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Effects of Rinsing on Residue Level of Chlorpyrifos Ethyl, Acetamiprid and Penconazole in Grapes

Asiye AKYILDIZ^a, Erdal AĞÇAM^a, Seçil GÜRKAN^b, Berat ÇETİNKAYA^b, Emine KARACA^a, Hakan BENLİ^a

^a Çukurova University, Department of Food Engineering, 01330, Adana, TURKEY

^b Mersin Provincial Control Laboratory, 33130, Mersin, TURKEY

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Corresponding Author: Asiye AKYILDIZ, E-mail: asiye1@cu.edu.tr, Tel: +90 (322) 338 65 37

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ABSTRACT

Effects of various rinsing conditions were investigated to remove residues of three pesticides including chlorpyrifos ethyl, acetamiprid and penconazole from grapes. The rinsing conditions included five different temperatures of rinsing water, three different fruit-to-water ratios and three different dipping times. The residue levels of all three pesticides decreased with decreasing the rinsing water temperature while in most cases, 10, 20 and 30 °C produced lower pesticide residue values when compared to 40 and 50 °C within each of combined treatments. In addition, 4 minutes of dipping time was not as effective as 2 and 3 minutes dipping times to eliminate chlorpyrifos ethyl residue from grape samples at all temperatures.

Keywords: Pesticide residue; Grape; Rinsing treatment; Chlorpyrifos ethyl; Acetamiprid; Penconazole

Yıkama Uygulamalarının Üzümde Chlorpyrifos Ethyl, Acetamiprid ve Penconazole Kalıntısı Üzerine Etkileri

ESER BİLGİSİ

Araştırma Makalesi

Sorumlu Yazar: Asiye AKYILDIZ, E-posta: asiye1@cu.edu.tr, Tel: +90 (322) 338 65 37

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ÖZET

Üzümde uygulanan çeşitli yıkama koşullarının, chlorpyrifos ethyl, acetamiprid ve penconazole içeren üç farklı pestisit kalıntılarının uzaklaştırılmasındaki etkileri incelenmiştir. Yıkama koşulları beş farklı sıcaklığı, üç farklı meyve/su oranını ve üç farklı daldırma süresini içermektedir. Üç pestisit de kalıntı seviyeleri, yıkama suyu sıcaklığının düşürülmesi ile azalmışken, kombine uygulamaların her biri içinde, 40 ve 50 °C ile karşılaştırıldığında 10, 20 ve 30 °C'de daha düşük pestisit kalıntı değerleri elde edilmiştir. Buna ek olarak, bütün sıcaklıklarda, üzüm örneklerinden chlorpyrifos ethyl kalıntısının uzaklaştırılmasında, 4 dakikalık daldırma süresi, 2 ve 3 dakikalık daldırma süreleri kadar etkili olmamıştır.

Anahtar Kelimeler: Pestisit kalıntısı; Üzüm; Yıkama uygulamaları; Chlorpyrifos ethyl; Acetamiprid; Penconazole

1. Introduction

In commercial agriculture, farm productivity can be increased using pesticides with reasonably low costs. Thus, a wide variety and abundance of agricultural commodities can be produced by a relatively small number of farmers. However, pesticide residues remained on agricultural commodities may be a disadvantage of pesticide use. Many of these pesticides residues are also known carcinogens and/or toxins, and therefore, reducing these residues is desirable from a public health point of view (Krol et al 2000). Durmusoğlu et al (2010) reported that the number of the pesticide active ingredients registered in EU countries for use in agriculture is around 250 at the end of 2009. On the other hand, 111 pesticides were registered for use in agriculture in Turkey according to Turkish Food Codex Regulation in 2011 (TGK 2011).

Grapes are one of the most important fruits in the Mediterranean area. Grapes are also suitable to produce juice, raisin, wine and jam and they are also consumed directly as a refreshing fruits. Rinsing the fruits is the most common form of processing which is a preliminary step in both household and commercial preparation. Various types of rinsing processes are available to remove loosely held residues of several pesticides with reasonable efficiencies (Street 1969; Kaushik et al 2009). Foods are generally washed before a further process applied (like washing followed by cooking, washing and drying, washing and peeling and washing, peeling and juicing) to allow for effective decontamination from pesticides (Kaushik et al 2009). There are several studies in that the effectiveness of the rinsing were examined as a part of larger home processing studies (Burchat et al 1988; Çelik et al 1995; Schattenberg et al 1996; Ramesh & Balasubramanian 1999; Krol et al 2000; Ling et al 2011). In addition, a wide variety of rinsing processes to remove pesticide residues have been reported in literature as a step in commercial fruit processing (Mergnat et al 1995; Cabras et al 1997; Cabras et al 1998a; Cabras et al 1998b; Abou-Arab 1999; Krol et al 2000). However, there are limited studies that examined the effectiveness

of various rinsing conditions (rinsing temperature, fruit/water ratio and dipping time) to remove pesticide residues in grapes.

