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DETERMINATION OF PESTICIDE RESIDUES IN PICKLED VINE (*Vitis vinifera* L.) LEAVES BY A VALIDATED LC-MS/MS METHOD

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ABSTRACT

Pesticides are chemicals used to combat insects, rodents, fungi and weeds, which are agricultural pests. In this study, it was aimed to determine pesticide residues of the pickled vine leaves produced by industrial and traditional methods from Narince variety grown in Tokat. The amounts of pesticides in the pickled vine leaves were determined by the QuEChERS (quick, easy, cheap, effective, rugged and safe) method. As a result of pesticide analysis performed on pickled vine leaves, 13 different pesticide active ingredients were determined and 8 pesticides were found to be above the maximum residue limit (MRL) value. While, the highest substance amounts according to MRL values were cyhalothrin, pyraclostrobin, cypermethrin, boscalid, the most detected pesticide active ingredients were ethiofencarb, isocarbofos, cyhalothrin, respectively. As a consequence of the investigation, it was found that detected some pesticide residue amounts from pickled vine leaves were at a level that would pose a health risk.

Keywords: Method validation, pesticide residue, QuEChERS method, vine leaf

VALİDE EDİLMİŞ BİR LC-MS/MS METODUYLA ASMA YAPRAKLARINDA PESTİSİT KALINTILARININ BELİRLENMESİ

ÖZ

Pestisitler tarım zararlıları olan böcek, kemirgen, mantar ve yabani otlarla mücadele de kullanılan kimyasallardır. Bu çalışmada, Tokat ilinde yetiştirilen Narince çeşidinden endüstriyel ve geleneksel yöntemlerle üretilen salamura asma yapraklarında pestisit kalıntılarının belirlenmesi amaçlanmıştır. Salamura asma yapraklarındaki pestisit miktarları QuEChERS (hızlı, kolay, ucuz, etkili, dayanıklı ve

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güvenli) yöntemi ile belirlenmiştir. Salamura asma yapraklarında yapılan pestisit analizi sonucunda 13 farklı pestisit etken maddesi tespit edilmiş olup 8 pestisit maksimum kalıntı limiti (MRL) değerinin üzerinde bulunmuştur. MRL değerlerine göre en yüksek pestisit miktarları sihalotrin, piraklostrobin, sipermetrin, boskalid iken en çok tespit edilen pestisit maddeleri sırasıyla etiyofenkarb, izokarbofos, sihalotrin olmuştur. Araştırma sonucunda, salamura asma yapraklarında tespit edilen bazı pestisit kalıntı miktarlarının sağlık açısından risk oluşturacak düzeyde olduğu belirlenmiştir.
Anahtar kelimeler: Metot validasyonu, pestisit kalıntısı, QuEChERS metodu, asma yaprağı

INTRODUCTION

Grape cultivation and viticulture are geographically spread over a very wide area in the world. Grapes are grown between 20°-50° latitudes in the Northern Hemisphere and 20°-40° latitudes in the Southern Hemisphere (Dağlıoğlu, 2005).

Turkey has favorable conditions for viticulture in terms of mathematics, geographical location and climatic characteristics. According to the 2020 data of the Turkish Statistical Institute (TurkStat), there are 23136 thousand hectares of agricultural land in Turkey. Viticulture activity are carried out in 4010 thousand decares of this area. When these data are evaluated, it is determined that about 17% of the total cultivated agricultural area is viticulture (Anonymous, 2021). In Turkey, grapes are mostly consumed as table, dried and processed into wine. It is also used in the production of many products specific to Turkey such as rakı, pickles, bastık, pekmez, tarhana (Cangi and Yağcı, 2017). Vine leaves, which are consumed fresh or in brine, which is one of the most important income sources, whose production and trade have been increasing in recent years, have even left the grape fruit in the background in some regions. Its production is mostly made in Manisa and Tokat provinces in Turkey. Especially in Tokat, Manisa and Mersin, the production of fresh and pickled vine leaves took the first place and grapes started to take place in the second plan as a source of income (Cangi and Yağcı, 2012). Due to its structure, vine leaves are not suitable for long-term storage and consumption. For this reason, it is processed with different methods and its shelf life is extended and marketed. Vine leaves can be frozen, dried, fermented (dry salted, in brine), canned and preserved without brine (Cangi and Yağcı, 2017). Sultani Çekirdeksiz, Narince, and Yapıncak types are the most preferred ones for making pickled leaves. Narince variety is mostly found in Tokat and Amasya regions. Almost all of the vineyards in these provinces are of this variety. It is a white, thin-skinned and intensely flavored grape variety (Eren, 2014). The leaves of Narince cultivar are broad and angular, long-stalked, medium hairy, less sliced and medium hard (Demirhan, 2006).

Vine leaves have an important export potential for Turkey. In Turkey, approximately 13.5 million dollars of revenue is obtained from the export of vine leaves and 135 million dollars from the stuffed grape leaves (Kuşaksız and Çimer, 2019). As in all commercial agricultural products, irrigation and fertilization are carried out in order to increase the yield and obtain more products. Chemical pesticides are used in the fight against diseases and pests such as powdery mildew, mildew and vineyard scabies, which are common in the region (Bal et al., 2016; Pertot et al., 2016). Chemical applications are the most used method in the fight against various diseases in grape and vine leaves because they give quick and precise results (Hayar et al., 2021). Chemical control methods are harmless when used consciously and in a controlled manner. However, it is reported that it poses a threat to food safety with its unconscious or uncontrolled use (Şık et al., 2012). Recent research have revealed that even when the use of chemicals in agricultural production is under control, it can pose serious risks to humanity. Applications in food safety, environmental pollution, toxicology, and occupational health are just a few of the areas where pesticide residues are examined (Niessen, 2010). With the development of modern agriculture in terms of food safety, pesticide residue analysis has become a very important issue due to their intensive use. It is very important to analyze and monitor pesticide residues and to evaluate the level of exposure of people to pesticides through their food consumption (Sannino et al., 2004). Since viticulture has an important place in the Tokat region, grapes and their products contain pesticide residues are one of the important problems (Cangi et al., 2014; Bal et al., 2016). Discussions about residue issues have begun as a result of the rise in vine leaf exports. In addition to these problems, residue declarations were transmitted in vine leaves from Turkey to Germany, Bulgaria and Austria in 2020-2022, and from Egypt to Cyprus, Austria, Germany, Bulgaria, Ireland and Netherlands in 2020 and 2021 (Balkan and Kara, 2023; Anonymous, 2023). Food products in Turkey are subject to inspection according to the Turkish Food Codex Maximum Residue Limits of Pesticides regulation. This regulation has been prepared taking into account the Regulation (EC) No 396/2005 of the European Parliament and of the Council on Maximum Residue Limits of Pesticides in Foods of Plant and Animal Origin, dated 23/2/2005. It is also updated according to the updates of the Council of the European Union. It is critical that analytical techniques for tracking pesticide residues in plants be developed or modified. QuEChERS is the most often used technique for determining pesticide residues, and it works well when combined with mass spectrometry detectors. It is highly recommended to use gas chromatography tandem mass spectrometry (GC-MS/MS) and liquid chromatography tandem mass spectrometry (LC-MS/MS). As numerous pesticides can be analyzed using a single injection thanks to the great sensitivity and selectivity of GC-MS and LC-MS (Balkan and Karaağaçlı, 2023).

