Food Chemistry 268 (2018) 264–270

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

# Industrial prune processing and its effect on pesticide residue concentrations

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ARTICLE INFO

*Keywords:*
Plums
Insecticides
Processing factor
Food safety

ABSTRACT

The aim of this study was to determine the insecticide residue processing factor (*PF*) from plums to prunes and the effect of the industrial processing of prunes residue concentrations. Our results show an increase of insecticide concentrations during plum dehydration that is explained by fruit water loss; however, the normalized insecticide residue concentration, based on plum dry weights to compensate dehydration, was reduced. The water washing and tenderizing of prunes produced insecticide residue reductions of 22.9 ± 4.5% and 21.9 ± 4.2%, respectively. *PF* were: 1.157, 1.872, 1.316, 0.192, 2.198, 0.775 and 0.156 for buprofezin, L-cyhalothrin, spirodiclofen, indoxacarb, acetamiprid, imidacloprid and emamectin benzoate, respectively, being directly related to water solubility, aqueous hydrolysis and degradation point and inversely related to molecular mass and melting point. In plums for the dehydrated agroindustry the final product is prunes, therefore, it is crucial to consider the *PF* to determine the specific preharvest interval for this important agroindustry.

## 1. Introduction

Raw agricultural products are mainly produced using conventional farming techniques, which often make use of many pesticides to control different pests during the production season. There are more than 300 different pesticides registered worldwide (EU Pesticides Database, 2018). Use of these pesticides in orchards and crops is regulated according to the Maximum Residue Level (MRL). According to the MRL and pesticide efficacies, chemical companies develop their technical recommendations. However, residues can remain in raw products at harvest, resulting in a potential residue transfer to primary processed food (PPF).

According to studies performed in Italy, approximately 30% of foods showed residues below MRLs. The main products contributing residues were fruits and wine, comprising 77 and 15% of intake residues, respectively (Lorenzini, 2007; Pasarella, Elia, Guarino, Bourlot, & Négre, 2009). In a study that determined exposure of the Belgian population to pesticide residues, the authors found pesticides residues in 72% of food samples such as potatoes, orange pulp, banana pulp, dried fruits, oil, wine, and others (Claeys et al., 2011). Nougadere et al. (2012), monitoring vegetables, fruits and PPFs in 36 cities in France, reported that 37% of the samples contained one or more pesticide or metabolites. This finding is a large concern for consumers.

Consumers demand healthy foods with functional properties ("functional foods") and non-detectable levels of pesticide residues. However, agroindustry processes do not always remove pesticides residues because pesticide retention by fruits or other raw products depends on the pesticides' physico-chemical properties (e.g., LogKow, volatility, solubility, etc.) and raw product characteristics (e.g., pH, cuticle, waxes and lipid content) (Athanasopulus & Pappas, 2000; Cabras et al., 1997; Elkins, 1989). Moreover, some agroindustry processes can increase the levels of some pesticide residues as items are turned from raw ingredients into PPFs (e.g., olive oil or raisins) (Amvrazi, 2011; Cabras & Angioni, 2000; Đorđević & Đurović-Pejčev, 2016).

During agroindustry processes, pesticide residues can be dissipated via washing, heating, pasteurization, peeling, storage and/or degraded by photolysis, hydrolysis, oxidation, metabolism, temperature and pH (Amvrazi, 2011; Bajwa & Sandhu, 2014; Kaushik, Satya, & Naik, 2009). However, the current knowledge related to the effect of raw industrial processing is limited, and the majority of published studies have been performed under laboratory conditions (i.e., considering only part of the entire agroindustry process).

The worldwide prune demand has increased by approximately 12%

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https://doi.org/10.1016/j.foodchem.2018.06.090
Received 23 January 2018; Received in revised form 11 June 2018; Accepted 18 June 2018
Available online 19 June 2018

**Table 1**
Formulation and application concentration of studied insecticides, analytical parameters, selected physico-chemical insecticides properties and soil organic carbon adsorption coefficients.[1]

| Pesticide | Formulation | Insecticide concentrations in application solution (g 100 L$^{-1}$) | Recovery | LOQ | LD | Rt (min) | Detector conditions | | Solubility[2] (ppm) | Molecular mass[2] (g mol$^{-1}$) | Aqueous $DT_{50}$[2] (Days) | $HK$[2] (Pa m$^3$ mol$^{-1}$) | $Koc$[3] (L kg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (Average ± SD) | (mg kg$^{-1}$) | | | $m/z$ | λ | | | | | |
| Buprofezin | SC | 30 | 101.1 ± 5.4 | 0.016 | 0.005 | 17.370 | 105 | – | 0.46 | 305.44 | > 51.0 | $2.8 \times 10^{-3}$ | 5363 |
| L-Cyhalothrin | EC | 1.5 | 91.3 ± 4.2 | 0.024 | 0.008 | 29.211 | 181 | – | 0.005 | 449.85 | 7.0 | $2.0 \times 10^{-2}$ | 283,707 |
| Spirodiclofen | SC | 14.4 | 92.4 ± 3.8 | 0.023 | 0.008 | 25.820 | 71 | – | 0.05 | 411.32 | 52.0 | $2.0 \times 10^{-2}$ | 31,037 |
| Indoxacarb | WG | 5.1 | 89.3 ± 4.1 | 0.027 | 0.009 | 31.216 | 59 | – | 0.2 | 527.83 | 22.0 | $6.0 \times 10^{-5}$ | 6450 |
| Acetamiprid | WP | 10.5 | 93.5 ± 3.3 | 0.021 | 0.007 | 17.822 | – | 246 | 2950.0 | 222.67 | > 100.0 | $5.3 \times 10^{-8}$ | 200 |
| Imidacloprid | WP | 21 | 90.7 ± 2.8 | 0.030 | 0.010 | 19.211 | – | 270 | 610.0 | 255.66 | > 100.0 | $2.0 \times 10^{-10}$ | 225 |
| Emamectin benzoate | SG | 1.5 | 102.2 ± 4.3 | 0.001 | 0.0004 | 17.910 | – | Excite: 365 Emission: 470 | 24.0 | 931.0 | > 20 | $1.7 \times 10^{-4}$ | 377,000 |