In this study, effects of various rinsing conditions (rinsing temperature, fruit/water ratio and dipping time) were investigated to remove chlorpyrifos ethyl, acetamiprid and penconazole residues in grapes. In addition, degradation kinetics of pesticides was studied during storage in fresh grapes.

2. Material and Methods

Pesticide standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Ammonium formate was obtained from Fluka (Buchs, Switzerland) while primary secondary amine (PSA) was obtained from Supelco (Bellefonte, USA). In addition, magnesium sulphate anhydrous, sodium acetate anhydrous, acetonitrile, glacial acetic acid and methanol were obtained from Merck (Darmstadt, Germany).

2.1. Pesticide applications

In the present study, 3 pesticides were used including two insecticides; chlorpyrifos ethyl and acetamiprid and one fungicide; penconazole. A mixed stock solution of pesticides was prepared by dissolving the commercial preparations of 50 mL of chlorpyrifos ethyl (Dursban 4), 50 g of acetamiprid (Mostar 20 SP) and 39.5 mL of penconazole (Topas 100 EC) in 100 L of tap water. The mixture was applied to the grape bunches on vines uniformly using a garden sprayer. The grapes were then harvested after two days of treatment. The harvested grape bunches were placed in transportation containers and transported to the laboratory for the treatments.

2.2. Rinsing

Several grape bunches were randomly selected from the transportation containers and the fruits were collected in a kitchen container. Then, the grape fruits were randomly assigned for following treatments. Rinsing conditions included five different temperatures of rinsing water (10, 20,

30, 40 and 50 °C), three different fruit/water ratios (grape/water: 1/2, 1/4 and 1/6) and three different dipping times (2, 3 and 4 min). The rinsing treatments were applied in one liter jars that were placed in a water bath shaker. After the rinsing treatments, the rinsing water was removed and the pesticides were extracted from the fruits. All rinsing conditions were replicated three times. Initial pesticides levels were determined using untreated (control) samples to calculate percentages of residues removed from the grapes by various rinsing procedures.

2.3. Extraction and Analysis

Anastassiades et al (2003) recently introduced a quick, easy, cheap, effective, rugged, and safe (QuEChERS) method of pesticide residue analysis that was also used in our study (Lehotay et al 2005). A test portion of 15 g sample was weighed in a 50 mL PTFE centrifuge tube. Subsequently 15 mL of 1% glacial acetic acid in acetonitrile was added into test tube. 6 g anhydrous magnesium sulphate and 1.5 g anhydrous sodium acetate were added and shaken vigorously for 1 min by hand. Tube was centrifuged at 5000 rpm for 3 min. Four mL of the upper layer extract was transferred into dispersive-SPE tubes containing 200 mg PSA + 600 mg anhydrous magnesium sulphate. Tube was shaken for 1 min by hand and centrifuged at 5000 rpm for 3 min. The upper layer of the extract was filtered with 0.45 µm filter and analyzed with LC-MSMS. The flow rate of the mobile phase was 0.25 mL min⁻¹. Injection volume was 10 µL and mobile phase A was 50 mM ammonium formate in water and mobile phase B was 50 mM ammonium formate in methanol. A gradient elution program as follows: initial condition of 20% solution B ramped to 90% linearly over 8 min then held for an additional 6 min. After 15 min, mobile phase was returned to 20% and held to 5 min.

For LC-MSMS analysis, an Applied Biosystems (Toronto, Canada) API 3200 triple quadrupole instrument with electrospray ionization (ESI) was used. The LC instrument was Shimadzu (Japan). The analytical column was a

Phenomenex Synergi 4u Fusion – RP 80A and security guard ODS C₁₈ column. Oven of column was kept at 30 °C in the method (Torrance, CA, USA).