In the literature, it has been determined that vine leaves are rich in phenolic compounds and have several biological activities (Lacerda et al., 2016). However, pesticide residues used in vine cultivation can cause various health problems. In addition, pesticide residues create economic losses in terms of domestic and foreign markets (Gazioğlu-Şensoy et al., 2017). Since viticulture has an important place in the Tokat region, pesticide residues on vine leaves are one of the important problems. In present research, it was aimed to detected pesticide amounts of pickled vine leaves, which are traditionally and commercially produced from the leaves of Narince grape variety in Tokat province in the Central Black Sea Region of Turkey, and to determine their compliance with the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides. For this purpose, it was worked up determine pesticide residues from wine leaves by the QuEChERS method, which consists of three stages (extraction, clean-up and chromatography).

MATERIAL and METHODS

Sample collection

In the study, pickled vine leaves (15 samples) produced from Narince grape variety (peculiar to Tokat region) were used. These 15 brands dominate the majority of the Tokat market. Industrially produced vine leaves belonging to different brands were obtained from the Merkez district (Tokat province) and traditionally produced vine leaves were obtained from Erbaa and Niksar districts (Tokat province) (Figure 1). All samples were collected from the market in June 2020. Because, the vine leaves that are harvested and fermented for the first time in the year are release to the market in this month. For each brand, two samples of one kilogram each with the same production dates and batch numbers were obtained. Selection criteria for pickled vine leaves were based on the Narince variety grown in the Tokat region in 2020. Because the pickled vine leaves of the Narince variety, which are grown and processed in Tokat, have a significant market share in Turkey. The brine leaf samples produced industrially are expressed with the E code, and the traditionally produced samples with the G code. After the samples were obtained, they were stored at 4-8 °C under refrigerator conditions in the laboratory of the Tokat Gaziosmanpaşa University Faculty of Engineering and Architecture, Department of Food Engineering. Analyses were carried out in Tokat Gaziosmanpaşa University Food Engineering Department and Scientific and

Technological Research Application and Research Center laboratories.

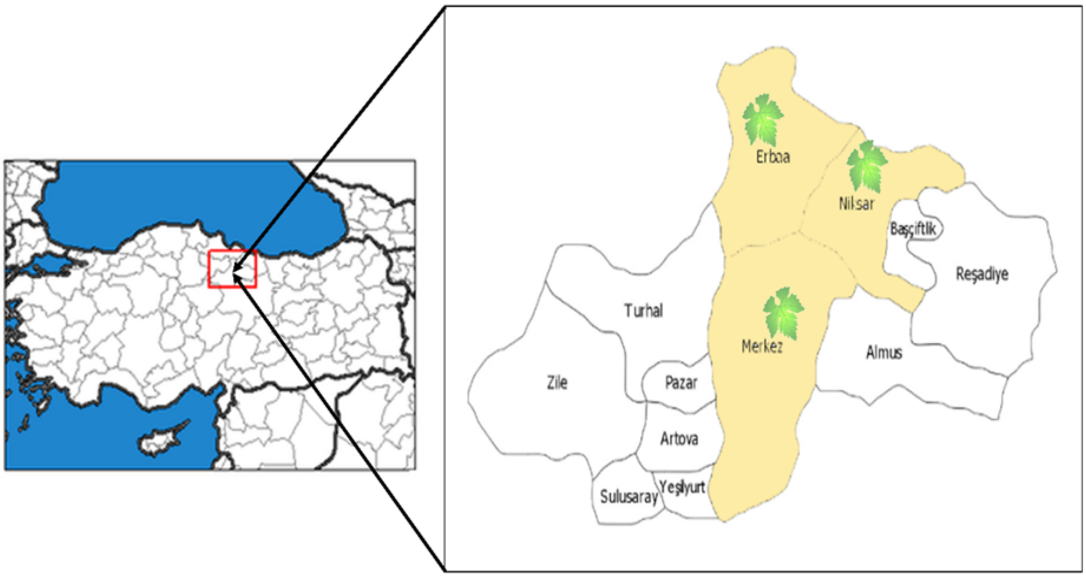

Figure 1. Sampling points on the map of Tokat province

Chemical materials and equipments

Ammonium formate, acetic acid and methanol were obtained from Merck (Darmstadt, Germany). Pesticide reference standards were supplied Dr. Ehrenstorfer Laboratories GmbH (Augsburg, Germany). Q-sep packages (magnesium sulfate anhydrous ($MgSO_4$), sodium acetate (NaOAc), ($MgSO_4$+PSA (primary secondary amine)+C18) were purchased from Restek (France). Precise balance (Radwag, Poland), grinder (Premier, Turkey), distilled water instrument (Merck, Germany), LC-MS/MS device (Shimadzu, Japan) were used in various research stages.

Sample extraction and clean-up for pesticide residue analysis

243 different pesticides on pickled vine leaves were analyzed using the QuEChERS method. This method consists of three stages: extraction, clean-up and chromatography (Figure 2). With LC-MS/MS, each sample was examined in triplicate (Lehotay, 2007).

LC-MS/MS analyses

This research was conducted using a Shimadzu® LC-MS 8050 model. LC-MS/MS system equipped with UPLC: LC-30AD pump x 2, SIL-20A autosampler, DGU-20A3R degasser, CTO-20ACV column oven and triple quadrupole MS/MS detector. The LC column was made by GL Sciences Inc. (Tokyo, Japan) and was an Inertsil (ODS IV) C18 column (2.1 mm x 150 mm, 3 µm particle size). A gradient elution procedure was used to carry out the chromatographic separation, using eluents A and B made up of dH_2O + 5 mM ammonium formate and methanol + 5 mM ammonium formate, respectively. Analysis started with 5% eluent B, which was increased linearly to 60% in 3 min, 70% in 4 min, 80% in 6 min, 95% in 7 min. The gradient elution was started at 5 % of B (held 1 min), then increased linearly to reach 95% of B in 4 min (held 2 min), and decreased to initial stage (5% of B) at 6 min, holding until 9 min. There was a 0.40 mL/min flow and 10 µL injection volume was used. The autosampler was kept at 4 °C, and the column oven was kept at 35 °C. For MS/MS detection, the electro spray ionization (ESI) interface was used positive polarity with the following; 3 kV of capillary voltage, 3V of extractor voltage, 350 °C of heat block temperature, 250 °C of desolvation line (DL) temperature, Nitrogen (N_2) as nebulizer gas of 2.9 L min^{-1} and drying gas of 10 L min^{-1}. N_2 gas of 99% purity produced by a Peak Scientific nitrogen generator (Billerica, MA, USA) was used in the ESI source and the collision cell. Collision induced dissociation (CID) gas is argon (Ar, 99.999%) of 230 kpa with flow rate 0.15 mL min^{-1}. LabSolution® software (version 4.91) was used to regulate all instrument parameters. (Balkan and Yılmaz, 2022).