[1] Referential pesticide properties in: http://sitem.herts.ac.uk/aeru/footprint/es/index.htm.
[2] Solubility at 20 °C; Hydrolysis at pH 7 and 20 °C; Henry Constant at 25 °C.
[3] Soil organic carbon adsorption coefficient.

in the last 10 years. On average, people consume 30 g person$^{-1}$ year$^{-1}$ of prunes; levels can be as high as 420 g person$^{-1}$ year$^{-1}$ in some countries like France (INC, 2017). Given the continuous increase in the world consumption of this healthy food, the aim of this study was to determine the processing factor (*PF*) for plums to prunes for seven insecticides that are currently used by the primary plum-producing countries and the effect of industrial processing steps on insecticide residue concentrations.

## 2. Materials and methods

### 2.1. Plums insecticide applications and the industrial prune-producing process

This study was performed from January through July 2017. Plums, cultivar D'Agen, were harvest at maturity from a commercial orchard located in the Teno, Maule region of Chile (latitude 34°51′S and longitude 71°19′W) and carried to SIDAL Experimental Station facilities in the Casablanca Valley of the Valparaiso region, Chile (latitude 33°14′S and longitude 71°24′W). The plums were then exposed to selected insecticides (Table 1).

The plums (180 kg) were dipped for 1 min in 200 L of insecticide solutions, which were kept on constant recirculation, and then taken out from the pesticide solution. As soon as they dried ( ± 30 min after dipping), the plums were spread on a polyethylene film placed over the soil and exposed to sunlight during the day and covered with another polyethylene film at night to prevent rehydration.

During the sunlight period, the average air temperature was 17.6 °C (maximum: 28.4 °C; minimum: 8.3 °C). The average relative humidity was 67.3%, and the average solar radiation 546.3 W m$^{-2}$; no rain fell. The total dehydration period was 26 days and the plums reduced their water content from 79 ± 4% to 22 ± 2%. After the drying period, the prunes were stored for 77 days at an air temperature of 18.2 °C and 50.5% humidity, which are similar to the conditions that occur in farm cellars.

At the end of the storage period, the prunes were transported for industrial processing to the Pacific Nut Company Chile S.A plant, located in San Bernardo, Metropolitana region, Chile, where they underwent an industrial process. Industrial unitary processes include washing (cold water bath at 13 °C for 1 min; pressure water washing at 13 °C for 1 min and water/solid separator at 15 °C for 0.5 min), tenderizing (tender chamber at 87 °C and 100% humidity for 30 min), pitting, calibration, selection and packaging.

### 2.2. Sampling procedure and pesticide analysis

Three replicated samples ( ± 300 g) of plums or prunes were collected before and after the insecticide applications and after the dehydration period, storage, and the unitary operations noted above. These samples were stored in plastic bags at 4 ± 1 °C until they were carried to the laboratory, where they were stored at −19 ± 2 °C until the residue analysis occurred.

The analytical procedure was obtained from Alister, Araya, Becerra, Saavedra, and Kogan (2017). All of the samples were homogenized using a Grindomix® Knife Mill (Retsch, Germany), and the pesticide residues were analyzed using the QuEChERS method. Five grams of the samples were placed in 50-mL conical polypropylene tubes (Jet Biofil®, Jet Bio-Filtration Co. Ltda, China) and into each tube 5 mL of water was placed to rehydrate the prune samples for 5 h. Then, 10 mL of acetonitrile was added (LiChrosolv®, Merck Millipore, Germany). After agitation (30 min at 180 rpm) (VWR Orbital Shaker DS-500E, VWR International Ltda, USA), the polypropylene tubes were placed into an ultrasonic bath (Branson model 3510, KIMCO, USA) for 10 min. Then, a QuEChERS UCT® (United Chemical Technologies, USA) sachet containing 4 g magnesium sulfate ($MgSO_4$), 0.5 g of disodium citrate ($C_6H_6Na_2O_7$), 0.5 g of trisodium citrate ($Na_3C_6H_5O_7$) and 1 g of sodium