 with a planting space of 3.9×4.7 m. A random-block design with four replications was used, and each block contained 69 plants in a single row. Treatments were carried out with a KWH 1500 pneumatic sprayer (C. Martignani, Lugo, Ravenna, Italy). The following commercial formulations were used: Cuman (containing 26.9% ziram), Fenitrocap (containing 23.15% fenitrothion), and Stigor (containing 38% dimethoate) at the doses 807, 694, and 570 g of active ingredient/ha, respectively, using a volume of 350 L/ha. A first treatment with fenitrothion and ziram was performed on June 7, 1996, while a second treatment with dimethoate was performed on June 10, 1996. The weather conditions were continuously recorded with an SM 3800 automatic weather station (SIAP, Bologna, Italy). Rainfall was continuously recorded with an AD-2 automatic weather station (Silimet, Modena, Italy). During the experiments, total rainfall was 23 mm. Maximum and minimum average temperatures were 29.6 and 14.1 °C, respectively. Samplings on dry plants started about 1 h after the first treatment and were repeated at 3, 10, 17, 24, 31, and 38 days. Sixty-nine fruit samples were randomly collected from each block and immediately analyzed for pesticide residues.

Sample Preparation. The apricots were counted and weighed to determine the average weight. At the last sampling at commercial ripening, double the number of fruits was

collected and divided into two groups. A part was immediately analyzed for pesticide residues, and the rest was dried prior to residue analysis. Each sample was chopped and homogenized with a Workset Cutter 4L instrument (Malvasi, Bologna, Italy).

Fruit Drying Conditions. At harvest the fruits were washed for 5 min in running water, cut into halves, and pitted. They were then placed in a ventilated oven at 100 °C for 30 min and at 70 °C for 12 h. The moisture content of the dried fruits was reduced to about 21–23%. The dried fruits were rehydrated to 33–35% moisture content by immersion for 20 min in water containing 1% ascorbic acid at 20 °C. The samples were analyzed immediately after rehydration.

Chemicals. Fenitrothion, dimethoate, omethoate, and ziram were analytical standards purchased from Ehrenstorfer (Augsburg, Germany). Triphenyl phosphate (99%) was used as the internal standard (i.s.) and was of analytical grade (Janssen, Geel, Belgium). Ethyl acetate and methanol were HPLC grade solvents (Carlo Erba, Milan, Italy), while benzene and ethanol were analytical grade solvents. Sodium hydroxide, hydrochloric acid, tin(II) chloride dihydrate, copper(II) acetate monohydrate, carbon disulfide, and diethanolamine were of analytical grade (Carlo Erba). Stock standard solutions of the pesticides (ca. 500 mg/kg each) were prepared in methanol. Working standard solutions were obtained by dilution with the extract of untreated fruits in ethyl acetate containing the i.s. at 0.3 mg/kg.

Apparatus and Chromatography. An HRGC Mega 5160 gas chromatograph (Carlo Erba) was employed. It was fitted with an N-40 nitrogen-phosphorus detector, an AS 550 autosampler (Carlo Erba), and a split-splitless injector, connected to an HP 3396-II reporting integrator (Hewlett-Packard, Avondale, PA). A Durabond fused silica column (30 m \times 0.25 mm i.d., film thickness 0.25 μ m) (J&W Scientific, Folsom, CA) was employed, with a DB 1701 liquid phase (14% (cyanomethyl)propylmethyl silicone). The injector and the detector were operated at 250 and 260 °C, respectively. The sample (2 μ L) was injected in the splitless mode (60 s), and the oven temperature was programmed as follows: 90 °C for 1 min, to 180 °C (15 °C/min), then to 250 °C (5 °C/min), and to 280 °C (10 °C/min), and held for 6 min. Helium was the carrier and make-up gas at 120 and 130 kPa, respectively, while hydrogen and air were both at 100 kPa. Calibration graphs for the pesticides were constructed with the i.s. method by measuring peak heights vs concentrations. Good linearities were achieved in the 0–5 mg/kg range, with correlation coefficients between 0.998 and 0.999. A Varian DMS 90 UV–vis spectrophotometer was employed.

Residue Analysis. Analyses of dimethoate, omethoate, and fenitrothion were performed by gas chromatography, while ziram was determined by spectrophotometry using the classical method for dithiocarbamate analysis (Manuale UNICHIM, 1981). UNICHIM method is based on the acid hydrolysis of dithiocarbamate with release of CS₂. The carbon disulfide