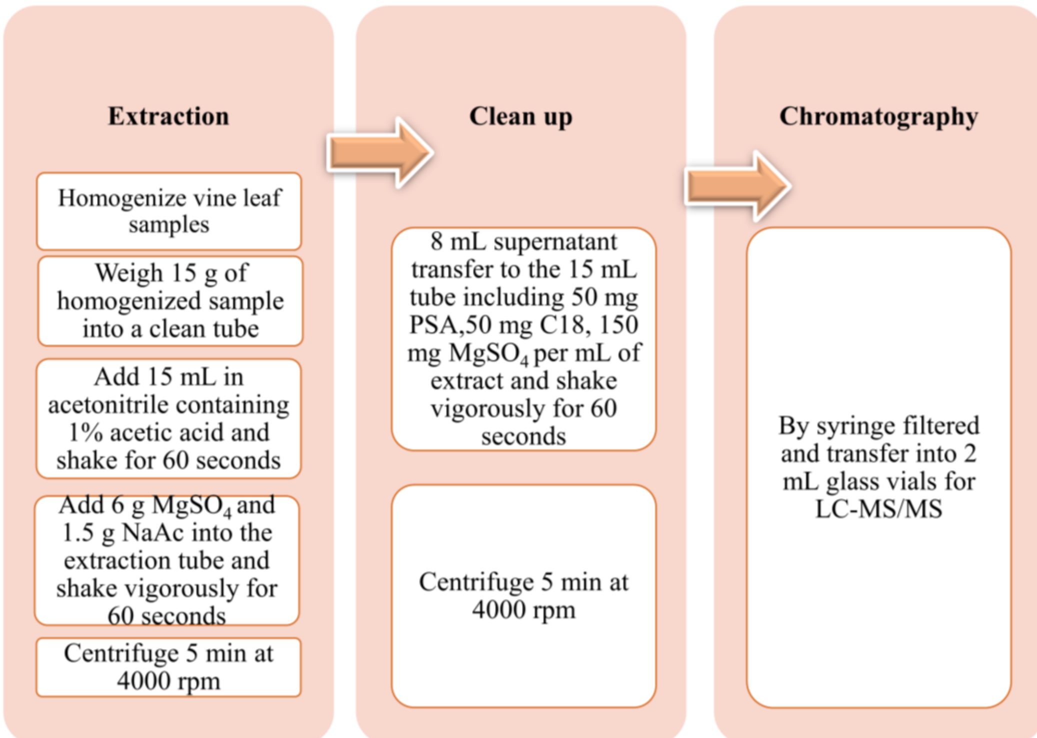

Figure 2. Analytical steps of the QuEChERS-AOAC Official Method 2007

Method validation

Using the European SANTE/11312/2021 Guideline (EC, 2021), the analytical method was internally validated by evaluating linearity, mean recovery, limit of detection (LOD), limit of quantification (LOQ), and precision (repeatability and within-laboratory reproducibility). Using matrix-matched calibration standards at six doses ranging from 5 to 200 g/kg, the method's linearity was evaluated. Linear regression coefficients (R^2) values of>0.99 were acceptable. After 10 mg/L of multistandard working solution was added to samples of blank matrix (grape leaves), 10 replicate analyses were carried out. Three times the relevant standard deviation (SD) was used to determine the LODs. According to SANTE Guideline, the LOQs were determined as 10 times the SD of the 10 replicate analyses that can be quantified with respect to acceptable recoveries (between 70 and 120%) and repeatability ($RSD_r \leq$ 20%) (EC, 2021). The recovery of pesticides from matrix and precision of the method were determined by the analyses of blank samples fortified at two concentration levels (10 and 50 µg kg^{-1}) in five replicates. On the same day, the repeatability (RSD_r) was assessed. On five consecutive days, the within-laboratory reproducibility (RSD_{WR}) test was run. The precision values were expressed as the relative standard deviation (RSD) (Magnusson and Örnemark, 2014).

RESULTS and DISCUSSION

Method validation

In the validation studies, the blank samples were examined and checked for the presence of any of the target pesticides before being added to the analytical sections with the necessary quantity of pesticide mixtures. The 243 pesticides (acaricide, fungicide, herbicide, insecticide, and plant grow regulator) were utilized to validate the method. These pesticides are listed in Table 1. Total Ion Chromatogram (TIC) was given in Figure 3.

For all pesticides, linearity was achieved with coefficients of determination (R^2) better than 0.990. The mean recoveries (RM%) over the analytical ranged from 71.17 to 119.37 % as shown in Table 1. The within-laboratory repeatability (RSD_r%) and reproducibility (RSD_{WR}%) of the recovery results were used to evaluate the method's accuracy and precision (Table 1). Both RSD_r% and RSD_{WR}% were less than 20% in all cases, which is in accordance with the guidelines (EC, 2021). In studies conducted on vine leaves, the recovery values of pesticides were found between 70% and 120% (RSD_r% and RSD_{WR} ≤20%) (Balkan and Kara, 2023; Hayar et al., 2021). Our study has some advantages over other studies. Hayar et al. (2021), and Balkan and Kara (2023) validated 33 and 9 pesticides in grape leaves, respectively. While 243 pesticides were validated on grape leaves in this study, much fewer pesticides were validated in published studies. In another study conducted on grapevine leaves, it was reported that 400 pesticides were recovered between 70% and 120%, but the RSDs of some pesticides exceeded 20%.

LOQ and LOD were lower than the corresponding default EU-MRLs for vine leaves rendering the method acceptable for checking compliance to MRLs. The values are listed in Table 1. The method's performance satisfied the EU SANTE/11312/2021 guideline's analytical quality control requirements, and as a result, it was considered appropriate for its intended use (EC, 2021). The method was used monitoring for pesticide residues in vine leaves (Balkan and Kara, 2023; Hamzawy, 2022; Hayar et al., 2021).

Table 1. Validation data of method

Pesticide				Spiking Level (0.01 mg kg^{-1})			Spiking Level (0.05 mg kg^{-1})		
	R^2	LOD	LOQ	RM	RSD_r	RSD_{WR}	RM	RSD_r	RSD_{WR}
		ug kg^{-1}			(%)			(%)	
2.4-D	0.9998	1.87	6.23	100.99	17.23	8.96	103.30	7.47	8.23
Abamectin	0.9946	2.17	7.23	84.49	5.78	14.93	99.75	6.46	12.27
Acephate	0.9981	2.16	7.20	112.04	4.44	2.74	98.17	3.51	2.15
Acequinocyl	0.9980	2.15	7.15	89.71	11.28	10.24	83.93	12.14	12.75
Acetamiprid	0.9999	1.99	6.65	96.74	1.26	6.00	100.69	1.06	1.86
Acetochlor	0.9909	1.38	4.58	101.36	7.28	8.93	109.41	6.86	2.70
Acrinathrin	0.9987	1.00	3.32	96.03	11.02	13.63	99.59	4.90	10.65
Alachlor	0.9932	2.30	7.66	102.31	6.63	6.94	109.86	3.43	2.64
Aldicarb	0.9979	0.69	2.29	91.51	4.86	13.93	101.98	14.63	17.24
Aldicarb-sulfone	0.9999	1.69	5.64	104.63	2.88	2.28	107.06	1.84	0.78
Aldicarb-sulfoxide	0.9999	2.68	8.93	104.04	5.30	9.74	109.68	5.99	5.01
Ametoctradin	0.9999	2.85	9.50	81.40	1.00	4.19	96.24	0.64	2.27
Amitraz	0.9996	1.72	5.73	93.87	9.42	6.79	106.71	6.36	3.48
Atrazine	0.9962	0.91	3.02	75.33	4.76	5.67	110.15	1.51	0.83
Azinphos-ethyl	0.9909	1.46	4.86	89.92	2.50	7.79	114.85	12.86	7.13
Azinphos-methyl	0.9916	1.68	5.62	91.96	14.18	5.03	115.11	3.25	4.35
Azoxystrobin	0.9998	2.21	7.38	107.60	5.37	1.01	112.31	2.68	8.96

