Environ Monit Assess (2022) 194: 570
https://doi.org/10.1007/s10661-022-10253-y

Monitoring of pesticide residues in peppers from Çanakkale (Turkey) public market using QuEChERS method and LC–MS/MS and GC–MS/MS detection

İsmet Yıldırım · Uğur Çiftçi

Received: 16 February 2022 / Accepted: 28 June 2022 / Published online: 7 July 2022
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Abstract Residue analyses were conducted for 283 pesticide active ingredients on pepper samples collected from the local markets (between April and November) of Çanakkale province of Turkey by using QuEChERS method and LC–MS/MS and GC–MS/MS devices. In present pepper samples, 35 different pesticide residues were detected. About 25.0% (27 samples) of present samples had single residue and 43.5% (47 samples) had multiple residues. Of the detected pesticides, acetamiprid, triadimenol, imidacloprid, boscalid, pirimiphos-methyl, tebuconazole, and metalaxyl were the most common ones, while carbendazim/benomyl, fenpropathrin, and thiram were the banned ones. Moreover, 24 of the pesticide residues detected were above the MRL values, 19 pesticides were in the "moderately hazardous (II)," and two pesticides were in the "extremely hazardous (Ib)" class (WHO). Present findings revealed that consumer health may be in danger despite all legal measures by the Ministry of Agriculture and Forestry of Turkey, thus greater emphasis should be put on monitoring of pesticide use and residues.

Keywords Pepper · Pesticide residue · QuEChERS · Monitoring · MRL

Introduction

Agricultural production should be increased to meet the food demands of continuously increasing world population. For this purpose, besides using new production techniques and cultivating high-yielding varieties, yield losses induced by pests, diseases, and weeds should also be minimized. Pesticides are widely and intensively used in plant production today. In terms of pesticide consumption in 2019, Turkey with annual pesticide consumption of 51,297 tons has the 11th rank worldwide after China, the USA, and Brazil, respectively (Food and Agriculture Organization (FAO), 2021). Pesticides used in Turkey consist of 19,698 tons of fungicides, 13,733 tons of insecticides, and 12,644 tons of herbicides. Proper use of pesticides provides sufficient protection against pests, diseases, and weeds. However, improper uses may result in residues on foodstuffs and agricultural products. Such residues may have serious sub-acute and chronic toxic impacts on human and animals consuming these products (Aktar et al., 2009; Forget, 1993; Tiryaki et al., 2010; Wang et al., 2017). Pesticides may have acute impacts on human health in short run or chronic impacts in long run.

İ. Yıldırım (✉)
Department of Plant and Animal Production, Çal Vocational College, Pamukkale University, 20000 Denizli, Turkey
e-mail: ismety@pau.edu.tr

U. Çiftçi
Republic of Turkey Ministry of Agriculture and Forestry, Çanakkale Food Control Laboratory Directorate, 17100 Çanakkale, Turkey

Short-term exposure of highly hazardous pesticides (HHPs) may have hazardous impacts on the liver, kidneys, blood, lungs, immune system, and gastrointestinal system and may negatively influence the skin, eyes, nervous system, cardiovascular system, gastrointestinal system, liver, kidneys, reproductive system, endocrine system, immune system, and blood (Sabarwala et al., 2018; WHO, 2020). Dithiocarbamate-containing pesticides and their metabolites (carbon disulfide, ethylene thiourea) may result in hypersensitivity, allergic dermatitis, cancer, Parkinson's, brain damage, reduction in activity of brain enzymes, and lymphocyte sensitivity (Rath et al., 2011). HPPs result in cancer especially in small children at development ages and potential health impacts of these pesticides may be encountered in more severe levels in pregnant or nursing women, babies and children, individuals with weakened immune system, and insufficiently nourished individuals (Food and Agriculture Organization (FAO) & World Health Organization (WHO), 2016).

Consumer exposure of pesticides is mostly encountered through the residues on consumed foodstuffs. To prevent consumers from the negative impacts of pesticides, high-risk pesticides are banned and Maximum Residue Limits (MRL) are set for low-risk ones. Such limits are set by World Health Organization (WHO) and Codex Alimentarius Commission (CAC) of United Nations Food and Agriculture Organization (FAO), USA Environmental Protection Agency (EPA), and EU commission and designated with regulations. In Turkey, pesticide residue limits are set by Turkish Food Codex (TFC) of Ministry of Agriculture and arranged so as to comply with the EU pesticide residue limits. Such limits are updated in certain intervals. It was indicated in EU 2017 pesticide residue reports that 25.8% (73 samples) of 283 chili pepper samples investigated in EU countries and the others and 5.7% (340 samples) of 5968 sweet pepper (bell pepper) samples had pesticide residue levels greater than the MRL values (European Food Safety Authority (EFSA), 2019). In various other countries, residue levels on agricultural commodities have been investigated and such levels were assessed through national standards or CAC-specified MRL values.

Number of studies on residue analyses in peppers is quite limited (Chu et al., 2019). In a study conducted in China, 15 black pepper samples were collected from the markets of 11 provinces and samples were analyzed for pesticide residues. It was found that clothianidin in 1 sample and acetamiprid in 6 samples were below the MRL, but carbendazim in 6 samples and metalaxyl-M in 2 samples exceeded MRL set by EU (Yao et al., 2019). In another study conducted in China, 299 bell pepper samples were collected from 17 provinces and 25 pesticides (15 OPs, 7 PYs, 3 CBs) were encountered in 86 samples and 7.36% of these samples had more than one pesticide and pesticide residue levels of 5.35% of these samples were greater than MRL set by China (Chu et al., 2019). Residue analyses were conducted in 160 local vegetable samples collected from large markets in Al-Qassim region of Saudi Arabia and it was reported that 58 of 89 samples had residue levels greater than the MRL and the greatest carbaryl residue level (2.228 mg /kg) was observed in peppers (Osman et al., 2010). In Turkey, Golge et al. (2018) analyzed 725 pepper and cucumber samples and reported that pesticide residue levels were within EU-MRL values and identified the most common pesticides in peppers respectively as acetamiprid, boscalid, azoxystrobin, and triadimenol. Besides, Kaya and Tuna (2019) analyzed limited number of fruit and vegetable samples (42 samples) collected from 3 public markets of İzmir province and did not observe over-limit pesticide residues in peppers. Ersoy et al. (2011) encountered over-limit pesticide residues (ethion, triazophos, and benomyl) in samples collected from local markets of Konya province.

