

Original article (Orijinal araştırma)

Effect of washing method on the reduction of insecticide residues and quality characteristics of sweet cherry fruits¹

Yıkama yönteminin kiraz meyvelerindeki insektisit kalıntılarının azaltılmasına ve ürün kalitesi üzerine etkisi

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Abstract

Sweet cherry trees were sprayed with 5 insecticides (acetamiprid, dimethoate, lambda-cyhalothrin, malathion, tau-fluvalinate) at the recommended field doses in this study. Fruits were harvested after the pre-harvested interval for each pesticide completed and then they were immersed into tap water and three different washing solutions (with three different concentrations) for 3 minutes (at 20°C). Insecticide concentrations were detected with a multi-residual analysis method using LC-MS/MS in Bursa Uludağ University in 2022. Following the treatments, changes in the quality characteristics of fruits were also investigated by quality (colour, texture and fruit cracking rate, water-soluble dry matter) and sensory analysis (fruit and stem colour, firmness, appearance, general acceptability). The results revealed that washing method with tap water during 3 min decreased insecticide residue level by 7-45% depending on insecticide active compound. Higher reduction rates were observed by washing with citric acid (10%), sodium bicarbonate (2.5%) and sodium hydroxide (0.5%). But significant reductions were detected only in lambda-cyhalothrin and malathion residues when compared with the newly harvested fruit samples. Processing factors (PF) of all washing methods were generally lower than 1 except for three treatments. PF values showed variations depending on the type of washing solution and the active compound of insecticides. Although washing with citric acid (10%), sodium bicarbonate (2.5%) and sodium hydroxide (0.5%) solutions caused reduction in residue levels, their negative effects on the quality and sensory characteristics of the fruits cannot be ruled out.

Keywords: Cherry, insecticide, LC-MS/MS, pesticide residues, processing factor, washing method

Öz

Bu çalışmada, kiraz ağaçlarına 5 insektisit formülasyonu (acetamiprid, dimethoate, lambda-cyhalothrin, malathion, tau-fluvalinate) önerilen dozlarda meyvelere uygulanmıştır. Hasat öncesi bekleme süresinden sonra hasat edilen meyveler musluk suyu ve üç farklı yıkama solusyonuyla (üç farklı konsantrasyonda) 3 dakika süreyle (20°C'de) yıkılmıştır. İnsektisit kalıntıları LC-MS/MS cihazı kullanılarak çoklu kalıntı analizi yöntemiyle Bursa Uludağ Üniversitesi'nde 2022 yılında tespit edilmiştir. Yıkama uygulamalarının ardından meyvelerin kalite özelliklerinde meydana gelen değişiklikler (renk, doku ve meyve çatlama oranı, suda çözünür kuru madde) ve duyusal özellikleri (meyve ve gövde rengi, sertlik, görünüm, genel kabul edilebilirlik) ayrıca araştırılmıştır. Araştırma sonuçlarına göre, musluk suyuyla 3 dakika süreyle yıkama yöntemi, insektisit etken maddesine bağlı olarak kalıntı seviyesini %7-45 oranında azalttığı ortaya konulmuştur. Diğer taraftan, sitrik asit (%10), sodyum bikarbonat (%2.5) ve sodyum hidroksit (%0.5) ile yıkamada daha yüksek etkiler gözlemlenmiştir. Ancak hasat edilen meyve örnekleriyle karşılaşıldığında sadece lambda-cyhalothrin ve malathion kalıntılarında istatistikî anlamda önemli azalmalar tespit edilmiştir. Tüm yıkama yöntemlerinin işleme faktörleri (PF), üç işlem dışında genellikle 1'den düşük bulunmuştur. PF değerleri yıkama solusyonunun cinsine ve insektisitlerin aktif bileşigine bağlı olarak değişiklik göstermiştir. Sitrik asit (%10), sodyum bikarbonat (%2.5) ve sodyum hidroksit (%0.5) solusyonları ile yıkama, kalıntı düzeylerinde azalmaya neden olsa da meyvelerin kalitesi ve duyusal özellikleri üzerinde göz ardı edilemez olumsuz etkiler oluşturmuştur.

Anahtar sözcükler: Kiraz, insektisit, LC-MS/MS, pestisit kalıntısı, işleme faktörü, yıkama metodu

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Introduction

Previous studies have shown that fruits have protective effects against the development of serious human diseases such as cardiovascular problems, diabetes, obesity and cancer (Ferretti et al., 2010). Their protective roles could be originated from the various nutrients such as dietary fiber, vitamins and phytonutrients. Several studies on phenols originated from fruits have demonstrated that they are bioavailable and have got a protective role against oxidative stress and free radical damages in human (Prior, 2003).

Cherries belonging to the subgenus *Cerasus*, *Prunus avium* L. of stone fruit family (Rosaceae) are known as "sweet cherry". Sweet cherries are characterized by high content of simple sugar, hydrosoluble (C) and liposoluble (A, E and K) vitamins, niacin, pantothenic acid, some carotenoids (beta carotene, lutein, zeaxanthin) and phenols. Some phenolic acids such as hydroxycinnamates, flavonols and flavan-3-ols and minerals like calcium, magnesium, phosphorous and potassium are also found in sweet cherry fruits (Gao & Mazza, 1995; Chaovanalikit & Wrolstad, 2004). Since sweet cherry fruits contain several antioxidants and particularly polyphenols, the fruits display many biological activities, such as antioxidant, anti-inflammatory and anticancer properties.

