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Verification of QuEChERS Method for the Analysis of Pesticide Residues and Their Risk Assessment in Some Fruits Grown in Tokat, Turkey

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ABSTRACT

This study sought to determine pesticide residues in some fruits in Tokat province, Turkey and to assess the health risks associated with the determined residues. QuEChERS analytical method was verified to determine 260 pesticides by using liquid chromatography-tandem mass spectrometry (LC-MS/MS). Pesticide solutions corresponded 10 and 50 µg kg^{-1} were applied to the pesticide-free apple matrix for the method verification. The linearities (R^2), limit of detections, limit of quantifications and mean recovery values of the pesticides ranged between 0.990-0.999, 0.83-3 µg kg^{-1}, 2.76-9.99 µg kg^{-1} and 70.3-119% (with relative standard deviation ≤20%), respectively. The results were evaluated according to the European Union maximum residue limits (EU-MRL). The residues were lower and higher than the EU-MRL with a ratio of 37.7% and 32.1% of the tested samples, respectively. The residue levels of diflubenzuron in apples, permethrin in cherries, and dimethoate in pears, apples, and peaches were higher than the EU-MRL. The results of health risk assessments indicated that omethoate and dimethoate have acute and chronic toxicity potential for consumers. Hence, the pesticide use in the study area must be reduced to avoid health risks. Furthermore, alternative management methods should be developed to lower the use of pesticides.

Keywords: LC-MS/MS, Fresh fruit, Method verification, Health risk, QuEChERS

1. Introduction

Fruits are an integral part of human nutrition for better health (Akhtar et al. 2010). The daily consumption of fruits reduces the risk of cardiovascular diseases, stroke, and cancers of the mouth, pharynx, esophagus, lungs, stomach, and colon (Aberoumand & Deokule 2010). Although fruits are very beneficial for consumers, pesticide residue problems occur in fruits from time to time and causes concerns for consumers. As in other crops, fruits are infected by numerous pests and diseases during the fruit maturation phase and post-harvest period (Sircu et al. 2019). Fruit producers intensively use pesticides in both field and warehouse against these pests. However, these chemicals cause residue problems on/in the product (Arias-Estévez et al. 2008) and they seriously threaten human health (Balkan & Yılmaz 2022b).

Since fruits are mainly consumed fresh (raw) and semi-processed, they contain higher pesticide residues in comparison to other foods of plant origin (Claeys et al. 2011). For this reason, it is important to assess the health risks associated with the intake of pesticides. Health risk assessments are a priority of food regulatory agencies to ensure consumers' food safety (Fan et al. 2019). The detection and monitoring of pesticide residues are extremely important. The monitoring of pesticide residues allows control over crop quality by identifying the potential risks of pesticides to public health. The pesticide residues data is often compared with the European Union (EU) standards which refer to maximum residue limits (MRL). Despite legal provisions concerning pesticide use in Turkey, incomplete and defective approaches persist. While studies on pesticide residues have been growing in Turkey, they remain unsatisfactory. The EU pesticides database provides technical guidance for legislation through EU database where >656 MRLs of pesticide residues can be found (EC 2023). The Federal Institute for risk assessment (BfR 2013) recommends that the accumulative risk should be evaluated

by hazard index (HI) and hazard quotients for the individual pesticides (Hamzawy 2022). The risk assessment of pesticide residues is vital for health by ensuring food quality.

The current study aimed at; 1) exploring pesticide residue levels in some fresh fruits grown in Tokat province, Turkey, by verified QuEChERS method and 2) health risk assessment based on pesticide exposure by evaluating the residue levels in fruit samples.

2. Material and Methods

2.1. Reagents and chemicals

Pesticide reference standards were supplied by Dr. Ehrenstorfer Laboratories GmbH (Bgm-Schlosser-STr. 6A, Augsburg, Germany). Acetonitrile (ACN), methanol (MeOH), magnesium sulfate anhydrous ($MgSO_4$), sodium acetate (NaOAc) and acetic acid (AcOH) were procured from Merck (Darmstadt, Germany). Primary-secondary amine (PSA) was purchased from Supelco Analytical (595 N Harrison Rd, Bellefonte, PA, USA).

2.2. Standard solution preparation

A mixture of 260 certified pesticide reference standards was used for the quantification of pesticide residues. The individual stock solution of each pesticide (1 mg mL^{-1}) was prepared in MeOH and stored at -18 °C. The mixed stock solution was prepared in extracts of blank samples (apple) at 1,000 µg L^{-1} and working standard solutions were prepared by serial dilutions with six levels of concentrations. All solutions were stored in amber vials at -18 °C.

2.3. Sample collection and storage

The samples were collected randomly from the orchards and vineyard located in Tokat, Turkey. Apple, pear, peach (at least 10 units) and cherry samples each of 1 kg, and grape samples of 2 kg (at least 5 bunches) were collected (EC 2002). The collected samples, which were placed in clean bags providing secure protection against contamination, damage and leakage, were immediately transported to the laboratory and stored in a freezer at -18 °C.

2.4. Sample extraction and clean up

The official QuEChERS AOAC Method 2007.01 was used for the extraction and clean-up procedures (Lehotay 2007). The QuEChERS steps followed are illustrated in Figure 1. Each of the samples were analyzed in triplicates with liquid chromatography-tandem mass spectrometry (LC-MS/MS).

For recovery studies, approximately 1 kg of apple sample was homogenized with a blender and 15 g of the homogenized sample were weighed in a 50-mL Falcon tube. Then, 150 µL of pesticide mixture was spiked to 15 g of sample and vortexed for 60 seconds. Fifteen minutes was waited for the pesticides to interact with the matrix. The next steps followed are illustrated in Figure 1 (Polat & Tiryaki 2019; Dülger & Tiryaki 2021).

