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Research Article/Araştırma Makalesi

Pesticide residues in vegetables and fruits from Istanbul by LC-MS/MS

İstanbul'da satışa sunulan bazı meyve ve sebzelerde LC-MS/MS ile pestisit kalıntılarının tespiti

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ABSTRACT

Selected pesticide active ingredients are used in various stages of production of fruits and vegetables in Turkey for the purpose of pest control. Due to their harm to humans, animals and the environment, pesticide active ingredients and their residue limits were determined by legal regulations. The aim of this study was to determine and highlight the pesticide residue risk in fruits and vegetables sold in markets and greengrocers and widely consumed in Istanbul, one of the most populated cities in Turkey. 393 pesticide active ingredients in 100 fruit and vegetable samples (tomatoes, green peppers, cucumbers, strawberries and apples in total) were screened using liquid chromatography coupled to mass spectrometry (LC–MS/MS) with Quick Easy Cheap Effective Rugged and Safe (QuEChERS) sample preparation method. The mean recoveries of the pesticides were between 76.5 % and 115.5 %, LOQ for them was 0.01 mg kg^{-1}. Pesticide residue was detected in 43% of the samples. A total of 7 (7%) samples contained pesticide residues above maximum residue limit (MRL). While pesticide residues were detected above MRL in tomato, strawberry and cucumber samples; no pesticide residues were found above MRL in pepper and apple samples. In the samples analyzed, 42 different pesticide residues were detected, the most detected pesticide active substance in the samples examined was Acetamiprid. Phorate Sulfone, one of the banned pesticides, was detected in a strawberry sample.

Key Words: Pesticide residue, Agricultural products, Fruits, Vegetables, LC-MS/MS

ÖZ

Türkiye'de meyve ve sebze üretiminin çeşitli aşamalarında zararlıların kontrolü amacıyla belirli pestisitler kullanılmaktadır. İnsanlara, hayvanlara ve çevreye zararlı etkilerinden dolayı pestisit etken maddeleri ve bunların kalıntı limitleri yasal düzenlemelerle belirlenmiştir. Bu çalışmanın amacı, Türkiye'nin en kalabalık şehri olan İstanbul'da market ve manavlarda satılan ve yaygın olarak tüketilen meyve ve sebzelerde pestisit kalıntılarının riskini belirlemek ve vurgulamaktır. 100 meyve ve sebze örneğinde 393 pestisit etken maddesi, QuEChERS numune hazırlama metoduyla kütle spektrometrisine bağlı sıvı kromatografisi (LC–MS/MS) kullanılarak taranmıştır. Pestisitlerin ortalama geri kazanımları %76.5 ve %115.5 arasında, LOQ değerleri ise 0.01 mg kg^{-1}'dır. Örneklerin %43'ünde pestisit kalıntısı tespit edilmiştir, 7 (%7)'si maksimum kalıntı limitinin (MRL) üzerinde pestisit kalıntıları içermektedir. Domates, çilek ve salatalık örneklerinde MRL üzerinde pestisit kalıntısı tespit edilirken, biber ve elma örneklerinde MRL'nin üzerinde pestisit kalıntısına rastlanmamıştır. İncelenen örneklerde 42 farklı pestisit kalıntısı tespit edilmiştir, en çok tespit edilen pestisit etken maddesi ise Acetamiprid'dir. Yasaklı pestisitlerden biri olan Phorate Sulfone ise bir çilek örneğinde tespit edilmiştir.

Anahtar Kelimeler: Pestisit kalıntısı, Tarım ürünleri, Meyveler, Sebzeler, LC-MS/MS

Introduction

Pesticides are chemicals that are widely used around the world to prevent or control pests, diseases, weeds and other plant pathogens in order to reduce and eliminate yield losses in agricultural products and to maintain high product quality (Damalas and Eleftherohorinos, 2011). In parallel with the increasing population both in Turkey and in the world, the demand for food has increased; thus, there are attempts to increase the agricultural production with various technical applications. The use of pesticides to combat diseases and pests is one of these technical measures (Kızılay and Akçaöz, 2009). With the increase in the use of pesticides in agriculture, the quality and quantity of food products have increased over the years (Goel and Aggarwal, 2007). Although pesticides have beneficial effects such as combating pests in order to obtain more products per unit area, they can cause unacceptably high levels of compounds in products if used improperly. These compounds cause a wide variety of harmful effects in humans, animals and the environment. In addition to the harmful effects of pesticides on the environment, they have been reported to have acute effects such as headache and nausea, acute neurological toxicity, neurological disorders, immune system disorders, reproductive and endocrine system diseases, cancer, and chronic kidney diseases in humans (Berrada et al., 2010; Guana et al., 2010; Chen et al., 2011; Bakırcı and Hışıl, 2012; Bakırcı et al., 2014). It is also known that pesticides remain in nature for years and their harmful effects continue to be a potential danger for a very long time (Issa and Çiftçioğlu, 2006). Therefore, it is important to control and regulate pesticide use and to monitor their levels in agricultural products (Gölge et al., 2018). In order to ensure food safety for consumers and protect human health, maximum residue limits (MRLs) have been determined by many organizations and countries around the world for pesticide residues in foods. MRL is the maximum level of pesticide residue legally permitted in foods and is expressed in mg kg^{-1} (Jallow et al., 2017). The relevant legal legislation in our country is the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides dated 05.11.2016 and numbered 29899. Pesticide residues in food should not exceed the maximum residue levels (MRL) specified in the legislation. When pesticide residue is detected above the MRL value, those foodstuffs are considered harmful for health (Lozowicka et al., 2015).