The geographic and climatic conditions in many regions of Türkiye are appropriate for sweet cherry production and Türkiye is an important sweet cherry producer with the production rate of 2.5 million tons (25.0%), followed by USA (12.0%), Uzbekistan (7.0%), Chile (6.0%), Iran (5.0%), and Italy and Spain (4.0%), respectively (TUİK, 2021; FAO, 2021). Dimethoate, tau-fluvalinate, lambda cyhalothrin and malathion are intensively used insecticides for the control of insect pests during sweet cherry growing (Hazarhun et al., 2022; BKUTARIM, 2023). The heavy use of these pesticides may end in environmental problems such as ecological imbalance, widespread pest resistance, environmental pollution, hazards to non-target organisms and wildlife (Simon, 2014). These pesticides may also cause some health problems like reproduction/development effects, and act as endocrine disruptor, skin irritant, respiratory tract irritant, skin sensitizer, eye irritant, acetyl cholinesterase inhibitor and neurotoxicant (PPDB, 2023). Although synthetic pesticides have the significant role in crop productivity and food security, their residues in agricultural products exert serious risks for human health (Çatak & Tiryaki, 2020). Therefore, there is an increasing interest in reducing pesticide residues over the surfaces or within the tissues of vegetables and fruits using different washing methods. Success of washing treatments on residues is highly dependent on the physicochemical properties of pesticide, such as mode of action (systemic or residual), water solubility, pH sensitivity, volatility and persistence. So, due to the different mode of action of pesticides, their removal is possible only by multiple methods of decontamination depending on the effects of these methods on the quality characteristics of the target commodity. The effect of washing on pesticide residue levels of cherry fruits is still not known. Effect of washing on the concentration of pesticide residues of different commodities (Al-Taher et al., 2013; Lozowicka et al., 2016; Acoglu & Yolci Omeroglu, 2021; Duman et al., 2021; Polat, 2021; Tiryaki & Polat, 2023) were studied previously with tap water and/or solutions containing different salts such as citric acid (CA), sodium bicarbonate (SB), sodium hydroxide (SH), potassium permanganate (PP) and acetic acid (AA). Harinathareddy et al. (2014) reported 37.0-73.2% reduction in the dimethoate, chlorpyrifos, quinophos, profenophos, phosalone, lamda-cyhalothrin, malathion and triazophos concentrations as a result of washing with tap water for 10 minutes (Harinathareddy et al., 2014). 24.0-97.41% reduction in the concentration of various pesticides were reported after washing with SB, PP, SH and CA solutions (Radwan, 2005; Harinathareddy et al., 2014; Polat & Tiryaki, 2020; Yalçın et al., 2023).

Industrial cherry packaging, involves a washing step (generally 3 minutes) for the removal of superficial dirt. For this purpose, fruits are washed with tap water during the sorting and classification processes by using automatic machines. Fresh sweet cherry fruits are very delicate, so for the protection of the fruit quality, they require painstaking processing and packaging precautions and also transportation conditions within the cold chain. Undesirable visible changes may easily occur on the fruit surface if these factors are not taken into consideration. The effects of pesticide removal applications on the quality characteristics of sweet

cherry fruits have not been studied yet. Previous studies have showed that chemical pre-treatments such as alkali solutions (sodium hydroxide) break down the wax on the cuticular surface of cherry and create microscopic cracks that increase moisture losses (Doymaz & İsmail, 2011). High amounts of dehydration (75%) were reported for sour cherry samples dipped in 1% (w/v) citric acid solution at room temperature in 50 h (Tarhan et al., 2006). The effect of SB solutions on postharvest decay of sweet cherry was investigated previously but how quality and sensory characteristics of fruits affected were not monitored concurrently (Karabulut et al., 2001). Presence of pesticide residues on agricultural commodities is an important food safety and public health issue and recently numerous studies were focused on their removal from the consumer products. The agents can safely take in low doses for human, but high concentrations could cause skin irritation or serious eye irritation (Merck, 2023). However, there is still a big gap about the reliability of these applications and how they affect the sensory and quality characteristics of the commodity. This study is conducted to fill the gap in this field by measuring the effectiveness of citric acid (CA), sodium bicarbonate (SB) and sodium hydroxide (SH) solutions for the removal of some pesticide residues and displaying their effects on the colour, texture and sensory characteristics of the sweet cherry fruits.

Materials and Methods

Pesticide applications

Unsprayed sweet cherry trees in an orchard in Bursa (Kestel) were used during 2022 season. Before insecticide spray, the samples collected from these trees were analysed to ensure there is no pesticide residue (Figure 1). Each plot size had four trees. The plots were with three replicates. Insecticides tested in current study were selected based on the results of our survey study during 2020–2021 seasons (Hazarhun et al. 2022). According to OECD (2008) guide, acetamiprid (Mospilan 20 SP), dimethoate (Poligor 40 EC), malathion (Malathion 65 EM), lambda-cyhalothrin (Sumosa 5 EC) and tau-fluvalinate (Mavrik 24 EW) were sprayed homogenously with an electric atomizer at the recommended field doses (Table 1). After pre-harvest interval (PHI) for each pesticide completed (7th and 14th days), 1 kg of sweet cherry sample were randomly collected and immediately transferred to laboratory in cold chain (Figure 1).