Table 1. continue

Pesticide				Spiking Level (0.01 mg kg-1)			Spiking Level (0.05 mg kg-1)		
	R^2	LOD	LOQ	RM	RSD_r	RSD_{WR}	RM	RSD_r	RSD_{WR}
		ug kg-1			(%)			(%)	
Benalaxyl	0.9967	1.50	5.00	103.80	3.52	14.57	99.15	1.16	2.69
Benfuracarb	0.9995	0.70	2.34	107.72	18.23	7.66	102.76	10.05	3.35
Bensulfuron-methyl	0.9964	2.53	8.42	88.68	9.59	4.08	111.81	3.00	3.36
Bifenazate	0.9970	2.76	9.19	91.92	3.82	8.56	85.84	4.89	3.42
Bitertanol	0.9977	1.45	4.83	86.46	6.62	3.63	105.54	2.43	4.71
Boscalid	0.9930	2.20	7.32	75.92	5.39	6.62	114.10	4.23	3.19
Bromuconazole	0.9995	1.64	5.47	93.15	8.86	6.80	109.43	4.24	6.22
Buprimate	0.9920	0.91	3.02	98.37	15.22	4.75	118.10	3.35	6.95
Buprofezin	0.9991	1.48	4.94	81.73	10.25	3.08	106.05	2.39	4.49
Butralin	0.9995	1.65	5.50	82.68	3.66	3.89	83.65	10.21	9.20
Butylate	0.9999	1.60	5.32	116.42	2.57	6.10	110.94	8.53	4.26
Carbaryl	0.9999	2.32	7.73	109.38	3.15	1.12	111.78	6.72	1.31
Carbendazim	0.9995	2.37	7.89	87.63	5.82	7.94	104.95	4.27	2.04
Carbofuran	0.9974	0.80	2.65	89.54	6.55	6.56	117.65	3.04	3.21
Carbofuran-3-hydroxy	0.9996	1.99	6.62	92.70	7.09	7.10	104.53	3.78	1.55
Carbosulfan	0.9992	2.43	8.11	107.75	1.98	11.14	97.74	2.01	3.58
Carboxin	0.9923	1.47	4.91	95.17	7.90	8.99	118.99	3.66	5.76
Carfentrazone-ethyl	0.9981	1.13	3.78	88.31	14.52	10.65	107.29	3.03	2.61
Chlorantraniliprole	0.9914	1.70	5.65	80.35	3.35	5.75	94.79	7.07	5.29
Chlorbufam	0.9968	1.65	5.51	78.57	13.53	11.79	115.99	8.39	6.90
Chlorfluazuron	0.9990	1.40	4.65	91.10	10.47	5.52	98.95	4.74	12.25
Chloridazon	0.9978	2.02	6.72	106.51	9.67	4.28	106.51	2.24	3.74
Chlorsulfuron	0.9962	2.79	9.31	76.85	3.04	9.10	103.05	2.34	3.03
Clethodim	0.9981	0.60	2.01	78.10	5.75	4.91	113.97	5.40	3.69
Clofentezine	0.9929	2.60	8.68	80.71	5.55	7.68	116.02	3.76	5.86
Clothianidine	0.9980	2.18	7.28	75.76	7.24	8.35	104.63	2.95	4.76
Cyantraniliprole	0.9998	1.20	4.00	103.31	12.50	5.01	110.34	1.67	4.84
Cycloate	0.9996	1.65	5.50	103.43	5.61	6.78	116.87	8.28	2.51
Cycloxydim	0.9964	1.60	5.34	94.59	7.45	7.79	102.23	1.68	4.15
Cyflufenamid	0.9915	1.28	4.27	91.60	7.89	8.16	102.02	4.78	6.63
Cyhalothrin	0.9950	2.18	7.26	103.16	2.24	4.47	93.09	15.25	5.84
Cymoxanil	0.9997	1.17	3.91	92.83	3.44	3.57	104.35	2.05	1.24
Cypermethrin	0.9996	0.69	2.30	75.13	5.03	3.05	103.84	2.39	17.10
Cyproconazole	0.9992	1.67	5.55	88.74	9.47	13.92	94.51	5.18	5.80
Cyprodinil	0.9983	1.44	4.80	87.64	6.90	8.23	97.86	6.55	4.50
Dazomet	0.9998	1.70	5.67	101.47	7.57	12.59	104.24	1.26	2.45
Deltamethrin	0.9984	2.20	7.32	94.77	7.69	3.78	112.78	4.86	2.24
Demeton-s-methyl	0.9974	2.73	9.11	91.04	14.94	15.70	106.76	9.27	5.15
Demeton-s-methyl-sulfone	0.9999	1.81	6.03	105.26	3.35	1.08	101.06	1.61	3.62
Desmedipham	0.9975	1.59	5.30	75.89	4.69	6.38	107.53	3.63	2.61
Diafenthiuran	0.9998	1.22	4.08	79.47	3.33	15.26	88.22	8.64	6.01
Diazinon	0.9998	2.54	8.47	93.15	13.25	13.37	107.77	1.92	1.15
Dichlorfos	0.9990	1.53	5.09	96.64	5.53	14.84	117.98	4.56	1.43
Diclofop -methyl	0.9964	1.74	5.81	94.40	10.84	15.75	107.24	5.60	8.55
Dicrotophos	0.9999	1.21	4.04	97.37	3.58	4.54	99.75	3.17	2.28

