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Original article (Orijinal araştırma)

Assessing residues of some insecticides during household processing of lemon[1]

Limonun evde işlenmesi sırasında bazı insektisitlerin kalıntılarının değerlendirilmesi

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Abstract

The goal of this study was to assess the residues of some insecticides (abamectin, buprofezin, etoxazole) applied on the lemon fruits during its cultivation and to investigate the consequence of household processing such as peeling, jam production, freezing and storage on the residues. A multi-residual analysis method based on QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) procedure and liquid chromatography coupled with triple quadrupole mass spectrometry was used. Mean recovery (measure of trueness; 70-120%), precision (as repeatability and interim precision relative standard deviation <20%) and limit of quantification (0.01 mg/kg < MRLs) were in accordance with the criteria set in the international guideline. Lemon samples were purchased from Bursa markets in April 2018. The experimental studies and statistical evaluations were conducted at Bursa University Agriculture Faculty (Bursa -Türkiye) between 5 May 2018-30 July 2022. The results revealed that pesticide residues mostly dispersed on the peel, therefore, peeling step decreased the residue level by 90-100% in the pulp of the fruit. Fruit juice and jam production operations decreased the residue level by 87- 100%. Processing factors were less than 1 for fruit juice and jam processing, on the other hand, it was greater than 1 for the separation, grating, freezing and storage of the peels.

Keywords: Household food processing, insecticide residue, lemon, processing factor

Öz

Bu çalışmanın amacı, limon meyvelerinin yetiştirilmesi sırasında üzerlerine uygulanan bazı insektisit (abamectin, buprofezin ve etoxazole) kalıntılarının değerlendirilmesi ve soyma, reçel üretimi, dondurma ve depolama gibi evde yapılan işlemlerinin kalıntılar üzerindeki etkisinin araştırılmasıdır. QuEChERS (Hızlı, Kolay, Ucuz, Verimli, Sağlam ve Güvenli) prosedürüne ve üçlü kuadropol sıvı kromatografi kütle spektrometresine dayalı bir çoklu kalıntı analiz yöntemi kullanılmıştır. Ortalama geri kazanım (gerçekliğin bir ölçüsü olarak; %70-120), kesinlik (tekrarlanabilirlik ve ara kesinlik bağıl standart sapma <%20 olarak) ve yöntemin ölçüm limiti (0.01 mg/kg < MRLs) uluslararası kılavuzda belirlenen kriterlere uygun olarak elde edilmiştir. Nisan 2018'de Bursa marketlerinden limon örnekleri satın alınmıştır. Deneysel çalışmalar ve istatiksel değerlendirmeler 5 Mayıs 2018-30 Temmuz 2022 tarihleri arasında Bursa Uludağ Üniversitesi Ziraat Fakültesi'nde (Bursa-Türkiye) gerçekleştirilmiştir. Elde edilen sonuçlara göre, pestisit kalıntısının çoğunlukla meyvenin kabukları üzerinde dağıldığı, dolayısıyla soyma aşamasının meyvenin posasındaki kalıntı miktarını %90-100 oranında azalttığı gözlenmiştir. Meyve suyu ve reçel üretimini içeren işleme adımları nihai üründe kalıntı seviyesini %87-100 oranında azaltmıştır. Sonuç olarak işleme faktörleri (P_f), meyve suyu ve reçel işleme için 1'den küçük olarak, meyve kabuklarının ayrılması, rendelenmesi, dondurulması ve saklanması için ise 1'den büyük olarak elde edilmiştir.

Anahtar sözcükler: Evsel gıda işlemleri, insektisit kalıntısı, limon, işleme faktörü

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Introduction

Citrus fruits, known for their extensive nutritional value and health benefits, are grown in more than 80 countries and are among the most popular fruits consumed worldwide (Cicero et al., 2015; Calvaruso et al., 2020). The lemon fruit is the third most produced citrus fruit after oranges and tangerines (Gonzalez-Molina et al., 2010). Lemon production in Turkey was reported as 1.4 million tons in 2022. Due to the increased consumption demand, it is aimed to reach 9.5 million tons in lemon production with an increase of 4% in Turkey, America and Mexico (USDA, 2022). Lemon has health-promoting effects due to its high content of flavonoids, vitamin C, citric acid, minerals, dietary fiber, essential oils and carotenoids (Anagnostopoulou et al., 2006; Gonzalez-Molina et al., 2009; Gonzalez-Molina et al., 2010; Guimaraes et al., 2010; Lorente et al., 2014; Hassan et al., 2022). Therefore, it constitutes a very important place in a daily diet, having a role in the prevention of obesity, diabetes, cardiovascular diseases, and some of the cancer types and lowering blood lipid (Gonzalez-Molina et al., 2009). Lemon is an extremely juicy and aromatic fruit and is popular with its color and flavor. It has smooth peels with medium thickness and each fruit contains seeds up to nine (Kafa, 2015). Lemon are consumed as fresh fruit, moreover it can be processed into jam, marmalade, fruit juice and frozen form for household or industrial applications (Uysal & Polatöz, 2017; Ayyıldız, 2018). In addition, it is known that lemon is commonly used in salad dressings and pickles as a flavor enhancer and preservatives.

Various pests such as thrips, mites and aphids can attack citrus trees during the fruit growth and development (Li et al., 2020). Like other citrus, the lemon crop is prone to pests so pesticides must be applied at various stages of agricultural production (Ortelli et al., 2005; Kariathi et al., 2016; Carvalho, 2017; Elgueta et al., 2017; Rodrigues et al., 2019). Insecticides and acaricides are common type of pesticides used for citrus (Li et al., 2022). Abamectin, buprofezin and etoxazole are common active compounds of different type of commercial formulations used for citrus production as insecticides for curing pests including passer citrus rust mite *Phyllocoptruta oleivora* (Ashmead, 1879) (Acari: Eriophyidae), citrus leaf miner *Phyllocnistis citrella* (Stainton, 1856) (Lepidoptera: Gracillariidae), citrus whitefly *Dialeurodes citri* (Ashmead, 1885) (Hemiptera: Aleyrodidae), oriental yellow scale *Aonidiella citrina* (Craw, 1890) (Hemiptera: Diaspididae), citrus red scale *Aonidiella aurantii* (Maskell, 1879) (Hemiptera: Diaspididae), and citrus red mite *Panonychus citri* (McGregor, 1916) (Acari: Tetranychidae) (Anonymous, 2023a).