In recent years, multi-residue analyses have been conducted for trace quantities of the pesticides on vegetable, fruit, and other commodities with the use of GS-MS/MS (gas chromatography/mass spectrometry) or LC–MS/MS (liquid chromatography/mass spectrometry) devices. Extraction method plays a significant role in residue analyses. Therefore, QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method is employed in pesticide residue analyses for extraction and clean-up (Dülger & Tiryaki, 2021; Liu et al., 2016; Morais et al., 2018; Polat & Tiryaki, 2020; Poulsen et al., 2017; Zhang et al., 2015). In the present study, existence of 283 pesticides in pepper samples was investigated with the use of QuEChERS extraction method in two different devices as of LC-MC/MC (Waters Acquity ULPC, Acquity TQD) and GC–MS/MS (Thermo Trace 1310, TSQ 8000 Evo).

The primary objective of the study was to monitor pesticide residues, with a potential risk on human

health, in pepper samples grown under greenhouse and field conditions and sold in local markets of Çanakkale province of Turkey. Prospective outcomes will reflect the pesticide residues on peppers grown in Turkey since peppers sold in Çanakkale public markets come from different regions.

Material and methods

Location

In this study, pesticide residues in pepper samples collected from local markets of Çanakkale province (Turkey) were analyzed and potential health risks of these residues were assessed. Çanakkale province is located between 25° 40′–27°30′ east longitudes and 39°27′–40°45′ north latitudes. It covers the Dardanelles connecting the continents of Asia and Europe, Biga and Gallipoli Peninsulas of northwestern Anatolia peninsula (Turkey), UNESCO World Heritage Troya National Park and down skirts of Kazdağları. Majority of the province is located within the boundaries of Marmara region and a small portion in Edremit Gulf in Aegean region. The province has a surface area of 9933 km^2. Products from all pepper-growing regions of Turkey are brought to Çanakkale public markets and sold in these markets.

Sampling

In the present study, 108 pepper (*Capsicum annuum* L.) samples were taken from randomly selected six stands in local markets of Çanakkale province for 6 months (April–November) in 15-day intervals. About 1 kg pepper samples (The European Communities (EC), 2002) were placed into different bags, labelled, and transported to Çanakkale Provincial Food Laboratory in cooler boxes and pesticide analyses were conducted in the same day.

Chemicals and reagents

Samples were analyzed for 283 different pesticide-active substances (Table 1). Since chemical structures, polarities, heat sensitivity, and reactions to ionization systems of active substance molecules are different, pesticide analyses were conducted in two different devices as of LC-MC/MC (Waters Acquity ULPC, Acquity TQD) and GC–MS/MS (Thermo Trace 1310, TSQ 8000 Evo). The method LOQ values of the detected active substances are provided in Table 1. Pesticide reference standards were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), with certified purity of ranging from 97 to 99% (Table 1). Chemicals used in this study include acetonitrile (CH_3CN, Merck Company, at ≥ 99.97% purity, hypergrade for LC–MS); acetic acid (CH_3COOH, Merck Company, at 100% purity, for HPLC LiChropur); QuEChERS extraction kit [6 g $MgSO_4$ + 1,5 g sodium acetate (CH_3COONa) (Agilent Company, QuEChERS Extraction Packets, AOAC Method)]; QuEChERS clean-up kit [1200 mg $MgSO_4$ + 400 mg PSA (Agilent Company, Dispersive SPE 15 mL, Fruits + Veg, AOAC)]; methanol (CH_3OH, Merck Company, at ≥ 99.97% purity, hypergrade for LC–MS), and ammonium acetate (CH_3COONH_4, Merck Company, at ≥ 98.0% purity).

Sample preparation and analytical method

Pesticide residue analyses in pepper samples were conducted at accredited Pesticide Analysis Laboratory of Çanakkale Food Control Directorate of Ministry of Agriculture and Forestry. Analyses were carried out with QuEChERS method and GC–MS/MS and LC–MS/MS devices. QuEChERS is a fast, easy, cheap, and efficient extraction method (Anastassiades et al., 2003; Payá et al., 2007). The sample extraction and clean-up procedures were carried out in accordance with QuEChERS-AOAC Official Method 2007.01 (Dülger & Tiryaki, 2021; Polat & Tiryaki, 2020).

Approximately 1 kg pepper samples were homogenized by using blender and placed in 200 mL polypropylene sample storage containers. Fifteen grams of homogenized pepper samples (analytical part) was weighed in two parallel to 50 mL falcon tubes and the remaining samples were stored in a deep freezer at − 20 °C to be used in case of repeating the analysis. Samples in falcon tubes were supplemented with 15 mL acetonitrile containing 1% acetic acid and shaken hardly for a minute. QuEChERS extraction kit including 6 g dehydrated $MgSO_4$ and 1.5 g CH_3COONa were added, shaken, and vortexed for a minute. Falcon tubes were centrifuged at 5000 rpm for a minute for phase separation. About 8 mL of upper supernatant was taken and transferred to another