Table 1. continue

Pesticide	R^2	LOD	LOQ	Spiking Level (0.01 mg kg^{-1}) RM	RSD$_r$	RSD$_{WR}$	Spiking Level (0.05 mg kg^{-1}) RM	RSD$_r$	RSD$_{WR}$
		ug kg^{-1}			(%)			(%)	
Diethofencarb	0.9991	1.88	6.26	96.97	4.61	3.61	112.84	1.94	0.80
Difenacozole	0.9997	1.84	6.15	116.55	3.91	2.30	106.74	5.36	0.63
Diflubenzuran	0.9941	1.68	5.61	71.98	12.05	6.88	101.35	7.29	7.05
Dimethenamid	0.9984	1.75	5.83	83.15	3.90	5.51	110.52	3.98	3.10
Dimethoate	0.9993	0.62	2.05	91.28	5.04	0.99	111.73	1.88	3.20
Dimethomorph	0.9993	1.92	6.40	91.96	3.01	8.82	108.30	3.06	7.01
Diniconazole	0.9999	1.61	5.36	106.90	5.00	10.29	111.94	2.67	4.28
Dioxacarb	0.9995	1.18	3.92	93.48	2.05	4.02	104.33	2.36	4.40
Diphenamid	0.9996	0.64	2.12	96.02	5.92	7.44	109.20	1.78	2.41
Diphenylamine	0.9982	2.02	6.72	97.87	3.55	2.68	106.12	5.09	12.78
Diuron	0.9967	1.20	4.01	75.46	3.71	8.34	113.24	1.68	3.90
DMF	0.9982	0.82	2.72	93.20	6.28	3.01	107.89	2.49	1.91
Dodine	0.9990	0.80	2.66	79.77	4.18	12.24	81.98	8.67	2.03
Emamectin	0.9991	1.76	5.86	85.42	4.67	10.43	101.00	7.95	2.69
Emamectin benzoat	0.9995	0.81	2.70	95.89	2.88	15.20	87.86	6.94	13.94
EPN	0.9958	1.39	4.62	78.57	6.60	3.93	104.14	7.41	2.92
Epoxiconazole	0.9931	1.31	4.38	83.94	7.35	18.31	90.88	1.35	2.16
EPTC	0.9992	1.10	3.65	103.02	17.74	2.29	107.80	5.94	5.74
Ethiofencarb	0.9950	1.22	4.07	104.73	2.68	1.32	106.85	4.94	2.74
Ethion	0.9986	1.11	3.71	94.91	9.91	13.21	100.19	3.41	5.92
Ethirimol	0.9968	1.03	3.44	98.31	10.97	18.39	86.24	2.16	0.73
Etofenprox	0.9967	2.25	7.49	90.40	8.35	9.37	96.59	18.34	3.48
Etoxazole	0.9999	0.92	3.08	85.20	6.92	8.30	78.82	2.07	3.70
Famaxadone	0.9952	2.07	6.90	90.48	10.84	8.01	109.85	9.46	6.80
Fenamidone	0.9983	0.99	3.31	80.05	7.63	5.16	105.51	3.30	2.47
Fenamiphos	0.9920	0.97	3.22	86.51	3.96	2.68	101.01	2.52	3.20
Fenamiphos-sulfone	0.9911	1.18	3.94	89.95	3.66	3.91	99.92	2.08	2.20
Fenamiphos-sulfoxide	0.9931	1.05	3.50	94.22	4.22	6.13	99.86	3.18	4.33
Fenarimol	0.9987	0.57	1.91	77.85	4.46	10.44	104.45	2.34	6.26
Fenazaquin	0.9991	1.26	4.20	102.06	2.71	8.31	108.07	3.52	1.20
Fenbuconazole	0.9956	1.23	4.11	84.94	4.62	10.07	109.45	4.48	6.47
Fenbutatin oxide	0.9991	0.91	3.04	83.73	3.64	4.85	91.15	2.83	6.78
Fenhexamid	0.9989	0.85	2.84	91.07	11.84	7.89	113.17	1.32	0.90
Fenoxycarb	0.9925	1.07	3.55	83.91	4.77	9.44	96.76	3.92	2.64
Fenoxyprob-ethyl	0.9998	1.33	4.42	102.56	8.36	18.13	113.65	3.04	5.25
Fenpropathrin	0.9986	0.78	2.61	80.42	8.35	9.55	87.36	15.29	8.61
Fenproxymate	0.9994	1.63	5.45	88.35	0.89	5.37	79.56	6.81	6.87
Fenthion	0.9992	1.01	3.36	83.78	5.05	11.46	117.05	3.57	5.62
Fenthion-sulfone	0.9989	1.03	3.42	86.66	4.00	2.89	104.63	3.43	5.00
Fenthion-sulfoxide	0.9998	0.76	2.52	90.41	3.39	4.63	102.61	2.60	1.56
Fipronil	0.9998	0.90	3.00	79.09	3.25	10.02	79.85	4.13	10.05
Fipronil-sulfone	0.9997	1.45	4.83	81.28	5.19	7.60	95.42	2.68	6.84
Fluazifop-p-butyl	0.9976	0.55	1.82	77.13	6.02	8.62	108.20	10.91	7.75
Fluazinam	0.9999	1.21	4.04	104.64	2.79	4.15	91.17	7.12	5.36
Flubendiamide	0.9972	1.29	4.31	84.62	2.30	19.61	86.11	14.95	14.27

Table 1. continue

Pesticide				Spiking Level (0.01 mg kg^{-1})			Spiking Level (0.05 mg kg^{-1})		
	R^2	LOD	LOQ	RM	RSD_r	RSD_{WR}	RM	RSD_r	RSD_{WR}
		ug kg^{-1}			(%)			(%)	
Fludioxinil	0.9999	0.46	1.55	84.90	12.33	9.86	88.21	2.26	1.49
Flufenoxuron	0.9977	0.83	2.78	82.70	2.33	10.93	98.31	7.66	8.96
Fluopicolide	0.9946	1.03	3.43	89.79	7.66	4.16	108.09	1.61	4.08
Fluopyram	0.9996	0.67	2.23	93.20	1.10	3.54	110.67	2.87	2.54
Fluquinconazole	0.9974	0.74	2.45	117.69	4.14	5.89	107.85	5.32	3.41
Flurochloridone	0.9990	0.96	3.19	106.12	14.91	6.35	110.67	3.93	10.57
Fluroxypyr	0.9995	0.98	3.27	89.60	5.94	13.13	113.68	5.52	12.32
Flusilazole	0.9948	1.60	5.34	78.35	7.94	18.40	106.90	3.90	5.56
Flutriafol	0.9990	1.60	5.32	88.79	8.10	7.39	101.11	5.04	4.14
Forchlorfenuron	0.9948	1.52	5.08	81.81	6.02	8.87	110.12	3.24	1.85
Formetanete hydrochloride	0.9940	1.22	4.06	89.69	7.99	12.19	102.42	7.70	6.23
Fosthiazate	0.9936	0.46	1.52	111.16	11.04	1.46	111.52	2.48	1.92
Furathiocarb	0.9994	0.86	2.88	87.84	3.88	4.18	107.99	3.52	1.43
Haloxyfop-R-methyl	0.9931	1.42	4.75	104.01	5.71	14.62	92.37	2.75	4.21
Hexaconazole	0.9966	0.93	3.11	83.75	13.89	8.94	113.20	2.74	2.59
Hexaflumuron	0.9908	1.39	4.62	93.59	12.90	6.60	84.62	8.47	15.51
Hexythiazox	0.9988	0.86	2.85	92.92	2.54	11.91	98.74	3.81	8.13
Imazalil sulfate	0.9999	0.91	3.05	89.78	15.12	7.16	101.26	5.28	5.29
Imidacloprid	0.9999	0.99	3.31	94.40	7.36	1.53	100.46	2.67	1.03
Indoxacarb	0.9995	1.10	3.66	98.86	4.33	10.72	103.96	4.43	8.89
Iodosulfuron-methyl-sodium	0.9985	1.40	4.66	74.42	7.12	4.82	97.95	3.85	4.39
Ioxynil	0.9995	1.01	3.38	81.71	7.05	15.76	88.13	11.89	12.86
Isocarbofos	0.9921	1.60	5.34	96.02	12.56	14.42	94.18	4.54	7.40
Kresoxim-methyl	0.9974	0.69	2.28	80.38	5.90	6.52	106.16	2.23	2.42
Lenacil	0.9910	0.72	2.38	85.01	3.87	9.41	117.26	1.99	3.61
Linuron	0.9957	1.05	3.49	83.79	14.36	3.15	114.72	4.86	9.04
Lufenuron	0.9997	0.64	2.13	89.21	5.12	11.89	102.53	3.98	4.65
Malaoxon	0.9996	0.70	2.34	86.73	4.11	2.80	102.14	0.99	2.06
Malathion	0.9985	1.35	4.49	85.10	7.31	1.60	115.20	0.83	0.87
Mandipropamid	0.9991	1.86	6.18	86.03	6.43	10.09	110.17	2.71	4.06
Mecarbam	0.9908	1.66	5.53	85.01	1.66	12.07	107.82	1.75	1.94
Mepanipyrim	0.9993	0.97	3.23	93.39	3.15	2.03	106.70	3.19	3.05
Mepanipyrim-hyroxypropyl	0.9985	0.99	3.30	84.91	9.13	15.85	107.21	2.01	3.31
Metaflumizone	0.9994	0.75	2.49	79.94	2.36	2.30	102.27	1.37	1.86
Metalaxyl-M	0.9908	0.95	3.17	103.21	9.42	9.17	106.12	9.17	3.97
Metamitron	0.9998	1.09	3.64	108.63	6.67	14.33	97.31	3.80	0.56
Methacrifos	0.9990	0.64	2.15	106.91	4.25	10.06	103.67	4.93	2.99
Methamidophos	0.9999	0.80	2.68	108.10	12.48	12.72	117.56	3.40	2.81
Methidathion	0.9973	2.39	7.96	104.31	2.89	4.69	97.86	3.72	3.49
Methiocarb	0.9923	1.73	5.75	79.21	4.26	4.66	112.58	6.72	4.17
Methiocarb-sulfone	0.9998	0.85	2.82	100.57	1.99	10.79	119.37	2.29	4.68
Methiocarb-sulfoxide	0.9999	0.76	2.53	99.43	4.08	3.88	102.72	4.92	2.76
Methomyl	0.9999	1.03	3.42	104.35	4.67	3.47	104.01	1.56	2.84