The application of pesticides throughout the agricultural production in the field or at the post-harvest stage dramatically increase the yield of crops. However, the misuse of pesticides can result in excess amount of residue in or on the crops which can cause health problems to the consumer and contaminates environment (Rodrigues et al., 2019; Philippe et al., 2021). Moreover, raw agricultural crops (RAC) are likely to contain pesticide residues above the maximum residue level (MRL) set at the national and international regulations in case they are harvested and consumed before the harvest period. The majority of RACs are processed before consumption (OECD, 2008). Concentration of pesticide residues in foods can be decreased by simple processing techniques such as washing, peeling, juicing, boiling, drying, fermentation or cooking (Shabeer et al., 2015; Lozowicka et al., 2016; Han et al., 2016; Acoglu et al., 2018; Catak et al., 2020; Maden & Yıldırım Kumral, 2020; Polat & Tiryaki, 2020; Yildirim Kumral et al., 2020; Acoğlu & Yolci Omeroglu, 2021; Duman et al., 2021; Balkan & Yılmaz, 2022; Polat 2021; Tiryaki & Polat, 2023; Luyinda & Yildirim-Kumral, 2023). On the other hand, toxic by-products or metabolites may also be formed at some specific food processing conditions (Han et al., 2013, 2016). The processing factor (P_f) is the ratio of the residue levels in processed products to residue level in raw agricultural crops (OECD, 2008). P_f is the main value that represents processing efficiency on the pesticide residue level. Physicochemical properties of pesticides (solubility in water, log Po/w, etc.) and application time can explain the differences in processing factor (Bonnechère et al., 2012; Scholz et al., 2017). P_f values should be taken into account for compliance of processed products (Anonymous, 2016).

There are some reported studies in literature dedicated to analysis of pesticide residue level in the lemon fruit and lemon products. Based on those studies, registered insecticides including abamectin and buprofezin and non-registered insecticide residues were reported in lemon fruits (Andrascikova & Hrouzkova, 2013; Bakirci et al., 2014; Cicero et al., 2015; Dincay & Civelek, 2017; Besil et al., 2019; Chen et al., 2021; Aslantas et al., 2023; Karaagaçlı, 2023). Moreover, the number of Rapid Alert System for Food and Feed (RASFF) notifications in 2021 for Turkey which was the most reported origin, increased from 191 to 361. Those numbers were mainly due to non-compliances for citrus fruits including lemons. Therefore, except for grapefruits, mandatory checking at the border was increased by 20% in October 2021 (EU, 2021). On the other hand, studies on the effect of household or industrial processing of lemon on pesticide residue levels are limited (Vass et al., 2015; M'hiri et al., 2018; Kowalska et al., 2022).

Pesticides having various modes of action can act in different ways after contact with the agricultural crops. Therefore, the fate of the residues depends on the physicochemical properties of the active ingredients in addition to the type of the matrix. Accordingly, P_f values for each combination should be determined separately (Han et al., 2016; Ma et al., 2019). Pesticides having systemic effect are diffused through leaves, stems or roots and are then moved within the plant by its circulatory system. Contact type of pesticides are directly applied to the outer surfaces of plants (Rodrigues et al., 2017, 2019). Therefore, the behavior of pesticides is associated not only with the processing methods, but also with their mode of action, application time, climate during plantation and physicochemical properties of the product (Lozowicka et al., 2016). The legal processing factor data base in Turkey does not provide any P_f values for abamectin and etoxazole residues in lemon products. On the other hand, the list covers only the processing factor of buprofezin for lemon juice as 0.58 (Anonymous, 2023b). To the best of our knowledge, this research was the first to determine the processing factors of those pesticides for lemon products.

The goal of this study was to assess the residues of some insecticides (abamectin, buprofezin and etoxazole) applied on the lemon fruits during cultivation and to investigate the effect of common household processing including peeling, heat treatments (blanching and boiling during jam production), freezing and storage on the fate of the residue.

Materials and Methods

Chemicals and solutions

QuEChERS extraction kits including 6000 mg anhydrous magnesium sulfate ($MgSO_4$) and 1500 mg anhydrous sodium acetate and QuEChERS clean-up kits consisting of 1200 mg $MgSO_4$ and 400 mg primary and secondary amines (PSA, 40 µm particle size) were provided from Chromabond (Germany). Solvents (acetonitrile, glacial acetic acid, methanol, formic acid), which are proper for pesticide residue analysis, were purchased from Merck (Germany) to be used in the study. Neat standards of abamectin, buprofezin and etoxazole (purity >99%) certified for pesticide residue analysis were purchased from Dr. Ehrenstorfer (Germany). Stock solutions of 1 mg/mL in acetonitrile containing 1% acetic acid were used to prepare working solutions at a concentration ranging between 20 and 800 µg /L through series of dilutions. Seven different levels of matrix matched calibration standards covering the concentrations of the target analytes in sample were diluted from working standards. Stock solutions were stored at deep-freezer (−18°C) in sealed brown glass bottles for 1 year. The other solutions were kept at 4°C for maximum 1 week. Deionized distilled water was used in the analysis (National Q purification system, Merck, Germany).