Table 1 The method LOQ values of the analyzed active substances

LOQ mg/kg	Active ingredient	
0.005	Acetamiprid; acetochlor; alachlor; aldicarb; atrazine; azinphos-methyl; azoxystrobin; beflubutamid; bensulfuron-methyl; bitertanol; bupirimate; buprofezin; carbaryl; carbendazim/benomyl; carbofuran; carboxin; carfentrazone-ethyl; clodinafop-propargyl ester; clofentezine; cymoxanil; cyproconazole; cyprodinil; demeton-S-methyl; diazinon; dicamba; dichlofluanid; diethofencarb; difenoconazole; dimethenamid; dimethoate; dimethomorph; diniconazole; diphenamid; diuron; dodine; DMA (0,05); emamectin benzoate; epoxiconazole; ethiofencarb; ethion; ethofumesate; fenamidone; fenamiphos; fenazaquin; fenbuconazole; fenhexamid; fenoxaprop-P-ethyl; fenoxycarb; fenpropathrin; fenpyroximate; fenthion; fluazifop-P-butyl; fluazinam; flutriafol; formetanate hydrochloride; fosthiazate; haloxyfop-2-ethoxyethyl; haloxyfop-R-methyl; hexaconazole; hexythiazox; ımazalil; ıodosulfuron-methyl sodium; lenacil; lufenuron; malaoxon; metalaxyl/metalaxyl-M; monocrotophos; oxamyl; phosalone; phosmet; pirimicarb; propargite; simazine; spinosad; thiodicarb; triadimenol	LC–MS/MS
0.006	Bromuconazole; chlorsulfuron; fludioxonil; flurochloridone	
0.007	Clothianidin; diclofop-methyl	
0.008	Chlorantraniliprole; clethodim; famoxadone; indoxacarb	
0.01	Aldicarb-sulfone; aldicarb-sulfoxide; amidosulfuron; amitraz; benalaxyl; benfuracarb; bentazone; bifenazate; boscalid; carbofuran-3-hydroxy; chlorfluazuron; chloridazon; chlormequat chloride; chlorpropham; chlorpyrifos; chlorpyrifos-methyl; climbazole; cycloate; demeton-S-methyl-sulfone; demeton-S-methyl-sulfoxide; diafenthiuron; dichlorvos; dithianon; DMF; DMPF; EPTC; etofenprox; etoxazole; fenbutatin-oxide; flufenoxuron; furathiocarb; imazamox; imazapyr; imazethapyr; imidacloprid; malathion; mandipropamid; metamitron; methabenzthiazuron; methidathion; methomyl; methoxyfenozide; metolachlor; metominostrobin; metribuzin; metsulfuron-methyl; mevinphos; molinate; monolinuron; myclobutanil; nicosulfuron; novaluron; omethoate; oxadixyl; paraoxon-methyl; penconazole; pendimethalin; phenmedipham; phenthoate; pirimiphos-methyl; prochloraz; profenofos; prometryn; propamocarb; propaquizafop; propazine; propiconazole; propyzamide; proquinazid; pymetrozine; pyraclostrobin; pyrazophos; pyridaben; pyridalyl; pyridaphenthion; pyridate; pyrimethanil; pyriproxyfen; quinalphos; quinoxyfen; quizalofop-ethyl; rimsulfuron; spinetoram; spirodiclofen; spirotetramat; spiroxamine; tebuconazole; tebufenozide; tepraloxydim; terbuthylazine; tetraconazole; thiabendazole; thiacloprid; thiamethoxam; thifensulfuron-methyl; thiophanate-methyl; tralkoxydim; triadimefon; tri-allate; triasulfuron; tribenuron-methyl; trichlorfon; trifloxystrobin; triflumizole; triflumuron; triticonazole	
0.02	Abamectin; acephate; cyhexatin; dazomet; fipronil; flusilazole; ioxynil; isoxaflutol; kresoxim-methyl; metrafenone; profoxydim-lithium; prothiophos; teflubenzuron; thiram; tolclofos-methyl; tolylfluanid	
0.03	Bifenthrin; clopyralid; deltamethrin; permethrin	
0.05	2,4-D; bromoxynil; carbosulfan; dinocap; triforine; fluvalinate, tau-; oxadiazon; oxyfluorfen; MCPA; tebufenpyrad	
Other	Hexaflumuron (0,009); fenarimol (0,011); diflubenzuron (0,03); mefenpyr-diethyl (0,04); mesotrione (0,04); metazachlor (0,1); pyrimidifen (0,1); sethoxydim (0,1); fosetyl-aluminum (1); gibberellic acid (3);	
0.01	2,4-DDD; 2,4-DDE; 2,4-DDT; 4,4-DDD; 4,4-DDE; 4,4-DDT; aldrin; bromopropylate; cadusafos; chinomethionat; chlordane, cis- (alpha); chlordane, trans- (gamma); cyfluthrin; cyhalothrin, gamma-; cyhalothrin, lambda-; cypermethrin; cypermethrin, -alpha; dicofol; chlorothalonil; dieldrin; endosulfan, alpha-; endosulfan, beta-; endosulfan-sulfate; endrin; endrin-aldehyde; endrin-ketone; ethalfluralin; ethoprophos; fenitrothion; fenvalerate/esfenvalerate; formothion; HCH, alpha-; HCH, beta-; HCH, delta; HCH, gamma- (Lindan); heptachlor; heptachlor-endo-epoxide; heptachlor-exo-epoxide; hexachlorobenzene; iprodione; parathion-methyl; procymidone; spiromesifen; terbutryn; tetradifon; trifluralin; vinclozolin	GC–MS/MS
0.02	Captan; folpet;	
0.05	Dinobuton;	
0.1	Dimethipin	

15 mL centrifuge tube including QuEChERS clean-up kit (1200 mg $MgSO_4$ + 400 mg PSA). The tube was vortexed for a minute and centrifuged at 5000 rpm for a minute. Upper clear portion was placed into vials and subjected to LC–MS/MS and GC–MS/MS detection. Resultant values were compared with the

MRL values of Turkish Food Codex (Plant Protection Products (PPPs), 2020) and EU-MRL Pesticide residues were also assessed for pesticide risk groups of World Health Organization (WHO, 2020).

