Pesticide Residues in Prune Processing

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Prunes are processed in three phases: washing, drying, and rehydration, which is performed immediately before packing. The entire drying process was subdivided into six steps. In this paper each of these steps was studied separately in order to determine which could be accountable for residue changes. The studied pesticides were diazinon, bitertanol, iprodione, phosalone, and procymidone. Although the drying process caused a fruit concentration factor of 3, the pesticide residues on the dried fruits were not higher than on the fresh fruits. Phosalone showed the same residue, while the values for procymidone, iprodione, and bitertanol were respectively 0.6, 2.3, and 3.2 times lower. The changes in residue values caused by the different steps were not the same in the different pesticides.

Keywords: *Prunes; drying process; pesticides; residues*

Prunes are dried only in ovens, while other fruits such as apricots, grapes, etc., are also sun-dried (Somogy, 1996). The technological process consists of three phases: washing, oven-drying, and rehydration, which is performed immediately before packing. Since the drying process causes a fruit concentration factor of 3−5 times, the amount of pesticide residues in prunes at harvest time should increase by a similar rate, reaching dangerous levels if the different steps of the drying process do not affect their level. A recent paper verified that the drying process affected residue levels with the complete disappearance of vinclozolin (Cabras et al., 1998). There are not many studies on pesticide residues on prunes during the drying process. This work is an attempt to contribute to the knowledge of the fate of some insecticide and fungicide residues (diazinon, bitertanol, iprodione, phosalone, and procymidone) during the drying process.

MATERIALS AND METHODS

Field Treatment. The trial was carried out in a plum orchard owned by Agricola Mediterranea S.p.A., located at San Giovanni di Uta, near Cagliari, Italy. The grove was planted in 1988 with the cultivar D'Ente 707 and a planting distance of 3.9 × 4.7 m. A random-block scheme with four replications for each experiment was used, and each block contained 80 plants on a single row. The treatments were carried out with an F320 pneumatic sprayer (Fox Motori, Reggio Emilia, Italia).

The following commercial formulations were used: Zolone (33.6% phosalone), Rovral (50% iprodione), Diazin 20E (19% diazinon), Sumisclex (50% procymidone), and Baycor 25PB (25% bitertanol), respectively at the doses of 672, 750, 475, 750, and 300 g/ha active ingredient. Two were carried out: one consists of bitertanol, diazinon, and procymidone, the other iprodione and phosalone. The plants were completely wetted with 2 L of solution/plant, up to a total volume of 1000 L/ha on August 19, 1997.

Sampling. Samples were collected at commercial ripening and following the preharvest time of 21 days after last treatment. Four random 180-fruit replicates were collected from each block. Each replicate was subdivided into four groups, two of 60 fruits and two of 30. One of the 30-fruit samples was analyzed immediately in order to determine the residue level in the fresh fruits; the other was subjected to the entire drying process (washing with water for 5 min, oven-drying, and rehydration). One of the 60-fruit samples was washed for 5 min (W_5) and subdivided into two subparcels of 30 fruits each. One of these subparcels was analyzed while the other was washed for another 20 min (W_{25}). The other 60-fruit sample was first dried without washing (D) and then divided in two 30-fruit subparcels, one of which was analyzed immediately while the other was rehydrated (D + R). Therefore six 30-fruit groups were determined for each replicate, namely, step 1, fresh fruit (control); step 2, fresh fruit washed for 5 min (W_5); step 3, fresh fruit washed for 25 min (W_{25}); step 4, oven-dried fruit (D); step 5, oven-dried and rehydrated fruit (D + R); and step 6, fruit from the entire drying process (washing, drying, and rehydration). Each sample represented one of six steps in which the drying process was subdivided in order to determine which steps could be accountable for changes in pesticide residues. Step 3 was included in the experimental plan in order to evaluate whether the decrease in residue due to washing could be attributed to pesticide solubilization.

Drying Technology. The prunes were washed in water for 5 min. After dripping, they were loaded onto drying trays. The trays were then placed in the oven with the following temperature program: 30 min at 95 °C, 30 min at 90 °C, and 16 h at 85 °C. Residual moisture on the fruit was 15−21%. The dried fruits were then rehydrated by immersion in water containing 1% ascorbic acid (20 min at 85 °C). The fruit moisture content was lower by 33−35%.