There are over 1000 pesticides in use (Wang et al., 2017). These pesticides are used during the cultivation or post-harvest storage of agricultural products (Guana et al., 2010; Bakırcı and Hışıl, 2012; Bakırcı et al., 2014). Pesticide residues have been detected above legal limits (Issa and Çiftçioğlu, 2006; Tiryaki, 2016; Dereumeaux et al., 2020) in a wide variety of foods such as cereals (Lozowicka et al., 2014), olive oil (Razzaghia et al., 2018), fish (Doğan and Karpuzcu 2019), vegetables and fruits (Ay et al., 2007; Chen et al., 2011; Ersoy et al., 2011a; Ersoy et al., 2011b; Lozowicka et al., 2015; Szpyrka et al., 2015; Tiryaki, 2016; Gölge et al., 2018; Hepsağ, 2019; Kaya and Tuna, 2019) drinking- utility water, and soil and sediment (Kumari et al., 2012; Doğan and Karpuzcu, 2019). They have also been found in both raw and processed food products (Keikotlhaile et al., 2010).

Turkey is one of the world's largest producers of fresh fruits and vegetables (Gölge et al., 2018). In 2019, tomato accounted for the 41.3% of the total vegetable production, cucumber 6.2% and charleston pepper 0.4%, and of the total fruit production, 16.2% was apple and 2.2% was strawberry (Turkish Statistical Institute, 2021).

The total use of pesticides in agricultural products in Turkey is 60.020 tons in 2018. Compared to pesticide utilization rates of 160 countries in the world in 2018, this amount constitutes 1.01%. However, Turkey is the 12th country among these 160 countries that uses the most pesticides, regardless of agricultural production rate (FAO, 2020).

In this study, it is aimed to examine the most consumed vegetable and fruit varieties in markets and greengrocers in Istanbul in terms of pesticide residue levels and pesticide residues in tomato, green pepper, cucumber, apple and strawberry samples were investigated for compliance with the Turkish legislation. A total of 393 pesticide active substances given in Table 1 were searched in a total of 100 samples by the analysis method validated in the LC-MS/MS device. Selected pesticide active ingredients are used in various stages of production of fruits and vegetables in Turkey for the purpose of pest control. Pesticide residue results were evaluated according to Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides and it was determined whether these foods contained pesticide residues within the legal limits permitted for human consumption.

Table 1. Pesticide active substances determined in the LC-MS/MS device in fruit and vegetable samples, LOQ values and recovery rate

No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)	No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)
1	1-Naphthylacetamide	0.01	105.7	198	Formetanate	0.01	109.7
2	2,4 Dimethylanilin	0.01	102.6	199	Fosthiazate	0.01	101.3
3	2,4 D	0.01	81.9	200	Fuberidazole	0.01	105.6
4	2,4,5 T	0.01	79.5	201	Furalaxyl	0.01	106.6
5	3,4,5 trimethocarb	0.01	101.6	202	Furathiocarb	0.01	103.7
6	Acephate	0.01	92.6	203	Halosulfuron Methyl	0.01	83.3
7	Acetamiprid	0.01	102.9	204	Haloxyfop	0.01	95.6
8	Acibenzolar-S-methyl	0.01	104.9	205	Haloxyfop-2-Ethoxyethyl	0.01	115.5
9	Aclonifen	0.01	105.5	206	Haloxyfop-methyl	0.01	106.3
10	Acrinathrin	0.01	91.2	207	Haloxyfop-r-methylester	0.01	106.3
11	Aldicarb	0.01	102.5	208	Hexaconazole	0.01	93.6
12	Aldicarb sulfone	0.01	106.0	209	Hexaflumuron	0.01	112.4
13	Aldicarb sulfoxide	0.01	99.3	210	Hexythiazox	0.01	102.9
14	Allethrin	0.01	103.7	211	Imazalil	0.01	95.9
15	Ametoctradin	0.01	91.7	212	Imazamox	0.01	86.9
16	Ametryn	0.01	101.0	213	Imazapic	0.01	79.8
17	Aminocarb	0.01	99.0	214	Imazapyr	0.01	98.4
18	Amisulbrom	0.01	78.0	215	Imazosulfuron	0.01	79.6
19	Amitraz	0.01	83.8	216	Imibenconazole	0.01	92.0
20	Anilazine	0.01	95.3	217	Indoxacarb	0.01	100.1
21	Anilofos	0.01	102.0	218	Iodosulfuron methyl	0.01	79.8
22	Aramite	0.01	100.9	219	Ioxynl	0.01	78.1
23	Asulam	0.01	92.5	220	Ipconazole	0.01	91.7
24	Atrazine	0.01	99.4	221	Iprodione	0.01	96.2
25	Azamethiphos	0.01	103.6	222	Iprovalicarb	0.01	92.4
26	Azimsulfuron	0.01	91.9	223	Isoproturon	0.01	98.8
27	Azinphos ethyl	0.01	105.0	224	Isopyrazam	0.01	97.3
28	Azinphos- methyl	0.01	109.2	225	Isoxadifen Ethyl	0.01	109.2
29	Aziprotryne	0.01	92.2	226	Isoxaflutale	0.01	97.3
30	Azoconazole	0.01	108.6	227	imidacloprid	0.01	97.8
31	Azoxystrobin	0.01	110.6	228	Kresoxim-methyl	0.01	100.6
32	Beflubutamid	0.01	108.1	229	Lenacil	0.01	92.8
33	Benalaxyl	0.01	112.9	230	Linuron	0.01	101.3
34	Bendiocarb	0.01	104.4	231	Lufenuron	0.01	106.1
35	Benfurocarb	0.01	108.0	232	Malaoxon		103.8
36	Benomyl-Carbendazim	0.01	102.8	233	Malathion	0.01	101.8