Chromatographic conditions

Samples were analyzed for 283 pesticide active substances in LC–MS/MS and GC–MS/MS devices. LC–MS/MS analyses were performed by liquid chromatography (Waters Acquity UPLC), sequential mass spectrometry (Waters Acquity TQD), and connected Waters Acquity UPLC BEH (C18 2.1×100 mm) column with 1.7 µm particle size. The 5% MeOH (Mobile Phase A) containing 10 mM ammonium acetate and 95% MeOH (Mobile Phase B) containing 10 mM ammonium acetate were used as mobile phase. The mobile phase flow rate was 0.3 mL/min. The column temperature was 50 °C and the injection volume was 20 µL. The gradient mobile phase flow program is given in Table 2. GC–MS/MS analyses were performed by gas chromatography (Thermo, Trace 1310), sequential mass spectrometry (Thermo, TSQ 8000 Evo), and Thermo TG-5MS (30 m×0.25 mm) 0.25 µm film thickness column. Helium was used as the carrier gas at a constant flow of 1.3 mL/min. About 2 µL sample was injected into the device. Oven temperature program is given in Table 3.

Method verification

The LOQ, calibration curve, repeatability, reproducibility, recovery, and precision parameters were assessed for method verification. The values were compared with SANTE guidelines (Çatak & Tiryaki, 2020; Dülger & Tiryaki, 2021). The first step of method validation is recovery assessment (SANTE, 2019).

Table 2 The gradient mobile phase flow program

Time	Flow rate	A %	B %
Initial	0.3	99.9	0.1
0.5	0.3	99.9	0.1
10	0.3	0.1	99.9
12.5	0.3	0.1	99.9
12.6	0.3	99.9	0.1
15	0.3	99.9	0.1

Table 3 Oven temperature program in GS-MS/MS

Time	Rate (°C/min)	Temperature (°C)	Hold time (min)
Initial		90.0	1.00
1	30.0	150.0	1.00
2	10.0	190.0	2.00
3	10.0	285.0	5.00

About 1 kg of blank pepper sample was homogenized with blander. Then, a 15-g well-homogenized pepper sample was spiked with 10 µg/kg level of pesticides standard dissolved in methanol and was incubated for 15 min, and then treated according to the procedure earlier described in sample preparation (Picó et al., 2018). Analyses were repeated 10 times. The standard deviation of the results was calculated and 10 times the standard deviation was accepted as the LOQ value. Matrix matched calibration was used to get the calibration curve. Mixtures were prepared at the concentrations of 1, 2, 5, 10, 20, 50, 100, and 200 µg/L on the phase obtained by analyzing the blank sample and each concentration was subjected for chromatographic analyses in 3 replicates. Acceptable calibration ranges were determined by performing residual control according to 20% acceptance criteria. For repeatability of control, 5 parallel spikes for each concentration were made on the blank sample at 10 and 50 µg/kg concentrations on the same day. The RSD values of the obtained results were calculated and evaluated according to the 20% acceptance criterion. For reproducibility of control, spikes at 10 and 50 µg/kg concentrations were prepared and analyzed on 5 different days and the RSD values of the obtained results were calculated and evaluated according to the 20% acceptance criterion. Recovery rates were determined for each analyte using the results obtained from the reproducibility and repeatability studies.

Results and discussion

Method verification

Validation of the analysis method was carried out with the use of method performance criteria such as LOQ (Limit of Quantitation, µg/kg), Linearity (µg/kg), Recovery (%), Repeatability (RSD%), and Reproducibility (RSD%). Resultant values (Table 4)

were evaluated according to the validation parameters and criteria in European SANTE Guideline (SANTE, 2019). In Repeatability studies, RSD values (%) varied between 1.4 and 10.2% in LC–MS/MS device and between 1.4 and 13.6% in GC–MS/MS device. These values were within the SANTE limits (≤ 20%) (SANTE, 2019). In Reproducibility studies, RSD (%) values varied between 3.1 and 16.8% in LC–MS/MS device, and between 8.2 and 18.3% in GC–MS/MS device. These values were also within the SANTE limits (≤ 20%). Recovery rates varied between 74.0 and 100.6% in LC–MS/MS device and between 82.9 and 95.7% in GC–MS/MS device. The rates obtained in the recovery rate analyses performed in both devices were compatible with the rates (70–120%) given for the reality parameter in the SANTE Document (SANTE, 2019).

Table 4 Validation data on LC–MS/MS device

Analyte	LOQ (µg/kg)	Linearity (µg/kg)	Repeatability (%RSD)	Reproducibility (%RSD)	Recovery (%)
Acetamiprid	4.3	1–200	3.3	6.1	74.0
Azoxystrobin	2.5	1–200	2.3	5.0	98.4
Bifenazate	10	10–200	5.4	7.7	91.8
Boscalid	10	1–200	5.6	8.3	96.8
Buprofezin	2.6	1–200	3.5	5.3	89.6
Carbendazim/benomyl	3.4	1–200	2.1	3.8	79.9
Chlorantraniliprole	7.6	1–200	3.9	10.7	100.6
Chlorpyrifos	8.9	1–200	6.5	10.6	90.6
Chlorpyrifos-methyl	10	10–200	6.8	16.8	92.6
Clofentezine	3.6	1–200	5.4	8.2	92.2
Deltamethrin	10	1–200	6.1	11.7	89.5
Dodine	3.6	1–200	2.8	7.1	88.0
Emamectin benzoate	2.8	1–200	3.9	6.2	93.8
Etofenprox	1.0	1–200	5.5	10.4	88.0
Etoxazole	5.8	5–200	4.1	12.2	86.4
Fenazaquin	3.7	1–200	4.0	8.8	83.5
Fenpropathrin	3.9	1–200	5.0	9.2	78.9
Fludioxonil	5.5	5–200	4.1	7.8	93.9
Formetanate HCL	2.6	1–200	1.4	4.0	87.2
Hexythiazox	4.2	1–200	3.6	6.4	85.6
Imidacloprid	9.7	1–200	4.6	7.4	80.0
Indoxacarb	7.5	1–200	4.9	7.9	95.1
Metalaxyl/metalaxyl-M	2.6	1–200	3.8	5.0	96.6
Methomyl	3.5	1.200	2.2	4.4	97.8
Methoxyfenozide	10	10–200	9.5	14.7	89.1
Metrofenone	10	10–200	6.4	11.2	90.1
Myclobutanil	10	1–200	8.1	8.5	90.3
Penconazole	10	1–200	4.3	10.6	91.1
Pirimicarb	2.4	1–200	1.5	3.1	90.3
Propamocarb	10	1–200	2.6	6.3	96.8
Pymetrozine	10	1–200	3.4	4.6	90.4
Pyraclostrobin	10	1–200	7.7	8.7	89.6
Pyrimethanil	10	1–200	3.6	5.8	89.0
Primiphos-methyl	10	1–200	10.2	10.2	88.9
Pyridaben	10	1–200	8.1	14.8	76.9