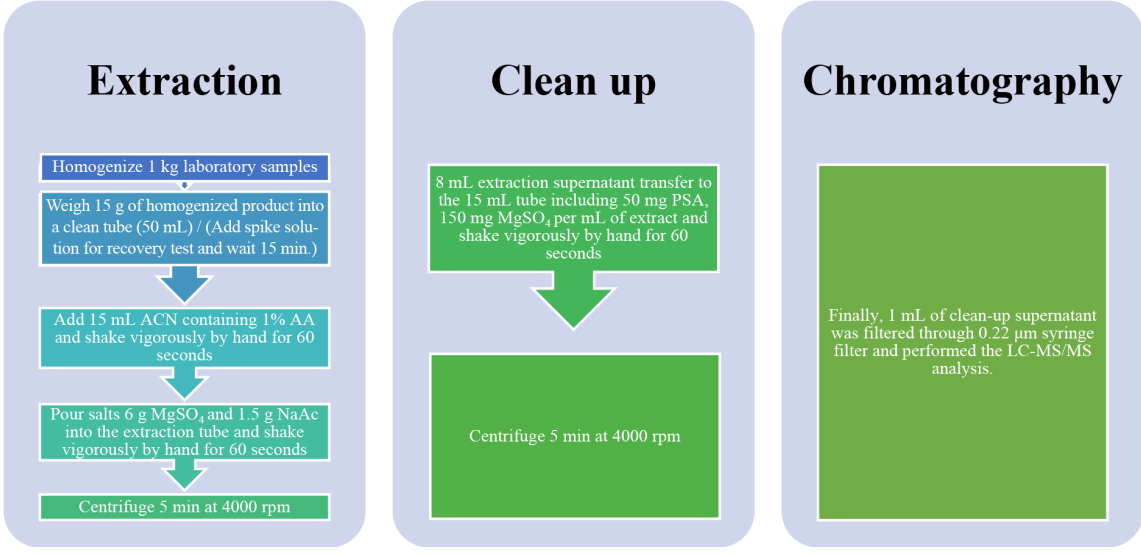

Figure 1- Analytical steps of the QuEChERS-AOAC Official Method 2007

2.5. LC-MS/MS analyses

The analyses were conducted on a LC-MS 8050 model (Shimadzu®. LC-MS/MS) 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 an Inertsil (ODS IV) C_{18} column (2.1 mm x 150 mm, 3 µm particle size) from GL Sciences Inc (Tokyo, JAPAN). Chromatographic separation was performed using a gradient elution program with eluent A consisting of distilled H_2O + 5 mM ammonium formate, eluent B consisted of MeOH + 5 mM ammonium formate. Analyses began with 5% eluent B, which was linearly increased to 60% in 3 min, 70% in 4 min, 80% in 6 min, and 95% in 7 min (held 1.50 min), and decreased to initial stage (5% of B) at 8.51 min, holding until 15 min. The flow rate, injection volume and total run time were 0.40 mL min^{-1}, 10 µL and 15 min, respectively. The column and autosampler temperatures were maintained at 35 °C and 4 °C, respectively. For MS/MS detection, the electro spray ionization (ESI) interface 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 temperature, nitrogen (N_2) as nebulizer gas of 2.9 L min^{-1} and drying gas of 10 L min^{-1}. The 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. The collision induced dissociation gas is argon (Ar, 99.99%) of 230 kPa with flow rate 0.15 mL min^{-1}. All parameters of instrument were controlled using LabSolution® software (version 4.91) (Balkan & *Yılmaz 2022*a).

2.6. Method verification

Method verification is the process of confirmation, through the provision of objective evidence, that specified requirements have been fulfilled. If a laboratory applies a standarized method or prevalidated method into its condition without any change in the procedure, the laboratory simply needs to verify that it can perform the method by meeting the method performance criteria. In that case "method verification" is more appropriate than "method validation" (Magnusson & Örnemark 2014; Dülger & Tiryaki 2022). The analytical method was in-house validated using the European SANTE/11312/2021 Guideline (SANTE 2021) by assessing linearity, mean recovery, limit of detection (LOD), limit of quantification (LOQ), and precision (repeatability and within-laboratory reproducibility) (Balkan & Yılmaz 2022a). The linearity of the method was determined using matrix-matched calibration standards at six level corresponding to 5-200 µg kg^{-1}. Linear regression coefficients (R^2) values of >0.99 were regarded as acceptable. To determine LOD and LOQ, a multi-standard working solution was spiked to the blank sample with a final concentration of 10 µg kg^{-1} and analyzed in 10 replicates. The LODs were calculated as three times the corresponding standard deviation (SD). The LOQs were calculated as ten times the SD (Magnusson & Örnemark 2014). The recovery of pesticides from the matrix and precision of the method were determined by the analyses of blank samples spiked at two concentration levels (10 and 50 µg kg^{-1}) in five replicates. The repeatability (RSD_r) was evaluated on the same day. The within-laboratory reproducibility (RSD_{wR}) was performed on five consecutive days. The precision values were expressed as the relative standard deviation (RSD).

2.7. Health risk assessment

Health risk assessments related to pesticides include estimated calculations of the extent to which the health of those who consume pesticide-containing foods will be at risk. Health risks from both acute and chronic exposure were included in the calculations. Dietary exposure assessments are based on the use of food consumption data in the relevant countries and data on the pesticide residues detected in the foods under study.

In assessing the acute and chronic risk of pesticide residues, estimated dietary exposure was compared to toxicological values known as acute reference dose (ARfD, mg kg^{-1} bw day^{-1}) and acceptable daily intake (ADI, mg kg^{-1} bw day^{-1}). The acute/short-term consumer health risk [acute hazard index (aHI)] was calculated based on the estimated short-term intake (ESTI, mg kg^{-1} day^{-1}) and the ARfD. The chronic/long-term consumer health risk (chronic hazard index, cHI) was calculated based on the estimated daily intake (EDI, mg kg^{-1} day^{-1}) and the ADI. The relevant formulas are given below (Liu et al. 2016);

ESTI=high residue level × food consumption/body weight (1)

aHI=ESTI/ARfD ×100 (2)

EDI=mean residue level × food comsumption/body weight (3)

cHI=EDI/ADI ×100 (4)

The average body weight of an adult was considered as 73.5 kg (TSI 2019; Balkan & Kara 2022). The daily consumption of apples, cherries, grapes, pears and peaches for the general population in Turkey were used as 0.08, 0.016, 0.077, 0.013 and 0.02 $kg^{-1}day^{-1}$ respectively (TSI 2021).

3. Results and Discussion

3.1. Method verification

In the verification experiments, blank samples taken from pesticide-free apple orchards were tested and checked for the absence of any of the target pesticides. The verification of the method was performed with the 260 pesticides listed in Table S1. The method performance criteria are also provided in Table S1.

The recovery (%) was calculated by dividing the measured concentration in the spiked blank sample by the true value (spiking level), multiplying by 100. The recovery for detected pesticides ranged varied between 80% and 117% (Table 1). Linearity was recorded for all pesticides, with coefficients of regression (R^2) ≥0.99. Method accuracy and precision were checked by the determination of within laboratory repeatability (RSD_r%) and reproducibility (RSD_{wR}%) of the recovery results (Table S1). Both RSD_r% and RSD_{wR}% were ≤20% in all cases, which is in accordance with the SANTE guidelines (SANTE 2021). The LOQs and LODs were lower than the corresponding default EU-MRLs for apples, cherries, grapes, pears, and peaches rendering the method acceptable for checking compliance to MRLs.

The method performance followed the analytical quality control criteria of the EU SANTE/11312/2021 guideline and therefore considered fit for the purpose (SANTE 2021). Therefore, the method was used for the monitoring of pesticide residues in apples, cherries, grapes, pears, and peaches.

