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Residue levels of pesticides in nuts and risk assessment for consumers

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RESEARCH ARTICLE

Abstract

The residue levels of 227 pesticides were analyzed in nuts (dried figs, dried apricots, raisins, walnuts, pistachios, hazelnuts, almonds, peanuts, dates, sunflower seeds, pumpkin seeds, white chickpeas and yellow chickpeas). The extraction of the samples was performed by using QuEChERS method, and the residue analyses were performed with LCMS/MS, GC-MS, GC-MS/MS. The results were evaluated according to the regulations of European Union and Turkish Food Codex (TFC), and a risk assessment for consumers was evaluated. At least one type of pesticide residue was detected in 29% of the samples. Thiacloprid in 4 pistachio and imidacloprid in 3 pumpkin seed, exceeded the maximum residue limit value given in the TFC. Trifluralin which is located in the list of prohibitted pesticides was detected in 9 pumpkin seed samples. The pesticides of chlorpyriphos, cypermethrin and chlorpyrifos-methyl were determined to pose an acute and chronic risk for children and adults. The target hazard quotient for all of the detected pesticides was calculated as <1. The Hazard Index value was determined as 0.264 for adults and 0.156 for children. When the amount of pesticide that people have with the consumption of other foodstuffs is also taken into consideration, people could be exposed to both acute and chronic health risks.

Keywords: nuts, pesticide, residue, risk assessment

1. Introduction

Arable and highly productive farm lands have decreased depending on the increase of environmental disasters around the world. Agricultural activities are still an important source of living due to increased population and living conditions of our country, so it has become an important issue to obtain high yields from arable lands. Pesticides used in agricultural activities in order to obtain high productivity have some advantages such as preventing the damages of rodents and other insects that damage crops; however, it causes pollutions of air, water and soil due to their being used unconsciously (Serrano *et al.*, 2004). When pesticides are used excessively and unconsciously in the agricultural area, they can hold onto soil and crop roots. Thus, they can cause food contamination and lead to acute and chronic poisoning in terms of human health (Mahmood *et al.*, 2014). Fortunately, after the harms of pesticides to the environment and to humans are understood better, a growing concern over this issue has appeared in the public not only in the scale of our country but also at the level of European Union and world countries, and thus countries have made various arrangements on the production and use of pesticides. Food and Agriculture Organization (FAO) and the World Health Organization (WHO) put the 'Codex Committee on Pesticide Residues (CCPR)' into effect in 1960. The CCPR is responsible for establishing maximum limits for pesticide residues in specific food items or in groups of food; issueing maximum limits for pesticide residues in certain animal feeding stuffs moving in international trade where this is justified for reasons of protection of human health; preparing priority lists of pesticides for evaluation by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR); considering methods of sampling and analysis for the determination of pesticide residues in food and feed; considering other matters in relation to the safety of food and feed containing pesticide residues and establishing maximum limits for environmental and industrial contaminants showing similarity to chemicals or other pesticides in specific food items or groups of food. In accordance with this purpose, the Turkish Food Codex (2018; TFC) regulation on maximum residue limits (MRLs) of pesticides entered into force in our country. MRLs of pesticides are evaluated together with the European Union (EU) harmonisation process and are published within the TFC regulation on MRLs of pesticides, which is renewed once a year. The regulation covers the maximum pesticide residue limits allowed to be present in fresh, unprocessed, processed or composite foods of plant and animal origin and the codes of practice of these limits. In the regulation, there are MRLs for the pesticides in the product groups that are included in the relevant legislation of the EU for the products that these limits will be applied to and maximum residue limits in the products or product groups of the pesticides whose evaluation is completed by the EU.

When studies in the literature are examined, there are some studies which have been conducted on residue levels of pesticides in various dried nuts and fruits. Liu *et al.* (2016) studied the residue level of pesticides in dried nuts such as chestnuts, walnuts, pine nuts collected from seven main production areas of China. As a result of the study in which 29 different pesticides were analyzed, four organophosphate pesticides (acephate, dimethoate, chlorpyrifos and paration-methyl) were detected in 11.4% of the samples at concentrations ranging from 19 μg/kg to 74 μg/kg. Moreover, six organochlorine pesticides (DDT, HCH, endosulfan, quintozene, aldrin and dieldrin) were detected in 18.2% of the samples at concentrations ranging from 2.0 μg/kg to 65.7 μg/kg. Similarly 25% of the hazelnut samples were found to have more than one pesticide residue, and the residue level of 15.9% exceeded the MRL value of China. The short term risk ratio of the tested hazelnuts was below 1.2%, whereas the long term risk was determined as 12.58%. The cumulative risk ratio of the tested pesticides was determined as 8.43% for organophosphates, 0.42% for chlororganic compounds and 0.15% for fungicides and the total cumulative risk was determined as 21.28%. In this study, no significant health risk was detected for consumers via hazelnut consumption. In a study conducted by Emami *et al.* (2017) in which fifty samples of pistachios of different brands were collected from different markets in Tehran, the detectable pesticide residue was found in 10% of the samples. Three samples had a contamination rate higher than the MRLs established by the Institute of Standard and Industrial Research of Iran (ISIRI) and that four samples had a contamination rate higher than the MRLs defined by EU. In the first study conducted to determine the pesticide levels of dates in Saudi Arabia, date samples were collected from local markets in Riyadh. The average levels of tested residues of pesticides, herbicides and fungicides in dates and their seeds were found to be below the MRL value. However, the residues of lindane (BHC gamma isomer), dieldrin, dimethoate, chlorpyrifos and all of the tested acaricide residues in dates were found to be above the MRL values and showed a dangerous orientation in date cultivation. The data have shown that the date seeds used as animal feed sometimes had higher concentrations of OP dimethoate (EL-Saeid and AL-Dosari, 2010). Similarly, Özkan (2015) identified the pesticide residues in some oil seeds and dried nuts (six pistachios, five sunflowers, six pumpkins, three watermelons, fifteen walnuts and eighy olive fruits) sold in local bazaars around Gaziantep. It was determined that two samples of pistachio had 0.13±0.032 and 0.296±0.074 mg/kg dichlorvos and one sample of pistachio had 0.021±0.001 mg/kg acetamiprid, and the values were higher than the MRL (0.01 mg/kg) value given for dichlorvos and acetamiprid in the TFC. On the other hand, ometoat was found to be below the TFC limit value (2 mg/kg) as 0.713±0.014 and 0.595±0.012 mg/kg in two olive samples.