Validation study was carried out according to SANCO (2011). During validation of the analytical method linearity, LOQ (limit of quantification), LOD (limit of detection), trueness and precision were studied. Linearity was studied with six calibration levels (5, 10, 25, 75, 100 ng mL⁻¹ (ppb)) by matrix-matched standard calibration in blank extract of grape. The linearity of each analyte was tested using the least square regression method and the coefficient of determination (R²) was calculated. The trueness and precision of the method was tested via recovery and reproducibility experiments. For each analyte in 6 replicates were analyzed at 3 levels (0.010, 0.050 and 0.1 mg kg⁻¹) to establish recovery. Recovery and RSD% (relative standard deviation) values were calculated for all pesticides and these values were given as Table 1. According to SANCO (2011), values of recovery (%) and RSD (%) should be between 70-120% and under 20% respectively. The values in the table are appropriate to SANCO (2011). LOQ (limit of quantification) and LOD (limit of detection) were determined by analyzing 10 grape. The standard deviation (SD) was calculated. The LOD was calculated for each pesticide as spiking level plus three times the standard deviation. The LOQ was calculated as spiking level plus ten times the standard deviation (Table 2).

LC-MSMS analyses were made duplicated. Control samples were analyzed and the results were determined as mg kg⁻¹ for each rinsing temperatures including 10, 20, 30, 40 and 50 °C. The residue levels of the pesticides following the rinsing treatments were also calculated for each rinsing temperatures and the results were presented as percentages of residues removed from grapes.

2.4. Statistical analysis

SPSS 16.0 for Windows (SPSS Inc., Chicago, IL, USA) software was used for variance analysis of the data and Duncan's multiple comparison test

Table 1- Mean recoveries and RSD values of pesticides*Çizelge 1- Pestisitlerin ortalama geri kazanım ve RSD değerleri*

<i>Pesticides</i>	<i>Spiking level (mg kg⁻¹)</i>	<i>Recovery (%) (n=6)</i>	<i>RSD (%)</i>
Chlorpyrifos ethyl	0.01	93	18.70
	0.05	78	5.56
	0.10	94	4.50
Acetamiprid	0.01	121	2.96
	0.05	90	2.66
	0.10	99	4.36
Penconazole	0.01	94	14.16
	0.05	87	4.60
	0.10	96	3.30

Table 2- LOD, LOQ and R² values of pesticides*Çizelge 2- Pestisitlerin LOD, LOQ ve R² değerleri*

<i>Pesticides</i>	<i>LOD (mg kg⁻¹) (n=10)</i>	<i>LOQ (mg kg⁻¹)</i>	<i>R²</i>
Chlorpyrifos ethyl	0.005	0.007	0.990
Acetamiprid	0.010	0.012	0.988
Penconazole	0.011	0.014	0.997

was used to determine which combined treatments were significantly different at each temperature. In addition, effects of the temperature were determined for each combined treatment. The data for the study were collected in three replications. The combinations evaluated were as follows: 1/2 fruit/water ratio plus 2 minutes dipping time (1/2FW-2M); 1/2 fruit/water ratio plus 3 minutes dipping time (1/2FW-3M); 1/2 fruit/water ratio plus 4 minutes dipping time (1/2FW-4M); 1/4 fruit/water ratio plus 2 minutes dipping time (1/4FW-2M); 1/4 fruit/water ratio plus 3 minutes dipping time (1/4FW-3M); 1/4 fruit/water ratio plus 4 minutes dipping time (1/4FW-4M); 1/6 fruit/water ratio plus 2 minutes dipping time (1/6FW-2M); 1/6 fruit/water ratio plus 3 minutes dipping time (1/6FW-3M); 1/6 fruit/water ratio plus 4 minutes dipping time (1/6FW-4M).

3. Results and Discussion

The efficacy of various rinsing conditions was evaluated to remove chlorpyrifos ethyl, acetamiprid, and penconazole residues in grape samples.