Table 1. Application dose, residue levels at the harvest day and maximum residue levels of the pesticides (BKUTARIM, 2023; EU, 2023)

Pesticides	Pesticide application dose (g /100 L water)	EU MRL ($\mu\text{g kg}^{-1}$)	TR MRL ($\mu\text{g kg}^{-1}$)	PHI (days)
Acetamiprid	5	1500	1500	7
Dimethoate	**	10	**	**
Lambda-cyhalothrin	2.5	300	300	14
Malathion	65	20	20	7
Tau-fluvalinate	7.2	400	400	14
Omethoate	*	10	**	**

* Not used due to the restrictions in Türkiye, but determined as dimethoate metabolite,

** No indicated; EU: European Union, MRL: Maximum residue limit, TR, Türkiye, PHI, Post Harvest Interval.

Experimental design

Tap water and three different washing solutions (with three different concentrations) were used during the experiments (Figure 1). 75 g portions of sweet cherry samples were immersed into 1.5 L washing solution (at 20°C) for 3 min. Following washing, samples were air-dried and prepared for the pesticide residue analyses. For the simulation of transport conditions to markets, a part of the samples was stored under cold conditions (4°C) during 8 days. Then, a series of fruit quality tests were performed on them. All of the analyses were done in triplicate.

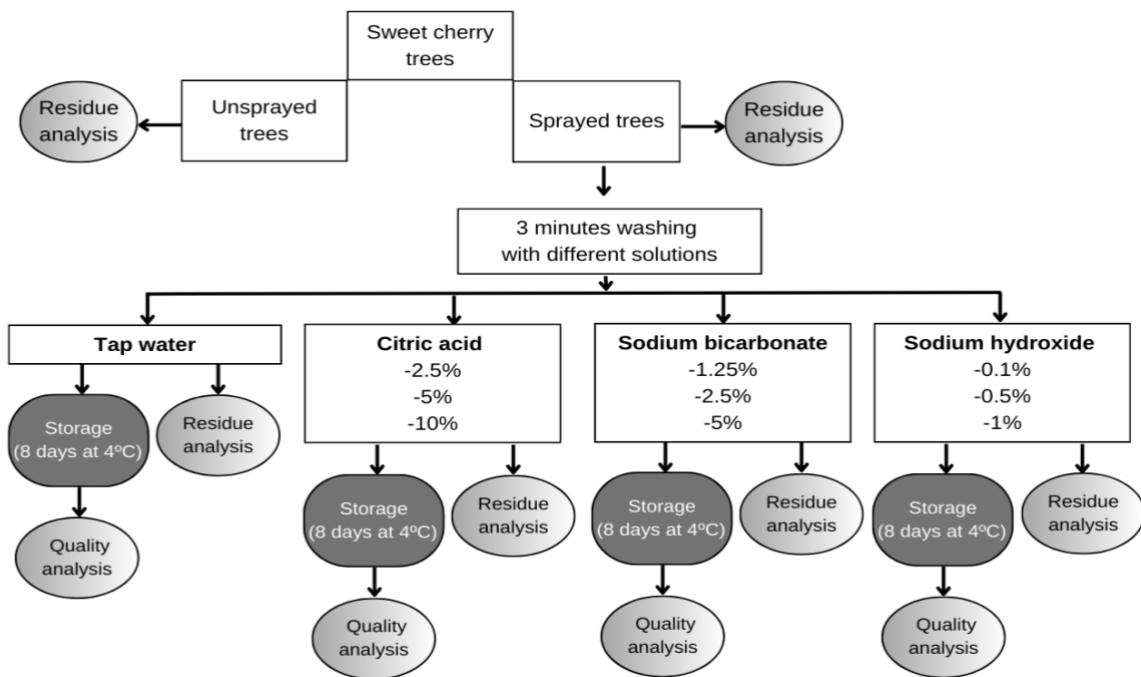


Figure 1. Processing steps and sampling details of different washing treatments.

Chemicals and reagents

The analytical standards used in validation studies were purchased from Dr. Ehrenstorfer GmbH (Germany), AccuStandard (USA) and CRM Labstandard (UK). The purity of all reference standards was higher than 96%. All other reagents, acetonitrile, ammonium formate, formic acid and methanol were of analytical grade and obtained from different manufacturers. Quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction (Q16E15E092) and clean-up (Q2A23Z592) kits were supplied from QuE Lab (Italy) (AOAC 2007.01 method). Chemical and toxicological characteristics of each pesticide tested in this study are presented in Table S1.

Pesticide analysis

Pesticide analysis were performed using Agilent 6470 Triple Quad Liquid–Mass Spectrometry (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was achieved using gradient elution with Agilent Poroshell SB-C18 analytical column ($3 \times 100 \text{ mm} \times 2.7 \mu\text{m}$) at 40°C . The mobile phase consisted of an aqueous solution of 0.1% formic acid and 1 mM ammonium formate (A) and methanol (B). The mobile phase flow rate was 0.52 mL min^{-1} . The gradient elution programme was as follows: 0–0.5 min 70% A, 0.5–8 min 70% A, 8–12.5 min 5% A, 8–12.6 min 5% A and 12.6–15 %70 A. The detection by the mass spectrophotometer (MS) was conducted in multiple-reaction monitoring and electrospray ionization mode. Nitrogen gas (N_2) was used as nebulizing and drying gas and supplied by a nitrogen generator (Peak Scientific Scotland, UK). Gas flow, gas capillary voltage and source temperature were set at 10 psi, 3500 V and 100°C respectively. Sample injection volume was $1 \mu\text{L}$. Experimental parameters (precursor and product ions, collision energy) for LC–MS/MS analysis of pesticides were displayed at Table S2. Sweet cherry fruits for each treatment were homogenised and used for pesticide analysis. Extraction and partition of pesticides were done using QuEChERS kits according to the manufacturer's instructions (QuE Lab, Italy). Sample preparation steps for pesticide analysis were summarised in Figure 2 (Lehotay, 2007; Hazarhun et al., 2022).