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Table 1. Residues (mg/kg \pm SD) of Some Pesticides in Apricots after Treatment and in Dried Apricots

days after first treatment	fruit weight (g \pm SD)	dimethoate ^b	omethoate	fenitrothion	ziram ^a
0	18 \pm 1			1.49 \pm 0.14	2.08 \pm 0.53
3	20 \pm 1	1.51 \pm 0.16	0.04 \pm 0.01	1.00 \pm 0.22	1.22 \pm 0.21
10	27 \pm 2	0.79 \pm 0.06	0.07 \pm 0.01	0.48 \pm 0.05	0.48 \pm 0.25
17	32 \pm 2	0.45 \pm 0.07	0.09 \pm 0.01	0.26 \pm 0.12	0.37 \pm 0.09
24	35 \pm 2	0.22 \pm 0.04	0.07 \pm 0.01	0.09 \pm 0.03	0.28 \pm 0.10
31	36 \pm 2	0.13 \pm 0.05	0.06 \pm 0.01	0.08 \pm 0.04	0.17 \pm 0.11
38	46 \pm 6	0.12 \pm 0.04	0.05 \pm 0.01	0.03 \pm 0.01	0.12 \pm 0.09
Drying Process					
dried fruits	8.6 \pm 0.2	0.14 \pm 0.01	0.10 \pm 0.01	<0.01	0.27 \pm 0.05
rehydrated fruits	10.5 \pm 0.3	0.09 \pm 0.03	0.08 \pm 0.01	<0.01	0.22 \pm 0.06

^a Expressed as CS₂. ^b Dimethoate was applied with a second treatment 3 days after fenitrothion and ziram.

reacts with a solution of copper acetate and diethanolamine. A colored complex is formed, and its absorbance at 435 nm is used for the spectrophotometric determination.

Extraction Procedure. A 5-g portion of sample was weighed in a screw-capped 30-mL tube, 10 mL of ethyl acetate containing the i.s. was added, and the mixture was agitated in a shaker (Stuart Scientific) for 20 min. The phases were allowed to separate, and the organic layer was transferred into another tube. The extraction was repeated, the organic extract was poured into the same tube, and then the combined extract was injected for GC analysis.

Recovery Assays. Untreated samples were fortified with appropriate volumes of standard solutions to reach concentrations of 0.05, 0.5, and 2 mg/kg. Samples were left to equilibrate for 30 min prior to extraction and were processed according to the above procedure. Average recovery from four replicates showed values ranging from 78% to 112% with a maximum coefficient of variation (CV) of 9%.

RESULTS AND DISCUSSION

The data relating to the residues in fruits and the average fruit weight are reported in Table 1. The weight of fresh fruits allowed to evaluate the residue dilution due to fruit growth, while that of dried fruits allowed to evaluate the concentration factor of the fruit due to the reduction in moisture content and to the theoretical residue concentration factor. The values of the preharvest interval (PHI) and maximum residue limits (MRL) used in this discussion are those established by Italian laws.

Residue Disappearance after Treatment.
Dimethoate. After the treatment, residues of dimethoate (1.51 mg/kg) and its metabolite, omethoate (0.04 mg/kg), were determined in the fruit. The residues of the active ingredient (AI) tended to decrease, showing pseudo-first-order kinetics ($r = -0.98$) with a half-life ($t_{1/2}$) of 9.0 days, while omethoate residues tended to increase up to its maximum concentration (0.09 mg/kg) 2 weeks after treatment and then progressively decreased up to 0.05 mg/kg at harvest. Three weeks after the treatment, dimethoate residue was 0.22 mg/kg; therefore, at PHI (20 days) the residue was considerably below the MRL (1 mg/kg).

Fenitrothion. This insecticide showed the fastest decay rate among the pesticides studied. In fact its half-life, calculated as pseudo-first-order kinetics ($r = -0.99$), was 6.9 days. In this experiment the residue, at PHI (20 days), was lower than the legal limit (0.5 mg/kg).

Ziram. The residue (expressed as CS₂) of this AI in fruit (2.08 mg/kg) was of the same magnitude as the MRL (2.0 mg/kg) just after treatment. Subsequently the residue tended to decrease following pseudo-first-order kinetics ($r = -0.97$), with a half-life similar to that calculated for dimethoate ($t_{1/2} = 9.9$ days). At PHI (10 days) ziram residue (0.48 mg/kg) was about one-fourth of the MRL.

The disappearance of all AIs is ascribed to two causes: the degradation process and fruit growth, which

determined a residue dilution of a factor of 2.3 (from 20 g just after treatment to 46 g at harvest) during the experiment.

Residue Disappearance after Drying Process. During the drying process the average fruit weight passed from 46 to 8.6 g, determining a concentration factor of 5.3. If the technological process were irrelevant, pesticide residues on the fruit should increase by this factor, but the data obtained in these experiments showed remarkably different behaviors. Omethoate and ziram residues have almost doubled, while fenitrothion disappeared and dimethoate remained constant. The residue decrease after the drying process could depend on the pesticide distillation during water evaporation. Each pesticide could be distilled in different amounts in accordance with their physicochemical properties.

The rehydration stage led to an increase of ca. 20% in fruit weight and determined a residue reduction of the same magnitude order. This fact indicates that fruit immersion in water, even for long periods, does not have any effect on residue solubilization.

Conclusions. All of the pesticides studied showed quite fast decay rates in apricots, with pseudo-first-order kinetics and $t_{1/2}$ ranging from 6.9 to 9.9 days. At PHI, pesticide residues were considerably below the legal limits. The drying process had a different influence on the residue concentration. Compared to a theoretical decrease of 5.3 times in fruit weight, omethoate and ziram residues almost doubled, while fenitrothion disappeared and dimethoate remained constant.

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