The rinsing conditions included five different temperatures (10, 20, 30, 40 and 50 °C), three different fruit-to-water ratios (grape/water: 1/2, 1/4 and 1/6) and three different dipping times (2, 3 and 4 min). Percentages of chlorpyrifos ethyl residues following various rinsing procedures are shown in Table 3. Chlorpyrifos ethyl is a non-systemic pesticide and the data indicated that removal of chlorpyrifos ethyl residues varied depending on the temperature. 1/2FW-2M produced the lowest chlorpyrifos ethyl residue in grape samples at 10 °C with a residue level of 33.37% ($p < 0.05$). Increasing water temperature to 20 °C resulted in 30.94 and 30.67% ($p < 0.05$) chlorpyrifos ethyl residues for 1/2FW-3M and 1/4FW-2M, respectively. 1/2FW-2M and 1/2FW-3M were the most effective treatments at 30 °C ($p < 0.05$) with residue levels of 23.07 and 29.52%, respectively. Although 1/4FW-3M and 1/6FW-2M resulted in the lowest residue levels for chlorpyrifos ethyl, considerably higher residue levels of 62.81 and 65.95% were obtained for 40 and 50 °C, respectively. Our results indicated that lower water temperatures up to 30 °C tended to remove chlorpyrifos ethyl residues more than higher

temperatures used during the rinsing procedure. Abou-Arab (1999) reported that tomato fruits were covered with a waxy layer and had a very thin skin and the pesticides might easily penetrate the fruits and accumulate inside the pulp. In another study, the solubility of the compounds in water increased and wax became fluid at a high temperature (85 °C) (Cabras et al 1998b). This could explain the penetration of the pesticide into fruit tissue at higher temperatures since chlorpyrifos ethyl is a contact pesticide and increasing water temperature may damage wax layer of the fruit and/or enlarge pore size of the skin.

In addition, 4 min of dipping time was not as effective as 2 and 3 min. dipping times to eliminate chlorpyrifos ethyl residue from grape samples at all temperatures. Similarly, in another study (of plums), two pesticides, iprodione and phosalone, were shown to decrease with a 5 min. wash in water, whereas 2 other pesticides, bitertanol and procymidone, did not show a decrease (Cabras et al 1998a). In addition, a 20 min wash did not change the results. Ling et al (2011) reported mixing results

related to washing with tap water for reduction of chlorpyrifos residue on vegetables. They stated that the tap water reduced the chlorpyrifos residue only by 0.23% in cabbage but 46.6% in tomato. In another study, Krol et al (2000) stated that rinsing time of 30 sec reduced many pesticide residues from a variety of food crops. These results indicated that extending the rinsing time or increasing the intensity of the rinsing procedure might not be an effective approach to eliminate all pesticide residues from fruit tissue due to the penetration of the pesticides into the plant tissue.

Percentages of acetamidrid residues following various rinsing procedures are shown in Table 4. Even though acetamidrid is a systemic pesticide, the data indicated a similar trend to chlorpyrifos ethyl and varied depending on the temperature of the rinsing water. The lowest acetamidrid residue levels of 40.05, 41.55 and 40.80% were obtained at 10 °C using 1/2FW-2M, 1/2FW-3M and 1/4FW-4M treatments as rinsing conditions ($p < 0.05$), respectively. 1/2FW-2M treatment produced also the lowest residue level ($p < 0.05$) of 37.85% in

Table 3- Percentages of chlorpyrifos ethyl residues following various rinsing procedures in grapes

Çizelge 3- Çeşitli yıkama uygulamalarını takiben üzümlerdeki chlorpyrifos ethyl kalıntısının yüzdeleri

Treatments ^a	10 °C	20 °C	30 °C	40 °C	50 °C
Control (mg kg ⁻¹)	0.733±0.21	0.805±0.24	1.080±0.25	1.152±0.28	1.142±0.31
1/2FW-2M	33.37±11.26 ^b	32.96±5.59 ^{BC} _b	23.07±3.29 ^D _c	86.44±1.14 ^{AB} _a	79.17±5.27 ^{AB} _a
1/2FW-3M	34.60±4.27 ^{BC} _c	30.94±5.68 ^C _c	29.52±5.84 ^D _c	86.15±6.89 ^{AB} _a	75.68±5.87 ^B _b
1/2FW-4M	41.33±4.86 ^{AB} _c	34.99±1.07 ^{BC} _d	75.11±4.13 ^A _b	92.03±3.68 ^A _a	76.55±7.44 ^B _b
1/4FW-2M	38.81±2.61 ^{ABC} _c	30.67±1.22 ^C _d	66.80±5.85 ^B _b	72.41±10.93 ^D _{ab}	78.54±6.00 ^{AB} _a
1/4FW-3M	45.21±2.28 ^A _c	40.02±7.77 ^{AB} _c	66.65±7.59 ^B _b	62.81±4.83 ^E _b	79.62±8.31 ^{AB} _a
1/4FW-4M	39.85±1.68 ^{ABC} _c	44.11±9.96 ^A _c	74.43±6.79 ^A _b	83.73±5.55 ^{BC} _a	87.39±9.97 ^A _a
1/6FW-2M	36.49±5.36 ^{BC} _d	47.47±1.25 ^A _c	65.32±6.01 ^B _b	76.94±8.01 ^{CD} _a	65.95±5.69 ^C _b
1/6FW-3M	40.01±6.35 ^{ABC} _c	43.49±1.77 ^A _c	60.68±3.40 ^{BC} _b	77.44±5.09 ^{CD} _a	78.54±6.75 ^{AB} _a
1/6FW-4M	40.26±4.01 ^{ABC} _c	45.91±10.84 ^A _c	57.56±4.97 ^C _b	80.89±7.06 ^{BCD} _a	73.20±6.52 ^{BC} _a