Table 1. continue

Pesticide				Spiking Level (0.01 mg kg^{-1})			Spiking Level (0.05 mg kg^{-1})		
	R^2	LOD	LOQ	RM	RSD_r	RSD_{WR}	RM	RSD_r	RSD_{WR}
		ug kg^{-1}			(%)			(%)	
Methoxyfenozide	0.9935	1.45	4.83	99.40	4.22	4.58	107.73	1.66	1.31
Metolachlor-S	0.9969	0.97	3.22	95.66	4.77	3.79	93.12	17.28	2.26
Metosulam	0.9961	1.02	3.39	82.98	4.75	5.98	110.28	2.36	1.23
Metrafenone	0.9935	1.07	3.55	74.44	12.84	7.94	100.79	0.93	3.22
Metribuzin	0.9998	0.81	2.72	93.61	19.82	15.24	108.02	2.54	1.62
Mevinphos	0.9913	0.77	2.56	106.41	6.55	7.48	112.98	2.62	2.92
Molinate	0.9977	0.96	3.21	102.65	3.48	12.48	111.34	12.79	2.70
Monocrotophos	0.9997	0.99	3.31	111.09	10.50	5.84	115.27	5.04	4.38
Monolinuron	0.9914	1.00	3.33	106.56	4.03	4.96	103.97	1.03	1.88
Myclobutanil	0.9962	0.94	3.12	107.50	8.67	9.70	78.52	4.54	7.93
Nicosulfuron	0.9959	0.80	2.67	86.20	14.95	7.17	113.34	4.12	6.49
Novaluron	0.9916	1.02	3.41	84.33	7.05	11.81	110.61	4.05	3.24
Nuarimol	0.9992	0.73	2.45	107.58	4.71	8.52	112.41	4.07	5.08
Omethoate	0.9996	0.96	3.20	102.49	6.53	19.01	117.54	3.78	2.22
Oxadixyl	0.9970	1.00	3.34	87.13	9.38	6.49	95.83	4.54	0.68
Oxamyl	0.9998	1.07	3.55	73.78	9.85	6.19	112.39	2.18	3.14
Oxycarboxin	0.9997	1.67	5.57	97.10	1.48	1.78	104.05	1.16	1.20
Oxydemeton-methyl	0.9999	1.20	3.99	108.39	1.28	3.15	104.20	1.69	2.44
Paclobutrazol	0.9982	2.01	6.69	100.30	8.19	14.16	101.02	2.82	4.84
Paraoxon-ethyl	0.9916	1.16	3.88	80.22	5.60	2.56	107.76	3.18	3.18
Paraoxon-methyl	0.9989	0.84	2.79	91.02	2.94	16.72	93.37	2.44	2.40
Pencycuron	0.9993	0.77	2.56	92.77	13.35	10.31	109.53	3.76	2.39
Pendimethalin	0.9990	0.94	3.13	76.09	9.30	9.22	111.09	6.24	4.23
Permethrin	0.9996	0.56	1.86	84.27	2.54	1.84	77.00	2.75	6.12
Phenmedipham	0.9979	0.87	2.91	93.24	7.55	16.14	102.23	2.58	19.25
Phorate	0.9981	1.70	5.66	82.92	2.66	5.80	98.23	3.75	3.39
Phorate-sulfone	0.9904	1.09	3.63	92.18	3.11	9.74	110.85	3.32	3.43
Phorate-sulfoxide	0.9971	0.55	1.83	90.37	7.54	7.48	80.43	5.44	4.24
Phosalone	0.9968	0.71	2.35	116.49	2.71	1.77	102.74	2.50	1.41
Phosmet	0.9936	0.75	2.50	91.40	6.66	11.52	116.71	3.94	9.52
Phosphamidon	0.9998	0.94	3.12	89.34	8.12	7.01	113.75	1.33	1.30
Pirimicarb-desmethyl	0.9997	1.09	3.64	93.22	9.61	3.24	103.08	2.51	1.35
Primicarb	0.9941	1.11	3.69	88.52	3.70	3.83	104.34	1.22	2.88
Primiphos-ethyl	0.9996	0.76	2.53	94.90	15.77	4.70	84.27	6.24	5.63
Primiphos-methyl	0.9985	0.92	3.05	98.94	9.51	5.85	106.08	1.78	2.75
Prochloraz	0.9979	0.67	2.22	82.45	8.63	6.08	106.53	3.19	4.39
Profenefos	0.9901	0.89	2.97	81.56	5.37	3.83	104.04	8.42	3.98
Profoxydim-lithium	0.9994	0.56	1.88	101.12	2.16	12.88	99.50	4.93	5.64
Promecarb	0.9976	1.06	3.53	117.98	3.65	4.93	113.17	3.48	4.66
Prometryn	0.9998	0.79	2.62	78.11	5.50	1.99	111.42	3.01	1.88
Propaquizafob	0.9984	0.76	2.55	115.46	6.24	5.91	112.52	5.87	3.46
Propargite	0.9999	0.66	2.21	93.68	13.86	5.89	107.01	6.56	5.77
Propazine	0.9984	0.94	3.12	106.78	6.43	6.88	100.00	4.89	3.89
Propiconazole	0.9935	0.54	1.79	86.93	4.07	1.38	115.16	3.09	1.72
Propoxur	0.9947	0.79	2.62	85.25	1.35	12.66	109.85	4.97	1.03
Propyzamide	0.9948	0.75	2.49	77.86	10.30	2.74	114.51	1.21	2.33