As a result of pesticide residue analyses conducted on different food matrices such as dried nut, fruit- vegetable, wheat and milk both in our country and in various countries around the world, it is seen that pesticide residues are generally detected, the detected values generally exceed the limit values such as TFC values for Turkey or EU values, and even prohibited pesticides are still detected mostly in food products. It is observed that pesticide residue analyzes are mostly carried out in food products such as vegetable, fruit or milk, and in dried fruits and that less study is done in dried nuts both in our country and in the world. Our country is one of the leading producer countries of dried nuts in the World, and according to the data provided by the Turkish Union of Chambers and Commodity Exchanges, the production capacity of the dried nut sector is approximately 3.2 million kg per year. Because dried nuts are both a means of entertaintment in our country and they are widely used as an auxiliary consumable material in foodstuffs, the annual consumption of nuts per capita has become 6.5 kg. Due to the fact that consumption of nuts has increased in these days and consumption of nuts has become widespread especially among primary school children, it is important that pesticide residue analyses be done and risks for consumers be determined.

2. Materials and methods

Sample collection

162 samples were taken from 13 different types of dried nuts and fruits such as dried figs, dried apricots, raisins, walnuts, pistachios, hazelnuts, almonds, peanuts, dates, sunflower seeds, pumpkin seeds, white roasted chickpeas and yellow roasted chickpeas served to the public in 2016 and 2017. The dried nuts and fruits were provided from the district bazaars, the wholesale market, and the markets which sell local products in the neighbourhoods where most of the city population lives. When taking the samples of the dried nuts and fruits, the fact that the dried nuts and fruits are frequently consumed by the public, they are taken from different points of production and sale, and they are of local production were taken into consideration. Among the products taken for the study, pistachios (15

samples) were produced in Gaziantep, Siirt and Karaman, almonds (15 samples) were produced in Mersin, Mersin-Gülnar and Muğla-Datça, and walnuts (15 samples) were produced in Konya-Hadim, Bursa-İnegöl, Kırşehir and Kırşehir-Kaman. Peanuts (15 samples) were produced in Osmaniye, sunflower seeds (15 samples) were produced in Bursa, Bursa/İnegöl, Konya, and Konya-Beyşehir, pumpkin seeds (12 samples) were produced in Nevşehir, Konya, and Konya/Altınekin. Dates (15 samples) were produced in Jerusalem, Medina and Iran, raisins (15 samples) were produced in Konya and Konya-Aksaray, dried apricots (14 pieces) were produced in Konya and Konya-Aksaray, the dried figs (14 samples) were produced in Aydın, nuts (15 samples) were produced in Ordu and Giresun, white chickpeas (8 samples) were produced in Denizli, yellow chicpeas (8 samples) were produced in Manisa-Kula and Denizli. The samples were provided in about 1 kg.

Sample preparation and analysis

The dried nuts such as walnuts, almonds, hazelnuts, and peanuts were provided shelled and unroasted and they were ground for analysis. The samples of sunflower seeds and pumpkin seeds were provided raw and they were ground with their shells. The samples of dates were ground after their stones were removed. The extraction of the dried nuts was carried out according to the method of QuEChERS (quick, easy, cheap, effective, rugged, and safe) (Paya *et al.*, 2007). A 5 g sample was taken from the homogenised sample to be analyzed after it was ground in a grinder. After the 5 g sample was homogenised with 7.5 g water, it was placed in a 50 ml falcon tube. Then, acetonitrile containing 15 ml of 1% acetic acid was added to the sample, and it was shaken vigorously for 1 minute. After that, 6 g of magnesium sulfate and 1.5 g of sodium acetate were added to the falcon tubes, and they were centrifuged for 5 minutes at 4,000 rpm by shaking for 1 minute. Later, 4 ml of the supernatant of the samples was taken and the cleaning stage was performed. For this, the mixture was transfered into 15 ml falcon tubes, and 0.6 g of magnesium sulphate and 0.2 g of primer secondary amine were added to the mixture. 0.2 g of C18 was also added in the oily samples. After the mixture was shaken vigorously for 1 min, it was centrifuged for 5 min at 4,000 rpm. Then, the suparnate was transferred into vials and the pesticide residue analyses were performed with LC-MS/MS, GC-MS and GC-MS/MS systems. Table 1 shows the list of the pesticides for which residue analysis was performed, the limit of measurement and the analysis method.