Pesticide residues in pepper samples

In the present study, 108 pepper samples were investigated for 283 pesticide active ingredients. As a result, no residue was detected in 34 samples (31.5%), while one or more pesticide residues were detected in 74 samples (68.5%). Of pesticide residues, 36.5% were single residue and 63.5% were multiple (Fig. 1). Of the pepper samples with multi pesticide residues, 3 samples had 6, 7, and 8 residues. In addition, 5 samples (4.6%) had 5 different pesticide residues, 10 samples (9.2%) had 4, 14 samples (13.0%) had 3, and 15 samples (13.9%) had 2 different pesticide residues (Fig. 1). Pesticide residues between 1 and 3 were determined in the pepper samples taking from between April and August, and October and November; 4 and 5 pesticide residues between April and July and in October 6 and 8 pesticide residues in April, and 7 pesticide residues in June were determined.

The pesticide contamination rate of pepper samples was higher than the values given in the EU's 2016 pesticide residue report for unprocessed peppers. According to the data obtained from the sweet pepper analyses conducted in various countries, 51% of 6451 sweet pepper samples were contaminated with pesticides and 20.9% had single residue and 32.5% had multiple residues (EFSA, 2018).

In previous studies, different pesticide residue rates were detected depending on the extraction methods, devices, chemicals, pesticides, number of samples, and compliance with the SANCO criteria (SANCO, 2014).

While single (4 samples) and multiple (4 samples) pesticide residues were detected in 40% of 10 pepper samples taken from the local markets of Konya province (Turkey) (Ersoy et al., 2011); single residues were detected in 12.8% of 211 pepper samples and multiple residues were detected in 55.4% of samples in Saudi Arabia (Ramadan et al., 2020). In another study, 26 pesticides were screened in 299 bell pepper samples collected from wholesale markets, supermarkets, and bazaars in Shandong Province of China and it was reported that 21.4% of the samples had single and 7.3% had multiple residues (Chu et al., 2019).

In the present study, the highest residue levels were observed in April (19.4%) and it was respectively followed by October (17.8%), June (16.8%), May (14%), and July (13.5%) (Table 5). Differences in pesticide residues of the months could be attributed to differences in farmer practices in pesticide treatments against pests and diseases under variable climate conditions and emergence of pests and diseases. Present findings revealed that growers intensively used pesticides against pests and fungal diseases throughout the sampling period. In addition, the use of pesticides registered against the pests in different crops but unregistered in pepper or of banned pesticides remained in hands of farmers from previous years may cause undesirable residues that are multiple or exceed MRL values. Present findings also revealed that following insecticides and fungicides, growers mostly used acaricides especially in May and October.

Of the pesticide residues encountered in pepper samples, 97 were insecticides, 68 were fungicides (18 were FST applied to soil or seeds), 18 were acaricides, and one was aphicide and miticide (Table 5). Insecticides were mostly composed of acetamiprid (15.1%), imidacloprid (6.5%), and pirimiphos-methyl (4.9%); fungicides were composed of triadimenol

