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Araştırma Makalesi

Sarımsakta Organoklorlu Pestisit Kalıntılarının Tespiti ve Sağlık Risklerinin Değerlendirilmesi[&]

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Öz

Tarihsel olarak yaygın olarak kullanılan kalıcı organik kirletici pestisitler, tarım ürünlerinde hala tespit edilebilmekte ve sağlık risklerine neden olabilmektedir. Bu çalışmada, Kastamonu il merkezinde potansiyel olarak kirlenmiş alanda bulunan farklı köylerin tarlalarında üretilen 23 sarımsak örneğinde yasaklı organoklorlu pestisit (OKP) kalıntı seviyeleri QuEChERS ekstraksiyon ve temizleme tekniği ile kombine GC/MS yöntemi ile belirlenmiştir. Çalışmamızda 23 örneğin 14'ünde en az bir OKP, çalışmamızda incelenen 23 OKP'nin 20'sinde en az bir örnekte saptanmıştır. Sarımsakta en sık saptanan OKP kalıntısı dikloro-difenil-trikloroetan (DDT) ve metabolitleridir. Örnek 16 hariç tüm sarımsak örneklerinin kalıntı seviyeleri maksimum kalıntı seviyelerinin (MRL) altında bulunmuştur. Çalışmamızda incelediğimiz OKP'lerin 18'i örnek 16'da belirlenmiştir ve bunların 14 tanesi çok yüksek konsantrasyonlardadır. Bir risk değerlendirmesi yapmak ve kabul edilebilir günlük alım (ADI) seviyelerinin aşıp aşılmadığını belirlemek için tüm numunelerin tahmini günlük alım seviyeleri (EDI) hesaplanmıştır. Örnek 16'daki kalıntı miktarları ele alınarak hesaplanan EDI değerlerinin hiçbiri ADI seviyelerini geçmemiştir. Ancak, gerçek sarımsak tüketimi hesaplanan miktarın üzerinde olan kişiler için örnek 16 gibi numunelerin maruz kalma riski oluşturabileceği unutulmamalıdır.

Anahtar kelimeler: Gıda güvenliği, GC-MS, OCP'ler, Pestisitler, QuEChERS, Toksisite.

Detection of Organochlorine Pesticides Residues in Garlic and Evaluation of Health Risks[&]

Abstract

Persistent organic polluting pesticides that have been used extensively historically can still be detected in agricultural products and cause health risks. In this study, banned organochlorine pesticide (OCP) residue levels in 23 garlic samples produced in the fields of different villages located in the potentially polluted area in the center of Kastamonu were determined by GC/MS method combined with QuEChERS extraction and clean-up technique. In our study, at least one OCP was detected in 14 of 23 samples and 20 of the 23 OCPs examined in our study, were detected in at least one sample. The most frequently detected OCP residue in garlic is dichloro-diphenyl-trichloroethane (DDT) and its metabolites. The residue levels of all garlic samples were below their maximum residue levels (MRL), except for sample 16. Eighteen of the OCPs examined in our study, were determined in sample 16 and 14 of them had very high concentrations. Estimated daily intake levels (EDI) of all samples were calculated to determine whether the acceptable daily intake (ADI) levels were exceeded in order to make a risk assessment. None of the EDI values calculated from the amounts of residues in the sample 16 exceeded the ADI levels. However, it should not be forgotten that samples such as sample 16 may pose a risk of exposure for people whose actual consumption of garlic is higher than the calculated amount.

Key words: *Cyamopsis tetragonolaba*, edible cluster bean, stability, plant seed yield.

Introduction

Pesticides are chemicals used to minimize the damage of pests (such as insects, viruses, bacteria, rodents, unwanted plants) during the stages of agricultural production (Miller and Leschewski, 2012). Both agricultural and domestic uses of pesticides are widespread, and the demand for them is increasing with the increasing supply of produce, fruit and vegetables, as well as the control of insect-borne diseases affecting humans, animals and livestock. Many pesticides are neurotoxicants that are acutely toxic at high doses, and at lower doses may have potentially milder effects due to different routes of exposure. An important group of pesticides found in the environment as a result of human activities is organochlorine compounds. Organochlorine pesticides (OCPs), which have negative effects on the environment and human health, are extremely toxic, persistent organic pollutants (POPs). These compounds have long biological half-lives and are chemically stable, and thus cause high biomagnification with a wide variety of nutrients in the food chain (Serrano et al., 2008). Due to its slow biotransformation and lipid solubility, organochlorine pesticides can accumulate in animal fat tissues through food and cause toxic effects (Gasull et al., 2010).

The Stockholm Convention addresses the issue of POPs and generally prohibits the production and use of persistent, bioaccumulative chemicals. This convention covers some chemicals and 9 organochlorine pesticides (12 substances in total) including dichloro-diphenyl-trichloroethane (DDT) (IISD, 2008). Two pesticides and 9 chemicals were added to this list in 2009, and endosulfan, which is also a pesticide, was added to the list in 2011. Despite being banned in most countries, persistent OCPs are still routinely detected in foods worldwide. Dichlorodiphenyldichloroethane (DDE), a degradation product or metabolite of DDT, is still one of the most studied OCP residues anywhere due to its potential toxicity (Roberts and Karr, 2012). Pesticides should be given particular attention because of the potential neurodevelopmental toxicity (adverse cognitive, behavioral, sensory and/or motor effects) posed by historically used and currently used pesticides. (Eskenazi et al., 2007-2008).