Table 1- Method verification data for detected pesticides

				Spiking level (10 µg kg^{-1})			*Spiking level (50 µg kg^{-1})*		
Pesticide	***R2***	***LOD***	***LOQ***	***Recovery***	***RSDr***	***RSD_{wR}***	***Recovery***	***RSDr***	***RSD_{wR}***
		µg kg^{-1}	*µg kg^{-1}*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*
Acetamiprid	0.999	1.76	5.88	102	7.89	1.98	107	4.49	1.49
Azoxystrobin	0.999	1.45	4.82	117	11.4	10.4	108	8.00	5.89
Boscalid	0.993	1.85	6.16	80.0	14.6	3.81	111	14.9	3.04
Carbendazim	0.999	2.73	9.10	97.0	5.01	4.29	107	5.19	3.09
Cymoxanil	0.999	2.50	8.35	96.3	4.38	1.80	96.6	3.78	1.00
Cypermethrin	0.999	2.70	9.00	110	2.95	5.80	98.8	1.87	4.59
Cyprodinil	0.998	2.45	8.17	111	5.18	6.20	103	7.41	3.69
Deltamethrin	0.998	2.35	7.84	90.1	5.34	7.61	85.0	5.34	3.61
Difenoconazole	0.999	1.01	3.36	104	5.74	2.72	99.0	2.98	1.13
Diflubenzuron	0.994	1.87	6.22	80.9	13.0	4.71	113	3.64	3.10
Dimethoate	0.999	2.37	7.91	104	5.99	1.74	111	1.39	2.92
Etoxazole	0.999	1.71	5.71	112	4.59	4.64	115	6.15	3.17
Fenhexamid	0.999	1.91	6.38	82.0	11.2	1.72	90.2	7.33	1.83
Imidacloprid	0.999	2.16	7.20	104	3.79	1.58	97.5	1.54	1.70
Metalaxyl-M	0.991	2.49	8.30	105	3.53	3.32	98.4	5.13	2.43
Metrafenone	0.994	2.46	8.20	101	5.27	3.51	103	8.69	1.01
Novaluron	0.992	2.45	8.17	108	7.15	5.33	106	6.28	7.77
Omethoate	0.999	2.34	7.79	95.2	7.57	2.94	101	4.78	1.37
Permethrin	0.999	2.91	9.70	105	3.49	7.72	101	3.98	2.05
Pyraclostrobin	0.999	1.91	6.37	101	1.83	3.87	110	7.85	3.43
Pyridaben	0.999	1.90	6.33	101	4.28	2.50	100	4.30	3.12
Pyrimethanil	0.999	2.04	6.79	103	8.04	3.00	102	6.37	3.17
Thiacloprid	0.999	2.67	8.91	91.7	4.32	2.86	106	3.90	2.06
Thiophanate-methyl	0.992	2.93	9.76	102	2.20	2.72	103	12.9	1.81

LOD: Limit of detection, LOQ: Limit of quantification, RSD_r: Relative standard deviation repeatability, RSD_{wR}: Relative standard deviation within-laboratory reproducibility

3.2. Pesticide residue concentrations in real samples

The pesticide residue analysis results are given in Table 2.

Table 2- Pesticide residue amounts and frequencies

Food commodity	*Number of sample detectable residue and percentage, (%)*	*Number of sample > MRL and percentage, (%)*	*Pesticide*	*Frequency of detection*	*Pesticide residue (mg kg^{-1})*	*Number of sample > MRL*	*MRL* (mg kg^{-1})*
Apple	13 (76.5%)	8 (47%)	Acetamiprid	4	0.018-0.058		0.4
			Boscalid	4	0.014-0.041		2
			Cypermethrin	1	0.058		0.1
			Diflubenzuron	4	0.059-0.485	4	0.01
			Dimethoate	6	0.021-0.402	6	0.01
			Etoxazole	1	0.0103		0.07
			Imidacloprid	1	0.023		0.5
			Novaluron	3	0.011-0.069		2
			Pyridaben	3	0.012-0.052		0.9
			Thiacloprid	4	0.022-0.064		0.3
			Thiophanate-methyl	2	0.010-0.080		0.5
Cherry	5 (62.5%)	2 (25%)	Cymoxanil	1	0.011		0.01
			Cypermethrin	2	0.012-0.015		2
			Permethrin	2	0.163-0.194	2	0.05
			Tebuconazole	1	0.046		1
			Thiacloprid	4	0.011-0.155		0.5
			Thiophanate-methyl	2	0.011-0.038		0.3
Grape	5 (55.5%)	-	Azoxystrobin	2	0.035-0.044		3
			Boscalid	1	0.055		5
			Cypermethrin	1	0.118		0.5
			Cyprodinil	1	0.035		3
			Difenoconazole	3	0.016-0.084		3
			Fenhexamid	2	0.023-0.116		15
			Metalaxyl-M	2	0.042-0.085		0.7
			Metrafenone	1	0.014		7
			Pyraclostrobin	2	0.011-0.12		2
			Pyrimethanil	2	0.034-0.177		5
Pear	6 (60%)	4 (40%)	Boscalid	3	0.020-0.036		1.5
			Cypermethrin	3	0.029-0.146		1
			Dimethoate	4	0.014-0.269	4	0.01
			Thiacloprid	1	0.177		0.3
			Thiophanate-methyl	1	0.116		0.5
Peach	8 (88.9%)	3 (33.3%)	Boscalid	2	0.055-0.061		5
			Carbendazim	2	0.014-0.021		0.2
			Cypermethrin	1	0.235		2
			Deltamethrin	1	0.020		0.2
			Dimethoate	3	0.024-0.038	3	0.01
			Pyraclostrobin	1	0.014		0.3
			Pyrimethanil	1	0.063		10
			Tebuconazole	4	0.014-0.031		0.6
			Thiophanate-methyl	4	0.040-0.276		2

*EU pesticide database (European Commission, 2022), MRL: Maximum residue limits

A total 11 different pesticides were detected in 17 apple samples. No active ingredient was found in 4 samples. Diflubenzuron residues exceeded the EU-MRL by 5.9, 15.2, 24.8 and 48.5 times in 4 apple samples, and dimethoate residues exceeded the EU-MRL value by 2.1, 2.3, 3.6, 7.2, 27.1 and 40.2 times in 6 apple samples. Ay et al. (2003, 2007), Ersoy et al. (2011c), Lozowicka (2015), Mutangwe et al. (2016), El Hawari et al. (2019) and Sircu et al. (2019) reported residue concentrations over MRL values in apple. In contrast, the residue concentration recorded by Thamani et al. (2021) were lower than the MRL values.

A total 10 pear samples were evaluated, and 5 different pesticides were detected. No active ingredient was found in 4 samples. Unlicensed dimethoate in pear exceeded the EU-MRL value in 4 samples (1.4, 2.3, 24.3 and 26.9 times). Ersoy et al. (2011c), Li et al. (2015), Mutangwe et al. (2016), and Sircu et al. (2019) reported residue concentrations over MRL values in pear.

No pesticide was detected in 1 of 9 peach samples tested, and 9 different pesticides were detected in the remaining 8 samples. Dimethoate residues exceeded the EU-MRL value by 2.4 times in 2 samples and 3.8 times in 1 sample. Ersoy et al. (2011b), Mutangwe et al. (2016), and Li et al. (2019) determined residue concentrations over MRL values in peach. In contrast, the residue concentration reported by Stachniuk et al. (2017), Kaya & Tuna (2019), and Dülger & Tiryaki (2021), were lower than the MRL values.

No pesticide was found in 4 out of 9 analyzed grape samples, and 10 different pesticides were detected from the remaining 5 samples. None of these samples exceeded EU-MRL values. Ersoy et al. (2011a), Mutangwe et al. (2016), and Yakar (2018) reported residue concentrations over MRL values in grape. In contrast, Nalcı et al. (2018), Sircu et al. (2019), and Thamani et al. (2021) determined residue concentrations lower than the MRL values in grape.