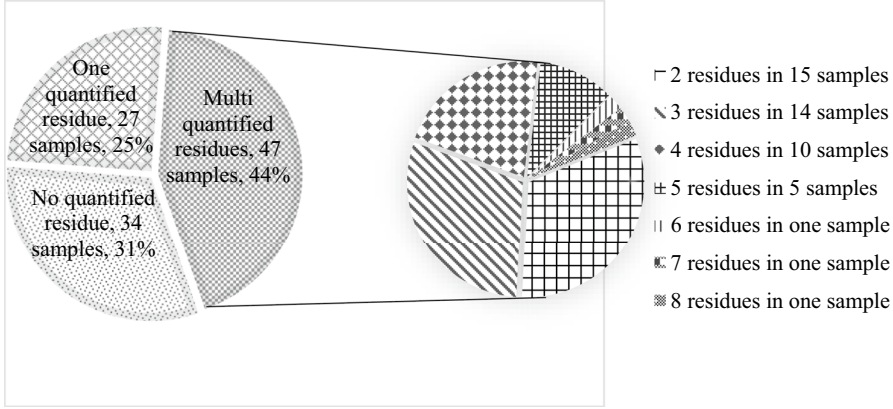

Fig. 1 Number of detected residues in individual pepper samples

Table 5 Monthly pesticide residues encountered on pepper samples

Active ingredient	Main use[d]	Active ingredient amount per sample by months (mg/kg)[e]								MRL[f] mg/kg	Risk class[g]
		April	May	June	July	August	September	October	November		
Acetamiprid	I	0.105; **0.402**; 0.012; 0.031	0.086; 0.071; 0.018	0.018; 0.055; 0.383	0.01; 0.207; 0.021; 0.019 0.023; 0.021	0.014; 0.116; **0.311**	0.012; 0.016; 0.035; 0.059	0.014; 0.013; 0.01; 0.009; 0.085		0.3	II
Azoxystrobin	F		0.102	0.077; 0.012		0.011	0.027	0.01	0.025; 0.028	3	U
Bifenazate	AC		0.031					0.068		3	U
Boscalid	F	0.258; 0.01	0.054; 0.032	0.013	0.076		0.013; 0.122	0.072; 0.02		3	U
Buprofezin	I		0.01		0.009					0.01	III
Carbendazim/ benomyl[a]	F						0.025			0.1	U
Chlorantraniliprole	I	0.026				0.01		0.015; 0.042; 0.011; 0.009		1	U
Chlorpyrifos	I	**0.19**	**0.178**; **0.016**	**0.625**	**0.011**; **0.051**			**0.037**		0.5 (0.01)	II
Chlorpyrifos-methyl	I	0.017; 0.432		0.032						0.5 (0.01)	III
Clofentezine	AC	0.018						0.006		0.02	III
Deltamethrin	I	0.042								0.2	II
Dodine[c]	F						0.022			0.05 (0.01)	II
Emamectin benzoate	I	0.015						0.012		0.02	II
Etofenprox[c]	I		**0.017**							0.01	U
Etoxazole	AC		**0.032**						**0.015**	0.02 (0.01)	III
Fenazaquin[c]	AC		**0.034**							0.01 (0.5)	II
Fenpropathrin[a]	I	0.008								0.01	II
Fludioxonil	F	0.027								2 (1)	U
Formetanate HCl[c]	AC		**0.08**		**0.106**; **0.537**	**0.037**		**0.243**		0.05 (0.01)	Ib
Hexythiazox	AC		0.008; 0.013					0.009		0.5	U
Imidacloprid	I		0.025; 0.02	0.021; 0.055; 0.038	0.189; 0.045	0.034	0.032	0.014; 0.075	0.016	1	II
Indoxacarb	I		0.021			0.039	0.082		0.123	0.3	II
Metalaxyl/ metalaxyl-M	F	0.014	0.036; 0.03		0.016	0.014		0.009; 0.046	0.016	0.5	II
Methomyl[b]	I								**0.082**	0.02 (0.04)	Ib
Methoxyfenozide	I						0.079	0.022		1 (2)	N

Table 5 (continued)

Active ingredient	Main use[d]	Active ingredient amount per sample by months (mg/kg)[e]								MRL[f] mg/kg	Risk class[g]
		April	May	June	July	August	September	October	November		
Metrafenone	F	**0.026**								0.01 (2)	U
Myclobutanil	F		0.014			0.077				0.5 (3)	II
Penconazole	F	0.03								0.2	III
Pirimicarb	AP				0.012					1 (0.5)	II
Propamocarb[c]	F			0.011						1 (3)	U
Pymetrozine[b,c]	I			0.042						10 (3)	III
Pyraclostrobin	F	0.055			0.024		0.021	0.017		1 (0.5)	N
Pyrimethanil[c]	F	0.599		0.033						0.5 (2)	III
Pirimiphos-methyl	I	0.047; 0.112; 0.043; 0.011; 0.545	0.01; 0.097	0.024	0.157					0.01	II
Pyridaben	AC		**0.018**	**0.014**; **0.018**						2 (0.01)	II

[a]Banned active ingredient in Turkey

[b]Active ingredients to be banned in 2021 in Turkey

[c]Unlicensed active ingredient for pepper

[d]*I* insecticide, *F* fungicide, *AC* acaricide, *AP* aphicide, *FST* fungicide for seed treatment, *MT* miticide

[e]Bold numbers indicate the values above the MRL according to TR MRLs or EU MRLs

[f]Turkish Food Codex MRL (Maximum Residue Limit) value, the values in parentheses indicate EU Codex MRL values

[g]WHO-recommended Classification of Pesticides by Hazard taking into account GHS (The Globally Harmonized System of Classification and Labelling of Chemicals) Ia: extremely hazardous, Ib: highly hazardous, II: moderately hazardous, III: slightly hazardous, U: unlikely to present acute hazard, N: non-classified (WHO, 2019)

(9.7%), boscalid (5.4%), and tebuconazole (4.9%) applied to soil and seeds; acaricides were composed of frometanate HCl (2.7%), hexythiazox (1.6%), and pyridaben (1.6%) (Table 5). Besides, miticide tebufenpyrad and aphicide pirimicarb were encountered in one sample each. The carbendazim/benomyl, fenpropathrin, and thiram encountered in samples were banned in Turkey, methomyl, triadimenol, and pymetrozine (unlicensed for pepper) are to be banned in 2021 and dodine, etofenprox, fenazaquin, formetanate HCl, propamocarb, pyrimethanil, and tebuconazole are unlicensed for pepper.

Ersoy et al. (2011) conducted pesticide residue analyses on limited number of vegetable samples (10 samples from each vegetable) collected from the markets and bazaars of Konya province (Turkey) and similar with the present findings, identified imidacloprid (3 samples), fludioxonil and carbendazim/benomyl (2 samples each), and acetamiprid and boscalid (one sample each), but different from the present findings, identified ethion, triazophos, and chlorothalonil (one sample each). In another study conducted in Hatay province of Turkey, 10 green and red pepper samples taken from different fields were analyzed for pesticide residues. Similar with the findings, acetamiprid, imidacloprid, pyriproxyfen, and triadimenol were identified in green peppers and different from the present findings, fenarimol was identified. Different from the green peppers, metalaxyl and thiabendazole were identified in red peppers (Sungur & Tunur, 2012).