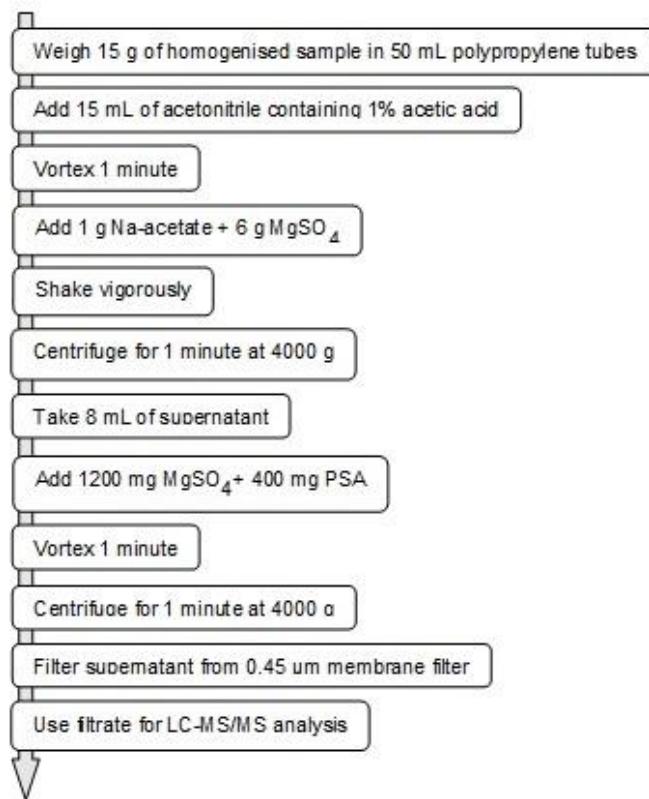


Figure 2. Sample preparation for LC-MS/MS analysis.

Method verification

The verification of the analysis method was tested according to SANTE/12682/2021 guidelines (SANTE, 2021). Within the guideline's context, selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), trueness (recovery %) and precision (intra-day and inter-day) parameters were tested. The selectivity was determined by analysing fortified and blank samples. The verification studies were performed on pesticide-free sweet cherry fruit samples. Linearity was evaluated by six levels matrix-matched calibration ranging from 2.5 to 250 µg L⁻¹. Trueness (recovery) and precision (repeatability and reproducibility) of the method calculated for five days using five replicates for two level (10 and 50 µg L⁻¹). The sensitivity of the method (LOD and LOQ) was calculated using the standard deviation (SD) of the analysis results of the lowest level (5 µg L⁻¹) spiked samples (Tiryaki, 2016; SANTE, 2021).

Calculation of processing factors

The effect of washing treatments was calculated (equation 1) similar to processing factor (PF) and obtained by the division of the residue concentration of washed fruits to the residue concentration of the unprocessed fruits (Chen et al., 2013, Đorđević et al., 2013).

$$PF = \frac{PRP}{PRR} \quad (1)$$

PF= Processing factor; PRP= Pesticide residue of processed material (mg kg⁻¹); PRR= Pesticide residue of raw material (mg kg⁻¹)

The PF value may indicate reduction (PF<1), no change (PF=1) or concentration increase (PF>1) of the pesticide residues (Chen et al., 2013). When residues were below the limit of quantification (LOQ) after processing, the PF value was accepted as zero (Aguilera et al., 2012). Additionally, the difference between

the initial pesticide concentration and the residue level of the final product was calculated by using the following formula (equation 2).

$$RR = \frac{PRR - PRP}{PRR} * 100 \quad (2)$$

RR= Residue reduction rate (%); PRR= Pesticide residue of raw material (mg kg⁻¹); PRP= Pesticide residue of processed material (mg kg⁻¹)

Determination of quality parameters

After performing different washing applications, the samples were divided into two equal parts. One group of samples were kept at +4°C for 8 days for the simulation of transportation stage of sweet cherries to markets. At the end of this storage period, changes in colour, texture, water soluble dry content and cracking levels were analysed. Additionally, visual and textural characteristics of the fruits were evaluated by an untrained test panel in terms of appearance, stem colour, firmness, colour and overall acceptance. Panellists were asked to evaluate samples in a random order using a numbered hedonic scale changing from 9 to 1 representing different levels from excellent to non-consumable (Kappel et al., 1996; Martínez-Romero et al., 2006).

For the determination of cracking level, 20 fruits were checked by eye and the number of fruits with cracks were noted. The percentage of cracked fruits were calculated by dividing the number of cracked fruits to the total number of fruits (Bilginer et al., 1999; Yıldırım & Koyuncu, 2010; Ozturk et al., 2018; Akkaya, 2021).

