# Pesticide Residues on Field-Sprayed Apricots and in Apricot Drying Processes

Paolo Cabras,*,† Alberto Angioni,† Vincenzo L. Garau,† Marinella Melis,† Filippo M. Pirisi,† Franco Cabitza,‡ and Mario Cubeddu‡

Dipartimento di Tossicologia, Università di Cagliari, viale Diaz 182, 09126 Cagliari, Italy, and Centro Regionale Agrario Sperimentale, 09100 Cagliari, Italy

The disappearance of bitertanol, diazinon, iprodione, phosalone, and procymidone on field-sprayed apricots and their fate during sunlight- and oven-drying processes were studied. After treatments in the field, diazinon disappeared completely after a week, whereas the other pesticides at preharvest time showed residues 50% below MRLs. The pesticides decreased with pseudo-first-order kinetics and half-lives ranging from 9.1 to 24.4 days. The sunlight- and oven-drying processes caused the fruit to concentrate by a factor of ~6 times. Nevertheless, the pesticide residues present in the dried fruit were lower than in the fresh fruit. The residue decreases were higher in the sunlight process than in the oven process. In the former, on average, the residues on the dried fruits were about half those on the fresh fruits, whereas in the latter they were about equal.

**Keywords:** *Apricots; drying processes; pesticides; residues*

Apricot is usually eaten both fresh and transformed (marmalade, juice, and dried fruits). Pesticide residues on the fruit at harvest time could undergo changes during food processing. Dicofol and triadimefon on the fruit at harvest time decreased by 80% during juice processing (Liapis et al., 1995; Miliadis et al., 1995). Since there was no dilution during the process, the decrease in pesticide was attributed to adsorption on the suspended solids removed by filtration. On dried fruit the concentration factor is ~5, but the oven-drying process caused different effects on the amount of residues on fruits at harvest time. Fenitrothion disappeared completely and dimethoate did not change, whereas omethoate and ziram almost doubled (Cabras et al., 1997). The drying process may also occur by sunlight (Scorza and Hui, 1996). In this case the effect on the pesticide residues could be different compared to the oven process because sunlight may have a degradative effect. There are not many studies on pesticide residues on apricots in field conditions and during food processing. In this work we studied the effect of two drying technologies (oven and sunlight) and the disappearance rate in field conditions of five pesticides (i.e., bitertanol, diazinon, iprodione, phosalone, and procymidone) that are commonly used in pest control on apricots.

## MATERIALS AND METHODS

**Field Trials.** The trials were carried out in an apricot orchard owned by Agricola Mediterranea S.p.A. at San Giovanni di Uta near Cagliari, Italy. The grove was planted in 1988 with the cultivar Boccuccia and 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 an F320 pneumatic sprayer (Fox Motori, Reggio Emilia, Italy). The following commercial formulations were used: Zolone (containing 33.6% phosalone), Rovral (containing 50% iprodione), Diazin 20E (containing 19% diazinon), Sumisclex (containing 50% procymidone), and Baycor 25PB (containing 25% bitertanol), respectively, at the doses of 672, 750, 475, 750, and 300 g/ha of active ingredient. Two experiments were carried out: a first treatment with bitertanol, diazinon, and procymidone, and a second treatment with iprodione and phosalone. Both experiments were performed on June 3, 1997, and the plants were sprayed until completely wet. The suspensions used were of ~2 L per plant, corresponding to a total volume of 1000 L/ha. The weather conditions (maximum and minimum average temperatures, relative humidity and rainfall) were continuously recorded with an SM 3820 automatic weather station (SIAP, Bologna, Italy). During the experiments it did not rain, and the maximum and minimum average temperatures were 29.6 and 16.3 °C, respectively.

**Sampling.** Each sample was made up of 25 fruits, randomly collected immediately after the first treatment on the dry plant and repeated at 7, 14, and 21 days. The apricots were counted and weighed to determine the average weight. They were then chopped and homogenized. The last sampling was carried out at commercial ripening, and 100 fruits were collected and divided into four groups. A section was immediately analyzed for pesticide residues, and the remaining part was processed prior to residue analysis.