Similar with the present findings, chlorpyrifos, fenpropathrin, and methomyl were identified in pepper samples in China (Chu et al., 2019), deltamethrin, pirimiphos-methyl, chlorpyrifos-methyl, imidacloprid, and metalaxyl were identified in Kuwait (Jallow et al., 2017), chlorpyrifos, pirimiphos-methyl, and triadimenol in Egypt (Doheim et al., 2002), pirimiphos-methyl in Korea (Cho et al., 2009), and methomyl, metalaxyl-M, carbendazim, acetamiprid, pyriproxyfen, chlorpyrifos-methyl, hexthiazox, penconazole, tebuconazole, and triadimenol in Saudi Arabia (Ramadan et al., 2020). Different from the present findings, dichlorvos, parathion, parathion-methyl, phorate, isofenphos-methyl, monocrotophos, triazophos, methidation, omethoate, acephate, carbofuran, aldicarb, fenpropathrin, and fenvalerate were identified in pepper samples in China (Chu et al., 2019), profenofos in Kuwait (Jallow et al., 2017), bromopropylate, dimethoate, cypermethrin, diazinon, dicofol, endosulfan, ipradion, malathin, metamidophos, phosalone, procymidone, profenofos, tetradifon, and vinclozoline in Egypt (Dogheim et al., 2002), ethoprophos, kresoxim-methyl, endosulfan, EPN, nuarimol, procymidone, and chlorothalonil in Korea (Cho et al., 2009), and ethion, diazinon, chlofenapir, hexaconazole, kresoxim-methyl, metribuzin, tebuconazole, thiocloprid, and triadimenol in Saudi Arabia (Ramadan et al., 2020).

In China, 26 pesticide residues of Organophosphate, Pyrethroid, and Carbamate groups were investigated on bell peppers (299 samples) and the most common residues were respectively identified as bifenthrin (5.01%), chlorpyrifos (4.35%), dichlorvos (3.68%), fenpropathrin (3.34%), monocrotophos and dimethoate (2.68%), methamidophos and omethoate (2.34%), and methomyl and cyhalothrin (1.67%) (Chu et al., 2019). Of these pesticides, chlorpyrifos and fenpropathrin were also identified in the present study. However, 14 pesticides (dichlorvos, parathion, parathion-methyl, phorate, isofenphos-methyl, monocrotophos, triazophos, methidation, omethoate, acephate, carbofuran, aldicarb, fenpropathrin, fenvalerate) identified in bell peppers of China were not encountered in the present study probably because they were banned in Turkey. Methomyl, cyfluthrin, and bifenthrin are among the pesticides to be banned in 2021. Similarly, 9 different pesticide residues were investigated on fruits and vegetables in Kuwait and deltamethrin, pirimiphos-methyl, chlorpyrifos-methyl, imidacloprid, and metalaxyl were identified in 83% (10 samples) of pepper samples and it was also found that pepper samples were contaminated with profenofos which was banned in Turkey (Jallow et al., 2017).

In a study investigating 54 pesticide residues on fruit and vegetable samples collected from markets in Egypt and similar with the present findings, the most common residues on 141 pepper samples were identified as dimethoate (15 samples), dicofol (15 samples), cypermethrin (7 samples), bromoproplate (6 samples), and profenofos (5 samples) (Dogheim et al., 2002). However, only two of 17 pesticides identified on pepper samples (chlorpyrifos, 4 samples and triadimenol, 1 sample) were also identified in the present study (Table 5). On the other hand, in a study conducted in Korea with 1207 pepper samples of which 0.9% contaminated with pesticides, the most common pesticide was identified as ethoprophos

(5 samples) (Cho et al., 2009). Similar with the present findings, pirimiphos-methyl, kresoxim-methyl, banned (in Turkey) pesticides of endosulfan, EPN, nuarimol, procymidone, and unlicensed (for pepper) pesticide of chlorothalonil were identified in that study.

Some of the pesticides identified in present pepper samples were also identified in vegetable samples collected from supermarkets in Saudi Arabia (Ramadan et al., 2020). About 50% (12 samples) of the samples were contaminated with pesticides and similar with the present findings, methomyl (7 samples), metalaxyl-M and carbendazim (4 samples each), acetamiprid (3 samples), pyriproxyfen and chlorpyrifos-methyl (2 samples each), hexthiazox, penconazole, tebuconazole and triadimenol (one sample each) were identified on samples. Apart from these pesticides, Ramadan et al. (2020) identified banned pesticides of ethion, diazinon, chlofenapir, hexaconazole, unlicensed pesticides (for pepper) of kresoxim-methyl, metribuzin and tebuconazole and pesticides of thiocloprid and triadimenol to be banned in 2021 in Turkey (PPPs, 2020).

Of the present 185 pesticide residues identified on pepper samples, 24 residues belonging to 9 different pesticides (13%) had levels greater than MRL specified in Turkish and EU Food Codex. Of these residues, 2 had greater levels than the MRL of TR, 13 had greater levels than the MRL of EU, and 9 had levels greater than the MRL of both EU and TR (Table 5). On the other hand, it was indicated in 2018 pesticide residue report of EU that 65 of 4361 samples (1.5%) analyzed in 2016 in Turkey violated the MRL values (EFSA, 2018). The differences between the violation ratios of EU and the present study were attributed to differences in study durations and number of samples.

Residue levels of formatanate HCL, listed in "highly hazardous" group (Ib) of WHO, in 4 samples (0.08, 0.106, 0.537, and 0,243 mg/kg) and methomyl level of one sample (0.082 mg/kg) were greater than the MRL of both Turkish and EU codex (Table 4). MRL value for formatanate is defined as 0.05 mg/kg (TR) and 0.01 mg/kg (EU) and MRL value for methomyl is defined as 0.02 mg/kg (TR) and 0.04 mg/kg (EU). Of these pesticides, formatanate is unlicensed for pepper and methomyl is banned in 2021. Residue levels of acetamiprid, listed in moderately hazardous group (II) in 2 samples (0.402, 0.311 mg/kg), chlorpyrifos in one sample (0.625 mg/kg), fenazaquin in one sample, and pyridaben in 3 samples (0.018, 0.014, 0.018 mg/kg) were greater than the MRL of Turkish and/or EU food codex (Table 4). On the other hand, residue levels of etofenprox, listed in "unlikely to present acute hazardous (U)" group in one sample (0.017 mg/kg) and metrafenone in one sample (0.026 mg/kg) were also greater than the MRL of TR and EU (0.01 mg/kg) and MRL of EU (0.01 mg/kg).