Chemicals. Bitertanol, diazinon, iprodione, phosalone, procymidone, and vinclozolin were analytical standards purchased from Ehrenstorfer (Augsburg, Germany); triphenyl phosphate was of analytical grade (99%) (Janssen, Geel, Belgium). Stock standard solutions of the pesticides (ca. 500 mg/kg each) were prepared in methanol. Working standard solutions were obtained by dilution with a hexane extract of untreated fruits containing the internal standard (i.s.). The i.s. used were vinclozolin at 0.3 mg/kg for iprodione and

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Table 1. Pesticide Residues in Plums during the Drying Process

steps in drying process	fruit weight (g ± SD)	pesticide residue (mg/kg ± SD)		fruit weight (g ± SD)	pesticide residue (mg/kg ± SD)	
		iprodione	phosalone		bitertanol	procymidone
fresh fruit	38.7 ± 1.3	0.68 ± 0.10	0.21 ± 0.06	38.9 ± 3.6	0.16 ± 0.04	0.37 ± 0.04
after washing for 5 min (W_5)	38.7 ± 1.0	0.27 ± 0.06	0.07 ± 0.01	38.0 ± 1.4	0.13 ± 0.03	0.38 ± 0.05
after washing for 25 min (W_{25})	38.3 ± 0.7	0.29 ± 0.08	0.08 ± 0.02	38.4 ± 0.9	0.15 ± 0.03	0.34 ± 0.06
after drying (D)	12.5 ± 1.2	0.55 ± 0.10	0.62 ± 0.16	12.5 ± 1.6	0.16 ± 0.03	0.35 ± 0.04
after drying (D) + rehydration (R)	14.0 ± 2.2	0.26 ± 0.10	0.49 ± 0.15	13.9 ± 1.7	0.07 ± 0.02	0.24 ± 0.05
after W_5 + D + R	14.5 ± 1.6	0.30 ± 0.09	0.24 ± 0.06	14.1 ± 1.4	0.05 ± 0.01	0.22 ± 0.03

phosalone and triphenyl phosphate at 0.1 mg/kg for bitertanol, diazinon, and procymidone. Hexane and methanol were HPLC-grade solvents (Carlo Erba, Milan, Italy).

Extraction Procedure. A 10-g portion of homogenized plums was weighed in a screw-capped 30-mL tube, and 10 mL of hexane solution containing the i.s. was added. The mixture was agitated in a rotary shaker (Stuart Scientific) for 30 min. The phases were allowed to separate and the organic layer was injected for gas chromatography (GC).

Chromatographic Determination. An HRGC Mega 2 Series gas chromatograph (Carlo Erba, Milan, Italy) was employed. It was fitted with an AS 800 autosampler (Carlo Erba) and a split−splitless injector and was connected to an HP 3396-A reporting integrator (Hewlett-Packard, Avondale, PA). The sample (2 μL) was injected in the splitless mode (30 s).

Iprodione and Phosalone Determination. An ECD 40 detector (320 °C; N_2 as makeup at 120 kPa) and an MDN-35 capillary column (35% phenylmethylsilicone, 25 m × 0.25 mm, film 0.25 μm, Supelco, Bellefonte, PA) were used. The injector temperature was 240 °C. The oven temperature was programmed as follows: 130 °C raised to 310 °C (30 °C/min) and held for 8 min. Helium was the carrier gas at 110 kPa and N_2 was the makeup gas at 150 kPa.

Diazinon, Procymidone, and Bitertanol Determination. An NPD-80 detector was used; the gases were H_2, 60 kPa, N_2, 80 kPa, and air, 130 kPa; the current was 2.75A and the voltage was 3.5 V. A CP-Sil 8 CB fused silica column (5% phenyl, 95% dimethylsiloxane liquid phase, 12 m × 0.32 mm i.d., film thickness 0.25 μm), (Chrompack, Middelburg, The Netherlands) was employed. The injector and detectors were at 240 and 300 °C, respectively. The oven temperature was programmed as follows: 110 °C (1 min) raised to 250 °C (7 °C/min). Helium was the carrier gas and nitrogen was the makeup gas; both were at 120 kPa.

