

DETERMINATION OF PESTICIDE RESIDUES IN SELECTED VEGETABLES FROM SANLIURFA, TURKEY, AND HUMAN HEALTH RISK ASSESSMENT

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Abstract— This study aims to evaluate the level of pesticide residues in vegetables such as tomatoes, peppers, eggplant, and cucumbers that are widely consumed in Sanliurfa. The presence of pesticide residues in continuously consumed agricultural products can cause serious health problems for consumers. This study illustrated a total of 83 fresh vegetable samples were analyzed for 130 pesticide residues using the QuEChERS extraction method and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) technique. As a result of the analysis, it was determined that 34% of the vegetable samples contained pesticide residues above the Maximum Residue Limits (MRLs). This rate was found to be 50%, 40%, 30%, and 18% in cucumber, eggplant, pepper, and tomato, respectively. A very high proportion of the analyzed samples contained residues that exceeded the limits. The cumulative risk index (cHI) calculated for tomatoes and peppers and the long-term consumer health risk (cHQ) value for acetamiprid residue detected in tomatoes were found to be greater than 1 for children. This case demonstrates that some precautions should be taken to protect consumers' health. In this regard, it is suggested that residue monitoring studies be carried out in a more planned and effective manner and that farmers and pesticide sellers be given training.

Keywords— Pesticide, residue, vegetable, LC-MS/MS, health

I. INTRODUCTION

The inability to provide good food products in parallel with the rapid increase in the world population is a severe problem. We, therefore, need to increase the production and efficiency of food products and take measures against food losses. In this context, we need to combat a variety of diseases and weeds which cause significant losses in agricultural products. In this struggle, various chemical compounds known as pesticides can also be used.

Pesticides are chemicals used against pests that cause damage to and decrease the nutritional value of food products during their production, preparation, storage, and consumption. These pests are parasites that carry various diseases, insects that harm agricultural products, weeds, and mushrooms, as well as flying and walking

creatures such as flies, lice, fleas, beetles, and cockroaches (Özdemir, 2017; Sircu *et al.*, 2019; Kailani *et al.*, 2021; Çavuşoğlu *et al.*, 2021; Si *et al.*, 2021).

Unless pesticides are used in accordance with the instructions, they will inevitably leave residues on agricultural products that are above limit values. Pesticide residues, particularly in fruits and vegetables, carry a potential risk for consumers. They may lead to the development of various acute and chronic disorders such as headaches, dizziness, rash, nausea, cancer, neurotoxicity, congenital disabilities, and endocrine disorders (Yuan *et al.*, 2014; Sircu *et al.*, 2019; Kumari and John, 2019; Ramadan *et al.*, 2020; Hepşağ and Kizildeniz, 2021; Kazar Soydan *et al.*, 2021).

Most institutions and countries worldwide have specified the maximum residue limits (MRLs) for pesticides in food products to ensure that food is safe for consumers and protects human health. MRLs are the maximum level of pesticide residue that is legally allowed in foods (Jallow *et al.*, 2017).

Within the scope of good agricultural practice (GAP), pesticide residues in foods should not exceed MRLs in order not to be contrary to law. MRLs are based on GAP data for food production. They are not toxicological limits. Exceeding MRLs is a strong indicator of GAP violation (Mebdoua *et al.*, 2017).

In Turkey, the regulations on MRLs in food products were prepared in 2016 based on the “European Parliament and Council on Maximum Residue Levels of Pesticides in or on Food and Feed of Plant and Animal Origin” dated 2/23/2005 and numbered 396/2005. They came into effect after being published by the Ministry of Agriculture and Forestry with the name “The Regulation on Maximum Residue Limits of the Turkish Food Codex Pesticides.”

Pesticide residues in vegetables and fruits vary according to the type of pesticide used, environmental conditions, the half-life of the pesticide, the type of crop, and the wait time between the last pesticide application and the harvest time.

Although it is a necessity to train the farmers on the correct pesticide use and to carry out periodic controls, and laboratory tests before reaching the consumer, these practices are not common in some regions.

Vegetables are primarily cultivated in the Mediterranean, Aegean, and Marmara Regions in Turkey. In

these regions, pesticide residue analyses are periodically performed, particularly in products that are cultivated for export. However, residue analyses are not adequately conducted in the Southeastern Anatolia Region, including Sanliurfa, which has a noteworthy share of vegetable cultivation. In addition, we have encountered no academic study conducted by scientists in this region. In this context, this study will be the first study conducted in this region.

The risk assessment of pesticide residues is important to ensure secure human health by maintaining food quality. In this manner, the current study aims to investigate pesticide residues in vegetable samples collected in 2020 from the Sanliurfa and to conduct a health risk assessment for children and adults on exposure to detected residue concentrations.

II. METHODS

A. Material

This study was conducted in Sanliurfa Province, located in the Southeastern Anatolia Region of Turkey. Sanliurfa is also situated in the Harran Plain which is one of the most fertile agricultural lands in Turkey. Its elevation from sea level is 518 m. Sanliurfa, which is dry and hot in summer, and mild and rainy in winter, receives 462 mm of rain annually on average (Anonymous, 2022).