No pesticide residues were found in 4 out of 8 analyzed cherry samples. In the other 4 samples, thiacloprid, tebuconazole, permethrin, cypermethrin, thiophanate-methyl active ingredients were detected. With the exception of permethrin and cymoxanil, the other active ingredients did not exceed EU-MRL values. Although the use of permethrin was prohibited, it was detected above EU-MRL values in 2 samples. Ersoy et al. (2011b) reported residue concentrations over MRL values in cherry samples in their study. Slowik-Borowiec et al. (2015), Stachniuk et al. (2017), Kaya and Tuna (2019) and Balkan and Kara (2020) determined residue concentrations lower than the MRL values in cherry samples. In addition, the samples taken from the cherry growing locations in Tokat were evaluated, and the pesticide residue levels were found to be below the MRL values.

3.3 Health risk assessment

A health risk analysis was conducted for 44 pesticides and the results are given in Table 3.

Table 3- Health risk estimation of pesticides residues in some fruits in Turkey

Food commodity	***Detected pesticide***	***ESTI (mg kg^{-1} d^{-1})***	***aHI (%)***	***EDI (mg kg^{-1} d^{-1})***	***cHI (%)***
Apple	Acetamiprid	6.37209E-05	0.2549	3.2061E-05	0.1282
	Boscalid	4.47189E-05	-	2.60687E-05	0.0652
	Cypermethrin	6.31604E-05	0.0316	6.31604E-05	0.1263
	Diflubenzuron	0.000532814	-	0.00026941	0.2694
	Omethoate	0.000104846	5.2423	4.50069E-05	15.0023
	Dimethoate	0.000232079	2.3208	0.000149092	14.9092
	Etoxazole	1.12979E-05	-	1.12979E-05	0.0282
	Imidacloprid	2.51565E-05	0.0314	2.51565E-05	0.0419
	Novaluron	7.4865E-05	-	4.61074E-05	0.4611
	Pyridaben	5.68081E-05	0.1136	3.18894E-05	0.3189
	Thiacloprid	7.01062E-05	0.2337	4.50129E-05	0.4501
	Thiophanate-methyl	8.77784E-05	0.0439	1.25782E-05	0.0157
Cherry	Cymoxanil	2.54376E-06	0.0032	2.54376E-06	0.0196
	Cypermethrin	3.35069E-06	0.0017	3.00981E-06	0.0060
	Permethrin	4.32796E-05	0.0029	3.98104E-05	0.0796
	Tebuconazole	1.02398E-05	0.0341	1.02398E-05	0.0341
	Thiacloprid	3.46603E-05	0.1155	1.14592E-05	0.1146
	Thiophanate-methyl	8.55668E-06	0.0043	1.15009E-06	0.0014

Table 3- Continued

Food commodity	*Detected pesticide*	*ESTI (mg kg^{-1} d^{-1})*	*aHI (%)*	*EDI (mg kg^{-1} d^{-1})*	*cHI (%)*
Grape	Azoxystrobin	8.55668E-06	0.0043	4.17501E-05	0.0209
	Boscalid	4.67334E-05	-	5.83718E-05	0.1459
	Cypermethrin	5.83718E-05	-	0.000125293	0.2506
	Cyprodinil	0.000125293	0.0626	3.72397E-05	0.1241
	Difenoconazole	3.72397E-05	-	3.96799E-05	0.3968
	Fenhexamid	8.88961E-05	0.0556	7.37927E-05	0.0369
	Metalaxyl-M	0.000123134	-	6.72699E-05	0.0841
	Metrafenone	8.96685E-05	0.0179	1.44422E-05	0.0058
	Pyraclostrobin	1.44422E-05	-	1.26541E-05	0.0422
	Pyrimethanil	1.32149E-05	0.0440	0.000111639	0.0657
Pear	Boscalid	6.76919E-06	-	4.98469E-06	0.0125
	Cypermethrin	2.72854E-05	0.0136	1.47043E-05	0.0294
	Omethoate	2.95747E-05	1.4787	2.02248E-06	0.6742
	Dimethoate	2.19561E-05	0.2196	6.49584E-06	0.6496
	Thiacloprid	3.29891E-06	0.0110	3.29891E-06	0.0330
	Thiophanate-methyl	2.16078E-05	0.0108	2.16078E-05	0.0270
Peach	Boscalid	1.73761E-05	-	1.73761E-05	0.0411
	Carbendazim	6.02231E-06	0.0301	6.02231E-06	0.0248
	Cypermethrin	6.64039E-05	0.0332	6.64039E-05	0.1328
	Deltamethrin	5.68254E-06	0.0227	5.68254E-06	0.0568
	Omethoate	6.65653E-06	0.3328	5.49284E-06	1.8309
	Dimethoate	4.23289E-06	0.0423	3.92427E-06	0.3924
	Pyraclostrobin	3.8365E-06	0.0128	3.8365E-06	0.0128
	Pyrimethanil	1.75686E-05	-	1.75686E-05	0.0103
	Tebuconazole	8.75457E-06	0.0292	8.75457E-06	0.0202
	Thiophanate-methyl	7.80918E-05	0.0390	7.80918E-05	0.0472

The symbol "-" represents that there was no authorized value for ARfD/ADI, and the corresponding risk index could not be computed. ESTI: Estimated short-term intake, aHI: Acute hazard index, EDI: Estimated daily intake, cHI: Chronic hazard index

The omethoate aHI value was 5.2423, cHI value was 15.0023, dimethoate aHI value was 2.3208, and cHI value was 14.9092 in apples. The omethoate aHI value was 1.4787 for pears, while the cHI value for peaches was 1.8309. Hamilton and Crossley (2004) mention a risk for consumers if the health risk index is greater than >1. Since the aHI and cHI values of omethoate and dimethoate for apples, the aHI value of omethoate for pears, and the cHI values of omethoate for peaches were >1, they were considered risky for consumers.

4. Conclusions

This study analyzed pesticide residues in some fruits produced in the Tokat province, and the health risks associated to the consumption of these fruits were quantified. The residual concentrations of 260 pesticides were determined in 54 fresh fruit samples. The fruit samples were monitored based on QuEChERS method followed by analysis using LC-MS/MS. The residue amounts were evaluated according to EU-MRL values. The pesticide residues were lower than EU-MRL values in 37.7% of the samples, and over EU-MRL values in 32.1% of the tested samples. The residues of diflubenzuron in apples, permethrin in cherries, and dimethoate in pears, apples, and peaches were over EU-MRL values. The aHI and cHI values of omethoate and dimethoate in apples, aHI value of omethoate in pears, and cHI values of omethoate in peaches were greater than the risk index of 1. The results indicated that chronic risk arising from pesticide exposure in fruits is significant for public health. Potential risks are possible due to prolonged dietary exposure. Residue levels of agrochemicals should constantly be monitored in the study region.