Risk assessment

The estimation of acute/short term consumer health risk (aHI) was calculated based on estimate short term intake (ESTI) and acute reference dose (ARfD). ESTI was calculated based on the highest pesticide residue level detected, daily nuts consumption and body weight. The formulas used in the calculation of ESTI and aHI values are given in Equation 1 and Equation 2 (Liu *et al.*, 2016).

$$\text{ESTI} = \frac{\text{Max. residue level} \times \text{amount of food consumption}}{\text{body weight}} \tag{1}$$

$$\text{aHI} = \frac{\text{ESTI}}{\text{ARfD}} \times 100 \tag{2}$$

The estimation of chronic/long term consumer health risk (HQ) was calculated based on estimated daily intake (EDI) and acceptable daily intake (ADI). EDI values vary according to average residue level, daily food consumption and body weight. The formulas used in the calculation of EDI and HQ values are given in Equation 3 and Equation 4 (Liu *et al.*, 2016).

$$\text{EDI} = \frac{\text{Mean residue level} \times \text{amount of food consumption}}{\text{body weight}} \tag{3}$$

$$\text{HQ} = \frac{\text{EDI}}{\text{ADI}} \times 100 \tag{4}$$

In the risk assessment conduceted for adults and children, the average adult body weight was taken as 73 kg and the child weight was taken as 32.7 kg (Jan *et al.*, 2010; Khan *et al.*, 2013). For the amount of daily consumption for adults and children, the values given in the Dietary Guidelines for Turkey (2004) prepared by Hacettepe University were taken into account. In this guide, the recommended portion for dried nuts (oil seeds, nuts) and dried fruit is given as 30 g. The recommended amount of daily portion for adults is 2.5-3 portions. For the calculations, 3 portions (90 g) were taken into consideration. The recommended daily portion for children is 1-1.5 portions and for the calculations in the study, 1.5 portions (45 g) were taken into consideration. ADI and ARfD values were used to find the risk caused by the consumption of pesticide contaminated nuts. The calculations were taken for the pesticides for which both ARfD and ADI values were present in the JMPR database (FAO/WHO, 1992, 2000, 2003, 2006) and the values are given in Table 2. Pesticide residues, daily consumption, and body weight are key factors for the calculation of the risk factor. Children face a higher health risk because of lower body weight and higher susceptibility. A calculated HQ value greater than 1 indicates an unacceptable risk.

Non-carcinogenic risk can be calculated based on EDI and ADI values. This value is referred to as THQ. The formula used in the calculation of THQ is given in Equation 5. The total value of THQ is called the hazard index (HI), which is a mixture of total pesticide pollution, and the formula used in its calculation is given in Equation 6 (Yu *et al.*, 2016).

Table 1. Pesticides for which residue analysis was performed, the limit of measurement and the analysis method.

Active substance	Limit of quantification (mg/kg)	Analysis method
acetamiprid, aldicarb, aldicarb sulfone (aldoxcarb), aldicarb sulfoxide, amitraz, atrazine, azoxystrobin, benfurocarb, bentazone, boscalid (nicobifen), bromuconazole, bupirimate, buprofezin, carbaryl, carbendazim (+benomil), carbofuran, carboxin, chlorfluazuron, chloridazon, chlormequat, chlorpropham, clethodim, clofentezine, cyanophos, cymoxanil, cyproconazole, cyprodinil, D,2,4-, Deltamethrin, Demeton-S-methyl, demeton-S-methyl sulfone, demeton-S-methyl sulfone (oxydemeton-methyl), desmedipham, diafenthiuron, diazinon, difenoconazole, dimethenamid, dimethoate, dimethomorph, diniconazole, dinocap, dithianon, diuron, dodine, epoxiconazole, ethiofencarb, ethofumesate, etofenprox, famoxadone, fenamidone, fenarimol, fenazaquin, fenbutatin-oxide, fenhexamid, fenoxycarb, fenpropathrin, fenpyroximate, fenthion, fludioxynil, flutriafol, formetanate (hydrochloride), furathiocarb, haloxyfop-2-ethoxyethyl, hexaconazole, hexythiazox, imazalil, imidacloprid, ioxynil, kresoxim-methyl, lenacil, lufenuron, malaoxon, malathion, metalaxyl-M, metamitron, methamidophos, methiocarb, methomyl, metribuzin, monolinuron, myclobutanil, omethoate, oxadixyl, oxamyl, penconazole, pendimethalin, phenthoate, phsalone, phosmet, phosphamidon, primicarb, prochloraz, prometryn, propamocarb, propaquizafop, propargite, propazine, propiconazole, propoxur, propyzamide, pyridaben, pyridaphenthion, pyridate, pyriproxyfen, simazine, spinosad, spinosad A, spinosad D, spiroxamine, tebuconazole, tepraloxydim, terbutryn, thiabendazole, thiacloprid, thiamethoxam, thiodicarb, thiophanate-methyl, triadimefon, triadimenol, tri-allate, trichlorfon, trifloxystrobin, triflumizole, vamidothion	0.01	LC-MS/MS
acetochlor, acrinathrin, alachlor, aldrin (HHDN), alpha-cypermethrin, azinphos-ethyl, benalaxyl, beta-cyfluthrin, bifenthrin, binapacryl, biphenyl (diphenyl), bitertanol, bromophos-ethyl, bromophos-methyl, bromopropylate, butylate, captan, carbosulfan, chiomethionate (quinomethionate), clorbenside, clordane-cis(alpha), clordane-trans(gamma), chlorfenvinphos, chlorobenzilate, chlorothalonil, chlorpyriphos, chlorpyriphos-methyl, cycloate, cyfluthrin, cyhalofop-butyl, cyhalothrin-lambda, cypermethrin, DDD, o-p, DDD, p-p, DDE, o-p, DDE, p-p, DDT, o-p, DDT, p-p, dichlofluanid, dichlorvos(DDVP), diclofop-methyl, dicofol, dieldrin, dimethipin, dinobuton, diphenamid, endosulfan,alpha-, endosulfan,beta-, endosulfan-sulfate-, endrin, esfenvalerate, ethalfluralin, ethoprophos, etrimfos, fenamiphos, fenchlorphos, fenitrothion, fenvalerate, fibronil, fluazifop-p-butyl, flucythrinate, flurochloridone, folpet, formothion, HCH, alpha-, HCH, beta-, HCH, delta-, heptaclor, heptachlor endo-epoxide (trans isomer), hexachlorobenzene, iprodine, isazofos, lindane (HCH, gamma-), mefenpyr-diethyl, metazachlor, methidathion, methoxychlor, metolachlor, mevinphos, molinate, oxyfluorfen, parathion-ethyl, parathion-methyl, permethrin, primiphos-methyl, procymidone, profenofos, prothiofos, pyrazophos, pyrimethanil, quinalphos, quinoxyfen, quintazone, tau-fluvalinate (fluvalinate), tecnezane, terbuthylazine, tetrachlorvinphos, tetradifon, tolcofos-methyl, tolylfuluanid, triazophos, trifluralin, vinclozolin	0.01	GC-MS; GC-MS/MS