We purchased a total of 83 vegetable samples including tomatoes (n:23), peppers (n:20), eggplants (n:20) and cucumbers (n:20), amounting to 2 kg of each vegetable, from markets, greengrocers, and district bazaars in the Karaköprü and Haliliye districts of Sanliurfa in August and September 2020. We took the samples to the Harran University Science and Technology Application and Research Center in Sanliurfa Province and kept them in a fridge at +4°C. After homogenizing the samples in a

blender, we kept them in sample containers of 100 at -18°C.

B. Chemicals

We procured the pesticide standards from Reference Chemistry Lab Devices Limited Company (Ankara, Turkey). We purchased acetonitrile (HPLC grade), methanol (HPLC grade), acetic acid (HPLC grade), magnesium sulfate heptahydrate, sodium acetate, graphitized carbon black, and primary secondary amine (PSA) from Merck (Darmstadt, Germany).

C. Extraction procedure

We extracted pesticide residues from the vegetables according to the AOAC 2007.01 version of the QuEChERS method (Lehotay et al., 2007).

D. Devices and Chromatographic Conditions

In order to determine pesticide residues in the vegetable samples, we used a Shimadzu model LC-MS/MS 8030 liquid chromatography-mass spectrophotometer (Kyoto, Japan) (LC-20ADXR pump, CBM-20 Alite controller SIL-20ACXR automatic sampler, CTO-20ASvp column oven). Other important equipment used included a Hettich centrifuge (Tuttlingen, Germany), analytical balance (Shimadzu ATX224), blender (Waring blender), vortex mixer (Velp Scientifica), GC vial (Agilent technologies), 20- and 50-ml Falcon tubes, and different volumes of micropipettes.

We used the ODS-4 C18 column for chromatographic distinction. We used water containing 10 mmol ammonium acetate for mobile phase A, and for mobile phase B, we used methyl alcohol. We set the maximum operating pressure at 400 bars. We performed the MS analyses in the multiple reaction monitoring (MRM) and positive ion modes. The m/z, regression equation, R² and LOQ values of pesticides are given in Table 1.

Table 1. m/z, regression equation, R² and LOQ values of pesticides

Pesticides	Precursor ion (m/z)	Product ions (m/z)	R ²	LOQ (µg/kg)
Abamectin	890.4	305.2/113.3	0.997	10
Acetamiprid	223.0	126.0/99.2	0.996	15
Alachlor	270.1	238.1/161.9	0.998	20
Ametryn	228.2	186.1/228.0	0.999	15
Azoxystrobin	404.1	371.9/344.2	0.994	15
Bifenthrin	440.1	181.1/166.2	0.998	10
Boscalid	343.0	307.0/140.2	0.999	20
Bupimate	317.1	166.0/108.0	0.999	10
Buprofezin	306.1	201.1/116.1	0.998	15
Carbendazim	192.0	160.0/132.2	0.997	15
Chlorbromuron	292.8	125.1/204.0	0.997	20
Chlorfenvinshos	358.9	98.9/155.0	0.998	15
Chloridazon	222.0	104.0/92.0	0.996	25
Chlorpyrifos	321.8	124.8/290.1	0.990	10
Chloroxuron	291.0	72.1/46.1	0.999	25
Chlorpyrifos ethyl	349.9	197.8/97.1	0.999	10
Clothianidine	249.7	169.0/132.1	0.999	20
Cyazofamid	324.9	108.1/44.1	0.997	25
Cycloxydim	326.1	180.1/100.9	0.999	20
Cyflufenamid	413.0	295.2/223.0	0.998	25
Cyproconazole	292.1	70.0/125.2	0.897	20

Table 1. (Continue)