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Table S1- Method verfication data for 260 pesticides

Pesticide	*R2*			*Spiking level (10 µg kg^{-1})*			*Spiking level (50 µg kg^{-1})*		
		LOD	*LOQ*	*Recovery*	*RSDr*	*RSD$_{wR}$*	*Recovery*	*RSDr*	*RSD$_{wR}$*
		µg kg^{-1}	*µg kg^{-1}*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*
2.4-D	0.999	2.75	9.17	96.1	12.4	5.64	99.5	11.4	4.23
Abamectin	0.995	2.94	9.80	89.7	9.35	7.28	103	5.91	7.89
Acephate	0.998	1.24	4.13	99.7	2.17	2.06	104	3.41	1.80
Acequinocyl	0.998	2.45	8.17	103	4.72	8.19	107	16.1	13.9
Acetamiprid	0.999	1.76	5.88	102	7.89	1.98	107	4.49	1.49
Acetochlor	0.991	2.28	7.59	97.0	4.43	7.64	112	4.65	4.50
Acrinathrin	0.999	2.67	8.92	97.4	12.4	9.84	81.4	9.63	12.1
Alachlor	0.993	1.94	6.45	102	5.11	2.03	110	4.60	2.97
Aldicarb	0.998	2.26	7.53	111	4.63	11.40	110	11.6	11.9
Aldicarb-sulfone	0.999	1.39	4.64	95.8	1.86	1.61	102	2.09	0.70
Aldicarb-sulfoxide	0.999	1.66	5.54	106	10.4	6.76	106	7.54	5.06
Ametoctradin	0.999	2.96	9.86	87.5	5.48	1.55	99.4	2.77	2.36
Amitraz	0.999	1.81	6.03	83.4	12.3	6.99	100	10.9	3.05
Atrazine	0.996	2.74	9.14	85.7	9.01	1.90	107	6.18	1.76
Azinphos-ethyl	0.991	2.95	9.83	104	7.75	9.16	111	5.47	6.17
Azinphos-methyl	0.992	2.97	9.90	90.4	13.4	3.34	102	3.52	2.15
Azoxystrobin	0.999	1.45	4.82	117	11.4	10.35	108	8.00	5.89
Benalaxyl	0.997	2.03	6.78	113	1.68	1.84	102	4.83	2.00
Benfuracarb	0.999	2.53	8.43	89.5	9.33	5.28	93.3	19.7	3.66
Benomyl	0.995	2.60	8.68	98.9	1.35	1.68	109	4.26	1.77
Bensulfuron-methyl	0.996	2.00	6.66	87.9	4.76	3.24	109	8.86	2.82
Bentazone	0.995	2.84	9.47	115	6.60	1.90	110	7.60	2.14
Bifenazate	0.997	1.81	6.05	111	3.73	1.50	95.5	2.68	4.25
Bitertanol	0.998	1.69	5.63	81.6	18.1	3.90	102	9.40	4.83
Boscalid	0.993	1.85	6.16	80.0	14.6	3.81	111	14.9	3.04
Bromoxynil	0.991	2.87	9.55	90.9	4.10	6.05	111	2.75	0.67
Bromuconazole	0.999	2.15	7.15	98.1	11.1	4.11	105	10.5	4.15
Buprimate	0.992	2.50	8.34	107	2.50	3.78	112	2.59	1.47
Buprofezin	0.999	2.34	7.80	94.2	5.99	2.66	99.4	6.13	2.81
Butralin	0.999	2.53	8.45	92.0	2.68	4.67	92.7	4.37	6.39
Butylate	0.999	2.66	8.86	92.2	5.78	6.36	101	2.51	2.83
Cadusafos	0.998	2.29	7.62	102	5.54	4.65	110	11.3	6.65
Carbaryl	0.999	2.22	7.39	113	3.12	3.58	105	4.67	2.80
Carbendazim	0.999	2.73	9.10	97.0	5.01	4.29	107	5.19	3.09
Carbofuran	0.997	2.50	8.33	93.1	4.73	2.20	113	5.55	1.87
Carbofuran-3-hydroxy	0.999	2.50	8.35	96.6	8.31	2.46	105	9.85	2.41
Carbosulfan	0.999	2.47	8.22	90.5	3.13	1.74	91.3	13.2	1.45
Carboxin	0.992	1.70	5.67	90.2	4.46	1.82	112	4.05	2.71
Carfentrazone-ethyl	0.998	2.21	7.36	78.4	5.24	2.90	93.3	7.56	2.54
Chlorantraniliprole	0.994	2.62	8.74	106	9.33	6.11	102	11.1	3.11

Table S1- Continued

Pesticide	*R2*	*Spiking level (10 µg kg^{-1})*					*Spiking level (50 µg kg^{-1})*		
		LOD	*LOQ*	*Recovery*	*RSDr*	*RSD$_{wR}$*	*Recovery*	*RSDr*	*RSD$_{wR}$*
		µg kg^{-1}	*µg kg^{-1}*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*
Chlorbufam	0.997	2.42	8.06	94.1	5.63	6.28	106	13.2	10.1
Chlorfenvinphos	0.994	1.63	5.43	109	4.64	6.74	110	2.42	11.2
Chlorfluazuron	0.999	2.92	9.73	107	6.05	5.68	104	7.01	2.83
Chloridazon	0.998	2.22	7.40	96.8	5.91	1.12	105	4.57	2.68
Chlorsulfuron	0.996	2.23	7.42	107	5.31	3.73	106	6.64	2.84
Clethodim	0.998	1.97	6.57	79.7	11.3	4.89	93.5	6.54	2.76
Clodinofop-propargyl	0.998	2.28	7.59	99.9	3.54	2.44	105	4.78	3.16
Clofentezine	0.993	2.10	6.99	94.2	6.28	3.79	96.5	7.10	4.08
Clothianidine	0.998	2.20	7.34	76.0	14.7	1.91	93.0	11.4	4.11
Cyantraniliprole	0.999	1.80	5.99	97.9	8.29	2.78	100	3.50	4.35
Cyazofamid	0.969	1.95	6.50	107	5.07	5.10	110	6.25	2.96
Cycloate	0.999	2.85	9.49	104	9.95	5.52	110	6.72	1.00
Cycloxydim	0.996	2.93	9.75	108	3.84	2.94	106	5.20	2.75
Cyflufenamid	0.992	2.12	7.05	106	5.41	3.51	99.1	6.30	4.19
Cyhalothrin	0.995	2.57	8.56	112	10.2	5.39	115	13.6	5.13
Cymoxanil	0.999	2.50	8.35	96.3	4.38	1.80	96.6	3.78	1.00
Cypermethrin	0.999	2.70	9.00	110	2.95	5.80	98.8	1.87	4.59
Cyproconazole	0.999	1.22	4.07	88.8	11.9	3.53	98.3	5.09	2.88
Cyprodinil	0.998	2.45	8.17	111	5.18	6.20	103	7.41	3.69
Dazomet	0.999	2.11	7.04	102	4.95	1.66	99.1	5.40	3.72
Deltamethrin	0.998	2.35	7.84	90.1	5.34	7.61	85.0	5.34	3.61
Demeton-s-methyl	0.997	2.65	8.85	80.4	14.7	13.31	95.4	16.6	7.49
Demeton-s-methyl-sulfone	0.999	1.76	5.87	106	3.15	1.58	98.9	2.17	2.17
Desmedipham	0.998	1.38	4.60	92.2	5.98	2.71	112	8.42	2.07
Diafenthiuran	0.999	2.88	9.59	103	7.14	6.97	105	12.1	6.46
Diazinon	0.999	2.59	8.62	102	2.12	2.43	93.3	4.56	2.55
Dichlofluanid	0.994	2.80	9.34	88.0	9.04	7.05	101	13.2	5.45
Dichlorvos	0.999	2.33	7.78	110	4.37	3.82	118	7.92	4.25
Diclofop-methyl	0.996	2.22	7.40	103	5.73	7.85	102	10.5	3.21
Dicrotophos	0.999	2.44	8.14	98.1	3.65	2.50	109	2.73	2.71
Diethofencarb	0.999	1.96	6.52	95.7	5.03	1.59	109	3.33	0.97
Difenoconazole	0.999	1.01	3.36	104	5.74	2.72	98.9	2.98	1.13
Diflubenzuron	0.994	1.87	6.22	80.9	13.0	4.71	113	3.64	3.10
Dimethenamid	0.998	2.20	7.33	89.3	4.22	2.38	104	5.25	2.88
Dimethoate	0.999	2.37	7.91	104	5.99	1.74	111	1.39	2.92
Dimethomorph	0.996	2.00	6.68	93.4	7.31	6.59	95.3	4.82	5.27
Diniconazole	0.999	1.30	4.34	103	5.22	4.46	113	9.04	2.91
Dinocap	0.955	2.36	7.87	97.7	7.26	9.43	102	6.98	7.24
Dioxacarb	0.999	2.78	9.26	92.7	4.92	1.95	99.6	3.64	2.92
Diphenamid	0.999	2.08	6.93	96.3	6.87	2.83	114	5.25	3.17
Diphenylamine	0.998	2.46	8.19	86.9	9.93	8.45	99.1	15.5	11.3