Equipment

A LC-MS-MS (Agilent 1260 II model LC-MS-MS-6470A) equipped with a 2.1 mm × 150 mm x 2.7 µm (Agilent Poroshell C18) analytical column was used for the analysis. At mass detector, heat block temperature, drying gas temperature, spray gas in ion source (N_2), drying gas in ion source (N_2), gas flow, nebulizer gas, and capillary voltage are 325°C, 400°C, 10 L/min, 11 L/min, 14 L/min, 40 psi, and 3000 V, respectively.

Positive electron spray ionization (ESI) mode was used for each pesticide. The mobile phase with 0.3 min/mL flow rate consisted of 5 mM ammonium acetate (A) and methanol in 0.1% formic acid water (B). The gradient program started with 80% A and 20% B for 0.5 min, increased linearly to 95% B in 10 minutes, hold at 95% B for 3 min. After the 13-min run time, 3-min post run followed using the initial 20% of B. The flow rate was 0.5 mL/min and the injection volume was 1 µL.

The other main equipment used in the study were homogenizator (Recht GM 200, Haan, Germany), refrigerated centrifuge (Sigma 2-16P, Osterode, Germany) top-loading balances (Shimadzu ATX224, Japan), polytetrafluoroethylene (PTFE) syringe (5mL), PTFE filter with 0.45 µm diameter, Eppendorf automatic pipettes (10, 100, 1000 µL) and LC-MS-MS vials (1.5 mL).

Sample

Approximately 30-40 kg of the lemon samples (*Citrus lamas*) were obtained from a market in Bursa in April 2018. The experimental studies and statistical evaluations were conducted at Bursa Uludağ University Agriculture Faculty (Bursa-Türkiye) between 5 May 2018 and 30 July 2022.

The samples were stored at 5-7°C and 90-95% relative humidity conditions until the further analysis. Since the mass of each lemon unit in the bulk sample ranged between 156 g and 185 g, laboratory samples not less than 1 kg and covering at least 10 units were taken from the bulk sample to comply with the criteria set in the legal legislation (EC, 2002). Except three laboratory samples separated as “non-treated control sample (C)” from the bulk sample, all laboratory samples were exposed to pesticide treatment step as explained follows.

Pesticide treatment

Active ingredients for lemon fruits were selected based on their popularity on the agricultural farming applications and their residue occurrence frequency (Andrascikova & Hrouzkova, 2013; Bakirci et al., 2014; Cicero et al., 2015; Dincay & Civelek, 2017; Besil et al., 2019; Chen et al., 2021; EU, 2021; Aslantas et al., 2023; Karaağaçlı, 2023). The commercial formulations of abamectin, buprofezin and etoxazole were selected as Asmition (18 g/L, emulsified concentrate), Korfezin (400 g/L, suspension concentrate) and Novamite (110 g/L, suspension concentrate), respectively and purchased from a local market. For calculation of processing factors, the important criteria include to have detectable level of the residues in RAC, therefore it is allowed to apply plant protection products more than the recommended dose and the RACs can be harvested before the harvest period (OECD, 2008). Based on the preliminary studies approximately one to four times of the recommended dose of the formulations were prepared (Acoglu & Yolci Omeroglu, 2021; Yolci Omeroglu et al., 2022). The laboratory samples were dipped into homogeneous solution of the formulations for 30 minutes to ensure a homogeneous distribution within and between samples and to obtain detectable residue level in the samples (Hassan et al., 2022). Accordingly, treated samples were left under sun light for 3-4 hours on polypropylene sheets allowing drying of fruit outer surface. Samples were kept at +4°C for 1 day till the further step.

Household processing

After treating samples with commercial formulations, three laboratory samples were kept as control samples (TC) without exposing any household processing (Figure 1). The experimental details were shown in Figure 2 and explained as follows. Each processing steps were repeated three times with three different treated laboratory samples. Prior to processing, each fruit unit in the laboratory samples were gently washed under tap water for 2-3 minutes.

Processing into lemon peels (LP) and pulp (LPu):

The peels were removed from the fruits with a knife. It has been determined that the mass of peel to pulp ranged between 26% and 32% in lemons (Figure 1b, c).

Processing into lemon juice (LJ):

Lemon samples were gently divided into two equal parts with a kitchen knife and lemon juice was produced by a kitchen processor (Arzum, Turkey). The mean pH of the juices was determined as 2.2±0.05 (Mettler Toledo Seven compact pH/Ion pHmeter, Canada) (Figure 1d).

Processing into lemon zest (LZ) and storage at frozen conditions:

Lemon peels were zested and stored at -20°C for three months. Analytical samples were taken monthly throughout the storage period (Figure 1f).

The lemon peels, pulps, juice and zest were stored in polypropylene sample vessels at -20°C till further analysis.

Processing into lemon jam (LJ):

The recipe described by Yolci Omeroglu et al. (2022) was applied for jam production. The average pH of the jams obtained was 3.45 ±0.06 and the water-soluble dry matter (Brix) was 72.65±0.64 g/100 g (RA-500 Model Kyoto Electronics Manufacturing Co. Ltd., Japan) (Figure 1e). Lemon jam was stored at room temperature till further analysis.