Pesticides	Precursor ion (m/z)	Product ions (m/z)	R ²	LOQ (µg/kg)
Cyprodinil	226.2	92.9/77.2	0.998	15
Deltamethrin	523.0	280.7/181.1	0.999	15
Desmedipham	318.2	181.9/136.0	0.998	20
Desmetryn	213.8	172.0/58.0	0.998	20
Diazinon	305.1	169.0/153.2	0.999	25
Diclobutrazol	328.0	70.0/159.0	0.999	25
Diclofop Methyl	340.0	280.9/120.1	0.999	25
Difenaconazole	406.0	250.9/187.9	0.999	20
Dimethenamid	275.9	243.8/168.1	0.999	25
Dimethoate	229.9	198.9/125.0	0.997	25
Dimethomorph	388.1	300.9/164.9	0.998	25
Dinocap	295.2	192.9/134.2	0.999	30
Diphenamid	240.2	134.1/165.1	0.997	30
Dithianon	295.9	264.0/208.9	0.998	25
Dodine	228.1	57.0/59.9	0.998	30
Ethiofencarb	226.0	107.0/78.9	0.998	25
Ethiofencarb sulfone	257.8	107.0/201.0	0.999	25
Ethiofencarb sulfoxide	241.9	107.0/184.9	0.997	30
Ethofumesate	304.0	121.0/241.0	0.996	25
Etofenprox	394.1	177.1/107.0	0.997	20
Etoxazole	359.9	141.0/113.1	0.997	25
Famoxadone	392.1	331.0/93.0	0.995	20
Fenamidone	312.0	92.1/236.2	0.995	15
Fenamiphos	304.1	216.9/121.0	0.999	15
Fenazaquin	307.1	161.2/147.1	0.999	20
Fenhexamide	301.9	97.1/55.1	0.998	25
Fenpropathrin	350.1	125.1/97.0	0.999	30
Fensulfothion oxon	293.0	94.0/140.0	0.996	25
Fenthion	279.1	168.9/105.2	0.999	25
Fenthion sulfoxide	295.0	109.0/280.0	0.995	25
Florasulam	359.9	129.0/81.6	0.994	20
Fluazifop-P-Buthyl	384.0	282.0/328.0	0.997	20
Fludioxinil	246.7	180.1/126.0	0.998	20
Flonicamid	230.1	174.0/148.2	0.996	15
Fluroxypr	255.0	180.8/208.8	0.999	25
Flutolanil	324.0	242.0/262.0	0.997	20
Fonofos	247.1	109.0/124.0	0.999	30
Fosthiazate	284.0	104.0/228.1	0.995	20
Hexythiazox	353.1	227.9/168.2	0.995	20
İmazalil	296.9	159.0/255.1	0.997	20
İmazethapyr	290.2	245.0/177.0	0.997	20
İmidachloropid	256.0	175.0/209.4	0.998	10
İndoxacarb	527.9	202.9/150.1	0.999	20
İsofenphos	345.8	216.9/245.0	0.999	15
İsofenphos-methyl	332.0	230.8/120.9	0.999	25
Kresoxim-M	314.1	206.0/131.1	0.998	20
Lufenuron	511.1	157.9/141.1	0.999	15
Malaoxon	315.0	127.1/99.1	0.998	15
Malathion	331.0	127.0/99.0	0.997	20
Mecarbam	330.0	227.1/97.0	0.999	20
Mefenpyr-diethyl	372.0	327.0/301.0	0.998	20
Mepanipyrim	223.8	106.1/104.1	0.997	15
Metaflumizone	507.1	178.0/116.0	0.999	10
Metalaxyl	280.0	220.1/160.2	0.999	15
Methabenzthiazuron	222.0	165.0/150.0	0.997	30
Methamidophos	141.9	94.1/47.1	0.996	25
Metrafenone	409.0	209.0/227.0	0.999	15
Metribuzin	215.0	187.0/126.0	0.994	20

Table 1. (Continue)

Pesticides	Precursor ion (m/z)	Product ions (m/z)	R ²	LOQ (µg/kg)
Metsulfuron-methyl	382.0	167.1/56.0	0.998	25
Mevinphos	225.1	126.8/193.1	0.981	25
Monocrotophos	224.0	127.0/98.1	0.998	30
Nuarimol	314.9	322.0/251.9	0.998	25
Omethoate	214.1	125.0/183.1	0.993	20
Oxadixyl	279.0	219.0/132.1	0.997	20
Oxamyl	237.0	72.0/90.0	0.995	20
Oxydemeton-methyl	246.9	169.0/125.0	0.995	20
Pencycuron	329.1	125.0/89.1	0.996	20
Pendimethalin	282.1	211.9/194.2	0.998	25
Permethrin	408.1	183.0/355.0	0.999	10
Phenthoate	321.0	134.9/247.1	0.999	30
Phosalone	367.9	181.9/110.9	0.997	20
Piperonyl-Butoxide	356.2	177.1/119.1	0.998	20
Pirimicarb-Desmethyl	225.2	72.1/168.1	0.996	20
Pirimiphos-methyl	306.0	164.1/108.2	0.998	25
Profenefos	372.9	302.8/96.9	0.997	15
Profoxydim-lithium	466.0	280.1/125.1	0.998	20
Propaquizafob	444.0	298.9/100.1	0.998	20
Propargite	368.1	231.1/175.1	0.998	20
Propazine	230.0	188.0/86.1	0.999	25
Propethamphos	282.0	138.0/156.1	0.991	25
Propiconazole	342.0	69.0/159.0	0.999	15
Propyzamide	255.9	189.9/173.0	0.999	20
Prosulfocarb	252.2	91.0/65.1	0.999	20
Pymetrozine	218.2	105.0/79.3	0.996	20
Pyrethrins	328.9	160.9/143.1	0.999	15
Pyridaben	365.1	147.1/309.3	0.997	10
Pyridaphenthion	341.0	188.9/92.0	0.998	20
Pyridate	379.0	207.0/351.1	0.998	20
Pyrimethanil	199.9	107.0/82.0	0.999	15
Pyriproxypen	322.1	96.0/77.9	0.997	15
Quinalphos	299.1	147.0/163.1	0.999	25
S-Metolachlor	284.2	252.0/176.2	0.997	20
Spinetoram	748.4	142.1/98.1	0.999	20
Spinosyn A	732.3	142.0/98.3	0.999	20
Spinosyn D	746.3	142.1/98.4	0.999	20
Spiromesifen	371.2	273.0/255.0	0.999	20
Spirotetramat-enol	302.1	216.1/270.2	0.997	20
Spirotetramat-enol-glicoside	464.4	302.2/447.2	0.999	15
Spirotetramat-keto-hydroxy	318.1	300.1/268.2	0.996	20
Spirotetramat-mono-hydroxy	304.1	119.1/211.2	0.999	15
Tebuconazole	308.1	70.0/125.0	0.991	15
Tebufenpyrad	334.0	145.0/117.0	0.999	15
Tepraloxydim	342.1	250.1/166.0	0.998	20
Terbumeton	226.0	170.1/114.2	0.998	20
Thiacloprid	253.2	125.9/98.9	0.998	20
Thiamethoxam	292.0	210.9/181.2	0.999	20
Thiodicarb	354.9	88.0/108.1	0.999	15
Triadimenol	296.0	70.0/69.4	0.998	15
Triticonazole	318.0	70.1/125.1	0.999	20