Table S1- Continued

Pesticide	*R2*	*Spiking level (10 µg kg^{-1})*					*Spiking level (50 µg kg^{-1})*		
		LOD	*LOQ*	*Recovery*	*RSDr*	*RSD$_{wR}$*	*Recovery*	*RSDr*	*RSD$_{wR}$*
		µg kg^{-1}	*µg kg^{-1}*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*
Diuron	0.997	2.77	9.24	72.2	13.1	1.89	98.9	6.50	2.85
DMF	0.998	2.11	7.04	94.1	4.71	2.44	107	3.58	2.05
Dodine	0.999	2.71	9.02	112	2.40	2.21	110	2.45	3.89
Emamectin	0.999	1.95	6.51	77.4	8.59	2.79	99.8	8.24	3.40
Emamectin benzoat	0.999	2.25	7.49	95.1	9.16	3.64	101	11.5	4.26
EPN	0.996	2.62	8.75	88.1	7.92	6.99	105	3.02	2.85
Epoxiconazole	0.993	2.84	9.46	102	7.39	0.94	104	4.51	2.11
EPTC	0.999	2.23	7.42	102	13.8	9.42	112	9.23	7.97
Ethiofencarb	0.995	1.80	6.00	103	8.74	2.66	117	3.92	4.78
Ethion	0.999	1.97	6.57	96.6	3.24	2.66	96.9	7.76	3.36
Ethirimol	0.997	1.19	3.96	75.4	7.19	1.73	90.9	5.59	2.02
Etofenprox	0.997	1.15	3.83	102	5.65	4.18	111	3.84	4.38
Etoxazole	0.999	1.71	5.71	112	4.59	4.64	115	6.15	3.17
Famoxadone	0.998	2.52	8.40	112	8.41	6.40	112	10.6	4.91
Fenamidone	0.998	1.72	5.74	88.8	6.64	3.21	105	7.97	2.47
Fenamiphos	0.992	2.74	9.13	94.8	3.11	2.48	91.7	3.81	2.63
Fenamiphos-sulfone	0.995	2.49	8.29	84.7	16.6	3.62	108	8.25	1.71
Fenamiphos-sulfoxide	0.993	1.64	5.48	93.1	2.82	2.12	97.5	6.95	3.79
Fenarimol	0.999	2.95	9.82	99.5	13.1	2.53	111	10.1	4.63
Fenazaquin	0.999	0.99	3.30	91.8	2.49	1.03	90.6	6.11	0.57
Fenbuconazole	0.996	2.15	7.18	104	3.29	3.13	107	6.97	4.81
Fenbutatin oxide	0.999	1.67	5.57	112	4.13	7.44	111	3.54	3.97
Fenhexamid	0.999	1.91	6.38	82.0	11.2	1.72	90.2	7.33	1.83
Fenoxycarb	0.998	1.66	5.52	113	6.16	2.37	112	6.02	2.82
Fenoxyprob-ethyl	0.999	1.89	6.31	107	9.56	8.47	119	4.54	2.66
Fenpropathrin	0.999	2.37	7.92	102	8.12	9.75	110	13.2	5.90
Fenproxymate	0.999	0.83	2.76	100	1.63	2.35	88.9	3.19	3.95
Fenthion	0.999	1.32	4.38	108	3.75	4.67	115	2.74	3.31
Fenthion-sulfone	0.999	2.19	7.31	105	7.21	4.97	112	14.5	2.74
Fenthion-sulfoxide	0.999	2.98	9.93	89.9	4.75	3.18	99.2	5.36	1.95
Fipronil	0.999	1.62	5.41	89.2	6.06	4.79	88.1	7.29	2.24
Fipronil-sulfone	0.999	2.13	7.09	95.6	10.7	2.75	101	5.61	4.41
Fluazifop-p-butyl	0.998	2.19	7.29	85.7	10.2	7.95	110	6.04	4.98
Fluazinam	0.999	2.26	7.54	107	13.3	7.54	107	6.24	6.54
Flubendiamide	0.999	2.98	9.92	87.6	6.78	6.90	101	7.23	3.64
Fludioxonil	0.999	2.71	9.05	98.9	6.11	4.29	94.1	3.84	4.68
Flufenoxuron	0.998	2.89	9.64	96.2	4.09	4.07	99.0	4.37	5.18
Fluopicolide	0.995	2.96	9.87	117	2.80	2.76	110	4.10	3.82
Fluopyram	0.999	2.82	9.41	82.1	3.69	2.16	89.5	2.42	2.28
Fluquinconazole	0.997	2.42	8.07	118	4.92	4.30	97.1	6.38	5.73
Flurochloridone	0.999	2.85	9.50	95.4	14.7	6.05	108	5.79	4.60