$$THQ = \frac{EDI}{ADI} \times 100 \quad (5)$$

$$HI = \Sigma_{k=1}^{i} THQ_n \quad (6)$$

3. Results and discussions

Pesticides in dried nuts and fruits

No pesticide residue was detected in the samples of almonds, walnuts, hazelnuts, peanuts, sunflower seeds, yellow chickpeas and white chickpeas, whereas pesticide residues were detected in the samples of pistachios, pumpkin seeds, dates, raisins, and dried apricots. As a result of the pesticide residue analyses carried out in 15 pistachios, pesticides (acetamiprid and thiacloprid) were detected in 4 samples. The detected pesticides are in the insecticide group. The concentration of acetamiprid was 0.009-0.018 mg/kg, whereas the concentration of thiacloprid was 0.012-0.024 mg/kg. Acetamiprid was detected to be below the MRL value of 0.07 mg/kg given in the TFC, while thiacloprid was detected to be slightly above the MRL value of 0.02 mg/kg given in the TFC. In a study conducted by Özkan (2015), acetamiprid concentration was found to be 0.021±0.001 mg/kg in one sample, and dichlorvos concentration was found to be 0.13±0.032 and 0.296±0.074 mg/kg in two samples, whereas in the study conducted by Poulsen and Andersen (2003), no significant pesticide residues were detected in pistachio samples.

The samples of pumpkin seeds (PS) in the study were taken from the products that were produced in Nevşehir, Konya, Konya-Altınekin and presented to sale in district

Table 2. Acute reference dose (ARfD) and acceptable daily intake (ADI) values for the pesticides.

Sample	Type of the pesticide	ADI	ARfd
Dried fig	chlorpyriphos	0.01	0.10
	malathion	0.30	2.00
Dried apricot	carbendazim (+benomil)	0.03	0.10
	dodine	0.10	0.20
	thiacloprid	0.01	0.03
	acetamiprid	0.07	0.01
	thiamethoxam	0.08	1.00
Raisin	indoxacarb	0.01	0.10
	acetamiprid	0.07	0.01
	chlorpyriphos	0.01	0.10
	cypermethrin	0.02	0.04
	deltamethrin	0.01	0.05
	dimethomorph	0.20	0.60
	famoxadone	0.006	0.60
	chlorpyriphos-methyl	0.01	0.10
Date	imidacloprid	0.06	0.40
Pumpkin seed	chlorpyriphos	0.01	0.10
	imidacloprid	0.06	0.40
Pistachio	acetamiprid	0.07	0.10
	thiacloprid	0.01	0.02

Table 3. The level of pesticide residues detected in the pumpkin seeds (PS) and their Turkish Food Codex (TFC) maximum residue limit (MRL) values.[1]

No	Name of pesticide	Type of pesticide	Level of residue (mg/kg)	TFC MRL value (mg/kg)
PS1	trifluralin	herbicide	0.011±0.006	banned
PS2	trifluralin	herbicide	0.011±0.006	banned
PS3	trifluralin	herbicide	0.010±0.005	banned
PS4	chlorpyriphos	insecticide	0.013±0.007	*
	trifluralin	herbicide	0.010±0.005	banned
PS5	chlorpyriphos	insecticide	0.012±0.006	*
	trifluralin	herbicide	0.010±0.005	banned
PS6	chlorpyriphos	insecticide	0.013±0.007	*
	trifluralin	herbicide	0.010±0.005	banned
PS7	imidacloprid	insecticide	0.082±0.041	0.05
	trifluralin	herbicide	0.048±0.024	banned
PS8	imidacloprid	insecticide	0.082±0.041	0.05
	trifluralin	herbicide	0.047±0.024	banned
PS9	imidacloprid	insecticide	0.079±0.040	0.05
	trifluralin	herbicide	0.046±0.023	banned
PS10	–	–	–	
PS11	–	–	–	
PS12	–	–	–	