E. Risk assesment

To assess the possible health risks of pesticide residues for consumers, we calculated the short-term consumer health risk (aHQ), the long-term consumer health risk (cHQ), and the cumulative risk index (cHI) values.

We calculated the aHQ based on the estimated short-term intake (ESTI) and the acute reference dose (ARfD) (Eq. 1 and Eq. 2). We obtained information about the ARfDs and the ADIs from the AB pesticide database.

$$aHQ = \frac{ESTI}{ARfD} \quad (1)$$

$$ESTI = \frac{\text{highest residue level} * \text{food consumption}}{\text{body weight}} \quad (2)$$

We specified the cHQ according to the estimated daily intake (EDI) and the acceptable daily intake (ADI) (Eq. 3 and Eq. 4).

$$cHQ = \frac{EDI}{ADI} \quad (3)$$

$$EDI = \frac{\text{mean residue level} * \text{food consumption}}{\text{body weight}} \quad (4)$$

A hazard coefficient (HQ) value above 1 indicates an unacceptable health risk. We calculated the cumulative risk index (cHI) expressing the multiple pesticide residues to which the consumer is exposed by summing up the HQs for each pesticide in the sample (Eq. 5) (Liu *et al.*, 2016).

$$cHI = \sum HQ \quad (5)$$

III. RESULTS

A. Evaluation of results

In this study, we examined a total of 83 tomatoes, pepper, eggplant, and cucumber samples in terms of 130 pesticide residues. We evaluated the results of the analysis according to the “Regulation on Maximum Residue Limits of the Turkish Food Codex Pesticides” published by the Ministry of Agriculture and Forestry (Anonymous, 2016). We give the MRL values of the pesticides detected in the analyses, minimum and maximum amounts, and the rates below and above MRLs in Table 2.

B. Residue Contents of the Tomato Samples

In the analyses performed on 23 tomato samples, we detected 15 different pesticide residues. We detected pyridaben residues in two samples, spinetoram residues in one sample, and spirotetramat residues above MRLs in one sample. We found that nearly 18% of the samples contained no residues, 64% contained residues below MRLs, and 18% contained residues above MRL. Ramadan *et al.* (2020), and Bhandari *et al.* (2019) detected residues above MRLs in 19.2%, and 44% of the samples, respectively. Hamed *et al.* (2019) and Hu *et al.* (2020) detected residues below the limits in 3.6% and 10%, respectively. Some studies found that the values detected were not above MRLs (Sungur and Tunur, 2012; Zengin and Karaca, 2017).

C. Residue Contents of the Pepper Samples

In the analyses performed on 20 pepper samples, we detected 12 different pesticide residues. We detected acetamiprid residues in three samples, chlorpyrifos residues in four samples, pyridaben, spinetoram, spirotetramat and spirotetramat enol-glucoside residues above MRLs

in one sample each. We found that all pepper samples contained pesticide residues, 70% of them were below MRLs and 30% were above MRLs. The studies conducted by Bhandari *et al.* (2019) and Ramadan *et al.* (2020) detected residues in all samples. They found that 19% and 50% of these residues were above limits, respectively. The study conducted by Hamed *et al.* (2019) detected residues in 43.6% of the pepper samples. They found that 9.1% of these residues were above the MRL values. A study conducted in Egypt detected residues above MRLs in 53% of the samples (Abdelkader *et al.*, 2021). Hu *et al.* (2020) detected residues below limits in 15% of the samples they examined.

D. Residue Contents of the Eggplant Samples

In the analyses performed on 20 eggplant samples, we detected five different pesticide residues. We detected acetamiprid residues in eight samples and spirotetramat enol glucoside residues above MRLs in one sample.