Table S1- Continued

Pesticide	R2	Spiking level (10 µg kg^{-1})					Spiking level (50 µg kg^{-1})		
		LOD	LOQ	Recovery	RSDr	RSD_{wR}	Recovery	RSDr	RSD_{wR}
		µg kg^{-1}	µg kg^{-1}	(%)	(%)	(%)	(%)	(%)	(%)
Fluroxypyr	0.999	2.67	8.91	79.1	8.95	6.09	95.8	18.7	9.27
Flusilazole	0.995	2.66	8.87	101	8.30	5.49	101	5.17	5.25
Flutriafol	0.999	3.00	9.99	104	7.84	4.87	107	9.95	3.19
Forchlorfenuron	0.995	1.57	5.24	76.7	4.46	2.26	94.1	9.25	1.83
Formetanete hydrochloride	0.994	2.87	9.57	89.3	7.38	3.98	119	11.6	5.09
Fosthiazate	0.994	1.25	4.16	98.1	3.06	1.86	104	3.29	2.18
Furathiocarb	0.999	2.72	9.07	103	3.92	2.76	110	4.32	1.82
Haloxyfop-R-methyl	0.993	2.22	7.40	97.9	3.56	3.55	95.1	10.5	3.32
Hexaconazole	0.997	2.04	6.80	73.0	11.2	4.07	108	6.99	3.05
Hexaflumuron	0.993	2.66	8.87	93.6	10.1	10.54	104	6.59	6.33
Hexythiazox	0.999	2.38	7.93	88.7	5.31	5.65	92.9	5.32	5.21
Imazalil sulfate	0.999	1.11	3.71	102	13.8	8.12	104	7.31	4.91
Imazapyr	0.996	2.74	9.14	90.1	7.48	1.47	95.4	10.6	1.23
Imidacloprid	0.999	2.16	7.20	104	3.79	1.58	97.5	1.54	1.70
Indoxacarb	0.999	2.67	8.90	115	3.59	5.63	106	6.72	4.12
Iodosulfuron-methyl-sodium	0.999	2.40	8.01	83.7	6.39	2.25	99.7	4.46	4.40
Ioxynil	0.999	2.58	8.61	98.9	10.6	9.88	105	6.72	4.45
Isocarbofos	0.992	2.89	9.65	106	13.2	14.59	93.7	5.27	7.70
Kresoxim-methyl	0.997	2.50	8.35	112	2.79	2.75	110	5.87	1.88
Lenacil	0.991	2.19	7.31	95.8	3.71	2.64	112	3.86	2.71
Linuron	0.996	2.88	9.59	95.5	12.7	3.92	109	8.18	4.81
Lufenuron	0.999	2.74	9.13	99.0	5.61	4.57	98.3	4.43	2.26
Malaoxon	0.999	1.10	3.65	96.7	3.78	1.58	106	2.95	2.62
Malathion	0.999	2.15	7.15	81.5	5.93	1.16	108	3.62	0.99
Mandipropamid	0.999	2.28	7.61	92.0	7.12	2.64	101	8.16	2.72
MCPA	0.997	1.94	6.46	105	4.93	1.44	108	8.15	3.26
Mecarbam	0.999	2.75	9.18	99.6	2.34	2.00	100	5.87	1.85
Mepanipyrim	0.999	2.01	6.69	92.0	3.48	5.45	90.7	3.48	6.14
Mepanipyrim-hyroxypropyl	0.998	2.53	8.42	85.9	6.09	1.66	110	3.54	1.55
Metaflumizone	0.999	2.83	9.42	96.8	10.7	9.03	109	6.97	5.08
Metalaxyl-M	0.991	2.49	8.30	105	3.53	3.32	98.4	5.13	2.43
Metamitron	0.999	2.43	8.09	94.1	9.00	3.54	94.5	9.38	3.78
Methacrifos	0.999	2.15	7.18	100	7.36	4.69	98.2	7.78	1.58
Methamidophos	0.999	2.10	7.01	113	3.13	2.74	105	5.00	2.84
Methidathion	0.999	2.95	9.84	86.4	7.71	6.02	112	5.69	4.44
Methiocarb	0.992	1.79	5.97	80.2	7.55	2.48	111	6.35	2.58
Methiocarb-sulfone	0.999	1.75	5.84	99.6	7.29	2.58	99.5	5.27	2.17
Methiocarb-sulfoxide	0.999	1.68	5.61	103	3.80	2.95	101	3.51	2.00
Methomyl	0.999	2.06	6.86	100	4.30	1.70	105	3.19	1.17
Methoxyfenozide	0.994	1.46	4.86	110	8.27	10.05	111	13.6	8.44
Metolachlor-S	0.997	2.57	8.56	86.4	7.98	1.99	102	4.92	2.07

Table S1- Continued

Pesticide	R2	Spiking level (10 µg kg^{-1})					Spiking level (50 µg kg^{-1})		
		LOD	LOQ	Recovery	RSDr	RSD_{wR}	Recovery	RSDr	RSD_{wR}
		µg kg^{-1}	µg kg^{-1}	(%)	(%)	(%)	(%)	(%)	(%)
Metosulam	0.996	2.68	8.93	70.3	6.88	2.21	99.0	4.64	2.68
Metrafenone	0.994	2.46	8.20	101	5.27	3.51	103	8.69	1.01
Metribuzin	0.999	2.67	8.90	106	5.77	2.68	112	5.71	1.93
Mevinphos	0.991	2.30	7.67	106	6.20	13.45	106	3.69	3.08
Molinate	0.998	2.28	7.59	106	14.3	4.91	106	5.49	3.58
Monocrotophos	0.997	1.49	4.95	107	5.08	1.33	104	3.21	1.53
Monolinuron	0.997	1.10	3.67	92.9	4.87	4.20	92.4	4.37	4.32
Myclobutanil	0.996	1.76	5.86	87.1	5.56	1.99	109	7.23	2.13
Nicosulfuron	0.996	2.36	7.87	76.0	6.07	3.78	105	13.2	4.26
Novaluron	0.992	2.45	8.17	108	7.15	5.33	106	6.28	7.77
Nuarimol	0.999	1.53	5.09	105	8.11	2.62	116	12.7	3.38
Omethoate	0.999	2.34	7.79	95.2	7.57	2.94	101	4.78	1.37
Oxadixyl	0.997	2.68	8.95	88.8	9.22	1.68	104	2.42	3.13
Oxamyl	0.999	0.94	3.13	101	1.56	1.37	109	2.81	1.60
Oxycarboxin	0.999	2.80	9.34	111	2.95	1.73	106	2.99	2.91
Oxydemeton-methyl	0.999	1.17	3.90	96.2	6.64	3.33	100	11.1	3.95
Paclobutrazol	0.998	1.62	5.40	93.0	7.22	3.72	111	4.57	2.93
Paraoxon-ethyl	0.992	2.18	7.27	85.9	4.66	3.12	109	9.80	2.02
Paraoxon-methyl	0.999	2.45	8.16	90.2	14.7	4.78	108	9.75	4.02
Penconazole	0.991	2.80	9.33	106	5.91	4.28	110	3.68	2.78
Pencycuron	0.999	1.95	6.50	95.6	11.8	4.89	111	4.95	5.96
Pendimethalin	0.999	1.33	4.43	84.9	2.80	2.99	89.7	4.07	3.58
Permethrin	0.999	2.91	9.70	105	3.49	7.72	101	3.98	2.05
Phenmedipham	0.998	2.67	8.90	94.6	7.63	5.32	104	7.71	5.80
Phenthoate	0.998	2.38	7.95	97.1	5.63	2.27	98.0	4.22	4.26
Phorate	0.998	2.66	8.85	89.5	7.98	6.45	107	9.24	4.39
Phorate-sulfone	0.995	2.20	7.34	100	6.91	5.48	88.2	10.4	5.18
Phorate-sulfoxide	0.997	2.48	8.27	115	2.64	3.59	107	2.70	1.18
Phosalone	0.997	1.08	3.61	86.3	5.28	2.24	109	9.33	2.65
Phosmet	0.994	2.75	9.18	78.5	8.20	1.26	112	5.04	1.87
Phosphamidon	0.999	2.67	8.90	99.9	8.02	2.80	106	2.24	2.30
Pirimicarb-desmethyl	0.999	2.59	8.63	93.6	4.27	1.27	104	4.49	2.31
Primicarb	0.994	2.04	6.81	94.5	4.87	8.63	92.7	7.45	4.36
Primiphos-ethyl	0.999	2.92	9.74	108	7.56	2.84	100	6.10	1.77
Primiphos-methyl	0.999	2.21	7.36	91.4	8.23	2.31	110	5.83	2.94
Prochloraz	0.998	1.95	6.49	101	6.20	5.09	105	12.8	7.68
Profenefos	0.990	2.79	9.29	103	4.27	3.58	106	4.24	3.37
Profoxydim-lithium	0.999	2.24	7.47	85.4	3.27	3.47	96.6	5.09	4.56
Promecarb	0.998	2.49	8.29	94.1	6.49	2.22	108	2.56	1.68
Prometryn	0.999	2.06	6.87	95.6	4.39	5.68	97.7	5.16	3.79
Propaquizafob	0.998	2.35	7.85	93.7	15.3	3.28	101	6.45	7.35