[1] – = not determined; * = MRL value is not defined in TFC.

markets, markets and wholesalers in Konya. No pesticide residue was detected in 3 of the 12 samples (Table 3). Trifluralin and chlorpyriphos were found in the samples of PS1, PS2 and PS3 in concentrations of 0.011±0.006, 0.011±0.006, 0.010±0.006 mg/kg respectively, and chlorpyriphos and trifluralin were detected as 0.013±0.007, 0.010±0.005 mg kg in PS4, 0.012±0.006, 0.010±0.005 mg/kg in PS5 and 0.013±0.007 and 0.010±0.005 mg/kg in PS6, respectively. Imidacloprid and trifluralin were detected as 0.082±0.041, 0.048±0.024 mg/kg in PS7, 0.084±0.042, 0.047±0.024 mg/kg in PS8, and 0.079±0.040, 0.046±0,023 mg/kg in PS9 respectively. In 9 of the 15 samples, trifluralin, which is a banned pesticide, was detected, in 6 samples chlorpyriphos, which is an insecticide, was detected, and in 3 samples, imidacloprid was detected. The detected imidacloprid concentrations exceeded the MRL value of TFC of 0.05 mg/kg in 3 samples. 15 samples were taken from the dates (D) produced in Jerusalem, Medina and Iran and sold in Konya. While pesticide residues were detected in 4 date samples, no residue was detected in 11 samples. Imidacloprid was detected as 0.020±0.010, 0.020±0.010, 0.019±0.010 and 0.019±0.010 mg/kg in D5, D6, D7 and D8 samples, respectively. These values appear to be below the MRL value of 0.05 mg/kg given in TFC for imidacloprid. In the study conducted by EL-Saeid and AL-Dosari (2010), cypermethrin was found to be 0.02 mg/kg in Khalas species, and deltarmethrin was found to be 0.03 and 0.01 mg/kg in Khalas and Sukkari species of dates, respectively.

The pesticides detected in the raisin (R) samples produced in Konya, Konya-Aksaray and offered for sale in Konya are given in Table 4.

Pyrimethanil in R4 sample with a concentration of 0.79±0.40 mg/kg, and iprodione in R15 sample with a concentration of 0.50±0.25 mg/kg were the most intensely detected pesticides. In the study conducted for raisin by Tatlı (2006), chlorpyriphos-ethyl in 4 samples at between 0.009 and 0.038 mg/kg, lambda cyhalothrin in 6 samples at between 0.01 and 0.061 mg/kg, procymidone in 6 samples at between 0.013 mg/kg, and 0.174 mg/kg, cypermethrin in 4 samples at between 0.018 and 0.096 mg/kg, pyrimethanil (0.101 mg/kg), deltamethrin (0.032 mg/kg), dichlofluanide (0.113 mg/kg), xeroxim-methyl (0.022 mg/kg) and monocrotophos (0.096 mg/kg) were dedected. In all of the analyzed samples, pesticides in fungicide, insecticide and acaricide group were detected. MRL values were not defined in the TFC for the detected pesticides.

At least one pesticide residue was detected in all of the samples except for dried apricot (DA) 7 sample of the apricots produced in Malatya and sold in Konya district markets, markets and wholesalers (Table 5).

Table 4. The level of pesticide residues detected in the raisins (R).[1]