No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)	No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)
37	Bensulfuron-methyl	0.01	100.0	234	Mandipropamid	0.01	104.8
38	Bentazone	0.01	94.2	235	MCPA	0.01	101.7
39	Benthiovalicarb Isopropyl	0.01	94.8	236	Mecarbam	0.01	102.5
40	Benzoximate	0.01	106.2	237	Mecoprop (MCPP)	0.01	79.9
41	Bifenazate	0.01	98.0	238	Mecoprop-P (MCPP-P)	0.01	82.0
42	Bifenox	0.01	107.4	239	Mepanipyrim	0.01	100.1
43	Bispyribac	0.01	78.3	240	Mepanipyrim-hydroxypropyl	0.01	102.7
44	Bitertanol	0.01	95.9	241	Metalaxyl	0.01	102.1
45	Boscalid	0.01	101.1	242	Metalaxyl-m	0.01	110.3
46	Bromacil	0.01	91.4	243	Metamitron	0.01	94.7
47	Bromoxynil	0.01	80.5	244	Methacrifos	0.01	100.0
48	Bromuconazole	0.01	96.6	245	Methamidophos	0.01	100.9
49	Bupirimate	0.01	95.8	246	Methiocarb	0.01	99.6
50	Buprofezin	0.01	94.4	247	Methiocarbsulfone	0.01	106.6
51	Butocarboxim	0.01	97.0	248	Methiocarbsulfoxide	0.01	104.8
52	Butocarboxim sulfoxide	0.01	97.7	249	Methomyl	0.01	101.8
53	Butralin	0.01	97.9	250	Methoxyfenozide	0.01	105.4
54	Buturon	0.01	103.6	251	Metolachlor	0.01	93.7
55	Carbaryl	0.01	105.2	252	Metosulam	0.01	89.6
56	Carbendazim	0.01	106.4	253	Metrafenone	0.01	105.2
57	Carbofuran	0.01	111.1	254	Metribuzin	0.01	96.1
58	Carbofuran-3-hydroxy	0.01	99.6	255	Metsulfuron-methyl	0.01	86.4
59	Carbosulfan	0.01	96.8	256	Molinate	0.01	96.7
60	Carboxin	0.01	106.7	257	Monocrotophos	0.01	99.0
61	Carfentrazone - ethyl	0.01	103.8	258	Monolinuron	0.01	107.0
62	Chlorantraniliprole	0.01	97.0	259	Myclobutanil	0.01	100.2
63	Chlorbufam	0.01	104.6	260	N-2,4 Dimethylphenyl formaide (DMF)	0.01	101.3
64	Chlorfenvinphos	0.01	98.5	261	Naled	0.01	87.4
65	Chlorfluazuron	0.01	83.6	262	Nicosulfuron	0.01	77.3
66	Chloridazon	0.01	98.4	263	Norfluazuron	0.01	104.3
67	Chlormequat chloride	0.01	78.5	264	Novaluron	0.01	110.4
68	Chlorotoluron	0.01	108.1	265	Nuarimol	0.01	90.6
69	Chloroxuron	0.01	106.2	266	O.O-Tepp	0.01	87.8
70	Chlorpyriphos	0.01	103.0	267	Omethoate	0.01	96.9
71	Chlorpyriphos Methyl	0.01	100.8	268	Orthosulfamuron	0.01	79.6
72	Chlorsulfuron	0.01	81.0	269	Oxadiazon	0.01	104.1
73	Chlorthiamid	0.01	98.0	270	Oxadixyl	0.01	98.6
74	Chromafenozide	0.01	103.1	271	Oxamyl	0.01	92.6
75	Cinidon Ethyl	0.01	107.0	272	Oxasulfuron	0.01	77.7
76	Clethodim	0.01	87.5	273	Oxycarboxin	0.01	97.0
77	Climbazole	0.01	96.3	274	Oxyfluorfen	0.01	81.6
78	Clodinafop-propargyl ester	0.01	103.9	275	Paclobutrazole	0.01	97.4
79	Clofentezine	0.01	97.3	276	Paraoxon Methyl	0.01	104.4
80	Clomazone	0.01	108.2	277	Paraoxon-ethyl	0.01	109.2