**Fruit Drying Conditions.** The fruits were cut into halves and pitted. They were then dipped in an aqueous solution of sodium metabisulfite (6 g/L) for 5 min. After dripping, they were placed in a baking pan and dried under the two different conditions: by sunlight for 7 days (from 8:00 a.m. to 8:00 p.m.) and in a ventilated oven at 100 °C for 30 min and at 70 °C for 12 h. During the sunlight experiments the maximum and minimum average temperatures were 32.4 and 20.4 °C, respectively. The moisture content of the dried fruits was reduced to ~21−23%. The dried fruits were rehydrated to a 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.** Bitertanol, diazinon, iprodione, phosalone, procymidone, and vinclozolin were analytical standards purchased from Ehrenstorfer (Augsburg, Germany). Triphenyl phosphate (99%) was used as the internal standard (i.s.) and

* Author to whom correspondence should be addressed (fax 39 70 300740; e-mail pcabras@unica.it).

† Università di Cagliari.

‡ Centro Regionale Agrario Sperimentale.



Published on Web 05/23/1998

**Table 1. Residues of Some Pesticides on Apricots after Field Treatment**

| days after treatment | wt, g | bitertanol mg/kg ± SD | bitertanol av[a] | diazinon mg/kg ± SD | diazinon av[a] | procymidone mg/kg ± SD | procymidone av[a] | wt, g | iprodione mg/kg ± SD | iprodione av[a] | phosalone mg/kg ± SD | phosalone av[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 24.9 ± 3.6 | 1.21 ± 0.26 | 1.21 | 0.87 ± 0.14 | 0.87 | 1.19 ± 0.26 | 1.19 | 28.3 ± 2.5 | 2.25 ± 0.42 | 2.25 | 2.40 ± 0.36 | 2.40 |
| 7 | 32.5 ± 3.5 | 1.05 ± 0.12 | 1.37 | 0.02 ± 0.01 | 0.03 | 0.92 ± 0.17 | 1.19 | 34.2 ± 5.1 | 1.54 ± 0.32 | 1.86 | 1.26 ± 0.29 | 1.52 |
| 14 | 37.7 ± 4.0 | 0.80 ± 0.01 | 1.21 | <0.01 | <0.01 | 0.78 ± 0.13 | 1.17 | 38.5 ± 3.1 | 1.24 ± 0.21 | 1.68 | 0.76 ± 0.18 | 1.03 |
| 21 | 43.3 ± 3.3 | 0.50 ± 0.13 | 0.86 | <0.01 | <0.01 | 0.65 ± 0.08 | 1.12 | 42.5 ± 2.0 | 1.09 ± 0.21 | 1.63 | 0.48 ± 0.14 | 0.72 |
| $t_{1/2}$ (days) | | 16.9 | | | | 24.5 | | | 20.3 | 45.4 | 9.1 | 12.1 |
| $r$ | | −0.97 | | | | - 0.99 | | | −0.97 | −0.95 | −0.99 | −0.99 |

[a] Average residues corrected by dilution due to fruit growth.

**Table 2. Pesticide Residues in Apricots during the Drying Process**

| | fruit wt, g | bitertanol, mg/kg ± SD | diazinon, mg/kg | procymidone, mg/kg ± SD | fruit wt, g | iprodione, mg/kg ± SD | phosalone, mg/kg ± SD |
|---|---|---|---|---|---|---|---|
| fresh fruit | 43.3 ± 3.3 | 0.50 ± 0.13 | <0.01 | 0.65 ± 0.08 | 42.5 ± 2.0 | 1.09 ± 0.21 | 0.48 ± 0.14 |
| sulfitation[a] | | 0.39 ± 0.14 | <0.01 | 0.41 ± 0.10 | | 0.90 ± 0.22 | 0.47 ± 0.17 |
| sunlight drying | 7.7 ± 0.8 | 0.27 ± 0.08 | <0.01 | 0.20 ± 0.10 | 7.6 ± 0.6 | 0.47 ± 0.12 | 0.76 ± 0.19 |
| sunlight drying + rehydration | 9.7 ± 1.1 | 0.22 ± 0.09 | <0.01 | 0.24 ± 0.12 | 9.5 ± 0.9 | 0.29 ± 0.09 | 0.64 ± 0.10 |
| oven-drying | 6.6 ± 0.6 | 0.63 ± 0.20 | <0.01 | 0.34 ± 0.10 | 7.6 ± 1.1 | 1. 45 ± 0.45 | 1.56 ± 0.37 |
| oven-drying + rehydration | 8.5 ± 0.4 | 0.52 ± 0.08 | <0.01 | 0.35 ± 0.10 | 8.7 ± 0.5 | 1.25 ± 0.20 | 1.43 ± 0.23 |

[a] Dipped in an aqueous solution of $Na_2S_2O_5$ at 6 g/L for 5 min.

was of analytical grade (Janssen, Geel, Belgium). Stock standard solutions of the pesticides (~500 mg/kg each) were prepared in methanol. Working standard solutions were obtained by dilution with the extract of untreated fruits in hexane containing the i.s. Hexane and methanol were HPLC grade solvents (Carlo Erba, Milan, Italy).