No	Name of pesticide	Type of pesticide	Level of residue (mg/kg)
R1	cyprodinil	fungicide	0.04±0.02
	indoxacarb	insecticide	0.018±0.009
	pyrimethanil	fungicide	0.027±0.014
R2	cyprodinil	fungicide	0.059±0.03
	indoxacarb	insecticide	0.028±0.014
	pyrimethanil	fungicide	0.036±0.018
R3	acetamiprid	insecticide	0.17±0.09
	azoxystrobin	fungicide	0.11±0.06
	boscalid (nicobifen)	fungicide	0.062±0.031
	chlorpyriphos	insecticide	0.30±0.15
	cypermethrin	insecticide	0.10±0.05
	cyprodinil	fungicide	0.014±0.007
	fenbutatinoxide	acaricide	0.011±0.006
	iprodione	fungicide	0.42±0.21
	myclobutanil	fungicide	0.014±0.007
	pyrimethanil	fungicide	0.38±0.19
	trifloxystrobin	fungicide	0.029±0.015
R4	azoxystrobin	fungicide	0.17±0.09
	boscalid (nicobifen)	fungicide	0.12±0.06
	chlorpyriphos	insecticide	0.041±0.021
	cyprodinil	fungicide	0.46±0.23
	deltamethrin	insecticide	0.018±0.009
	dimethomorph	fungicide	0.038±0.019
	famoxadone	fungicide	0.026±0.013
	fenbutatinoxide	acaricide	0.094±0.047
	fludioxonil	fungicide	0.029±0.015
	imidacloprid	insecticide	0.090±0.045
	metalaxyl-m	fungicide	0.013±0.007
	penconazole	fungicide	0.011±0.006
	pyrimethanil	fungicide	0.79±0.40
R5	acetamiprid	insecticide	0.010±0.005
	cyprodinil	fungicide	0.069±0.035
	iprodione	fungicide	0.061±0.031
	pyrimethanil	fungicide	0.040±0.020
R6	cyprodinil	fungicide	0.062±0.031
	pyrimethanil	fungicide	0.063±0.032
R7	cyprodinil	fungicide	0.051±0.026
	pyrimethanil	fungicide	0.033±0.017
R8	boscalid (nicobifen)	fungicide	0.014±0.007
	cyprodinil	fungicide	0.072±0.036
	deltamethrin	insecticide	0.018±0.009
	pyrimethanil	fungicide	0.035±0.018
R9	boscalid (nicobifen)	fungicide	0.27±0.14
	cyprodinil	fungicide	0.014±0.007
	pyrimethanil	fungicide	0.025±0.013
R10	kresoxim-methyl	fungicide	0.037±0.019
R11	kresoxim-methyl	fungicide	0.043±0.022
R12	kresoxim-methyl	fungicide	0.024±0.012
R13	kresoxim-methyl	fungicide	0.037±0.019
R14	acetamiprid	insecticide	0.012±0.06
	azoxystrobin	fungicide	0.20±0.10
	boscalid (nicobifen)	fungicide	0.044±0.022
	chlorpyriphos	insecticide	0.38±0.19
	cypermethrin	insecticide	0.077±0.039
	cyprodinil	fungicide	0.022±0.011
	fenbutatinoxide	acaricide	0.013±0.007
	fludioxonil	fungicide	0.013±0.007
	iprodione	fungicide	0.43±0.22
	metalaxyl-M	fungicide	0.012±0.006
	pyrimethanil	fungicide	0.28±0.14
	trifloxystrobin	fungicide	0.040±0.020
R15	acetamiprid	insecticide	0.16±0.08
	azoxystrobin	fungicide	0.11±0.06
	boscalid (nicobifen)	fungicide	0.062±0.031
	chlorpyriphos-methyl	insecticide	0.30±0.15
	cypermethrin	insecticide	0.072±0.036
	cyprodinil	fungicide	0.014±0.007
	iprodione	fungicide	0.50±0.25
	myclobutanil	fungicide	0.014±0.007
	pyrimethanil	fungicide	0.38±0.019
	trifloxystrobin	fungicide	0.029±0.015
	myclobutanil	fungicide	0.014±0.07

[1] Maximum residue limit value is not defined in Turkish Food Codex.

The detected pesticides were in the fungicide and insecticide groups. Since there was no MRL value for dried apricots in the TFC, no evaluation could be made. Carbendazim(+benomil) detected in DA1 sample was the most intensely detected pesticide with a concentration value of 0.12±0.06 mg/kg. 14 samples of dried figs (DF) were taken from the products produced in Aydın and offered for sale in Konya. Only two insecticides, chlorpyriphos and malathion, could be detected in the dried fig samples of DF1 and DF2 and their concentrations were determined as 0.025±0.013 and 0.070±0.035 mg/kg, respectively. Since there was no MRL value for dried figs in the TFC, no evaluation could be made. In the study conducted by Tatlı (2006), no pesticide residues were found in the dried fig samples.

Health risk assessment

The acute and chronic term risk assessment conducted in the study were determined for pesticides having the values of both ADI and ARfD that are presented in the JMPR database and vary for each type of pesticide. As a result of the risk assessment, the values of ESTI, EDI, aHI, HQ and THQ detected for adults and children are given in Table 6. aHI value of 20 pesticides subjected to risk assessment was found to be greater than 1 for 1 pesticide (acetamiprid) for adults and 3 pesticides (chlorpyriphos,

Table 5. The level of pesticide residues detected in the dried apricots (DA).[1,2]

No	Name of pesticide	Type of pesticide	level of residue (mg/kg)
DA1	carbendazim (+benomil)	fungicide	0.12±0.06
	dodine	fungicide	0.066±0.033
	pyriproxyfen	insecticide	0.012±0.006
DA2	dodine	fungicide	0.065±0.033
	tiacloprid	insecticide	0.028±0.014
DA3	acetamiprid	insecticide	0.018±0.009
	azoxystrobin	fungicide	0.045±0.023
	carbendazim (+benomil)	fungicide	0.024±0.012
	thiophanate-methyl	fungicide	0.033±0.017
DA4	acetamiprid	insecticide	0.024±0.012
	azoxystrobin	fungicide	0.062±0.031
	carbendazim (+benomil)	fungicide	0.024±0.012
DA5	acetamiprid	insecticide	0.016±0.008
	azoxystrobin	fungicide	0.044±0.022
	carbendazim (+benomil)	fungicide	0.026±0.013
DA6	dodine	fungicide	0.055±0.028
	thiamethoxam	insecticide	0.012±0.006
DA7	n.d.	n.d.	n.d.
DA8	acetamiprid	insecticide	0.028±0.014
	azoxystrobin	fungicide	0.071±0.036
	carbendazim (+benomil)	fungicide	0.030±0.015
	thiophanate-methyl	fungicide	0.013±0.007
DA9	dodine	fungicide	0.071±0.036
DA10	acetamiprid	insecticide	0.010±0.005
	carbendazim (+benomil)	fungicide	0.010±0.005
	dodine	fungicide	0.078±0.039
DA11	dodine	fungicide	0.030±0.015
DA12	dodine	fungicide	0.035±0.018
DA13	dodine	fungicide	0.052±0.026
DA14	dodine	fungicide	0.078±0.039
	thiacloprid	insecticide	0.024±0.012