No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)	No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)
81	Cloquintocet-methylhexyl ester	0.01	97.8	278	Parathion- methyl	0.01	101.8
82	Clothianidin	0.01	96.2	279	Pebulate	0.01	94.8
83	Coumaphos	0.01	105.1	280	Penconazole	0.01	103.3
84	Crimidine	0.01	89.2	281	Pencycuron	0.01	98.4
85	Cyanazine	0.01	97.6	282	Penoxsulam	0.01	76.9
86	Cyazofamid	0.01	108.5	283	Phenmedipham	0.01	99.9
87	Cycloate	0.01	98.8	284	Phorate Sulfone	0.01	96.9
88	Cycloloxydim	0.01	91.0	285	Phoratesulfoxide	0.01	107.4
89	Cyflufenamid	0.01	95.6	286	Phosmet	0.01	107.4
90	Cymoxanil	0.01	108.1	287	Phoxim	0.01	98.9
91	Cypermethrin	0.01	97.5	288	Picloram	0.01	94.7
92	Cyproconazole	0.01	97.3	289	Picolinafen	0.01	101.1
93	Cyprodinil	0.01	94.4	290	Picoxystrobin	0.01	98.5
94	Dazomet	0.01	94.6	291	Pinoxaden	0.01	109.7
95	Demeton-s methyl-sulfone	0.01	99.2	292	Pirimicarb	0.01	95.7
96	Demeton-s methyl-sulfoxide	0.01	99.4	293	Pirimicarb Desmethyl	0.01	105.2
97	Demeton-s-methyl	0.01	102.8	294	Pirimicarb Desmethyl Formamido	0.01	92.2
98	Desmetryn	0.01	99.1	295	Pirimiphos-methyl	0.01	92.6
99	Diafenthiuron	0.01	81.4	296	Primiphos-ethyl	0.01	98.5
100	Dichlofenthion	0.01	109.0	297	Prochloraz	0.01	99.7
101	Dichlofluanid	0.01	100.2	298	Profenofos	0.01	101.7
102	Dichloprop	0.01	80.5	299	Profoxydim	0.01	109.1
103	Dichlorvos	0.01	108.2	300	Promecarb	0.01	105.4
104	Diclobutrazol	0.01	88.4	301	Prometryn	0.01	100.9
105	Diclofop Methyl	0.01	107.4	302	Propachlor	0.01	99.8
106	Diethofencarb	0.01	102.6	303	Propamocarb	0.01	83.7
107	Difenconazole	0.01	99.1	304	Propanil	0.01	102.3
108	Diflubenzuron	0.01	103.9	305	Propaquizafop	0.01	100.7
109	Diflufenican	0.01	102.7	306	Propargite	0.01	96.7
110	Dimefox	0.01	98.7	307	Propazine	0.01	102.0
111	Dimethachlor	0.01	104.6	308	Propetamphos	0.01	93.1
112	Dimethenamid	0.01	103.6	309	Propham	0.01	108.1
113	Dimethoate ve Omethoate Toplamı Dimethoate cinsinden	0.01	99.5	310	Propiconazole	0.01	96.7
114	Dimethomorph	0.01	107.7	311	Propisochlor	0.01	91.6
115	Dimetilan	0.01	98.5	312	Propoxur	0.01	105.0
116	Diniconazole	0.01	90.8	313	Propyzamide	0.01	105.8
117	Dinocap	0.01	105.5	314	Proquinazid	0.01	92.6
118	Dinoseb	0.01	83.7	315	Prosulfocarb	0.01	95.3
119	Dinoterb	0.01	77.7	316	Prosulfuron	0.01	78.5
120	Dioxacarb	0.01	104.7	317	Prothioconazole	0.01	94.0
121	Diphenamid	0.01	106.0	318	Pymetrozine	0.01	76.8
122	Dipropetryn	0.01	99.6	319	Pyraclostrobin	0.01	98.2
123	Disulfoton-Sulfone	0.01	106.8	320	Pyraflufen ethyl	0.01	105.9
124	Disulfoton-Sulfoxide	0.01	102.5	321	Pyrasulfotole	0.01	76.8
125	Dithianon	0.01	102.3	322	Pyrazophos	0.01	100.0
126	Diuron	0.01	105.6	323	Pyrethrins	0.01	105.6
127	DMPF	0.01	95.1	324	Pyridaben	0.01	90.5