The changes in the fruit colour characteristics were measured based on the L*, a*, and b* criteria determined by the International Lighting Commission (CIE). The L* coordinate represented the lightness of the colour, a* indicated the position between green and red, and b* was the extent of blueness/yellowness. Measurements were made on 20 fruits using Konica Minolta CR-400 colorimeter (Tokyo, Japan). Average of minimum 2 measurements taken from the 2 opposite poles of the equatorial part of each fruit under luminous conditions (McGuire, 1992).

For the determination of fruit flesh firmness, 20 fruits were analysed using TA XT Plus (Stable Micro Systems, Surrey, UK) texture analyser. For this purpose, HDP/BS probe of the device was used in compression mode, 2 mm/s speed and 20% deformation rate (Kumral et al., 2019).

Water-soluble dry matter content of the fruits was measured using refractometer (Kem RA500, Kyoto Electronics Manufacturing Co. Ltd.) after the pitted fruits were homogenised with a household blender (Sinbo, Türkiye) and strained through a cotton cloth (Kappel et al., 1996).

Statistical analysis

All analyses and trials were conducted in triplicate. The insecticide concentrations and fruit quality data obtained at each treatment were subjected to one-way variance analysis using JMP 7.0 Software (SAS, Cary, NC). For the detection of different groups, Tukey's multiple comparison test was performed with a significance level of 0.05 (α) after normality testing with the Shapiro-Wilk test.

Results and Discussion

Verification results

The results of linearity, limit of detection and quantification, trueness and precision for each pesticide were given at Table S3. Matrix matched calibration curves of the 6 insecticides were linear ($R^2 = 0.997\text{-}0.999$). The LOQ values (2.70 to 4.04 µg kg⁻¹) were quite lower than the MRLs of each insecticide (Table 1 & S3). The recovery rates of the insecticides for two spike levels were calculated between 101.391-113.74 and 100.91-112.16, respectively. For repeatability and reproducibility parameters, the highest RSD_r and RSD_{wr} did not exceed 20% for both spike levels. All verification parameters were compatible with SANTE 11312/2021 criteria (SANTE, 2021).

Changes in pesticide residues and processing factor

Pesticide residue levels in sweet cherries harvested at the end of PHI, the processing factors (PF) and the reduction rates (RR) are shown in Table 2. In all the washing methods, the differences are significant for lambda-cyhalothrin and malathion during washing with different solutions (lambda cyhalothrin: $F_{10,36}=2.98$, $P=0.01$; malathion: $F_{10,36}=3.35$, $P=0.006$). Whereas only washing with 2.5% sodium bicarbonate yielded significant reductions in residue levels of lambda-cyhalothrin. Similarly, significant declines in malathion residues were observed when washing with citric acid (10%), sodium bicarbonate (1.25%) and sodium hydroxide (0.5 and 1%) solutions compared with residue level in the raw material. Reductions in the concentrations of all active substances were detected during washing treatments, but majority of these were statistically insignificant (acetamiprid: $F_{10,36}=1.09$, $P=0.41$; dimethoate: $F_{10,36}=0.94$, $P=0.52$; fluvalinate: $F_{10,36}=1.67$, $P=0.14$; omethoate: $F_{10,36}=2.12$, $P=0.06$). Processing factors (PF) of all washing methods were generally lower than 1. PF values were showed variations depending on the washing solution and the insecticide active compound (Table 2). The lowest PFs were obtained with citric acid (10%), sodium bicarbonate (2.5%) and sodium hydroxide (0.5%) solutions complying with the previous studies reporting lower PFs for fruits washed with acid or basic solutions (Osman et al., 2014; Polat & Tiryaki, 2020).

Table 2. Insecticide residue levels, their removal rates and the processing factor after different washing treatments