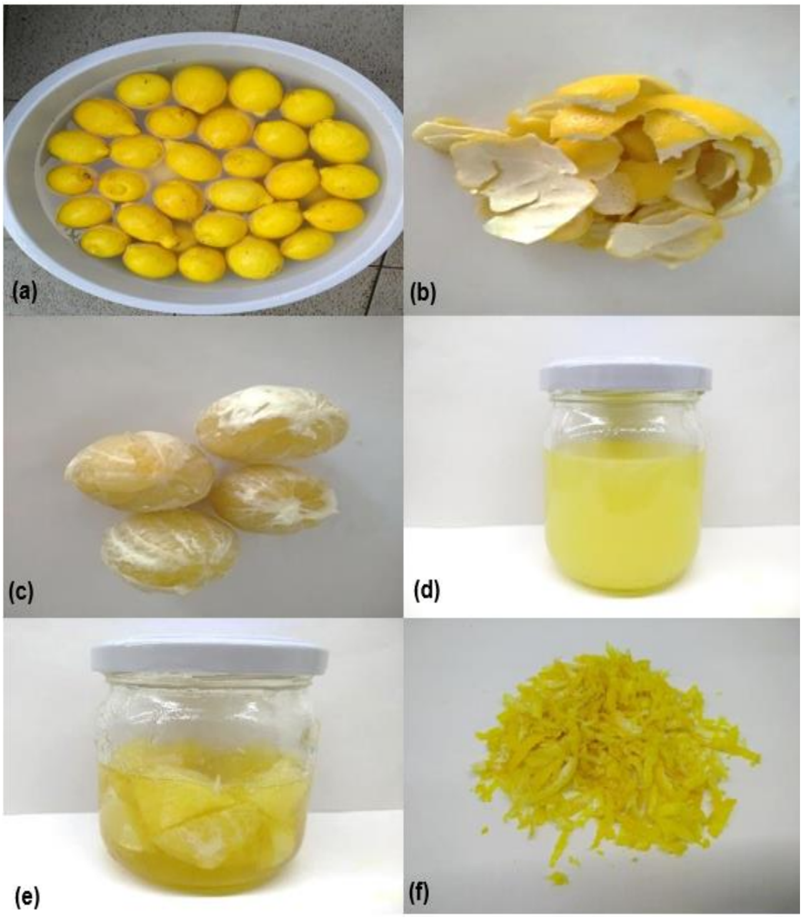

Figure 1. Household processing of lemon; a) Pesticide treatment, b) Lemon peel (LP), c) Lemon pulp (LPu), d) Lemon juice (LJ), e) Lemon jam (LJ), f) Lemon zest (LZ).

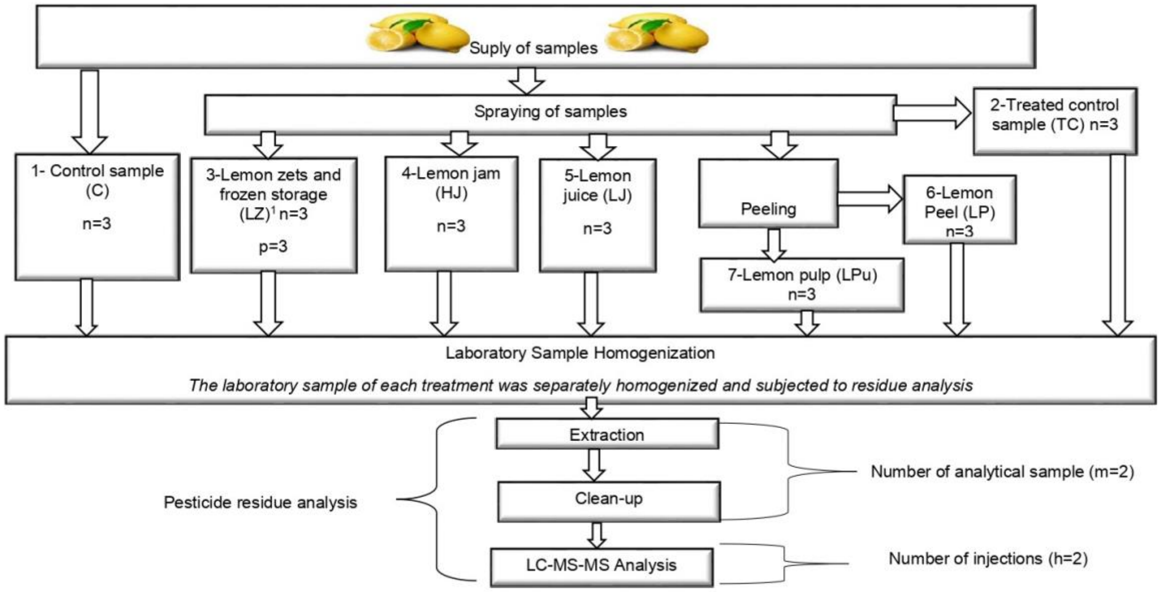

Figure 2. Experimental pattern ("n" represents the replicate number of the processing and the number of the laboratory samples"; "p" represents number of storage period" ([1] Samples were taken each month during three months of frozen storage period).

Pesticide residue analysis

Each laboratory samples were handled separately throughout the pesticide residue analysis explained below.

Lemon jams (LJ) were homogenized thoroughly with a food chopper (RechtGM 200, Haan, Germany). Lemon pulp (LPu), lemon peel (LP) and control samples (C, TC) were homogenized with the chopper till obtaining particle size of 2-3 mm. Lemon juice and lemon zest did not go through a sample processing step. Analytical samples taken from the laboratory sample were kept in PTFE sample vessels at -20°C for till extraction and cleanup step as explained in Figure 2.

Pesticide residue analysis including extraction, clean-up and LC-MS-MS steps was based on a validated standard multi-residue method, namely QuEChERS (AOAC, 2007). The details of the method were provided in Figure 2 and Figure 3. The information on LC-MS-MS identifications are given in Table 1.

Table 1. LC-MS-MS identification details

Analyte	Molecular formula	Mode of Action	MRL (mg/kg)	LOQ[a] (mg/kg)	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Cone Voltage (V)	Collusion Energy (V)
Abamectin	$C_{18}H_{72}O_{14}$	Semi-Systemic	0.04	0.01	12.822	895.9 895.9	751.4 327.2	100	-48 -8
Buprofezin	$C_{16}H_{23}N_3OS$	Contact	0.01	0.01	11.815	306.2 306.2	201.1 116.1	150	-6 -9
Etoxazole	$C_{21}H_{23}F_2NO_2$	Contact	0.1	0.01	12.147	360.3 360.3	141.1 340.2	140	-15 -30

[a] LOQ represents limit of quantification.