**Extraction Procedure.** A 10 g portion of homogenized apricot was weighed in a screw-capped 30 mL tube. Ten milliliters of hexane containing the i.s. (vinclozolin at 0.5 ppm for iprodione, and phosalone and triphenyl phosphate at 0.1 ppm for the others) were added, and the mixture was agitated in a shaker (Stuart Scientific) for 30 min. The phases were allowed to separate, and the organic layer was injected for gas chromatopgraphy (GC).

**Apparatus and Chromatography.** An HRGC Mega 2 gas chromatograph (Milano, Italy), with a split−splitless injector and an AS 800 autosampler, connected to an HP 3396-II reporting integrator (Hewlett-Packard, Avondale, PA) was employed. A CP Sil 8 CB silica column (5% phenylmethylsilicone, 25 m × 0.25 mm i.d., film thickness 0.12 $\mu$m, Chrompack, Middelburg, The Netherlands) was employed. The injector and the detector were operated at 240 and 300 °C, respectively. The sample (2 $\mu$L) was injected in the splitless mode (30 s), and the oven temperature was programmed as follows: 110 °C for 1 min, raised to 250 °C (7 °C/min). Helium was the carrier gas at 120 kPa. To determine iprodione and phosalone, an ECD 40 detector was used, with a temperature of 300 °C and nitrogen as makeup at 120 kPa. To determine diazinon, procymidone, and bitertanol, the detector was an NPD-80, the gases were $H_2$ 60 kPa, $N_2$ 80 kPa, and air 130 kPA, the current 2.75 A, and the voltage 3.5 V. Calibration graphs for the pesticides were constructed with the i.s. method by measuring peak heights versus concentrations. A good linearity was achieved in the 0−5 mg/kg range, with correlation coefficients between 0.9987 and 0.9993.

**Recovery Assays.** Samples of untreated apricots were fortified with appropriate volumes of standard solutions to reach concentrations of 0.05, 0.5, and 2 mg/kg. The samples were allowed to settle for 30 min prior to extraction and were then processed according to the above procedure. Average recovery from four replicates showed values ranging from 91 to 108% with a maximum coefficient of variation (CV) of 9%.

## RESULTS AND DISCUSSION

Tables 1 and 2show the evolution of pesticide residues during the drying process and after treatment. The values of the preharvest interval (PHI) and the maximum residue limits (MRL) used in this discussion are those established by Italian laws. The half-lives ($t_{1/2}$) of the residues were calculated following a pseudo-first-order kinetics.

**Residue Disappearance after Field Treatment.** *Bitertanol.* After treatment, the residue level of this active ingredient (AI) in fruit was 1.21 mg/kg, and at harvest time, that is, 3 weeks later (according to the preharvest interval), it was 0.50 mg/kg, which is remarkably lower than the MRL (1.0 mg/kg). The half-life was 16.9 days. Similar results were obtained in supervised trials carried out in France (FAO/WHO, 1988). The disappearance of residues after treatment was mainly due to a dilution effect due to fruit growth and not to degradation. In fact, residue corrected values showed a constant residue in the first 2 weeks, while in the third week there was a loss of ~30%.

*Diazinon.* This pesticide showed a very fast decrease rate. The residue on the fruit after treatment (0.87 mg/kg) almost completely disappeared in less than a week (0.02 mg/kg). These results suggest excessive caution in establishing legal limits (MRL = 0.5 mg/kg and PHI = 15 days).

*Procymidone.* The residue of this AI disappeared in the same way as in bitertanol. After treatment, the residue level was 1.19 mg/kg, whereas at harvest time it was 0.65 mg/kg. Its MRL is 1.5 mg/kg and its PHI 14 days. Just after treatment the residue level was below this value. The half-life ($t_{1/2}$) was 24.5 days. Disappearance of its residue after treatment was due to only dilution due to fruit growth. In fact, the corrected residue values showed a constant residue in all experiment times, showing that the AI did not degrade.