No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)	No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)
128	DNOC (4,6-DINITRO-o-CRESOL)	0.01	82.0	325	Pyridalyl	0.01	86.7
129	Dodine	0.01	90.0	326	Pyridaphenthion	0.01	98.9
130	Emamectin	0.01	105.5	327	Pyridate	0.01	83.5
131	Emamectin-Benzoate	0.01	104.8	328	Pyrimethanil	0.01	100.1
132	EPN	0.01	106.3	329	Pyriproxyfen	0.01	93.3
133	Epoxiconazole	0.01	97.4	330	Quinclorac	0.01	102.4
134	EPTC	0.01	99.8	331	Quinoxyfen	0.01	95.2
135	Etaconazole	0.01	92.0	332	Quizalofop Ethyl	0.01	103.8
136	Ethametsulfuron Methyl	0.01	92.6	333	Rimsulfuron	0.01	85.1
137	Ethiofencarb	0.01	102.5	334	Rotenone	0.01	99.1
138	Ethion	0.01	98.8	335	Sethoxydim	0.01	84.4
139	Ethiprole	0.01	103.7	336	Simazine	0.01	99.2
140	Ethirimol	0.01	93.5	337	Spinetoram	0.01	101.4
141	Ethofumesate	0.01	107.8	338	Spinosad	0.01	103.1
142	Ethoprophos	0.01	91.4	339	Spinosad - Spinosyn D	0.01	106.9
143	Ethoxysulfuron	0.01	100.0	340	Spirodiclofen	0.01	99.8
144	Etofenprox	0.01	90.8	341	Spiromesifen	0.01	83.2
145	Etoxazole	0.01	78.9	342	Spirotetramat	0.01	95.1
146	Famoxadone	0.01	102.7	343	Spirotetramat-Enol	0.01	106.5
147	Famphur	0.01	105.0	344	Spirotetramat-Enol-Glucoside	0.01	105.6
148	Fenamidone	0.01	96.4	345	Spiroxamine	0.01	94.4
149	Fenamiphos	0.01	107.0	346	Sulcotrione	0.01	97.7
150	Fenamiphossulfone	0.01	109.6	347	Sulfosulfuron	0.01	88.3
151	Fenamiphossulfoxide	0.01	104.1	348	Sulfotep	0.01	99.3
152	Fenarimol	0.01	100.7	349	Sulprofos	0.01	98.2
153	Fenazaquin	0.01	80.8	350	Tebuconazole	0.01	93.7
154	Fenhexamid	0.01	101.3	351	Tebufenozide	0.01	111.0
155	Fenobucarb	0.01	107.3	352	Tebufenpyrad	0.01	98.4
156	Fenoxaprop-ethyl	0.01	100.7	353	Tebupirimfos	0.01	99.0
157	Fenoxycarb	0.01	98.3	354	Teflubenzuron	0.01	93.7
158	Fenpiclonil	0.01	102.3	355	Temephos	0.01	96.1
159	Fenpropathrin	0.01	96.7	356	Tepraloxydim	0.01	93.2
160	Fenpropidin	0.01	102.0	357	Terbacil	0.01	105.7
161	Fenproprimorph	0.01	100.6	358	Terbufossulfone	0.01	106.7
162	Fenpyroximate	0.01	76.5	359	Terbufossulfoxide	0.01	105.4
163	Fensulfothion	0.01	105.5	360	Terbumeton	0.01	94.9
164	Fensulfothion-oxon	0.01	99.7	361	Terbuthlazine	0.01	92.2
165	Fensulfothion-oxonsulfone	0.01	106.6	362	Terbutryn	0.01	106.3
166	Fensulfothion-sulfone	0.01	107.4	363	Tetraconazole	0.01	94.0
167	Fenthion	0.01	101.9	364	Tetramethrin	0.01	99.8
168	Fenthion-Oxon	0.01	102.9	365	Thiabendazole	0.01	98.9
169	Fipronil	0.01	100.3	366	Thiacloprid	0.01	104.1
170	Fipronil sulfone	0.01	98.9	367	Thiamethoxam	0.01	102.4
171	Fipronilsulfone	0.01	103.4	368	Thidiazuron	0.01	93.7
172	Flamprop-M-Isopropyl	0.01	102.8	369	Thifensulfuron methyl	0.01	81.3
173	Flazasulfuron	0.01	77.4	370	Thiobencarb	0.01	101.2

No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)	No	Pesticide Active Ingredient	LOQ (mg kg^{-1})	Recovery Rate (%)
174	Florasulam	0.01	78.1	371	Thiodicarb	0.01	92.6
175	Fluazifop-p-butyl	0.01	110.1	372	Thiophanate-methyl	0.01	106.4
176	Fluazinam	0.01	91.0	373	Tolfenpyrad	0.01	90.3
177	Flubendiamide	0.01	96.1	374	Topramezone	0.01	99.4
178	Flubenzimine	0.01	96.6	375	Tralkoxydim	0.01	84.9
179	Fludioxonil	0.01	91.8	376	Triallate	0.01	93.4
180	Flufenoxuron	0.01	99.5	377	Triasulfuron	0.01	91.5
181	Flumioxazin	0.01	104.7	378	Triazophos	0.01	95.4
182	Fluometuron	0.01	105.6	379	Tribenuron-methyl	0.01	107.5
183	Fluopicolide	0.01	108.9	380	Trichlorfon	0.01	104.0
184	Fluopyram	0.01	94.4	381	Trichloronat	0.01	98.8
185	Fluoroglycofen Ethyl	0.01	104.3	382	Tricyclazole	0.01	97.6
186	Fluoxastrobin	0.01	89.5	383	Tridemorph	0.01	88.9
187	Flupyrsulfuron Methyl	0.01	80.6	384	Triflumizole	0.01	94.6
188	Fluquinconazole	0.01	102.0	385	Triflumuron	0.01	101.5
189	Fluroxypyr	0.01	95.9	386	Triflusulfuron-Methyl	0.01	86.4
190	Flurtamone	0.01	99.2	387	Triforine	0.01	103.9
191	Flusilazole	0.01	104.6	388	Trinexapac Ethyl	0.01	79.9
192	Flutolanil	0.01	109.2	389	Triticonazole	0.01	86.6
193	Flutriafol	0.01	95.0	390	Tritosulfuron	0.01	80.1
194	Fluxapyroxad	0.01	109.8	391	Uniconazole	0.01	96.5
195	Fonofos	0.01	106.7	392	Vamidathion	0.01	100.9
196	Foramsulfuron	0.01	76.5	393	Zoxamide	0.01	98.9
197	Forchlorfenuron	0.01	92.7				