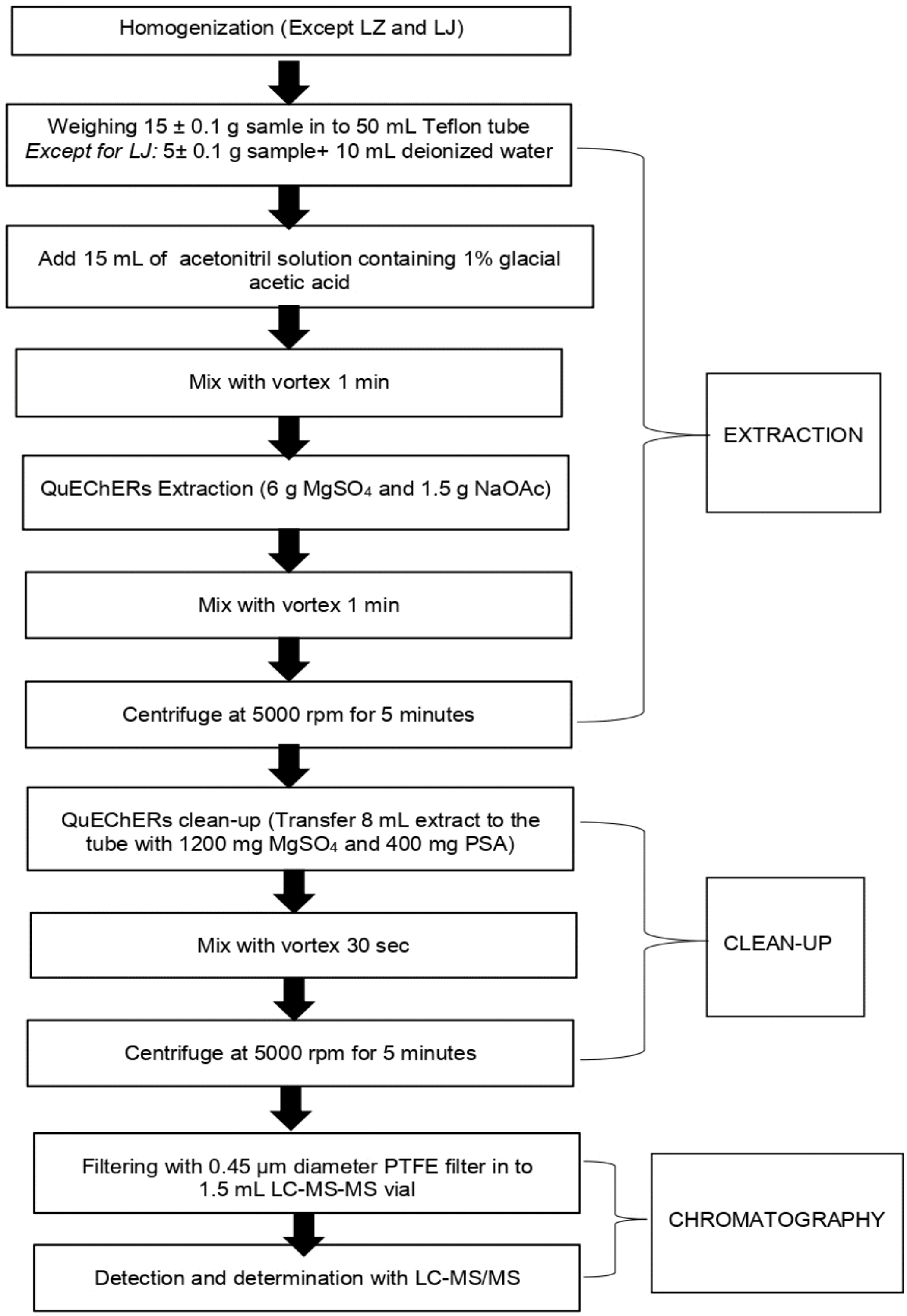

Figure 3. Pesticide residue analysis method based on QuEChERS extraction (AOAC, 2007).

Method verification study was conducted in our laboratory prior to application of the analytical method for the analysis of the sample, and quality control studies during each batch of analysis were performed according to principles recommended by European SANTE/11312/2021 Guidance Document (SANTE, 2021) and EURACHEM guidelines (EURACHEM, 2012, 2014).

Processing factor (P_F)

The processing factor (P_f) is the ratio of the pesticide amount in the processed product (PP) to raw agricultural crops (RAC) (OECD, 2008; Claeys et al., 2011; Scholz et al., 2017). A factor less than or greater than 1 indicates decrease or concentration, respectively. The equation of the processing factor is given in equation 1.

$$P_F = \frac{PP}{RAC} \qquad (1)$$

Where PP refers to the residue level in the processed lemon samples (GP, HJ, LJ, LP, and LPu). RAC refers to residue level in raw agricultural crops (TC). PP in Equation 1 was replaced with LOQ of the method if its nominal value was lower than LOQ. Accordingly, P_f value was expressed with an asterisk "<".

Experimental design and statistical analysis

Experimental design was illustrated at Figure 2. Each process was repeated three times with three different laboratory samples (n=3). Two analytical portions from each laboratory sample was taken for further pesticide residue analyses (m=2). Subsequently, from each analytical portion's duplicate measurements with LC-MS-MS (h=2) were performed. At Table 2 and Table 3, results were expressed as mean ± standard deviation (n=3). One-way analysis of variance (ANOVA) followed by a Tukey post hoc test was used to compare significance differences among household process in terms of pesticide residue levels and processing factors. The SPSS software (version 20.0; SPSS Inc., Chicago, IL, USA) was used for statistical analysis, and $p < 0.05$ was considered as statistically significant.