[1] n.d. = not detected; * = MRL value is not defined in TFC.
[2] Maximum residue limit value is not defined in Turkish Food Codex.

deltamethrin, chlorpyriphos-methyl) for children. When HQ values are taken into account, values greater than 1 were detected for 1 pesticide (acetamiprid) for adults and 3 pesticides (chlorpyriphos, deltamethrin, chlorpyriphos-methyl) for children. No pesticides were detected to pose both acute and chronic risks. Acetamiprid posed an acute risk for both adults and children, whereas chlorpyriphos, deltamethrin and chlorpyriphos-methyl posed a chronic risk both for adults and children. From this point of view, 5% of the pesticides subjected to risk assessment pose an acute risk for adults and children, while 15% of them pose a chronic risk for adults and children. When it is evaluated in terms of the products analyzed, chlorpyriphos and malathion concentrations were determined in dried fig samples as 0.025±0.013 and 0.070±0.035 mg/kg respectively, and chlorpyriphos and malathionin were found not to pose a danger to adults and children in terms of acute and chronic risks. However, it seems that children are at a higher chronic risk than adults. It is thought that this situation is caused because of the fact that children are always more vulnerable to harmful chemicals than adults and they have lower weights. The reason why malathion posed less risk for adults and children although the detected amount of malathion was higher than that of chlorpyriphos is due to the difference in the values of ADI and ARfD between the two pesticides.

The pesticides in dried apricot samples subjected to risk assessment were not pose any acute or chronic risks for both adults and children. Among the pesticides in raisin samples subjected to risk assessment, chlorpyriphos posed an acute risk both for adults and children, whereas cypermethrin and deltamethrin posed a chronic risk both for adults and children. Chlorpyriphos has been the pesticide that poses the highest chronic risk for adults and children. The only pesticide subjected to risk assessment in date samples is imidacloprid. As a result of the evaluation, it was determined that imidacloprid did not cause any acute or chronic risks in adults and children. The pesticides subjected to risk assessment in pumpkin seed samples were chlorpyriphos and imidacloprid. These two pesticides were determined not to cause any acute or chronic risks in adults and children. The pesticides subjected to risk assessment in pistachio samples were acetamiprid and thiacloprid. Thiacloprid did not pose any risks for adults, whereas it posed both acute and chronic risks for children. Acetamiprid did not cause any acute or chronic risks both for children and adults. In the study conducted by Liu *et al.* (2016), the level of pesticide residues was analyzed in chestnuts, walnuts and pine nuts, and four orgonophosphate pesticides (acephate, dimethoate, chlorpyrifos and paration-methyl) were detected in concentrations varying from 19 to 74 μg/kg. While the short term risk ratio of the dried nuts tested was less than 1.2%, the long term risk was determined as 12.58%.

In humans, poisonings occur when pesticides are taken through skin, inhalation or digestion. In all three ways, pesticides are the most harmful substances. Poisining occurs in two kinds such as acutely or chronically. As a result of chronic poisoning resulting from ingestion of pesticide residues in foods, some health problems such as lung diseases, cancer, brain damage, and nephrosis in liver and kidney can occur. There are also pesticides that show teratogenic (abnormalities in the development of the fetus) mutagenic (genetic disorders) and allergic effects. The use of some organic phosphorus compounds without wearing protective clothing and masks can cause sudden deaths. Pesticide-related poisonings usually occur in pesticide

Table 6. Results of the risk assessment for adults and children.[1]

Sample	Type of the pesticide	Adult					Children				
		ESTI	EDI	aHI	HQ	THQ	ESTI	EDI	aHI	HQ	THQ
Dried fig	chlorpyriphos	3.082E-05	3.082E-05	0.030	0.308	0.003	3.440E-05	3.440E-05	0.034	0.344	0.003
	malathion	8.630E-05	8.630E-05	0.004	0.02	0.0002	9.633E-05	9.633E-05	0.004	0.032	0.0003
Dried apricot	carbendazim (+benomil)	1.479E-04	4.993E-05	0.1479	0.1664	0.001	1.651E-04	5.573E-05	0.1651	0.1858	0.001
	dodine	9.616E-05	7.260E-05	0.0481	0.0726	0.0007	1.073E-04	8.104E-05	0.0537	0.0810	0.0008
	thiacloprid	3.452E-05	3.205E-05	0.1151	0.3205	0.003	3.853E-05	3.578E-05	0.1284	0.3578	0.003
	acetamiprid	3.452E-05	2.367E-05	0.3452	0.0338	0.0003	3.853E-05	2.642E-05	0.3853	0.0377	0.0003
	thiamethoxam	1.479E-05	1.479E-05	0.0015	0.0185	0.0001	1.651E-05	1.651E-05	0.0017	0.0206	0.0002
Raisin	indoxacarb	3.452E-05	2.836E-05	0.0345	0.2836	0.002	3.853E-05	3.165E-05	0.0385	0.3165	0.003
	acetamiprid	2.096E-04	1.085E-04	**2.0959**	0.1550	0.001	2.339E-04	1.211E-04	**2.3394**	0.1730	0.001
	chlorpyriphos	4.685E-04	2.963E-04	0.4685	**2.9630**	0.029	5.229E-04	3.307E-04	0.5229	**3.3073**	0.033
	cypermethrin	1.233E-04	1.023E-04	0.3082	0.5116	0.005	1.376E-04	1.142E-04	0.344	0.5711	0.005
	deltamethrin	2.219E-04	1.221E-04	0.4438	**1.2205**	0.0002	2.477E-04	1.362E-04	0.4954	**1.3624**	0.013
	dimethomorph	4.685E-05	4.685E-05	0.0078	0.0234	0.005	5.229E-05	5.229E-05	0.0087	0.0261	0.0002
	famoxadone	3.205E-05	3.205E-05	0.0053	0.5342	0.020	3.578E-05	3.578E-05	0.006	0.5963	0.005
	chlorpyriphos-methyl	3.699E-04	3.699E-04	0,3699	**3.6986**	0.036	4.128E-04	4.128E-04	0.4128	**4.1284**	0.041
Date	imidacloprid	2.466E-05	2.404E-05	0.0062	0.0401	0.0004	2.752E-05	2.683E-05	0.0069	0.0447	0.0004
Pumpkin seed	chlorpyriphos	1.603E-05	1.562E-05	0.0160	0.1562	0.001	1.789E-05	1.743E-05	0.0179	0.1743	0.001
	imidacloprid	1.036E-04	1.007E-04	0.0259	0.1678	0.001	1.156E-04	1.124E-04	0.0289	0.1873	0.001
Pistachio	acetamiprid	2.219E-05	2.219E-05	0.0222	0.0317	0.0003	2.477E-05	2.477E-05	0.0248	0.0354	0.0003
	thiacloprid	2.959E-05	2.866E-05	0.1479	0.2866	0.002	3.303E-05	3.200E-05	0.1651	0.3200	0.003