Material and Method

Solvents and chemicals

Chemicals and solvents used in the LC-MS/MS were "MS Grade", chemicals used in sample preparation were of "HPLC" purity. They were provided from Merck and J.T. Baker. Pesticide standards were purchased from Dr. Ehrenstorfer, Sigma, and HPC. Standard solutions were prepared by dilution of stock solutions with acetonitrile and stored at 4 °C.

The ultrapure water used in the analysis was obtained from the Human UP 900 S-UV water purification system (Conductivity: 0.5 µs cm^{-1})

Sample collection

A total of 100 vegetable and fruit samples including 20 tomatoes, 20 green peppers, 20 cucumbers, 20 strawberries and 20 apples were collected from markets and greengrocers in various districts of Istanbul, Turkey. Samples were randomly taken from various market and greengrocers. The average weight for samples was approximately 2 kg. The samples taken were sent immediately to the laboratory under cold conditions. All samples were analyzed for pesticide residues without washing and within 24 hours.

Sample preparation and extraction

These products were analyzed for pesticide residues using a standard and validated method approved by the Ministry of Agriculture and Forestry an accredited food analysis laboratory. The samples were homogenized in blender to obtain thoroughly mixed homogenates before the analysis. AOAC Official Method 2007.01 method was used for the extraction of the samples (AOAC, 2007). 15 g of these homogenized samples for extraction were taken in a polypropylene centrifuge tubes and 15 mL of extraction solution (25 mL of acetic acid on 2475 mL acetonitrile) was added on top and shaken for 15 minutes by vortex. When the shaking process was completed, one Quechers Extraction Salt (6 g $MgSO_4$, 1.5 g NaOAc) was added and vigorous shaking was continued. Then, after being centrifuged at 4500 rpm for 5 minutes, 8 mL of the upper phase (acetonitrile phase) was removed, transferred to a 15 mL dSPE clean-up tube and vortexed for 1 minute. The dSPE tube was centrifuged at 4500 rpm for 5 minutes and the solution was passed through a 0.45 µm syringe filter and taken into two different vials.

LC-MS/MS analysis

The pesticide residue amounts were determined by scanning the vials on LC-MS/MS devices and averaging the results. Information and chromatographic operating conditions of the LC-MS/MS device are shown in Table 2. When a result fell outside the calibration range, the sample was diluted to fall within the calibration range.

Table 2. LC-MS/MS chromatographic operating conditions

LC MS/MS	Agilent 6420 Triple Quad / G6420A / SG 13387002
Mobile Phase	**HPLC Mobile Phase (A):** 0.252 g Ammonium Formate was dissolved in 1000 ml MS grade water and 1ml Formic Acid was added. **HPLC Mobile Phase (B):** 0.252 g Ammonium Format was dissolved in 1000 mL MS grade Methanol and 1 ml Formic Acid was added on it.
Mobile Phase Flow	0.5 mL min^{-1}
Column	2.1 mm x 50 mm x 3 µm C18 column
Column Temperature	30 ^{o}C

Results and Discussion

Method validation and quality assurance

In validation studies; linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision (repeatability and reproducibility) and recovery studies have been done. For linearity; 8 different concentrations (0-1- 2.5 - 5 - 10 - 25 - 50 and 100 ng ml^{-1}) were prepared and given to the device. In the calibration curve, it has been paid attention that the concentration variation between the current and the calculated does not show more than ± 20%. For LOQ; at the lowest level, 10 independent analyzes were performed with contamination on the blank sample. The level that provides the 70-120% recovery rate and the precision requirement (R.S.D. lower than 20%) determined as the LOQ (Table 1). LOQ values were 0.01 mg kg^{-1} for all analysed pesticides. The recovery values ranged from 76.5% to 115.5%. For the purpose of internal quality control; blank and spiked sample and calibration vontrol samples were used before each run.

Pesticide residues in samples

393 pesticide active ingredients analyzed by LC-MS/MS were searched in 100 fruit and vegetable samples and results were evaluated according to the "Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides (Official Gazette: 25.11.2016-29899)".

Pesticide residues were detected in 43 (43%) of the 100 samples examined; 7 (7%) of these samples were above the MRL and 36 (36%) of these were below the MRL. In 57 samples (57%), no pesticide residues were detected at the measurement limit level. No pesticide residues were found above the MRL in green pepper and apple samples, but pesticide residues were detected below the MRL in 50% of these samples. Pesticide residues above the MRL were detected in 20% of the cucumber samples, 10% of the strawberry samples, and 5% of the tomato samples analyzed. The percentages of pesticide residues detected below the MRL of these samples were 30%, 20%, and 35%, respectively. Pesticides detected above MRL are Primicarb, Acetamiprid, Tebuconazole, Phorate Sulfone, Pirimiphos-methyl, Chlormequat chloride, Pyridaben, Chlormequat (Table 3). A total of 41 types of pesticides (above the MRL and below the MRL) were detected in the analyzed samples. Pesticide residues and the samples in which they were detected are as in Table 4.