		Pesticides					
Treatment		Acetamiprid (μgkg^{-1})	Dimethoate (μgkg^{-1})	Lambda-cyhalothrin (μgkg^{-1})	Malathion (μgkg^{-1})	Tau Fluvalinate (μgkg^{-1})	Omethoate (μgkg^{-1})
Initial residue level		37.67 \pm 4.05 ^a	223.75 \pm 8.61 ^a	30.00 \pm 0.00 ^a	6.33 \pm 1.45 ^a	10.00 \pm 3.51 ^a	10.75 \pm 0.25 ^a
Citic acid solutions	Tap water	PR (mg/kg) RR (%) PF	32.00 \pm 1.00 ^a 15.02 0.85	186.50 \pm 4.50 ^a 16.65 0.83	25.00 \pm 2.88 ^{ab} 16.67 0.83	3.50 \pm 0.29 ^{ab} 44.71 0.55	6.00 \pm 1.16 ^a 40.00 0.60
	2.5%	PR (mg/kg) RR (%) PF	32.00 \pm 1.73 ^a 15.02 0.85	191.67 \pm 9.14 ^a 14.34 0.86	27.50 \pm 2.50 ^{ab} 8.33 0.92	3.25 \pm 0.75 ^{ab} 48.66 0.51	6.00 \pm 1.16 ^a 40.00 0.60
	5%	PR (mg/kg) RR (%) PF	36.33 \pm 0.88 ^a 3.55 0.96	212.50 \pm 6.76 ^a 5.03 0.95	30.00 \pm 0.00 ^{ab} 0 1.00	3.33 \pm 0.33 ^{ab} 47.39 0.53	7.00 \pm 0.41 ^a 30.00 0.70
	10%	PR (mg/kg) RR (%) PF	29.00 \pm 1.53 ^a 22.96 0.77	212.75 \pm 7.28 ^a 4.92 0.95	25.00 \pm 2.90 ^{ab} 16.67 0.83	2.67 \pm 0.33 ^b 57.82 0.42	4.25 \pm 0.63 ^a 57.50 0.43
	1.25%	PR (mg/kg) RR (%) PF	30.50 \pm 4.41 ^a 18.99 0.81	177.33 \pm 35.22 ^a 20.75 0.79	22.50 \pm 2.50 ^{ab} 25.00 0.75	2.25 \pm 0.63 ^b 64.46 0.36	4.67 \pm 0.33 ^a 53.30 0.47
	2.5%	PR (mg/kg) RR (%) PF	29.33 \pm 2.33 ^a 22.09 0.78	199.25 \pm 13.83 ^a 10.95 0.89	20.00 \pm 0.00 ^b 33.33 0.67	3.00 \pm 0.57 ^{ab} 52.61 0.47	5.00 \pm 0.58 ^a 50.00 0.50
	5%	PR (mg/kg) RR (%) PF	31.50 \pm 3.59 ^a 16.34 0.84	192.00 \pm 14.01 ^a 14.19 0.86	20.00 \pm 0.00 ^{ab} 33.33 0.67	3.67 \pm 0.88 ^{ab} 42.02 0.58	5.50 \pm 1.04 ^a 45.00 0.55
	0.1%	PR (mg/kg) RR (%) PF	33.33 \pm 1.45 ^a 11.49 0.89	212.33 \pm 16.23 ^a 5.10 0.95	30.00 \pm 0.00 ^{ab} 0 1.00	4.00 \pm 0.00 ^{ab} 36.81 0.63	6.00 \pm 0.00 ^a 40.00 0.60
	0.5%	PR (mg/kg) RR (%) PF	28.00 \pm 1.00 ^a 25.61 0.74	202.67 \pm 16.25 ^a 9.42 0.91	22.50 \pm 2.50 ^{ab} 25.00 0.75	2.00 \pm 0.41 ^b 68.40 0.32	4.75 \pm 0.85 ^a 52.50 0.48
Sodium hydroxide	1%	PR (mg/kg) RR (%) PF	29.67 \pm 1.76 ^a 0 1.05	212.33 \pm 1.45 ^a 5.10 0.95	26.67 \pm 3.33 ^a 11.10 0.89	2.00 \pm 0.41 ^b 68.40 0.32	5.50 \pm 0.50 ^a 45.00 0.55

PR, pesticide residue; RR, reduction rate; PF, processing factor;

*Means with different letters are significantly different at $p<0.05$.

Similarly, PFs as low as 0.12-0.27 were reported for neonicotinoid and organophosphate insecticides for fruits treated with 2-9% citric acid solutions (Osman et al., 2014; Randhawa, 2014; Polat & Tiryaki, 2020). Radwan et al. (2005) revealed that washing with 0.1% sodium hydroxide solution exhibited PFs of 0.08-0.35 for profenofos on pepper and eggplant. Moreover, Yang (2017) reported decrease in PF of phosmet during washing of apples with sodium bicarbonate solutions.

Water solubility and octanol-water partition coefficient (Log P) are the most significant environmental fate features for removing pesticide residues from agricultural commodities (Holland et al., 1994). Especially, highly soluble pesticides with a low octanol-water partition coefficient can easily be eliminated from these commodities (Randhawa et al., 2014; Lozowicka et al., 2016). In current study, malathion displayed high reduction rate (44.67%) in tap water with a low 2.75 Log P and a high water solubility (148 mg l⁻¹). On the contrary, acetamiprid, dimethoate and omethoate exhibited low reduction rates (15.02, 16.65, 6.98%, respectively), despite having high water solubility (2950, 25900 and 500000 mg l⁻¹, respectively) and low logP (0.80, 0.75 and -0.9 Log P, respectively). High solubility does not always have the same impact, mode of action also plays a significant role in the removal of pesticide residues from agricultural commodities. Since acetamiprid, dimethoate and its metabolite omethoate have xylem systemic mode of action, they displayed less reduction rates (0-25.61%, 4.92-20.75%, 6.98-23.26% respectively) during different washing treatments. On the other hand, higher reduction rates were observed for contact insecticides malathion and tau-fluvalinate compared with the systemic ones. In compliance with our results, Yang et al. (2017) reported that sodium bicarbonate solutions were more effective in removing surface-contact pesticides from apples, while it was not completely effective in removing systematic insecticide residues which have penetrated into the fruit.