Table S1- Continued

Pesticide	R2	Spiking level (10 µg kg^{-1})					Spiking level (50 µg kg^{-1})		
		LOD	LOQ	Recovery	RSDr	RSD_{wR}	Recovery	RSDr	RSD_{wR}
		µg kg^{-1}	µg kg^{-1}	(%)	(%)	(%)	(%)	(%)	(%)
Propargite	0.999	2.85	9.51	92.2	3.58	4.10	96.9	5.71	6.45
Propazine	0.998	2.08	6.95	93.0	3.03	2.39	103	3.09	1.76
Propiconazole	0.994	1.72	5.74	98.2	8.33	4.89	109	10.1	7.12
Propoxur	0.995	2.67	8.89	92.1	7.03	1.60	113	3.73	1.93
Propyzamide	0.995	1.22	4.07	89.3	7.02	2.04	111	9.75	1.47
Prothiophos	0.999	2.70	8.99	87.2	8.32	3.02	89.6	5.36	4.26
Pymetrozine	0.999	1.66	5.55	75.5	7.35	2.18	97.2	5.22	2.30
Pyraclostrobin	0.999	1.91	6.37	101	1.83	3.87	110	7.85	3.43
Pyrazophos	0.996	2.28	7.60	86.9	5.96	3.04	99.2	5.16	3.07
Pyridaben	0.999	1.90	6.33	101	4.28	2.50	100	4.30	3.12
Pyridaphenthion	0.999	1.65	5.50	119	2.88	1.58	108	1.58	1.69
Pyridate	0.999	2.66	8.85	88.8	4.18	2.85	95.2	11.7	1.83
Pyrimethanil	0.999	2.04	6.79	103	8.04	3.00	102	6.37	3.17
Pyriproxyfen	0.999	2.75	9.15	96.6	5.51	4.11	99.0	5.73	4.53
Quinalphos	0.998	2.03	6.78	96.1	11.5	3.53	111	7.06	1.77
Quizalofop-ethyl	0.997	2.25	7.50	87.6	14.5	4.08	105	8.34	4.49
Rimsulfuron	0.999	2.43	8.08	99.2	4.99	3.95	104	9.84	4.23
Sethoxydim	0.990	1.83	6.11	96.5	2.38	1.28	106	2.52	1.78
Simazine	0.999	2.59	8.64	102	7.74	4.53	105	11.0	1.98
Spinosyn A	0.999	2.35	7.82	103	3.18	4.44	105	1.57	3.80
Spinosyn D	0.999	2.84	9.47	103	4.06	4.02	113	5.20	2.82
Spirodiclofen	0.999	2.92	9.73	97.1	9.17	2.62	95.5	9.25	6.96
Spiromesifen	0.991	2.59	8.63	95.3	11.2	5.61	98.8	5.07	8.84
Spiroxamine	0.999	1.14	3.81	88.7	13.5	9.26	99.2	13.6	5.89
Sulfoxaflor	0.999	2.17	7.23	93.9	8.11	4.08	99.8	5.65	3.68
Tebuconazole	0.994	1.38	4.60	101	7.20	2.75	112	6.46	2.73
Tebufenozide	0.995	2.73	9.09	94.9	5.40	7.02	91.5	4.48	6.85
Tebufenpyrad	0.997	2.59	8.64	113	7.16	8.91	106	11.6	9.16
Teflubenzuron	0.999	2.13	7.10	109	7.60	6.74	106	8.77	12.4
Tepraloxydim	0.999	2.49	8.31	89.5	8.88	5.99	96.1	5.34	8.97
Terbutryn	0.999	2.04	6.79	85.3	5.31	1.52	102	3.77	2.28
Terbutylazine	0.998	2.38	7.95	96.1	3.22	2.34	109	4.25	11.5
Tetraconazole	0.999	1.83	6.10	98.6	4.58	1.91	106	2.77	2.94
Tetramethrin	0.996	2.71	9.04	85.0	4.74	1.95	95.9	7.30	3.72
Thiabendazole	0.997	2.33	7.76	106	2.59	1.38	113	6.22	0.94
Thiacloprid	0.999	2.67	8.91	91.7	4.32	2.86	106	3.90	2.06
Thiamethoxam	0.998	2.59	8.63	92.2	8.13	1.30	107	2.86	1.10
Thifensulfuron-methyl	0.999	1.03	3.43	104	3.79	1.58	101	2.72	1.99
Thiobencarb	0.995	2.34	7.81	116	5.52	6.03	114	5.90	13.5
Thiodicarb	0.995	2.30	7.66	95.1	4.53	4.81	94.2	4.57	3.59
Thiophanate-methyl	0.992	2.93	9.76	102	2.20	2.72	103	12.9	1.81

Table S1- Continued

Pesticide	*R2*	*LOD*	*LOQ*	*Spiking level (10 µg kg^{-1})* *Recovery*	*RSDr*	*RSD_{wR}*	*Spiking level (50 µg kg^{-1})* *Recovery*	*RSDr*	*RSD_{wR}*
		µg kg^{-1}	*µg kg^{-1}*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*
Tolclofos-methyl	0.998	2.44	8.14	95.7	16.5	8.44	103	10.5	6.06
Tolfenpyrad	0.999	2.55	8.50	80.1	5.61	4.57	95.9	4.25	2.58
Tolyfluanid	0.996	2.63	8.77	109	4.77	3.57	108	5.45	4.12
Tralkoxydim	0.996	1.04	3.47	115	2.38	3.03	111	1.62	1.95
Triadimefon	0.990	2.32	7.74	98.2	6.41	2.44	110	8.11	1.57
Triadimenol	0.996	2.47	8.22	99.2	6.65	4.85	83.1	5.28	6.28
Tri-allate	0.998	1.74	5.81	95.0	12.9	4.78	91.4	4.98	8.31
Triasulfuron	0.998	2.27	7.58	103	3.14	3.83	91.7	7.68	2.61
Triazophos	0.999	1.49	4.98	74.3	3.42	3.22	97.7	3.71	2.41
Tribenuron-methyl	0.999	2.02	6.74	87.4	4.73	3.08	108	3.60	2.56
Trichlorfon	0.999	1.80	5.99	104	5.94	2.15	106	4.61	1.67
Trifloxystrobin	0.998	1.52	5.07	85.5	6.83	3.39	108	6.27	2.66
Triflumizole	0.999	2.34	7.80	85.2	4.46	5.02	110	6.99	3.03
Triflumuron	0.992	2.24	7.46	111	5.07	6.36	111	11.1	3.42
Triticonazole	0.999	1.54	5.15	106	3.61	1.39	103	1.55	1.02

LOD: Limit of detection, LOQ: Limit of quantification, RSD_r: Relative standard deviation repeatability, RSD_{wR}: Relative standard deviation within-laboratory reproducibility