We found that 25% of the eggplant samples contained no residues, 35% contained residues below MRLs, and 40% above MRLs. A study conducted in Nepal found that 93% of the samples examined contained residues. Of the samples, 56% contained multiple residues and 4% contained residues above limits (Bhandari *et al.*, 2019). Hu *et al.* (2020) detected residues above MRLs in 5% of the samples they analyzed. Another study detected residues in 85% of the samples. Of these samples, 65% contained residues below MRLs and 20% above MRLs (Ramadan *et al.*, 2020)

E. Residue Contents of the Cucumber Samples

In the analyses performed on 20 cucumber samples, we detected eight different pesticide residues. We detected acetamiprid residues in nine samples, chlorpyrifos residues in three samples and metalaxyl residues above MRL in one sample. We found that 10% of the samples contained no residues, 40% contained residues below MRLs and 50% above MRLs. Hamed *et al.* (2019) detected pesticide residues in 56.4% of the samples they examined. Of these residues, 7.3% were above limits. Another study detected residues in all samples analyzed. Of these residues, 58.3% were below limits and 41.7% were above limits (Ramadan *et al.*, 2020).

F. Regional comparison

In a study conducted in the Mediterranean Region, Türkiye, 12.2% of the tomato samples (Hepsağ and Kizildeniz, 2021), and in a study conducted in the Aegean Region, 8%, 9.6%, and 26% of the tomato, pepper, and cucumber samples contained residue above the MRL, respectively (Bakırcı *et al.*, 2021). In another study conducted in the Aegean Region, residues in tomato and pepper samples did not exceed MRLs (Kazar Soydan *et al.*, 2021).

When we compare the rates exceeding the MRLs, it is understood that the values obtained in the current study are higher than the values in the Aegean and Mediterranean Regions.

These results reveal that the controls are not carried out very often in the Southeastern Anatolia Region and

Table 2. Pesticide residues and levels detected in tomato, pepper, eggplant, and cucumber

Pesticide	MRL (mg/kg)	<LOQ %	LOQ > <MRL %	>MRL %	(min-max) (mg/kg)	Mean (mg/kg)
Tomato						
Acetamiprid	0.3	61	39	0	0.03-0.28	0.14±0.08
Azoxystrobin	3.0	52	48	0	0.02-0.25	0.09±0.08
Boscalid	3.0	87	13	0	0.04-0.31	0.22±0.15
Carbendazim	0.5	83	17	0	0.02-0.25	0.11±0.12
Chlorpyrifos	0.2	83	17	0	0.01-0.07	0.05±0.02
Deltamethrin	0.3	57	43	0	0.05-0.13	0.08±0.02
Difenacozole	2.0	87	13	0	0.09-0.30	0.17±0.12
Dimethomorph	1.0	81	19	0	0.05-0.29	0.17±0.17
Indoxacarb	0.5	57	43	0	0.02-0.07	0.04±0.01
Metalaxyl	0.2	87	13	0	0.04-0.12	0.08±0.04
Pyridaben	0.3	65	26	9	0.02-0.36	0.13±0.14
Spinetoram	0.5	78	18	4	0.03-1.22	0.36±0.49
Spirodiclofen	0.5	87	9	4	0.13-0.53	0.31±0.21
Tebuconazole	0.9	87	13	0	0.08-0.26	0.16±0.09
Triadimenol	1.0	74	26	0	0.09-0.22	0.17±0.05
Pepper						
Acetamiprid	0.3	30	55	15	0.02-2.21	0.36±0.62
Azoxystrobin	3.0	90	10	0	0.09-0.11	0.10±0.01
Boscalid	3.0	90	10	0	0.03-0.16	0.09±0.09
Chlorpyrifos	0.2	70	10	20	0.02-0.73	0.33±0.30
Deltamethrin	0.2	80	20	0	0.02-0.18	0.12±0.07
İmidachloropid	1.0	80	20	0	0.03-0.11	0.06±0.04
Metalaxyl	0.5	90	10	0	0.03-0.06	0.04±0.02
Pyridaben	0.5	90	5	5	0.47-0.59	0.53±0.09
Spinetoram	0.5	90	5	5	0.05-1.50	0.78±1.03
Spirodiclofen	0.2	85	10	5	0.07-0.24	0.14±0.09
Spirotetramat	2.0	85	10	5	0.02-2.42	1.05±1.23
Triadimenol	1.0	75	25	0	0.04-0.17	0.11±0.05
Cucumber						
Acetamiprid	0.3	30	25	45	0.02-0.91	0.45±0.33
Azoxystrobin	1.0	85	15	0	0.02-0.07	0.05±0.03
Boscalid	4.0	85	15	0	0.03-0.41	0.18±0.20
Buprofezin	1.0	85	15	0	0.07-0.10	0.07±0.02
Chlorpyrifos	0.05	85	0	15	0.06-0.38	0.18±0.18
Dimethomorph	0.5	75	25	0	0.03-0.10	0.07±0.03
Metalaxyl	0.5	35	60	5	0.02-0.58	0.14±0.15
Thiamethoxam	0.5	90	10	0	0.03-0.13	0.08±0.08
Eggplant						
Acetamiprid	0.3	30	30	40	0.02-1.60	0.370±0.44
İmidachloropid	0.5	95	5	0	0.01-0.34	0.176±0.23
Pyridaben	0.2	90	10	0	0.01-0.07	0.041±0.04
Spirotetramat	2	85	10	5	0.22-2.69	1.378±1.24
Thiacloprid	0.7	95	5	0	0.08-0.08	0.08

more importantly, the farmers do not have enough information about pesticides and their applications.