Results and Discussion

Method verification and quality control studies

Prior to application of a validated method into a routine analysis laboratory, method verification study should be performed to provide evidence that the validated method can be applied by the laboratory. In this context, the reliability of the method was successfully proved at our laboratory conditions and reported previously by Yolci Omeroglu et al. (2022) for orange matrix. Based on the results, mean recovery (as a measure of trueness; 70-120%), precision (as repeatability and interim precision relative standard deviation-RSD_r and RSD_{wR} <20%) and LOQ of the method (0.01 mg/kg< MRL) were in accordance with the criteria set European SANTE/11312/2021 Guidance Document (SANTE, 2021). Moreover, measurement uncertainty complied with the maximum default relative expanded measurement uncertainty set as 50%. To specify the linearity of the method and to determine the residue level in each of the sample, seven level matrix -matched calibration curve covering the concentrations of sample ranging between 10 µg/kg and 1500 µg/kg was constructed at each batch of analysis. Matrix matched calibration curve was prepared from the extract of control lemon samples (C) with a residue level lower than LOQ of the method. A weighted linear calibration function (R^2) > 0.9990) was obtained to determine the concentrations of the residues in the samples as µg/kg (Yolci Omeroglu et al., 2018).

Since both orange and lemon fruits are typical representative commodities for citrus fruits which are categorized under the commodity group with high acid content and high water content, the method verification study reported previously by Yolci Omeroglu et al. (2022) for orange matrix was considered as appropriate for lemon matrix (SANTE, 2021). On the other hand, during routine analysis of each of analytical batch, quality control studies including deviation of calculated concentration, recovery and duplicate samples were also conducted. Deviation of calculated concentration of the calibration standards by the calibration function from the true concentrations was calculated at each batch of the analysis for quality control purposes. It changed between -7.30% and 19.87%, which complied with the range (±20) specified at the SANTE/11312/2021 Guidance Document (SANTE, 2021). Moreover, recoveries of all analytes within the scope of the study measured at each batch of analysis were determined by spiking the blank lemon samples at LOQ level of the method. Individual recoveries ranged between 83% and 103% (n=7) and were compatible with the practical default range of 60-140% stated in the guideline (SANTE, 2021). The difference between the duplicate measurements of each analytical sample were less than the repeatability limit (r) at 95% confidence level (EURACHEM, 2014), which was based on the average RSD_r value (3%, n=72) obtained during method verification study.

Assessing residue of insecticides during household processing of lemon

Average concentration of abamectin, buprofezin, and etoxazole residues in pesticide treated control lemon samples (TC) were obtained as 0.011, 0.246, and 0.246 mg/kg, respectively. After processing of TC samples into LP, LPu, LJ, LZ, the levels of aforementioned pesticide residues changed from <LOQ to 0.043 mg/kg, 0.020 to 1.060 mg/kg, <LOQ to 0.593 mg/kg, respectively. Based on the statistical results shown in Table 2, different type of household processing changed the residue levels significantly ($p < 0.05$) from the levels found in TC samples.

Processing into lemon peels (LP) and pulp (LPu):

Peeling process increased the residue concentrations in lemon peels significantly ($p <0.05$) compared to control samples (TC). The increase in concentration changed from 3.3 to 8.5 fold. Pesticide residues were reduced as a result of the separation of the lemon peels from the fruit pulp. Peeling process eliminated totally abamectin residue in the pulp, while it reduced buprofezin concentration by 90%. In line with our findings, a study reported by Li et al. (2012) revealed that residues of imidacloprid, carbendazim, abamectin and cypermethrin in orange decreased by peeling process. Liu et al. (2016) concluded that spirotetramate, and its metabolites B-enol, B-glu and B-keto accumulated on the peel of citrus. Moreover, Calvaruso et al. (2020) reported that 43% of the fenhexamid residue in lemon peel was transferred from the peel to albedo, and 18% from albedo to the pulp resulting a low penetration through the pulp.

Similarly, other studies in the literature revealed that peeling substantially reduced pesticide residues in fruits (Boulaid et al., 2012; Reiler et al., 2015; Yolci-Omeroglu et al., 2015). For instance, it was reported that the reduction of pesticide residues by peeling of tomatoes accounted as 70% for pyridaben and 100% for pyrifenox and tralomethrin (Cengiz et al., 2007). Liu et al. (2014) prevailed a decrease in thiophanate-methyl by 84.2% with the peeling of tomatoes, while its metabolite carbendazim decreased by 87.3%. Naman et al. (2022) reported that mancozeb residue decreased by 72.59% by the peeling of apple. Likewise, Peng et al. (2014) reported that imidacloprid, pyraclostrobin, azoxystrobin and fipronil residues in jujube fruits decreased in the pulp of the fruit and the residues remained on the peel. In the same manner, residues of chlorpyrifos-methyl, phenitrothion and procymidone in peach (Balinova et al., 2006), thiophanate-methyl and carbendazim in tomato (Liu et al., 2014), chlorothalonil, difenoconazole and azoxystrobin residues in tomatoes (Rodrigues et al., 2017) remained on the peel after peeling process.

Peeling is an important step in the processing of many fruits and vegetables. Since the majority of pesticides are applied directly to crops, peeling is one of the most effective ways to reduce pesticide residues penetrated into the cuticle layer (Dorđević & Durović-Pejčev, 2016; Chung, 2018). The increase in residue concentration can be related to the physical and chemical properties of pesticides especially to the octanol-water coefficient (log Po/w) in addition to their mode of action. Abamectin has a semi-systemic effect while buprofezin and etoxazole have a contact effect. Abamectin, buprofezin and etoxazole have low water solubility but high log Po/w values (4.4, 3.8 and 5.6, respectively). Therefore, they tend to adhere to the cuticular waxes or deeper layers rather than diffusing through the pulp of the fruit (Holland et al., 1994; Kaushik et al., 2009). Kimbara et al. (2012) reported that cutin and waxes on the outer surface of the citrus have important functions on the protection of pesticide residues physically. Liu et al. (2016) reported that spirotetramate residue in citrus peels increased compared to the initial concentration. In a study reported by Peng et al. (2014), it was observed that residues of imidacloprid, pyraclostrobin, azoxystrobin and fipronil deposited on the peels of jujube fruits rapidly penetrated into the epicuticular waxes and the cuticle, so that the concentration of pesticide residues on the peels increased compared to the pulp of the fruit. Yolci Omeroglu et al. (2022) concluded the same findings for abamectin, buprofezin and etoxazole in orange. They attributed to these findings to the cuticular waxes which thought to be acted as a transport barrier to prevent forming residual deposits in the citrus pulp.