^a, The treatments evaluated were as follows: 1/2FW-2M (1/2 fruit/water ratio plus 2 minutes dipping time); 1/2FW-3M (1/2 fruit/water ratio plus 3 minutes dipping time); 1/2FW-4M (1/2 fruit/water ratio plus 4 minutes dipping time); 1/4FW-2M (1/4 fruit/water ratio plus 2 minutes dipping time); 1/4FW-3M (1/4 fruit/water ratio plus 3 minutes dipping time); 1/4FW-4M (1/4 fruit/water ratio plus 4 minutes dipping time); 1/6FW-2M (1/6 fruit/water ratio plus 2 minutes dipping time); 1/6FW-3M (1/6 fruit/water ratio plus 3 minutes dipping time); 1/6FW-4M (1/6 fruit/water ratio plus 4 minutes dipping time); *, Means followed by different capital letters in each column are significantly different ($p < 0.05$); **, Means followed by different lower case letters in each row are significantly different ($p < 0.05$)

grape samples at 20 °C. Similarly, the most effective rinsing conditions were 1/2FW-2M and 1/2FW-3M to eliminate acetamiprid residues at 30 °C ($p < 0.05$) with residue levels of 42.08% and 40.40%, respectively. In addition, 4FW-3M and 1/6FW-2M treatments produced the lowest acetamiprid residues of 85.94% and 69.88% at 40 and 50 °C, respectively. However none of the combined rinsing conditions at 30, 40 and 50 °C were as effective as the combined rinsing conditions at 10 and 20 °C to remove acetamiprid residues.

The results were similar to the results obtained for chlorpyrifos ethyl residue. Even though chlorpyrifos ethyl is classified as a non-systematic pesticide and acetamiprid is classified as a systematic pesticide our results indicated that similar residue levels were obtained for chlorpyrifos ethyl and acetamiprid following the treatments. This similarity might be explained by differences between some physicochemical properties of these two pesticides since water solubility of the pesticides are quite different. Following are some physicochemical properties of chlorpyrifos ethyl,

acetamiprid and penconazole; solubility in water (at 20 °C, mg L^{-1}) 1.05, 2950.00 and 73.00; melting points (°C) 41.50, 98.90 and 60.30; Kow (octanol-water partition coefficient, pH 7 at 20°C) 5.01×10^4 , 6.10×10^0 and 5.25×10^3 , respectively (PPDB 2013 a, b, c). In a study, Guardia-Rubio et al (2007) also stated that successive washing treatments were highly effective in eliminating several systemic or non-systemic pesticide residues from olive samples. In contrast, Boulaïd et al (2005) were reported that application of an intensive washing to tomato samples did not seem to reduce the residue levels of pyrifenoxy (systemic), pyridaben (non-systemic), and tralomethrin (non-systemic) pesticides.

Percentages of penconazole residues following various rinsing procedures are shown in Table 5. Similar trend to chlorpyrifos ethyl and acetamiprid were also observed with the residues of penconazole, another systemic pesticide, in grape samples following various rinsing procedures. 1/2FW-2M, 1/2FW-3M and 1/2FW-4M treatments produced the lowest residue levels of 30.20%, 35.98% and 36.67% ($p < 0.05$) at 10, 20 and 30 °C, respectively.