[1] The bold numbers in the table are the highest determined aHI and HQ values.

production facilities, during preparation of the pesticide and application of the pesticide, and after the ingestion of foods contaminated with pesticides. The most common ones are those caused by the ingestion of foods contaminated with pesticides. When there is exposure to pesticides for a long time, various damages occur in nervous system, respiratory system, cardiovascular system, stomach, intestinal and circulatory systems, internal organs such as liver and kidney, skin and eyes (Tatlı, 2006).

Another way of risk assessment is THQ, which is based on estimated and acceptable intake rates. Higher amounts of consumption (THQ>1) than tolerable amounts pose an unacceptable risk (Bedük *et al.*, 2017). All of the THQ values obtained in the study were detected to be <1. The potential risk that can be caused by all of the pesticides is determined as HI. The calculated HI value was detected as 0.415 for adults and 0.955 for children.

4. Conclusions

Since our country is one of the leading producers of nuts in the world and we as a society consume these products both as snacks and as auxilary ingredients in foodstuffs besides different products, it is necessary that a study be conducted for these products and the pesticide residue levels be revealed. Thus, a risk assessment can be conducted according to the data obtained from the study and to the international agreements. In the study, the residue levels of 227 pesticides were analyzed in total 162 dried nuts and fruits in 13 different products such as 15 walnuts, pistachios, hazelnuts, almonds, peanuts and dates, 13 sunflower seeds, 12 pumpkin seeds, 8 white chickpeas, 7 yellow chickpeas, 11 raisins and dried apricots and 10 dried figs. A risk assessment was made for adults and children by taking into account ADI and ArfD values. At least one pesticide residue was found in 6 of the 13 samples. 6 types (dried figs, dried apricots, raisins, dates, pumpkin seeds, pistachios) having pesticide residues constitute 46% of all of the samples analyzed. At least one pesticide residue was found in 47 of 162 samples. These detected pesticides constitute 29% of all of the samples. A banned pesticide was found in 9 of 162 samples and this constitutes 0.06% of all samples of the pesticides. In the study in which the risk assessments of 10 types of insecticides and 4 types of fungicides were conducted, 5% of the pesticides were found to pose an acute risk for adults and children, and 15% were found to pose a chronic risk for adults and children. Even though all of the THQ values obtained in the study were below 1, the calculated HI values were obtained as 0.2642 for adults and 0.11155 for children. These results show that adults are exposed to 2 times more total risks than children.

The values of the maximum residue limits for pesticides and products can be reached in the TFC on Regulation of MRLs of Pesticides. New updates are made in this regulation at certain periods and maximum residue limits of different products are added. There are no maximum residue limits for raisins, dried figs and dried apricots in the products analyzed in the study, so necessary legal regulations should be put into practice urgently by taking into account how intensely these products are consumed throughout our country. Both adults and children to a large extend are affected by potential hazards of pesticides. An unhealthy environment and unhealthy foods negatively affect not only the fate of children growing up in such environments but also the fate of countries. For this reason, the benefits brought by the regulations to be made should be in such a way that they can regulate not only a certain segment of the society, but also the health of the society and the environment. Pesticide residue analyses of foodstuffs should be made at regular intervals and the results should be evaluated according to the legislation. Turkish people consume not only the dried nuts and fruits analyzed in the study but also many products together for the continuation of their daily lives. In this respect, people are not only exposed to the risks of dried nuts and fruits but also they are exposed to both acute and chronic health risks in many aspects with the intake of other foods. It is impossible to find pesticides and products that do not carry any risks around the world. However, it may not help eliminate the risk completely but it will certainly help reduce the risk if the law-makers concerned in the matter are strict followers of legal regulations for pesticides and if the pesticide to be used is applied according to the instructions in the user manuals. Perhaps it is impossible to abolish the use of pesticides completely, but the measures to be taken will ensure that everyone in the community can have healthier foods in a healthier environment.

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Conflict of interest

The authors have declared no conflict of interest.

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