Calibration graphs for the active ingradient (AI) were constructed with the i.s. method by measuring peak heights vs concentrations. Good linearities were achieved in the 0.01−1 mg/kg range, with correlation coefficients between 0.9987 and 0.9993.

Recovery Assays. Untreated samples were fortified with appropriate volumes of standard solutions to reach concentrations of 0.01 and 1 mg/kg. The samples were left to settle for 30 min prior to extraction and were then processed according to the above procedure. The average recovery from four replicates showed values ranging from 91% to 104%.

RESULTS AND DISCUSSION

At harvest time diazinon was the only pesticide that was not found in the fruits analyzed. This pesticide degraded completely in the period between treatment and harvest. Average weight was calculated before pesticide analysis. The data are reported in Table 1.

Iprodione. The residue at harvest time was 0.68 ppm and became 0.30 ppm after the entire drying process (step 6). Considering that the concentration factor was 3 times, the real decrease in residue was about 6 times. Washing for 5 min (step 2) caused a decrease by a factor of 2. Since the residue level after drying (step 4) was similar to that in the fresh fruit, the decrease corresponded to the concentration factor (3 times). These data showed that the total decrease (~6 times) is due to washing for a factor of 2 (step 2) and to drying for a factor of 3 (step 4). The prolonged washing (step 3) of the fruit did not affect the residue level. This could be explained by considering that the pesticide penetrated the epicuticular layer and the cuticola after the treatment (Riederer and Schreiber, 1996), thus avoiding direct contact with water and consequently solubilization.

The decrease in residue after first washing was not attributable to a solubilization process. A reasonable hypothesis could be pesticide adsorption by dust on the fruit during treatment. Washing removed both the dust and the adsorbed residue.

Phosalone. The residue at harvest time was 0.21 mg/kg. The washed sample (step 2) showed a decrease by a factor of 3, from 0.21 to 0.07 mg/kg. After the drying process (step 6) the residue level was 3 times higher (from 0.21 to 0.62 mg/kg). This can be attributed to the concentration factor of the fruit that decreased from 38.7 to 12.5 g. Therefore in the drying process, the residue decrease due to washing was compensated by the residue increase due to drying, therefore the residue level did not change. Prolonged washing and rehydration did not cause any change in the residue level, as in the case of iprodione.

Bitertanol. The residue at harvest time was 0.16 mg/kg and 0.05 mg/kg after the drying process, which corresponds to a decrease of 3.2 times. The average weight decreased from 38.9 g in the fresh fruit to 14.1 g in the dried fruit. The concentration factor was 2.8; the real decrease was therefore about 9 times. Fruit washing for 5 or 25 min did not cause any residue decrease. Apparently the drying process (step 4) did not cause any decrease. Considering a concentration factor of 3.1 times (the fruit weight decreased from 38.9 to 12.5 g), the residue decrease was the same as the concentration factor. The rehydration process (step 5) caused a decrease in the residue level; the total decrease in the active ingredient (AI) was thus due to both these effects combined. Rehydration was carried out at 85 °C. At high temperature the solubility of the compounds in water increased and wax became fluid. This two effects could affect a decrease of residues according to the pesticide's physical−chemical properties.

Procymidone. The residue level after the drying process was 0.22 mg/kg, corresponding to 59% of the residue in the fresh fruit. Considering a concentration factor in the fruit of 2.8, the real decrease was 4.7 times. As for bitertanol, washing (step 2) did not affect the residue level, while drying and rehydration (steps 4 and 5) were the steps of the process that were responsible for the residue decrease.

CONCLUSIONS

Although the concentration factor due to the drying process in prunes was ca. 3, the studied residues were lower in the dried fruit than in the fresh fruit: phosalone showed the same value, while the residue values of procymidone, iprodione, and bitertanol were lower: 0.6, 2.3 and 3.2 times, respectively.

Washing caused an important decrease in iprodione and phosalone, while it did not affect the level of bitertanol and procymidone. Since prolonged washing did not affect residue levels, the residue decrease cannot be attributed to solubilization. The drying phase caused a decrease that was equal to the concentration factor in iprodione, bitertanol, and procymidone, while it did not affect phosalone. Rehydration caused the same effect as washing only in the case of iprodione, while a moderate decrease was found in phosalone and procymidone and a large decrease was found in bitertanol.

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