The most detected pesticide active substance in the samples examined is Acetamiprid. Acetamiprid is a broad-spectrum insecticide widely used to control some pests in vegetables, fruits and teas, with low mammalian toxicity but potentially posing a health risk to humans (Jin et al., 2016; Verdian 2017; Imamura et al., 2010).

The use of banned pesticides Phorate Sulfone in Turkey was detected in a strawberry. Phorate Sulfone is an extremely toxic an organophosphorus pesticide that can dissolve in water, therefore it can pass from soil to groundwater (Henderson et al., 2004; Bala et al., 2015; Jariyal et al., 2018). Phorate Sulfone is the oxidized product of Phorate and Phorate has been banned in Europe since 2004 (Xiao et al., 2021).

The results of this study show that there are pesticide residues above the Maximum Residue Limit in fruits and vegetables in Turkey. The results of pesticide inspections carried out in laboratories affiliated to the Ministry of Agriculture and Forestry General Directorate of Food Control also support this. 1.7% of the 15921 samples analyzed in 2007 and 2.3% of the 23322 samples analyzed in 2008 were found to be above the MRL values in the legislation (Tiryaki, 2016).

However, some findings in this study do not support some pesticide residue studies previously conducted in Turkey. For example, no pesticide was detected above the maximum residue limits in green pepper and apple samples; however, in a study conducted on 46 apple samples in Konya, pesticide residues were detected above the limit value in 1 sample (Ersoy et al., 2011).

There are many studies to determine pesticide residue levels in various foodstuffs and environmental sources in the world. In these studies, materials such as cereals (Kumari et al., 2012; Lozowicka et al., 2014), olive oil (Razzaghia et al., 2018), milk and dairy products (Raab et al., 2008), soil and water (Kumari et al., 2012; Doğan and Karpuzcu, 2019) were examined. The number of studies conducted on pesticide residue in agricultural products in Turkey. There are also studies on fish (Uluocak and Egemen, 2005; Doğan and Karpuzcu, 2019), milk and dairy products (Dervişoğlu et al., 2013), and seedless table grapes (Yakar, 2018) in Turkey. Pesticide residue studies carried out in recent years on samples of green pepper, apple, strawberry, tomato and cucumber in Turkey and around the world are as follows:

In 2019, 74% of tomato samples collected from 30 farmers in and around the province of Mersin were found without residue, while 26% was detected with pesticides below MRL levels (Hepsağ, 2019). In 2017, 7 random samples of strawberry, tomato, pepper and cucumber were collected from farmers' markets in 3 districts in İzmir province. While no pesticide residue was detected at the limit of measurement in peppers, pesticide residues were found below the limit value in samples of strawberry, tomato and cucumber (Kaya and Tuna, 2019). Between 2014 and 2016, 325 green pepper and 400 cucumber samples were collected from various markets, supermarkets and other retail outlets in Adana, Mersin, Antalya regions and these were analyzed for 170 pesticide residues. Pesticide residues were found below the EU MRL in 12.9% of peppers and 13.5% of cucumbers (Gölge et al., 2018). Between 2010 and 2012, 268 apple, 57 strawberry, 42 tomato, 40 cucumber and 9 pepper samples were analyzed in Poland. Pesticide residue was detected above the maximum residue level only in 1.5% of the apple samples (Szpyrka et al., 2015). In a study by Ersoy et al. (2011), pesticide named Oxamyl was detected above the limit value in 1 of the 10 tomato samples, and pesticides above the limit value were detected in 2 of 10 pepper samples (Ersoy et al. 2011). In 2006, an investigation was carried out in terms of the residues of five commonly used pesticides in the samples taken from the apples that were newly placed in the warehouses during the harvest season in the province of Isparta and its districts. Of the 82 apple samples, 21 (25.6%) had diazinon, 24 (29.3%) paration-methyl, 14 (17.1%) methidathion, 29 (35.4%) chlorpyrifos, 53 (64.6%) 3-5-6 trichloro-2-pyridinol and 55 (67.1%) carbendazim residues (Ay et al., 2007). Between

2006-2009, no pesticides above the MRL were detected in any of the 41 apple samples collected from wholesalers and supermarkets in 5 counties in Xiamen, China. Pesticides were detected above the MRL in 3.9% of 258 cucumber samples and 10.4% of 231 tomato samples (Chen et al., 2011). 878 samples (255 tomatoes, 280 cucumbers, 243 peppers, 100 apples) collected from Antalya, Fethiye and İzmir regions between 1990-1994 were examined for insecticides; 89.4% of tomato, 89.3% of cucumber, 88.5% of pepper and all of the apple samples were determined to be within the legal limit. In the examination of these samples in terms of fungicide with dithiocarbamat, 95.6% of cucumber and all of the tomato, pepper and apple samples were found to be within the legal limit (Tiryaki, 2016). In the examination performed on 82 tomato and cucumber samples in Kazakhstan, 184 pesticide residues were investigated. Pesticide residue was detected above the maximum residue levels in 28% of the samples. No pesticide residue was found in 34% (Lozowicka et al., 2015).