Existence of etofenprox, fenazaquin, and formatanate, which was banned to be used in peppers in Turkey, and methomyl, listed in "highly hazardous (1b)" group, at levels greater than the MRL of TR and EU Codex revealed that public health was under danger. Thusly, active ingredients and formulations of the pesticides listed in "highly hazardous (1a or 1b)" group have carcinogenic, mutagenic, reproductive toxicity and pose serious irreversible health risks on humans and environment (FAO & WHO, 2016).

Similar with the present findings, pesticide residue levels of pepper samples exceeding MRL values were also reported in previous studies conducted in Turkey. Ersoy et al. (2011) investigated pesticide residues (203) on vegetable samples collected from markets and bazaars of Konya province (Turkey) and identified the residue levels of banned pesticides of ethion, triazophos, and benomyl-carbendazim as greater than the MRL values. Of these pesticides, triazophos is listed in "highly hazardous (Ib)," ethion in "moderately hazardous (II)," and benomyl-carbendazim in "slightly hazardous (U)" group (WHO, 2020). In another study conducted on vegetables collected from the markets of Aegean region, residue levels of acetamiprid, carbendazim/benomyl, clofentezine, dimethomorph, imidachloprid, methomyl, oxamyl, and trifloxystrobin were greater than the MRL values (Bakırcı et al., 2014). Of these pesticides, oxamyl is listed in "extremely hazardous (Ia)" and methomyl in "highly hazardous (Ib)" group (WHO, 2020).

Contrary to the present findings, Kaya and Tuna (2019) conducted pesticide residue analyses on limited number of fruit and vegetable samples (42 samples) collected from three different bazaars of İzmir province and did not encounter any residue levels in peppers exceeding MRL values. In another province of Turkey (Hatay), Sungur and Tunur (2012) investigated the existence of 175 pesticide residues on fruits and vegetables and did not encounter residue levels of greater than MRL in pepper samples (10 samples). The reason not to see residue levels greater than MRL

values might be attributed to limited number of samples in those studies.

In other studies, conducted in Turkey with green pepper (325 samples) and cucumber (400 samples) samples collected from the markets and bazaars of Adana, Mersin, and Antalya provinces, pesticide residues were encountered in 13.2% (96 samples) of the samples, but none of them was exceeding MRL values of EU (Golge et al., 2018). Existence of 170 pesticides was investigated in several number of samples in that study and 9 pesticides were encountered in pepper samples and 5 different pesticides were identified in cucumber samples.

On the other hand, it was indicated in EU 2018 report on pesticide residues in foodstuffs that 284 of 6451 pepper samples (4.4%) analyzed in 2016 had residue levels greater than the MRL values (EFSA, 2018). In the same report, it was indicated that violation of MRL values was encountered in 14 of 111 samples (12.6%) in Dominican Republic, 12.6% of pepper samples in Egypt, and 6 of 74 chili pepper samples (8.1%) in Thailand.

Besides EU 2018 reports (EFSA, 2018), violation of MRL values was reported for samples collected from markets and bazaars of different countries. Pesticide residue levels were greater than MRL values in peppers for 11 pesticides (bromopropylate, chlorpyrifos, cypermethrin, diazinon, dicofol, dimethoate, tetradifon, and triadimenol) in Egypt (Dogheim et al., 2002), half of 14 chili pepper samples had residue levels of 5 pesticides (cyproconazole, ethion, methomyl, prefenofos, and chlorfenopyr) greater than the MRL values in Saudi Arabia (Ramadan et al., 2020), 8 of 15 black pepper samples had residue levels of 2 pesticides (carbendazim in 6 samples, metalaxyl-M in two samples) greater than the MRL values in China, again residue level of one pesticide (bifenthrin) in bell peppers was greater than the MRL values of China (Chu et al., 2019), and 12 of 1207 pepper samples had residue levels of 7 pesticides (chlorotharonil, endosulfan, EPN, ethoprophos, kexosim-methyl, nuarimol, pirimiphos-methyl, procymidone) greater than the MRL values in Korea (Cho et al., 2009).

As it was in pesticide analyses conducted on peppers in Turkey, violation of residue limits was not encountered in some other countries. For instance, Mutengwe et al. (2016) identified existence of 74 commonly used pesticides in fruit and vegetable samples collected from two large markets of South Africa, but none of them were exceeding MRL values. Non-compliance with MRL values was not encountered for 34 pesticide residues in 150 fruit samples in Kuwait (Jallow et al., 2017).

Conclusion

Ministry of Agriculture and Forestry of Turkey encourages farmers to implement Good Agricultural Practices and Integrated Pest Management (IPM) for providing healthy products that do not contain risky pesticide residues to consumers. In addition, "Prescription Pesticide Sales" and to keep "Producer Registry Book (33 products including pepper)" have been made mandatory for monitoring and control of pesticide use. However, present findings revealed that unlicensed pesticides or banned pesticides for all crops are still able to be used in pepper cultivation in Turkey. Therefore, consumers and producers should be trained to raise awareness on pesticide residues and risks, pesticide uses. Residues should better be monitored and integrated management, and organic and good agricultural practices should be widespread.

Acknowledgements This work was a part of the master thesis of Uğur Çiftçi (School of Graduate Studies, Department of Plant Protection, Çanakkale Onsekiz Mart University). The authors are also grateful to Prof. Dr. Zeki Gökalp (Certified English Translator) for his critical reading and through syntactic corrections of the manuscript. Pesticide analyses of pepper samples were conducted at Residue Laboratory of Çanakkale Food Control Directorate of Ministry of Agriculture and Forestry, Accredited (ISO 17025i) by TÜRKAK for 156 pesticide active ingredients in accordance with TS EN ISO/IEC 17025.

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethical approval All applicable international, national, and institutional guidelines were followed for collecting samples and while handling in the laboratory for analysis.

Conflict of interest The authors declare no competing interests.

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