Table 1. continue

Pesticide				Spiking Level (0.01 mg kg^{-1})			Spiking Level (0.05 mg kg^{-1})		
	R^2	LOD	LOQ	RM	RSD_r	RSD_{WR}	RM	RSD_r	RSD_{WR}
		ug kg^{-1}			(%)			(%)	
Prothiophos	0.9992	0.82	2.73	82.99	5.79	11.16	112.61	1.89	16.28
Pymetrozine	0.9987	0.96	3.19	83.39	4.75	7.83	74.39	5.74	8.46
Pyraclostrobin	0.9999	0.68	2.25	103.54	4.69	2.92	86.05	1.58	0.75
Pyrazophos	0.9964	1.00	3.34	113.86	1.76	3.99	119.30	0.35	2.45
Pyridaben	0.9996	0.94	3.13	77.47	2.04	5.55	109.65	2.79	2.43
Pyridaphenthion	0.9992	0.86	2.87	101.30	5.56	4.73	107.48	5.23	7.20
Pyridate	0.9999	0.77	2.57	113.32	4.45	7.91	107.49	0.88	1.39
Pyrimethanil	0.9998	0.89	2.97	93.14	5.59	11.40	92.44	4.47	5.57
Pyriproxyfen	0.9999	0.91	3.05	110.11	5.69	5.99	106.83	3.20	3.93
Quinalphos	0.9976	1.26	4.19	87.07	6.23	5.34	77.24	6.25	1.06
Quizalofop-ethyl	0.9972	0.89	2.97	98.61	12.88	6.73	116.89	3.90	4.33
Rimsulfuron	0.9995	1.87	6.23	77.71	8.93	16.06	111.67	3.87	3.46
Sethoxydim	0.9901	0.79	2.63	98.48	4.35	10.63	109.30	4.67	6.24
Simazine	0.9996	0.81	2.69	94.50	1.33	4.94	108.74	3.99	1.35
Spinosyn A	0.9998	0.64	2.12	100.62	6.06	10.35	105.69	5.60	1.37
Spinosyn D	0.9997	0.77	2.57	106.95	7.45	4.03	116.87	4.04	5.54
Spirodiclofen	0.9997	1.11	3.71	110.63	3.81	9.75	118.72	4.05	7.95
Spiroxamine	0.9999	0.76	2.52	103.98	5.66	4.20	96.32	6.99	9.78
Sulfoxaflor	0.9999	1.40	4.67	96.43	6.17	12.64	90.62	5.46	6.60
Tebufenozide	0.9957	1.38	4.60	105.64	5.66	3.79	104.40	5.39	3.36
Tebufenpyrad	0.9968	0.84	2.79	104.89	4.67	5.10	99.83	3.06	5.35
Teflubenzuron	0.9995	0.72	2.40	102.94	6.81	4.21	111.11	8.82	13.03
Tepraloxydim	0.9995	1.46	4.87	78.21	6.59	6.55	92.56	5.81	18.45
Terbutryn	0.9985	2.40	7.99	85.87	5.67	11.84	79.51	6.31	6.77
Terbutylazine	0.9977	1.22	4.06	81.41	7.22	3.69	106.89	1.51	0.40
Tetraconazole	0.9998	1.64	5.47	79.96	7.53	11.29	110.38	3.83	6.06
Tetramethrin	0.9959	0.48	1.61	112.37	4.45	5.02	110.74	2.18	3.58
Thiabendazole	0.9971	1.49	4.96	77.16	5.05	10.35	107.75	2.73	5.81
Thiacloprid	0.9987	0.78	2.59	116.17	4.48	4.26	108.97	1.10	1.17
Thiamethoxam	0.9983	1.37	4.58	71.17	4.92	3.63	97.79	3.49	1.61
Thifensulfuron-methyl	0.9999	0.82	2.74	100.34	3.82	11.06	103.13	1.42	1.56
Thiodicarb	0.9949	0.74	2.48	105.86	3.94	2.70	104.13	1.98	1.91
Tolclofos-methyl	0.9979	1.79	5.98	97.66	11.37	4.66	89.27	3.65	5.09
Tolfenpyrad	0.9998	1.07	3.55	101.91	16.78	12.78	110.65	5.86	4.53
Tolyfluanid	0.9917	1.19	3.97	99.00	10.26	5.58	110.38	3.25	4.05
Tralkoxydim	0.9947	0.86	2.87	91.86	3.57	4.45	111.64	8.03	10.60
Triadimefon	0.9905	0.85	2.84	103.78	10.47	11.79	111.19	3.05	1.56
Triadimenol	0.9959	0.64	2.14	80.91	7.87	8.64	109.39	2.68	4.21
Tri-allate	0.9984	1.68	5.60	96.47	9.75	9.24	97.21	10.80	2.44
Triasulfuron	0.9984	1.62	5.41	83.07	7.43	5.32	97.61	5.18	2.14
Triazophos	0.9987	0.73	2.42	92.56	5.06	4.10	93.15	4.39	4.40
Tribenuron-methyl	0.9994	0.97	3.22	86.09	9.39	12.19	97.10	2.64	3.65
Trichlorfon	0.9986	1.42	4.72	79.52	0.74	2.63	100.91	4.16	2.80
Trifloxystrobin	0.9983	1.28	4.25	97.27	4.21	19.26	110.22	1.91	3.52
Triflumizole	0.9989	1.66	5.53	90.98	2.25	9.96	94.95	1.18	4.09
Triflumuron	0.9924	1.77	5.90	92.34	2.90	2.38	106.21	2.00	4.35
Triticonazole	0.9999	0.94	3.13	93.40	4.03	12.82	108.33	7.45	5.41