Table 4- Percentages of acetamiprid residues following various rinsing procedures in grapes

Çizelge 4- Çeşitli yıkama uygulamalarını takiben üzümdeki acetamiprid kalıntısının yüzdeleri

Treatments ^a	10 °C	20 °C	30 °C	40 °C	50 °C
Control (mg kg^{-1})	0.244±0.36	0.260±0.40	0.322±0.47	0.338±0.51	0.404±0.69
1/2FW-2M	40.05±0.39 ^{C_b}	37.85±13.38 ^{D_b}	42.08±2.65 ^{E_b}	89.84±3.33 ^{DE_a}	88.49±1.23 ^{AB_a}
1/2FW-3M	41.55±1.73 ^{C_d}	57.36±16.10 ^{AB_c}	40.40±0.82 ^{E_d}	93.31±7.00 ^{BCD_a}	78.71±2.09 ^{CDE_b}
1/2FW-4M	46.63±5.42 ^{BC_c}	64.77±4.04 ^{A_b}	94.36±4.65 ^{BC_a}	97.12±2.73 ^{AB_a}	91.30±12.09 ^{A_a}
1/4FW-2M	52.95±1.80 ^{AB_c}	46.52±3.90 ^{CD_d}	97.25±1.39 ^{AB_a}	99.56±1.29 ^{A_a}	86.14±6.90 ^{ABC_b}
1/4FW-3M	57.69±4.48 ^{A_c}	49.98±2.54 ^{BC_d}	98.88±1.74 ^{A_a}	85.94±0.95 ^{E_b}	84.08±1.01 ^{ABC_b}
1/4FW-4M	40.80±1.77 ^{C_c}	51.71±4.12 ^{BC_b}	92.73±1.09 ^{C_a}	92.25±4.38 ^{CD_a}	86.19±16.88 ^{ABC_a}
1/6FW-2M	47.06±6.88 ^{BC_d}	51.57±1.89 ^{BC_c}	97.58±3.05 ^{A_a}	97.20±2.81 ^{AB_a}	69.88±2.19 ^{E_b}
1/6FW-3M	46.76±8.53 ^{BC_c}	43.84±3.08 ^{CD_c}	85.65±1.28 ^{D_b}	98.00±0.86 ^{A_a}	80.12±6.00 ^{BCD_b}
1/6FW-4M	46.18±8.77 ^{BC_c}	46.20±3.84 ^{CD_c}	92.58±2.53 ^{C_a}	95.59±3.30 ^{ABC_a}	72.60±1.26 ^{DE_b}

^a, The treatments evaluated were as follows: 1/2FW-2M (1/2 fruit/water ratio plus 2 minutes dipping time); 1/2FW-3M (1/2 fruit/water ratio plus 3 minutes dipping time); 1/2FW-4M (1/2 fruit/water ratio plus 4 minutes dipping time); 1/4FW-2M (1/4 fruit/water ratio plus 2 minutes dipping time); 1/4FW-3M (1/4 fruit/water ratio plus 3 minutes dipping time); 1/4FW-4M (1/4 fruit/water ratio plus 4 minutes dipping time); 1/6FW-2M (1/6 fruit/water ratio plus 2 minutes dipping time); 1/6FW-3M (1/6 fruit/water ratio plus 3 minutes dipping time); 1/6FW-4M (1/6 fruit/water ratio plus 4 minutes dipping time); *, Means followed by different capital letters in each column are significantly different ($p < 0.05$); **, Means followed by different lower case letters in each row are significantly different ($p < 0.05$)

Table 5- Percentages of penconazole residues following various rinsing procedures in grapes

Çizelge 5- Çeşitli yıkama uygulamalarını takiben üzümlerdeki penconazole kalıntısının yüzdeleri