Table 2. The effect of different processing techniques on pesticide residue in lemon samples (n=3)[1]

		Pesticides (mg/kg, *average±standard deviation*)					
No	Process	Abamectin[2,3]		Buprofezin[2,4]		Etoxazole[2, 3]	
1	Treated control lemon sample (TC)	0.011±0.001	c	0.246±0.030	d	0.040±0.003	e
2	Lemon peel (LP)	0.036±0.003	a	0.660±0.017	c	0.343±0.032	d
3	Lemon pulp (LPu)	<LOQ		0.024±0.001	e	<LOQ	
4	Lemon juice (LJ)	<LOQ		0.035±0.001	e	<LOQ	
5	Homemade jam (HJ)	<LOQ		0.020±0.001	e	<LOQ	
6	Frozen lemon zest (1st month of storage) (LZ_1)	0.043±0.005	a	1.060±0.034	a	0.593±0.011	a
7	Frozen lemon zest (2nd month of storage) (LZ_2)	0.042±0.009	a	0.910±0.020	b	0.530±0.010	b
8	Frozen lemon zest (3rd month of storage) (LZ_3)	0.019±0.002	b	0.650±0.036	c	0.490±0.010	c

[1] "n" represents the replicate number of the laboratory samples"; "m" refers to the number of analytical samples taken from each laboratory sample; "h" refers to the number of injections made for each analytical sample;
[2] There is a difference between the averages indicated by different lowercase letters in the same column ($P < 0.05$);
[3] Since the abamectin and etoxazole concentrations of pulp, juice and jam <LOQ of the method, they were excluded from the statistical analyses. Therefore, degrees of freedom (df) between group = 5-1= 4; df within group = (5 x3)-5=10;
[4] Degrees of freedom (df) between group = 7-1= 6; df within group =(7 x3)-7=14.

Processing into lemon juice (LJ):

Consumption of fruit juice is a very convenient way to consume more fruits (Lozowicka et al., 2016). During the extraction of juice from the plant tissues, the diffusion of the residues throughout the fruit juice is based on the distribution behavior of the residue between the peel and pulp in addition to their physicochemical properties (Dordevic & Durovic-Pejcev, 2016). In this study, for non-polar compounds (log Po/w ≥ 5.6), complete disappearance of abamectin and etoxazole residues were observed in lemon juice, while a reduction of 86% of buprofezin residue was prevailed (Table 1). Since any heat treatment process for sterilization/pasteurization of homemade juice was not included in the production step, the reduction of the pesticide residues in juice can only be attributed to deposition of the residues on the wax and cuticular section of the outer surface, which is related with their higher octanol-water partition coefficient (log Po/w). Yolci Omeroglu et al. (2022) observed the same findings for orange juice. Furthermore, Tang et al. (2023) stated that degradation or dissipation of five pesticides including etoxazole occurred at a rate of at least 37.6 % in sterilized citrus juice compared with the residual levels in raw citrus. On the other hand, for concentrated citrus juice due to the heat concentration, the degradation rate was diverse compared to sterilized citrus juice.

In line with our findings, Athanasopoulos & Papas (2000) reported that azinphos-methyl residues totally disappeared in lemon juice during processing step. In another study, it was found that abamectin, residue decreased by 46.0% during fruit juice production (Li et al., 2012). Naman et al. (2022) determined that chlorpyrifos residue reduced by 100% in pear juice. Likewise, mancozeb residue in apple juice was reduced by 100%. The findings reported by Hendawi et al. (2013) prevailed that reduction of imidacloprid residue in strawberry juice was related with its lower water solubility (514 µg/mL) and higher octanol-water coefficient (2.7). Moreover, the other studies in the literature supported the relation between the fate of the pesticide during fruit juice production and the physicochemical properties of pesticide (Rasmusssen et al., 2003; Martin et al., 2013; Kwon et al., 2015; Li et al., 2015; Lozowicka et al., 2016; Hassan et al., 2022).

Processing into lemon zest (LZ) and storage at frozen conditions:

Lemon peels are processed into zest form and commonly used for baking purposes to provide pleasant aroma. Lemon zest can be stored in frozen forms to prolong the shelf life. Freezing, as one of the most widely used food preservation methods, provides better preservation of taste, texture and nutritional value in foods than other methods (Kaushik et al., 2009). In Table 1, the changes of pesticide residues during production of lemon zest and throughout the storage period at -20°C were shown. After processing into lemon zest, concentration of abamectin, buprofezin and etoxazole residues were found to be significantly more compared to their concentration in control lemon samples (TC) ($P < 0.05$). This observation can be attributed to the accumulation of the pesticide on the exocarp of the lemon fruit. Higher oil solubility affinity of the pesticides analyzed within the scope of the study lead to absorption of their residues by waxy outer surface of the lemon. The findings reported by Yolci Omeroglu et al. (2022) supported our conclusions. According to results shown in Table 1, throughout the frozen storage period for three months, pesticide residue level decreased significantly ($P<0.05$) with a ratio ranged between 17% and 55%. Similarly, it has been reported in literature for different type of pesticide and matrix combinations, even though storage of agricultural crops at frozen conditions, pesticide residue level decreased throughout the increasing storage period (Abou-Arab, 1999; Hamilton et al., 2004; Chauhan et al., 2012; Öğüt et al., 2014; Bouzari et al., 2015). On the other hand, study reported by Oliva et al. (2017) revealed that after freezing and during storage of the zucchini, residue levels of trifloxystrobin and myclobutanil decreased less than 1%. In the same study, the losses in imidaclorpid and diethofencarb were observed much greater (31.7 and 9.8%, respectively), with no significant variations observed between the storage period of 15 days and 30 days.