*Iprodione.* This pesticide belongs to the chemical class of the dicarboximides, as procymidone. It showed a disappearance rate that was similar to that of procymidone with a half-life ($t_{1/2}$) of 20.3 days. The residue level was below the MRL (5.0 mg/kg) just after treatment (2.40 mg/kg). The disappearance of the residue after treatment was ascribed both to dilution due to fruit growth and to degradation. The corrected data showed a degradation of 30%, which not considering fruit growth showed a $t_{1/2}$ of 45.4 days.

*Phosalone.* This pesticide showed the highest disappearance rate second only to diazinon with a $t_{1/2}$ of 9.1 days. At PHI (21 days) the MRL (1.0 mg/kg) was met with a residue at harvest time of 0.48 mg/kg, despite a residue after treatment of 2.40 mg/kg. The data corrected by dilution showed that degradation affects residue decrease by ∼70%. Therefore, not considering fruit growth the $t_{1/2}$ was 12.1 days.

**Residue Disappearance after the Drying Process.** *Sulfite Treatment.* The fruits were cut into halves and pitted; they were then dipped for 5 min in an aqueous solution of sodium metabisulfite at 6000 mg/kg (Ramaswamy and Abbatemarco, 1996); therefore, the fruits were also washed. As a result of this, the residues did not decrease with the exception of procymidone, which decreased by 37%.

*Sun-Drying.* Sun-drying caused a fruit concentration factor of 5.6 in both experiments; therefore, theoretically in dried fruits the residues should have increased by the same factor. In all experiments the residue values found after the drying process were almost half those on fresh fruits with the exception of phosalone, for which it increased by 50%.

*Oven-Drying.* Oven-drying caused concentration factors of 5.6 and 6.5 in both experiments. The residue values found in the dried samples were almost the same as in the fresh fruit except for phosalone, which tripled.

Comparison of the residues on fruits after drying with the two processes show that oven-drying gives much higher residues than sun-drying (that are on average double). This could be attributed to photodegradation.

*Rehydratation.* Rehydratation did not involve appreciable changes in residues for any of the pesticides.

**Conclusion.** At harvest time fruits have residue values below 50% of the MRLs. Diazinon disappeared almost completely in a week, whereas the others had decrease rates with $t_{1/2}$ ranging between 9.1 and 24.4 days. In some pesticides the disappearance rate is ascribed only to the dilution effect due to fruit growth (procymidone), whereas in the others there is also a contribution due to degradation, which is the main factor in the disappearance of phosalone.

Despite a weight concentration factor of ∼6 times, the pesticide residues present in the dried fruit were lower than in the fresh fruit. In the sunlight process the residue decreases were higher than in the oven process. In the former on average the residues on the dried fruits were about half those on the fresh fruits, while in the latter they were about equal. The only exception is phosalone, which increases by ∼50% for sun-dried fruit and by 3 times when oven-dried.

## LITERATURE CITED

Cabras, P.; Angioni, A.; Garau, V. L.; Minelli, E. V.; Cabitza, F.; Cubeddu, M. Residues of some pesticides in fresh and dried apricots. *J. Agric. Food Chem.* **1997**, *45*, 3221−3222.

FAO/WHO. *Pesticide Residues in Food*−*1988. Evaluations, Part I*−*Residues*; Paper 93/1; FAO/WHO: Rome, 1988; pp 17−30.

Liapis, K. S.; Miliadis, G. E.; Aplada-Sarlis, P. Dicofol residues on field sprayed apricots and in apricot juice. *Bull. Environ. Contam. Toxicol.* **1995**, *54* (4), 579−583.

Miliadis, G. E.; Aplada-Sarlis, P.; Liapis, K. S. Disappearance of tetradifon from field sprayed apricots and the apricot juice produced from them. *J. Agric. Food Chem.* **1995**, *43*, 1698−1700.

Ramaswamy, H. S.; Abbatemarco, C. Thermal processing of fruits. In *Major Processed Products*; Somogyi, L. P., Barret, D. M., Hui, Y. H., Eds.; Technomic Publishing: Lancaster, PA, 1996; Vol. 1, p 49.

Scorza, R.; Hui, Y. H. Apricots and peaches. In *Major Processed Products*; Somogyi, L. P., Barret, D. M., Hui, Y. H., Eds.; Technomic Publishing: Lancaster, PA, 1996; Vol. 2, pp 37−76.

Received for review January 20, 1998. Revised manuscript received March 29, 1998. Accepted April 1, 1998.

JF980059D