G. Risk assessment

According to the Turkish Statistical Institute's (TÜİK) 2020 data, the annual tomato, pepper, eggplant, and cucumber consumption per person in Turkey is 119, 80, 30 and 74 kg, respectively. Daily consumption per person is 0.33, 0.02, 0.03 and 0.05 kg, respectively (TÜİK, 2021).

We calculated the diet exposure for children (aged 3 to 10 years) and adults (over 18 years). In calculating the diet, we used body weights of 70.8 kg for adults and 23.1

kg for children on the basis of the recommendations of the European Food Safety Authority Scientific Committee (EFSA, 2015).

Table 3 shows the aHQ, cHQ, and HI values in children and adults. Examining the table, none of the aHQ values of the residues detected in all vegetables were above 1 (<1). Among the cHQ values, only the acetamiprid residue detected in the tomato samples was above 1, while the other values were below 1. The HI was above 1 for children in the tomato and pepper samples. The values in the eggplant and cucumber samples were below 1.

Table 3. The short-term and long-term exposure risk in children and adult

Pesticide	ARfD	Short Time Risk				ADI	Long Term Risk			
		Children		Adult			Children		Adult	
		ESTI	aHQ	ESTI	aHQ		EDI	cHQ	EDI	cHQ
Tomato										
Acetamiprid	25	3,59	0,14	1,18	0,05	1.6	1,77	1,11	0,58	0,36
Azoxystrobin	10	3,23	0,32	1,06	0,11	200	1,15	0,01	0,38	0,00
Boscalid	10	4,03	0,40	1,32	0,13	40	2,84	0,07	0,93	0,02
Carbendazim	20	3,22	0,16	1,06	0,05	30	1,47	0,05	0,48	0,02
Chlorpyrifos	100	0,93	0,01	0,30	0,00	10	0,63	0,06	0,21	0,02
Deltamethrin	10	1,64	0,16	0,54	0,05	10	1,02	0,10	0,33	0,03
Difenacozole	300	3,98	0,01	1,31	0,00	10	2,15	0,22	0,71	0,07
Dimethomorph	600	3,80	0,01	1,25	0,00	50	2,22	0,04	0,73	0,01
Indoxacarb	125	0,97	0,01	0,32	0,00	6	0,55	0,09	0,18	0,03
Metalaxyl	500	1,63	0,00	0,54	0,00	80	1,03	0,01	0,34	0,00
Pyridaben	50	4,72	0,09	1,55	0,03	10	1,71	0,17	0,56	0,06
Spinetoram	100	15,98	0,16	5,25	0,05	25	4,72	0,19	1,55	0,06
Spirodiclofen	10	6,95	0,70	2,28	0,23	15	4,02	0,27	1,32	0,09
Tebuconazole	30	3,40	0,11	1,12	0,04	30	2,05	0,07	0,67	0,02
Triadimenol	50	2,92	0,06	0,96	0,02	50	2,15	0,04	0,71	0,01
HI								2,50		0,73
Pepper										
Acetamiprid	25	6,64	0,27	2,18	0,09	1.6	1,07	0,67	0,35	0,22
Azoxystrobin	10	0,32	0,03	0,10	0,01	200	0,29	0,00	0,10	0,00
Boscalid	10	0,47	0,05	0,16	0,02	40	0,28	0,01	0,09	0,00
Chlorpyrifos	100	2,18	0,02	0,72	0,01	10	1,03	0,10	0,34	0,03
Deltamethrin	1	0,55	0,55	0,18	0,18	10	0,37	0,04	0,12	0,01
Imidacholoprit	80	0,34	0,00	0,11	0,00	6	0,18	0,00	0,06	0,00
Metalaxyl	500	0,17	0,00	0,06	0,00	80	0,13	0,00	0,04	0,00
Pyridaben	50	1,78	0,04	0,59	0,01	10	1,60	0,16	0,53	0,05
Spinetoram	100	4,53	0,05	1,49	0,01	25	2,34	0,09	0,77	0,03
Spirodiclofen	10	0,72	0,07	0,24	0,02	15	0,41	0,03	0,13	0,01
Spirotetramet	1000	7,25	0,01	2,38	0,00	50	3,14	0,06	1,03	0,02
Triadimenol	50	0,51	0,01	0,17	0,00	50	0,32	0,01	0,10	0,00
HI								1,17		0,37
Eggplant										
Acetamiprid	25	1,67	0,07	0,55	0,02	1.6	0,39	0,24	0,13	0,08
Imidacholoprit	10	0,06	0,01	0,02	0,00	60	0,06	0,00	0,02	0,00
Pyridaben	80	0,36	0,00	0,12	0,00	170	0,18	0,00	0,06	0,00
Spirotetramet	10	0,13	0,01	0,04	0,00	50	0,13	0,00	0,04	0,00
Thiacloprid	1000	2,80	0,00	0,92	0,00	10	1,44	0,03	0,47	0,01
HI								0,27		0,09
Cucumber										
Acetamiprid	25	1,98	0,08	0,65	0,03	1.6	0,97	0,61	0,32	0,20
Azoxystrobin	10	0,15	0,02	0,05	0,01	200	0,12	0,00	0,04	0,00
Boscalid	10	0,89	0,09	0,29	0,03	40	0,39	0,01	0,13	0,00
Buprofezin	500	0,23	0,00	0,07	0,00	10	0,16	0,02	0,05	0,01
Chlorpyrifos	100	0,83	0,01	0,27	0,00	10	0,40	0,04	0,13	0,01
Dimethomorf	600	0,23	0,00	0,08	0,00	50	0,15	0,00	0,05	0,00
Metalaxyl	500	1,26	0,00	0,41	0,00	80	0,31	0,00	0,10	0,00
Thiamethoxam	500	0,28	0,00	0,09	0,00	26	0,17	0,01	0,06	0,00
HI								0,69		0,22