Processing into lemon jam (LJ):

Jam is a product obtained by cooking the fruit to a certain consistency using sucrose and other additives. The recipe used in the scope of the study included the removing of the outer layer of the fruit gently by grating followed by the boiling of pulps in water 3 times for 15 min. To overwhelm the bitter taste of the outer layer, each time water was replaced with the fresh one. The other steps in the production were similar to common jam processing including cooking step at 95°C for 30 min (Yolci Omeroglu et al., 2022). In the scope of the study, abamectin and etoxazole residues was not detected in the final product, while 92% reduction in buprofezin residue was revealed. In line with our findings, Liu et al. (2016) reported that one of the metabolite forms of spirotetramat, namely B-keto, in marmalade was reduced by 68% compared to the initial concentration, while the other metabolites (B-enol, B-glu and B-mono) were completely removed. The more recent study by Naman et al. (2022) determined that the mancozeb residue decreased by 100% in apple jam. Those findings were mainly due to the steps included in the jam production as explained above. Moreover, it can be attributed to their chemical and thermal degradation during heat treatment process in addition to their water solubility (Kaushik et al., 2009; Bajwa & Sandhu, 2014; Dordevic & Durovic-Pejcev, 2016; Lozowicka et al., 2016).

Processing factor

Food processing may reduce or increase the level of the residues in final products compared to their initial level in raw agricultural crops depending on the physicochemical properties of the pesticide, type of the matrix and the operations included in the processing (Shabeer et al., 2015; Oliva et al., 2017). The effects of different type of household processing on the processing factors were summarized in Table 3.

Table 3. The effect of different processing techniques on average processing factors (n=3)[1,2]

		Average processing factor (Pf) ± std deviation					
No	Process	Abamectin		Buprofezin		Etoxazole	
1	Fruit peel separation (P)	3.307±0.448	Ba	2.701±0.327	Cb	8.598±0.646	Ab
2	Fruit pulp separation (LPu)	<0.050±0.001	Bc	0.101±0.017	Ac	<0.050±0.001	Bc
3	Fruit juice processing (FJ)	<0.862±0.080	Abc	0.146±0.010	Bc	<0.251±0.023	Bc
4	Homemade jam production (HJ)	<0.862±0.070	Abc	0.081±0.010	Bc	<0.251±0.023	Bc
5	Frozen storage of lemon zest (1st month) (GP_1)	3.752±0.740	Ba	4.329±0.399	Ba	14.921±1.530	Aa
6	Frozen storage of lemon zest (2nd month) (GP_2)	3.624±0.775	Ba	3.732±0.526	Ba	13.333±1.448	Aa
7	Frozen storage of lemon zest (3rd month) (GP_3)	1.669±0.184	Cb	2.649±0.177	Bb	12.315±1.122	Aa

[1] There is a difference between the means indicated by different lowercase letters in the same column ($P<0.05$); degrees of freedom (df) between group= 7-1= 6; df within group= (7 x3)-7=14);

[2] There is a difference between the means shown with different capital letters in the same row ($P<0.05$); degrees of freedom (df) between group=3-1= 2; df within group= (3 x3)-3=6.

Since concentration of pesticide residue in TC samples ranged from 0.011 mg/kg to 0.246 mg/kg (Table 2) was higher than the LOQ of the analytical method, calculation of processing factors met the criteria set in the OECD guideline (OECD, 2008).

It has been observed that there was a remarkable effect on the removal of pesticide residues by processing of lemon fruit into pulp, juice and jam. Therefore, P_f values for those steps for all of the three pesticides were determined to be less than 1. P_f values were found to be more than 1 due to the increase in the concentration of pesticide residues in the peel part and frozen grated peel part. These results were attributed to log Po/w values of pesticides. The highest processing factors were obtained for etoxazole and in addition, in some studies in the literature, processing factors have been calculated and it has been reported that the processing factor is bound on the type of the active ingredient, its physicochemical properties in addition to type of the carriers used in the formulation (Li et al., 2012; Han et al., 2013; Tiryaki & Özel, 2019; Polat & Tiryaki, 2020; Tiryaki & Polat, 2023). It can be indicated that the results of those studies are compatible with our findings.

Conclusions

Pesticides as plant protection products constitute an important place in boosting agricultural production. Even though pesticides can increase yield of the agricultural products at a limited extent, an abuse use may cause health risk both to human being and the environment. Therefore, to control products on the market with legal limits, extensive studies should be conducted to reveal the effects of processing on pesticide residue and to calculate related processing factors. In the light of needs, the current work was conducted to investigate effect of some representative household processing on insecticide residues in lemon. In the study, the required method performance criteria were met. The QuEChERS method was successfully applied for analysis of abamectin, buprofezin and etoxazole residue in lemon and its products. It was concluded that fate of pesticide residues depended on the type of treatment to be applied to the food, the physicochemical structure of pesticides and nature of the product. It was determined that the pesticide residue levels in lemon pulp, juice and jam obtained from lemon fruits were significantly reduced. It was observed that the insecticide residues were commonly distributed on the lemon peel due to the physicochemical properties of the pesticides and nature of the crop. Processing factors vary according to the physicochemical properties of pesticides and processing methods; therefore, future studies should be conducted for different combinations of pesticide, matrix and processing methods. Moreover, effect of pre-harvest interval on the fate of the pesticide should be examined in future risk assessment studies. Additionally, if possible, field treated samples should be used for the estimation of processing factor accurately.

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