Changes in fruit quality

Fresh cherry fruits are extremely delicate and may be easily damaged during the improper preparation or packaging steps (Gonçalves et al., 2007). Fruit size, fruit colour, stem colour, firmness, sweetness, total soluble solids, dry matter content and cracking are all considered as important fruit quality traits (Kappel et al., 1996; Gonçalves et al., 2007; Kovács et al., 2009; Romano & Cittadini, 2014). Fruit firmness is the combination of skin and flesh strength and affects consumer acceptance and shelf life (Kappel et al., 1996). Losses of firmness, colour and flavour in addition to dessication, stem discoloration and mould growth are the major causes of product rejection by the consumer (Habib et al., 2017). Changes in fruit characteristics after washing and during storage at 4°C for 8 days are shown in Table 3. The changes in water soluble dry matter content were statistically insignificant ($F_{9,29}=1.08$; $p>0.05$). Firmness and colour characteristics (L, a, b) of the fruits were affected by the treatments (firmness: $F_{9,29}=4.42$, $p<0.01$; L: $F_{9,29}=3.31$, $p=0.01$; a: $F_{9,29}=4.98$, $p<0.01$; b: $F_{9,29}=4.06$, $p<0.01$). Treatments of sodium hydroxide (1 and 0.5%) solutions caused slight changes in the firmness and colour characteristics of the fruits compared to washing with tap water. 5% sodium bicarbonate treatment caused a decrease in the value, that denotes a colour change towards green. The changes in cherry fruit qualities during transportation, storage and some pre-treatments were previously investigated by several researchers (Habib et al., 2017; Simsek & Sufer, 2021), but there is limited information about the effects of washing on the quality of the cherry fruits. Similar with our findings, Simsek & Sufer (2021) reported insignificant colour changes of cherries after citric acid pre-treatments compared with the control. Results of the sensory evaluation showed that (Table 4), the effects of treatments on the fruit and stem characteristics were significant and application of 5% sodium bicarbonate and 1 and 0.5% sodium hydroxide solutions caused marked decreases in the appearance, fruit colour, stem colour, texture and general acceptability scores of the samples.

Table 3. Changes in fruit quality characteristics after storage at 4°C for 8 days

Treatment	Water soluble dry matter (%)	Firmness (kg/cm ²)	Colour parameters		
			L	a	b
Tap water	14.30±1.27 ^{a*}	2986.95±79.39 ^a	22.31±0.08 ^{ab}	18.38±0.17 ^a	5.03±0.15 ^{ab}
Citric acid solutions	2.5%	15.37±0.84 ^a	2553.19±0.40 ^{ab}	22.86±0.40 ^{ab}	19.09±0.43 ^a
	5%	15.77±0.73 ^a	2484.40±136.41 ^{ab}	23.47±0.05 ^{ab}	18.33±0.53 ^a
	10%	16.23±0.82 ^a	2653.82±202.36 ^{ab}	23.46±0.14 ^{ab}	16.42±0.25 ^{ab}
Sodium bicarbonate	1.25%	16.50±1.00 ^a	2393.97±53.43 ^{ab}	22.49±0.79 ^{ab}	14.79±0.52 ^{ab}
	2.5%	15.10±0.82 ^a	2405.83±67.34 ^{ab}	23.32±0.10 ^{ab}	15.58±0.55 ^{ab}
	5%	16.50±0.21 ^a	3018.61±172.45 ^a	21.62±0.39 ^b	12.51±2.34 ^b
Sodium hydroxide	0.1%	16.07±0.82 ^a	2778.22±144.52 ^a	22.94±0.71 ^{ab}	15.08±0.89 ^{ab}
	0.5%	14.90±0.25 ^a	2456.48±251.18 ^{ab}	24.48±0.35 ^a	18.07±0.79 ^a
	1%	14.33±0.70 ^a	1956.72±174.85 ^b	23.81±0.58 ^{ab}	15.54±0.69 ^{ab}

*Means with different letters are significantly different at p<0.05.

Table 4. Sensory evaluation of textural and visual changes in sweet cherry samples

Treatment	Appearance	Colour	Stem colour	Texture	General acceptability
Tap water	6.63±0.38 ^{a*}	6.45±0.31 ^a	5.90±0.59 ^a	6.63±0.41 ^{ab}	6.27±0.38 ^a
Citric acid solutions	6.90±0.25 ^a	6.63±0.27 ^a	6.90±0.43 ^a	7.45±0.38 ^a	6.72±0.35 ^a
	5.18±0.26 ^{ab}	5.45±0.41 ^{ab}	5.72±0.44 ^a	6.09±0.56 ^{ab}	5.36±0.33 ^{ab}
	5.00±0.46 ^{abc}	5.54±0.43 ^{ab}	6.09±0.60 ^a	6.18±0.53 ^{ab}	5.36±0.43 ^{ab}
Sodium bicarbonate	6.63±0.41 ^a	6.54±0.34 ^a	6.36±0.50 ^a	6.45±0.38 ^{ab}	6.36±0.38 ^a
	5.81±0.48 ^a	6.09±0.36 ^a	5.27±0.48 ^a	5.90±0.54 ^{ab}	5.45±0.54 ^a
	3.81±0.56 ^{bc}	3.45±0.54 ^c	2.18±0.35 ^b	3.09±0.51 ^c	2.45±0.28 ^c
Sodium hydroxide	5.90±0.41 ^a	5.81±0.44 ^{ab}	5.36±0.54 ^a	5.54±0.56 ^{ab}	5.72±0.48 ^a
	3.09±0.57 ^{cd}	3.90±0.62 ^{bc}	4.81±0.61 ^a	4.72±0.55 ^{bc}	3.54±0.47 ^{bc}
	1.63±0.30 ^d	3.09±0.41 ^c	4.90±0.68 ^a	4.36±0.65 ^{bc}	2.27±0.33 ^c

*Means with different letters are significantly different at p<0.05.