Treatments ^a	10 °C	20 °C	30 °C	40 °C	50 °C
Control (mg kg ⁻¹)	0.079±0.18	0.086±0.20	0.111±0.22	0.118±0.30	0.146±0.39
1/2FW-2M	30.20±5.56 ^E _d	50.21±13.49 ^{CD} _c	36.67±2.73 ^E _d	84.43±8.97 ^A _a	70.10±4.99 ^B _b
1/2FW-3M	45.01±4.88 ^{CD} _{bc}	35.98±4.82 ^E _c	40.68±2.74 ^{DE} _c	54.24±18.93 ^C _{ab}	64.24±2.82 ^{AB} _a
1/2FW-4M	53.33±5.53 ^{AB} _b	87.11±10.29 ^A _a	82.36±2.55 ^A _a	80.21±5.28 ^{AB} _a	59.38±1.26 ^C _b
1/4FW-2M	51.96±1.56 ^{ABC} _c	40.07±1.06 ^{DE} _d	82.06±7.40 ^A _a	80.46±14.25 ^{AB} _a	62.47±6.27 ^{AB} _b
1/4FW-3M	56.57±3.13 ^A _b	48.81±4.34 ^{CD} _b	74.22±11.94 ^A _a	65.90±3.57 ^{BC} _a	68.31±6.10 ^{AB} _a
1/4FW-4M	42.18±2.99 ^D _c	54.98±11.01 ^{BC} _b	60.01±7.76 ^B _b	73.66±6.50 ^{AB} _a	82.74±13.71 ^A _a
1/6FW-2M	42.03±8.74 ^D _b	61.45±4.40 ^B _a	72.81±12.82 ^A _a	74.19±16.01 ^{AB} _a	60.98±6.60 ^C _a
1/6FW-3M	48.22±8.78 ^{BCD} _b	49.08±0.91 ^{CD} _b	49.11±3.18 ^{CD} _b	73.32±8.49 ^{AB} _a	66.98±4.86 ^{AB} _a
1/6FW-4M	45.89±4.75 ^{CD} _d	59.62±12.87 ^{BC} _{bc}	50.82±5.95 ^{BC} _{cd}	80.31±4.65 ^{AB} _a	67.49±6.67 ^{AB} _b

^a, The treatments evaluated were as follows: 1/2FW-2M (1/2 fruit/water ratio plus 2 minutes dipping time); 1/2FW-3M (1/2 fruit/water ratio plus 3 minutes dipping time); 1/2FW-4M (1/2 fruit/water ratio plus 4 minutes dipping time); 1/4FW-2M (1/4 fruit/water ratio plus 2 minutes dipping time); 1/4FW-3M (1/4 fruit/water ratio plus 3 minutes dipping time); 1/4FW-4M (1/4 fruit/water ratio plus 4 minutes dipping time); 1/6FW-2M (1/6 fruit/water ratio plus 2 minutes dipping time); 1/6FW-3M (1/6 fruit/water ratio plus 3 minutes dipping time); 1/6FW-4M (1/6 fruit/water ratio plus 4 minutes dipping time); *, Means followed by different capital letters in each column are significantly different ($p < 0.05$); **, Means followed by different lower case letters in each row are significantly different ($p < 0.05$)

1/2FW-3M, 1/2FW-4M and 1/6FW-2M resulted in the lowest residue levels of 54.24% for 40 °C and 59.38% and 60.98% for 50 °C, respectively for penconazole.

In general, statistically higher residue levels were observed for all combined rinsing treatments at 40 and 50 °C except combined rinsing treatments at 30 °C which showed a different pattern than others. The residue levels of all pesticides at 30 °C were numerically higher and closer to the results observed at 40 and 50 °C excluding 1/2FW-2M and 1/2FW-3M treatments. However, the data indicated that the residual levels of all three pesticides decreased with decreasing the rinsing water temperature while 10 and 20 °C produced lower pesticide residue values when compared to 40 and 50 °C within each treatment combinations.

4. Conclusions

Our initial hypothesis was that increasing fruit/water ratio, dipping time and temperature of water would decrease the pesticide residue in grape. However our results indicated that higher residue

levels were obtained at higher temperatures during the rinsing procedures. In most cases 10, 20 and 30 °C resulted in lower pesticide residue values when compared to 40 and 50 °C within each of combined treatments. In addition, 4 minutes of dipping time was not as effective as 2 and 3 minutes dipping times to eliminate chlorpyrifos ethyl residue from grape samples at all temperatures.