Table 3. Number and ratio of samples without pesticide residue, with residues below and above the MRL and detected pesticide residue

Sample	No. of samples	No. of samples without residue (<LOD)	No. of samples with residue <MRL	No. of samples with residue >MRL	Pesticide actives substances detected above the MRL
		n (%)	n (%)	n (%)	
Green pepper	20	10 (50%)	10 (50%)	0 (0%)	
Apple	20	9 (45%)	11 (55%)	0 (0%)	
Strawberry	20	14 (70%)	4 (20%)	2 (10%)	Primicarb, Acetamiprid, Tebuconazole, Phorate Sulfone
Tomato	20	12 (60%)	7 (35%)	1 (5%)	Pirimiphos-methyl
Cucumber	20	10 (50%)	6 (30%)	4 (20%)	Chlormequat chloride, Pyridaben, Chlormequat
TOTAL	100	57 (57%)	36 (36%)	7 (7%)	

Table 4. Pesticide active ingredients detected in samples and MRL levels

Pesticide Active Substance	Green pepper			Apple			Strawberry			Tomato			Cucumber		
	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})
	>LOD, <MRL	>MRL		>LOD, <MRL	>MRL		>LOD, <MRL	>MRL		>LOD, <MRL	>MRL		>LOD, <MRL	>MRL	
Acetamiprid	6		≤ 0.3	5		≤ 0.8	2	1	≤ 0.01	1		≤ 0.2	4		≤ 0.3
Ametoctradin										1		≤ 2			
Azoxystrobin	1		≤ 3							1		≤ 3			
Benomyl-carbendazim				1		≤ 0.2									
Bifenazate							1		≤ 3						
Boscalid	2		≤ 3	1		≤ 2	3		≤ 6	3		≤ 3	1		≤ 4
Chlorantraniliprole				2		≤ 0.5									
Chlormequat														1	≤ 0.05
Chlormequat chloride													1	1	≤ 0.05
Cypermethrin	1		≤ 0.5												

Pesticide Active Substance	Green pepper			Apple			Strawberry			Tomato			Cucumber		
	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})	Number of samples		MRL (mg kg^{-1})
	>LOD, <MRL	>MRL		>LOD, <MRL	>MRL		>LOD, <MRL	>MRL		>LOD, <MRL	>MRL		>LOD, <MRL	>MRL	
Cyprodinil				1		≤ 2				2		≤ 1.5			
Dimethomorph										1		≤ 1	1		≤ 0.5
Etoxazole							1		≤ 0.2						
Famoxadone										1		≤ 2			
Fenhexamid										2		≤ 2			
Fluazinam										1		≤ 0.3			
Fluopyram	3		≤ 0.8				1		≤ 2	2		≤ 0.9	2		≤ 0.5
Hexythiazox	2		≤ 0.5				2		≤ 0.5				1		≤ 0.5
Indoxacarb				3		≤ 0.5				1		≤ 0.5			
Isopyrazam				1		≤ 0.7				1		≤ 0.5			
Metalaxyl	1		≤ 0.5										1		≤ 0.5
Metalaxyl-m													1		≤ 0.5
Methoxy fenozide				4		≤ 2									
Metrafenone	1		≤ 2												
Myclobutanil	2		≤ 0.5												
Novaluron				3		≤ 2									
Phorate Sulfone								1	≤ 0.01						
Pirimiphos -methyl											1	≤ 0.01			
Primicarb								1	≤ 1	1		≤ 0.5	3		≤ 1
Promecarb													2		≤ 5
Pymetrozine	1		≤ 3												
Pyra clostrobin							1		≤ 1.5	3		≤ 0.3			
Pyridaben	4		≤ 0.5				2		≤ 1					2	≤ 0.01
Pyridalyl										1		≤ 1			
Pyrimethanil	1		≤ 2	1		≤ 15	1		≤ 5	2		≤ 1	2		≤ 0.7
Pyriproxyfen	2		≤ 1							1		≤ 1			
Spirotetramat	2		≤ 2												
Spirotetramat -Enol-Glucoside	1	-	≤ 2							1		≤ 2			
Tebuconazole	1	-	≤ 0.6					1	≤ 0.01						
Tebufenpyrad							1		≤ 1						
Thiacloprid				8	-	≤ 0.3									
TOTAL	**32**	**0**		**30**	**0**		**15**	**4**		**26**	**1**		**19**	**4**	

Conclusion

For this study, fruits and vegetables that are widely consumed in Turkey were selected and samples were collected from markets and greengrocers where the people often prefer to shop. These results show that; In Turkey, pesticides can be found above the MRL in strawberry, tomato and cucumber samples. Also suggest that it may pose a risk to public health. It is important to use safe agricultural products in order to protect and sustain human, animal and environmental health. It is thought that tightening official controls, educating agricultural workers about pesticide applications and harms, and monitoring pesticide residues can reduce pesticide use.

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Author Contributions: Ö.E. designed the study, directed, supervised the work. B.Ç.S and M.A. designed validation study and analysis. B.Ç.S, M.A. and M.Ö. analyzed the data and searched the sources. B.Ç.S wrote the article. All authors have read, revised, and approved the manuscript.

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