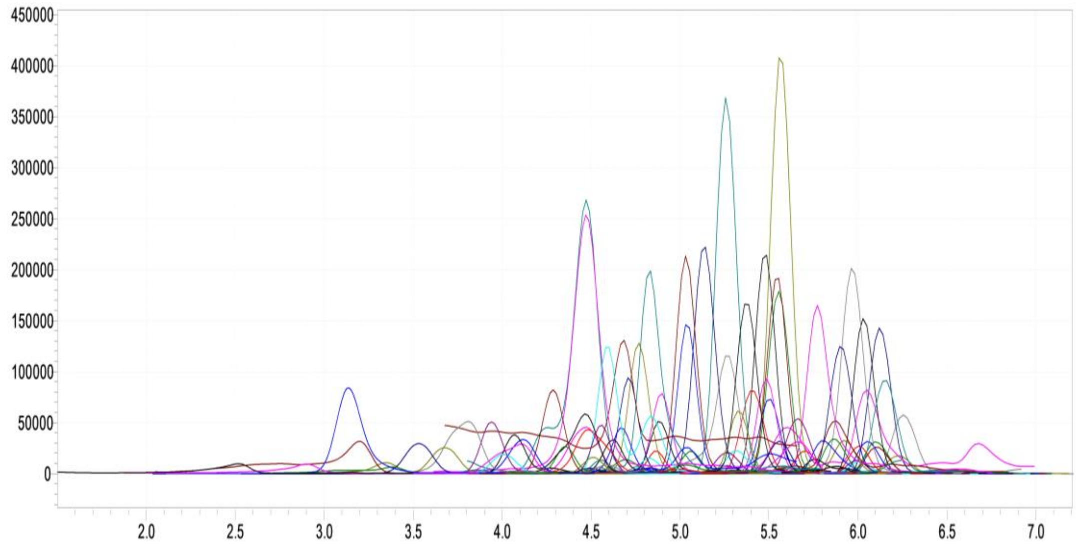

Figure 3. Total Ion Chromatogram (TIC) of pesticides

Pesticide residue concentrations in brined vine leaves

In the study, 13 of 243 pesticide active ingredients analyzed were determined in pickled vine leaves. In addition, 8 pesticide active ingredients were determined above the MRL value (Table 2). In the study, at least 1 pesticide residue was found in each of the 15 samples. Ethiofencarb is used as an insecticide and acaricide (Anonymous, 2012). Ethiofencarb was on the list of banned pesticides whose use has been terminated in Turkey according to the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides. Boscalid, carboxin, cyhalothrin, metalaxyl-m, methacrifos, pyraclostrobin, pyrimethanil, triticonazole fungicide; cypermethrin, ethiofencarb, isocarbofos, methacrifos are pesticides used as insecticides (Anonymous, 2016). Cypermethrin is used against the cluster moth, and cyhalothrin is used against *Lobesia botrana* and *Otiorhynchus sulcatus*. While metalaxyl m is used to combat vineyard mildew, metrafenone is used against vineyard powdery mildew. Pyraclostrobin is used against vineyard mildew and vineyard powdery mildew, and pyrimethanil is used against gray mold (Anonymous, 2015). Carboxin is used for *Pythium* spp. in wheat, barley and cotton. Hexythiazox is a acaricide used against red spider in viticulture (Anonymous, 2015).

The highest pesticide residues according to MRL values were cyhalothrin, pyraclostrobin, cypermethrin, boscalid. Their residues were 0.316 mg/kg, 0.294 mg/kg, 0.276 mg/kg and 0.215 mg/kg, respectively. The most common pesticide for all samples were ethiofencarb, isocarbofos, cyhalothrin, respectively. Although banned, ethiofencarb (in all samples), hexythiazox (in one sample), methacrifos (in three samples), isocarbofos (in six samples) were detected in brine leaf samples. Boscalid (in three samples), cyhalothrin (in five samples), metrafenone (in one sample), pyrimethanil (in one sample) were found to be higher than the MRL values, respectively. The samples with the highest pesticide residues are E1 and E2 samples, while the samples with the least pesticide residues are E6 and G3 samples (Table 2).

Bakırcı et al. (2019) analyzed 232 vine leaf samples from the province of Manisa (Turkey) in 2017 for pesticide residues using QuEChERS method and liquid chromatography-tandem mass spectrometry (LC-MS/MS). As a result of the study, 42 different pesticide types and 210 different results were obtained. 92 of the detected pesticide active ingredients were found above the MRL value. While the highest residue was cyhalothrin, the most detected pesticide was metalaxyl (Bakırcı et al., 2019). In another study, residue levels of vine leaves treated with cold brine (26.5 °C) and hot brine (80 °C) after 4 months of fermentation were investigated. Fungicides with active ingredients of tebuconazole, metrofenone and pyrimethanil were noted on the leaves. According to the results of the research, it was reported that the residue level in the vine leaves applied with hot and cold brine decreased, while the residue level was very high in the leaves without brine **(**Kuşaksız and Çimer, 2019). El-Din et al. (2018) investigated 26 pesticide residues in 96 grape leaves samples collected from Egyptian local markets. It was discovered that every pesticide residue found in leaf samples exceeded the MRLs. Another study, 78 samples of grape leaves were gathered from local markets of Egyptian. More than 400 pesticide residues in grape leaves were identified using a QuEChERS technique, followed by GC-MS/MS and LC-MS/MS. The results showed that 36 pesticide residues from various chemical groups were found in 78 samples over the MRLs (Hamzawy, 2022).

Table 2. Pesticide values of pickled vine leaves (mg/kg)

Pesticide	MRL****	E1**	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12	G1	G2	G3
Boscalid	0.01	–	0.215	–	0.040	–	–	–	–	–	0.035	–	–	–	–	–
Carboxin	0.01***	0.007	0.007	–	–	–	–	–	–	–	–	–	–	–	–	–
Cyhalothrin	0.02	0.09	0.053	0.138	–	–	–	–	–	–	0.109	–	–	–	0.316	–
Cypermethrin	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–	0.276	–
Ethiofencarb	****	0.011	0.009	0.009	0.009	0.008	0.009	0.009	0.008	0.008	0.009	0.009	0.009	0.009	0.009	0.009
Hexythiazox	0.5	–	–	–	0.018	–	–	–	–	–	–	–	–	–	–	–
Isocarbofos	****	0.029	–	0.016	0.045	0.054	–	–	0.052	–	0.015	–	–	–	–	–
Metalaxyl M	0.05	–	0.027	0.045	–	–	–	–	0.034	–	–	–	–	–	–	–
Methacrifos	****	0.007	0.006	–	–	–	–	0.011	–	–	–	–	–	–	–	–
Metrafenone	0.01	–	–	–	–	–	–	–	0.039	–	–	–	–	–	–	–

Pyraclostrobin	0.02	-	-	-	-	-	-	-	-	-	0.294	-	0.128	-	-	-
Pyrimethanil	0.01	-	-	-	0.062	-	-	-	-	-	-	-	-	-	-	-
Triticonazole	0.01***	0.004	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* MRL: Maximum residue limit
** Pickled vine leaf samples (E1, E2, E3….G1,G2…)
*** If there is no MRL or LOD in the evaluation section of clause 6 for the relevant pesticide in the product in Annex-1, 0.01 mg/kg value is used as MRL for processed food.
**** There is no active ingredient in the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides.

CONCLUSION

The production of pickled vine leaves, which has an important place in markets in Turkey, has experienced a downsizing in the domestic and foreign markets due to pesticide residues. The grape leaf of the Narince variety is a geographical indication registered product that has a high economic contribution to the region and has an important place in the promotion of the region. However, the fact that vine leaves are a secondary product after grapes has led to the absence of established quality standards for the processing of vine leaves. This situation causes the end product with different characteristics and variable quality standards. Although studies on vine leaves have been carried out in recent years, the resources are still insufficient.

Pesticide active ingredients were found in pickled vine leaves above the maximum residue amounts allowed in the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides. In addition, some pesticides detected are included in the list of banned pesticides whose use has been terminated according to the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides. When the obtained data is evaluated, due to the lack of certain standards in the production of pickled vine leaves, serious differences were observed in quality parameters. Determination of standard production parameters for the production of pickled vine leaves is important in terms of establishing a reliable market. It is also seen that pesticide residues pose a serious risk for vine leaves.

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AUTHOR CONTRIBUTIONS

Tuba ZORLU ÜNLÜ: Sample collection, Analysis, Writing original manuscript. Semra TOPUZ: Methodology, Writing original manuscript, Reviewing & editing. MUSTAFA BAYRAM: Supervision, Evaulation, Writing-review & editing. Tarık BALKAN: Methodology, Analysis. Cemal KAYA: Writing-review & editing.

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