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References

- Abou-Arab A A K (1999). Behavior of pesticides in tomatoes during commercial and home preparation. *Food Chemistry* **65**: 509–514
- Anastassiades M, Lehotay SJ, Štajnbaher D & Schenck FJ (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of

- pesticide residues in produce. *Journal of AOAC International* **86**(2): 412-431
- Boulaid M, Aguilera A, Camacho F, Soussi A & Valverde M (2005). Effect of household processing and unit-to-unit variability of pyrifenoxy, pyridaben and tralometrin residues in tomatoes. *Journal of Agriculture and Food Chemistry* **53**: 4054-4058
- Burchat C S, Ripley B D, Leishman P D, Ritcey G M, Kakuda Y & Stephenson G R (1998). The distribution of nine pesticides between the juice and pulp of carrots and tomatoes after home processing. *Food Additives & Contaminants* **15**: 61-71
- Cabras P, Angioni A, Garau V L, Melis M, Pirisi F M, Karim M & Minelli E V (1997). Persistence of insecticide residues in olives and olive oil. *Journal of Agriculture and Food Chemistry* **45**: 2244-2247
- Cabras P, Angioni A, Garau V L, Minelli E V, Cabitza F & Cubeddu M (1998a). Pesticide residues in plums from field treatment to drying processing. *Italian Journal Food Sciences* **10**: 81-85
- Cabras P, Angioni A, Garau V L, Pirisi F M, Brandolini V, Cabitza F & Cubeddu M (1998b). Pesticide residues in prune processing. *Journal of Agriculture and Food Chemistry* **46**: 3772-3774
- Çelik S, Kuñç Ş & Aşan T (1995). Degradation of some pesticides in the field and effect of processing. *Analyst* **120**: 1739-1743
- Durmuşođlu E, Tiryaki O & Canhilal R (2010). Türkiye’de pestisit kullanımı, kalıntı ve dayanıklılık sorunları. Türkiye Ziraat Mühendisliđi 7. Teknik Kongresi, 11-15 Ocak 2010, Ankara. Bildiriler Kitabı 2, pp. 589-607.
- Guardia-Rubio M, Ayora-Canada M J & Ruiz-Medina A (2007). Effect of washing on pesticide residues in olives. *Food Chemistry Toxicology* **72**(2): 139-143
- Kaushik G, Satya S & Naik S N (2009). Food processing a tool to pesticide residue dissipation. *Food Research International* **42**: 26-40
- Krol W J, Arsenault T L, Pylypiw J R H M & Mattina M J I (2000). Reduction of pesticide residues on produce by rinsing. *Journal of Agriculture and Food Chemistry* **48**(10): 4666-4670
- Lehotay S J, Mařtovská K & Lightfield A R (2005). Use of buffering and other means to improve results of problematic pesticides in a fast and easy method for residue analysis of fruits and vegetables. *Journal of AOAC International* **88**(2): 615-629
- Ling Y, Wang H, Yong W, Zhang F, Sun L, Yang M, Wu Y & Chu X (2011). The effects of washing and cooking on chlorpyrifos and its toxic metabolites in vegetables. *Food Control* **22**(1): 54-58
- Mergnat T, Fritsch P, Saint-Joly C, Truchot E & Saint-Blanquat G (1995). Reduction in phosalone residue levels during industrial dehydration of apples. *Food Additives & Contaminants* **12**(6): 759-767
- PPDB (2013a). Pesticides Properties DataBase. Chlorpyrifos (Ref: OMS971) Available: <http://sitem.herts.ac.uk/aeru/footprint/en/> (Accessed 13 Nov 2013)
- PPDB (2013b). Pesticides Properties DataBase. Acetamiprid (Ref: NI 35) Available: <http://sitem.herts.ac.uk/aeru/footprint/en/> (Accessed 13 Nov 2013)
- PPDB (2013c). Pesticides Properties DataBase. Penconazole (Ref: CGA71818) Available: <http://sitem.herts.ac.uk/aeru/footprint/en/> (Accessed 13 Nov 2013)
- Ramesh A & Balasubramanian M (1999). The impact of house-hold preparations on the residues of pesticides in selected agricultural food commodities available in India. *Journal of AOAC International* **82**: 725-737
- SANCO (2011). Method Validation & Quality Control Procedures for Pesticide Residues Analysis in Food & Feed. (Document No: SANCO/12495/2011)
- Schattenberg H J 3rd, Geno P W, Hsu J P, Fry W G & Parker R P (1996). Effect of household preparation on level of pesticide residues in produce. *Journal of AOAC International* **79**: 1447-1453
- Street C (1969). Methodsof removal of pesticide residues. *Canadian Medical Association Journal* **100**: 154-160
- TGK (2011). Türk Gıda Kodeksi Pestisitlerin Maksimum Kalıntı Limitleri Yönetmeliđi, Resmi Gazete Tarihi: 29.12.2011 Resmi Gazete Sayısı: 28157 (3.mükerrer)