Conclusion

Pesticide residues on agricultural commodities may cause some adverse health effects for consumers but their use during agricultural practices is inevitable due to the prevention of product losses. Treatment of fruits with different washing solutions may be an alternative way of reducing pesticides residues on consumer products. Thus, applications of citric acid (10%), sodium bicarbonate (2.5%) and sodium hydroxide (0.5%) solutions resulted significant reductions in the residue concentrations of lambda-cyhalothrin and malathion. However further research is necessary for the optimisation of their use due to the restrictions caused by their negative effects on the sensory and quality characteristics of delicate agricultural commodities. Instead of relying on washing methods, it is recommended to take actions to reduce pesticide residue in growing sweet cherry. However, it is a positive development that the use of some systemic insecticides (dimethoate and omethoate) has been banned in Türkiye in recent years.

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Table S1. Chemical and toxicological characteristics pesticides (PPDB, 2023)

Pesticide	Chemical group	Mode of action	Toxicological features				
			ADI (mg kg ⁻¹ bw day ⁻¹)	ARfD (mg kg ⁻¹ bw day ⁻¹)	Oral LD ₅₀ (mg kg ⁻¹ bw)	Dermal LD ₅₀ (mg kg ⁻¹ bw)	Inhalation LD ₅₀ (mg kg ⁻¹ bw)
Acetamiprid	Neonicotinoids	Insecticide	0.025	0.025	146	2000	>1.15
Dimethoate	Organophosphorus	Insecticide	0.001	0.01	245	2000	1.68
Lambda-cyhalothrin	Synthetic pyrethroids	Insecticide	0.0025	0.005	56	632	0.066
Malathion	Organophosphorus	Insecticide	0.03	0.3	1778	2000	>5
Tau-fluvalinate	Synthetic pyrethroids	Insecticide	0.005	0.05	546	2000	>0.56
Omethoate	Organophosphorus	Insecticide	0.0003	0.002	50	145	0.3

ADI: Acceptable daily intake, ARfD: Acute reference dose, Oral LD₅₀: Acute oral lethal dose for mammals, Dermal LD₅₀: Dermal lethal dose for mammals, Inhalation LD₅₀: Inhalation lethal dose for mammals, WHO: World Health Organisation, 1b: Highly hazardous; II: moderately hazardous, III: slightly hazardous.

Table S2. Pesticide information and optimized LC-MS/MS conditions

Pesticide	CAS number	Molecular weight	Molecular formula	Ionization	Precursor ion	Product ion	Collision energy (V)	Retention time (min.)
Acetamiprid	135410-20-7	222.67	C ₁₀ H ₁₁ CIN ₄	[M+H] ⁺	223.1	126.1; 56.2	17, 11	2.67
Dimethoate	60-51-5	229.26	C ₈ H ₁₂ NO ₃ PS ₂	[M+H] ⁺	230.0	198.9; 125.0	3, 17	3.54
Lambda-cyhalothrin	91465-08-6	449.85	C ₂₃ H ₁₉ CIF ₃ NO ₃	[M+H] ⁺	467.1	450.0; 225.0	6, 14	7.88
Malathion	121-75-5	330.36	C ₁₀ H ₁₉ O ₄ PS ₂	[M+H] ⁺	330.9	285.0; 127.0	38, 4	6.33
Tau fluvalinate	102851-06-9	502.90	C ₂₆ H ₂₂ CIF ₃ N ₂ O ₃	[M+H] ⁺	503.1	208.1; 181.1	15, 25	8.92
Omethoate	1113-02-6	213.20	C ₅ H ₁₂ NO ₄ PS	[M+H] ⁺	213.9	182.9; 125.0	4, 16	1.27

Table S3. Validation parameters for the tested pesticides

Pesticide	Concentration range (μg kg ⁻¹)	R ²	LOD (μg kg ⁻¹)	LOQ (μg kg ⁻¹)	Spike level (μg kg ⁻¹)	Repeatability (μg kg ⁻¹)	RSD _r (%)	Reproducibility (μg kg ⁻¹)	RSD _{wr} (%)	Mean recovery (%)
Acetamiprid	2.5-250	0.9996	2.94	3.97	10 50	10.72-10.69 54.26-54.75	0.77-0.99 0.85-0.74	11.18 56.08	5.72 5.16	111.82 112.16
Dimethoate	2.5-250	0.9993	2.64	2.98	10 50	10.66-10.59 51.86-52.34	1.01-0.96 0.89-0.46	11.13 51.23	11.13 51.23	111.35 102.46
Lambda-cyhalothrin	2.5-250	0.9953	2.96	4.04	10 50	10.19-9.28 50.47-50.83	11.41-12.18 5.00-8.45	10.14 50.46	10.14 50.46	101.39 100.91
Malathion	2.5-250	0.9984	2.58	2.76	10 50	10.07-9.74 49.19-49.79	2.45-3.23 3.81-1.47	11.37 53.44	11.37 53.44	113.74 106.88
Tau fluvalinate	2.5-250	0.9968	2.75	3.34	10 50	10.63-10.45 52.50-53.60	3.39-5.21 1.85-2.71	10.52 52.08	10.52 52.08	105.24 104.16
Omethoate	2.5-250	0.9997	2.56	2.70	10 50	10.17-10.10 49.35-50.15	0.84-0.59 0.61-0.72	10.65 51.88	10.65 51.88	106.55 103.76