A study conducted in Bangladesh detected chlorpyrifos, quinalphos, diazinon, and dimethoate residues in eight needle squash samples. Five of these residues in adults and seven in children were above the acceptable value (1) of health risk. We calculated the risk indices for chlorpyrifos to be 2.24 and 10.87 in children and adults, respectively (Islam *et al.*, 2021).

A study conducted by Kazar Soydan *et al.* (2021) in the Aegean Region in Turkey found that the health risk was below 1 (<1) in a total of 3044 samples of 16 vegetables and fruits. The highest values (HQ) were found to be 0.120, 0.071, 0.027, 0.024 and 0.020 for chlorothalonil, famoxadone, pyridaben, chlorpyrifos and indoxacarb, respectively.

Omwenga *et al.* (2021) detected the aHQ values for chlorpyrifos in spinach to be 3.3 and 2.2 in children and adults, respectively. The chronic diet exposure was found to be below 1 (<1) in all samples. The HI value was calculated to be 0.54 and 0.34 in children and adults, respectively.

A study conducted in Nigeria detected the hazard indices to be below 1 in cabbage, lettuce, calyces and tiger nut samples in both children and adults (Maigari *et al.*, 2021).

A consumer's exposure to pesticides in food products may cause serious health issues, in particular, cancer, kidney disease, cardiovascular diseases, endocrine function disorders, birth defects, infertility, and neurological and behavioral disorders (Islam *et al.*, 2021). For this reason, studies aimed at decreasing pesticide residue amounts especially in vegetables should be completed as quickly as possible.

V. CONCLUSIONS

The current study revealed that tomatoes, peppers, eggplants, and cucumbers contained 20 different pesticide residues. Of these residues, acetamiprid, chlorpyrifos, metalaxyl, pyridaben, spinetoram, spirotetramat, and spiroticlofen were above the MRL values in the Turkish Food Codex. We detected residues above limits in nearly 34% of the samples examined. We concluded that the cHQ value calculated for the acetamiprid residue in the tomato samples posed a potential chronic health risk for children. In addition, we found that children were at risk of overall chronic exposure (HI) due to tomato and pepper consumption. We, therefore, recommend that the relevant institutions make regular and effective inspections and that farmers be trained about pesticide use in order to remove or minimize the health risks to consumers.

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REFERENCES

- Abdelkader, A., Ayoub, M. and Mohammed, A. (2021) Evaluation of pesticide residues in some commonly consumed vegetables in Egypt and their related chronic exposure. *Alfarama Journal of Basic and Applied Sciences*. **2**, 149–167.
- Anonymous (2016) *Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides*. Number: 29899, Prime Ministry Press, Ankara. (accessed on 5 October 2021)
- Anonymous (2022) <http://www.karakopru.gov.tr/co-grafi-yapisi>. (accessed on 1 January 2022)
- Bakırcı, G.T., Yaman Acay, D.B., Bakırcı, F. and Ötleş, S. (2014) Pesticide residues in fruits and vegetables from the Aegean region, Turkey. *Food Chemistry*. **160**, 379–392.
- Bhandari, G., Zomer, P., Atreya, K., Mol, H. G. J., Yang, X. and Geissen, V. (2019) Pesticide residues in Nepalese vegetables and potential health risks. *Environmental Research*, **172**, 511–521. 2
- Çavuşoğlu, D., Yalçın, E., Çavuşoğlu, K., Acar, A. and Yapar, K. (2021) Molecular docking and toxicity assessment of spiroticlofen: protective role of lycopene. *Environmental Science and Pollution Research*. **28**, 57372–57385.
- EFSA (2015) European Food Safety Authority. European Union report on pesticide residues in food. *Efsa J.* **15**, 1–134.
- Hamed, S., A. EL-Ghanam, A. and Elhefny, D. (2019) Fast and Easy Method of 55 Pesticide Residues Determination in Commonly Fruits and Vegetables Collected from Egyptian Local Markets. *Journal of Plant Protection and Pathology*. **10**, 587–595.
- Hepsağ, F., and Kizildeniz, T. (2021) Pesticide residues and health risk appraisal of tomato cultivated in greenhouse from the Mediterranean region of Turkey. *Environmental Science and Pollution Research*. **28**, 22551–22562.
- Hu, D., Jiang, M., Ge, T., Liu, X., Li, Z., Liu, J. and Zhu, K. (2020) Pesticide residues in vegetables in four regions of Jilin Province. *International Journal of Food Properties*. **23**, 1150–1157.
- Islam, M.S., Rahman, M.R., Prodhan, M.D.H., Sarker, D., Rahman, M.M. and Uddin, M.K. (2021) Human health risk assessment of pesticide residues in pointed gourd collected from retail markets of Dhaka City, Bangladesh. *Accreditation and Quality Assurance*. **26**, 201–210.
- Jallow, M.F.A., Awadh, D.G., Albaho, M.S., Devi, V.Y. and Ahmad, N. (2017) Monitoring of pesticide residues in commonly used fruits and vegetables in Kuwait. *International Journal of Environmental Research and Public Health*. **14**, 833.
- Kailani, M.H., Al-Antary, T.M. and Alawi, M.A. (2021) Monitoring of pesticides residues in soil samples from the southern districts of Jordan in 2016/2017. *Toxin Reviews*. **40**, 198–214.
- Kazar Soydan, D., Turgut, N., Yalçın, M., Turgut, C. and Karakuş, P.B.K. (2021) Evaluation of pesticide residues in fruits and vegetables from the Aegean region of Turkey and assessment of risk to consumers. *Environmental Science and Pollution Research*. **28**, 27511–27519.
- Kumari, D. and John, S. (2019) Health risk assessment of pesticide residues in fruits and vegetables from farms and markets of Western Indian Himalayan region. *Chemosphere*. **224**, 162–167.
- Lehotay, S.J., O'Neil, M., Tully, J., García, A.V., Contreras, M., Mol, H., Heinke, V., Anspach, T., Lach, G., Fussell, R., Mastovska, K., Poulsen, M. E., Brown, A., Hammack, W., Cook, J.M., Alder, L., Lindtner, K., Vila, M.G., Hopper, M. and Parker, A. (2007) Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: Collaborative study. *Journal of AOAC International*. **90**, 485–520.
- Liu, Y., Shen, D., Li, S., Ni, Z., Ding, M., Ye, C. and Tang, F. (2016) Residue levels and risk assessment

- of pesticides in nuts of China. *Chemosphere*. **144**, 645–651.
- Maigari, A.U., Sulaiman, M.B., Buhari, M. and Abdul-lahi, A.O. (2021) Pesticide residues in selected vegetables from gombe markets, gombe state, nigeria: assessing the health impact. *Ife Journal of Science*, **23**, 77-87.
- Mebdoua, S., Lazali, M., Ounane, S. M., Tellah, S., Nabi, F. and Ounane, G. (2017) Evaluation of pesticide residues in fruits and vegetables from Algeria. *Food Additives and Contaminants: Part B Surveillance*. **10**, 91–98.
- Omwenga, I., Kanja, L., Zomer, P., Louisse, J., Rietjens, I.M.C.M. and Mol, H. (2021) Organophosphate and carbamate pesticide residues and accompanying risks in commonly consumed vegetables in Kenya. *Food Additives and Contaminants: Part B Surveillance*. **14**, 48–58.
- Özdemir, N. (2017) Neonikotinoid Pestisitler ve Arı Sağlığına Etkileri. *Uludağ Arıcılık Dergisi*. **17**, 44-48.
- Ramadan, M.F.A., Abdel-Hamid, M.M.A., Altorgoman, M.M.F., Al Garamah, H.A., Alawi, M.A., Shati, A.A., Shweeta, H.A. and Awwad, N.S. (2020) Evaluation of pesticide residues in vegetables from the Asir region, Saudi Arabia. *Molecules*. **25**,1–20.
- Si, W.S., Wang, S.Y., Zhang, Y.D., Kong, C. and Bai, B. (2021) Pesticides and risk assessment in Shanghai fruit and raw eaten vegetables. *Food Additives and Contaminants: Part B Surveillance*. **14**,245–255.
- Sircu, R., Turcanu, G., Opopol, N., Pinzaru, I., Manceva, T. and Scurtu, R. (2019) Pesticides residue determination in vegetables and fruits commonly used in Republic of Moldova and estimation of human intake. *Chemistry Journal of Moldova*. **14**,62–71.
- Sungur, Ş. and Tunur, Ç. (2012) Investigation of pesticide residues in vegetables and fruits grown in various regions of Hatay, Turkey. *Food Additives and Contaminants: Part B Surveillance*. **5**, 265–267.
- TÜİK (2021) Turkish Statistical Institute https://data.tuik.gov.tr/Kategori/GetKategori?p=tarim-111anddil=1_tuketim_miktarlari (accessed on 18 November 2021)
- Yuan, Y., Chen, C., Zheng, C., Wang, X., Yang, G., Wang, Q. and Zhang, Z. (2014) Residue of chlorpyrifos and cypermethrin in vegetables and probabilistic exposure assessment for consumers in Zhejiang Province, China. *Food Control*. **36**, 63–68.
- Zengin, E. and Karaca, İ. (2017) Uşak İlinde Örtü Altı Üretimi Yapılan Domateslerdeki Pestisit Kalıntılarının Belirlenmesi. *Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Dergisi*. **21**, 554.

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