In recent years, great progress has been made in residue detection studies aiming to minimize pesticide damage, and as a result of these studies, highly advanced multiple residue analysis methods have emerged and started to be used. In such multiple residue analyzes examining agricultural products, residue levels of more than 100 pesticides can be determined simultaneously (Yu et al., 1997). Although traditional pesticide analysis methods (such as liquid-liquid partitioning, solvent extraction, liquid solid adsorption) are still frequently used, multiple residue analyzes that have been used recently include more selective extraction methods (QuECHERS, supercritical liquid extraction etc.). In the "QuECHERS" (Quick, Easy, Cheap, Effective, Rugged, Safe) method, which allows the analysis of a high number of pesticides with different structures in different matrices on fruits and vegetables, the extraction of pesticides with both polar and non-polar characteristics can be performed with a single type of solvent, and at the same time without the need for additional concentration process. Analysis can be done with both Gas chromatography-mass spectrometry (GC/MS) and Liquid chromatography-mass spectrometry (LC/MS-MS) without the need for further processing. The positive aspects of the QuECHERS method are quite high compared to many of the traditionally used pesticide analysis methods. With this method, high recoveries (> 85%) were obtained in pesticides with different polarities and volatility. It is possible to work with more than one sample at the same time and the analysis time is short. In the QuECHERS method, the labor cost is very low and the solvent consumption and amount of waste from the process are also very low. Extraction can be done with limited space and equipment (Anastassiades et al., 2003). The GC-MS technique is a constantly evolving and growing technique that has several advantages over GC techniques used with other detectors, such as confirmability, sensitivity, quantitative detection, distinguishing overlapping peaks, universal detection with high selectivity, and the use of spectral libraries (Maštovská et al., 2001). Therefore, GC-MS analysis technique combined with QuECHERS sample preparation technique was preferred in this study.

The aim of our study is to find out that residual amounts of OCP in garlic that is one of the main agricultural product whose waste is also valuable (Tahmas Kahyaoğlu, 2021) and grown in the villages in potentially contaminated areas in the center of Kastamonu. The second aim in this study to reveal the possible toxic effects and health risks by examining whether these residue amounts exceed the legal limits. This potentially contaminated area was determined as a result of interviews with Kastamonu Chamber of Agriculture, the oldest pesticide dealers of Kastamonu province and Kastamonu Provincial Directorate of Agriculture. According to the literature review, no study has been found that examines the residual amounts of banned OCP

used in the past in this region or that has made a risk assessment.

Material and Methods

Sample collection

Kastamonu Chamber of Agriculture provided vehicle and technical personnel support for sample collection. According to the data obtained by the researches, it has been revealed that the possible polluted area is the central villages from Kastamonu city center to the Taşköprü plain and 3 km away from the Kastamonu Sugar Factory. 23 garlic samples, 1 kg each, were collected from farmers producing in 18 different villages, including the agricultural areas within the scope of the study, and kept in a cold room at -18 ° C until analysis.

Chemicals

OCP Mix Standard (aldrin, endrin, cis-chlordane, trans-chlordane, alpha-HCH, beta-HCH, gamma-HCH (Lindane), o,p'DDD, p,p'DDD, o,p'DDE, p,p'DDE, o,p'-DDT, p,p'DDT, methoxychlor, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, hexachlorobenzene, dieldrin, alpha-endosulfan, beta-endosulfan, technazene, quintozen) Pesticide-Mix 71 was obtained from Dr. Ehrenstorfer (Germany) company. Q-sep QuEChERS Q110 kit and Qsep QuEChERS Dspe Clean-up used in sample extractions and cleaning were purchased from RESTEK Turkey. ISOLAB (Germany) brand chromatographic purity acetonitrile was used as extraction solvent.

Methods

Sample extraction

The crushed garlic samples were weighed 10 gram portions and taken into 50 ml clean falcon tubes and 10 ml of acetonitrile was added. It was shaken first by hand and then by vortex for a total of 3 minutes. Then, the contents of the Q-sep Q110 QuEChERS kit containing 4 g $MgSO_4$, 1 g NaCl, 1 g trisodium citrate dihydrate, 0.5 g disodium hydrogen citrate sesquihydrate chemicals were added to the tubes. The tubes, which were shaken rapidly for about 2 minutes, were centrifuged for 5 minutes at 3500 rcf using a cooled centrifuge (Hermle Z 326 K, Germany).

Sample clean up

The supernatants formed in the centrifuged tubes at the extraction step were taken into 15 ml falcon tubes containing the Q-sep QuEChERS dSPE mixture and shaken for about 2 minutes, and then the tubes were centrifuged at 5000 rcf for 2 minutes in a cooled centrifuge. The supernatant formed was taken with a syringe and passed through a 0.25 µm micro filter and taken into vials. The vials were analyzed by placing them in the autosampler of the GC-MS device.

GC-MS analysis

OCP residue analyzes were performed in Kastamonu University, Central Research Laboratory Application and Research Center as service procurement. SHIMADZU GC-MS QP 2010 ULTRA brand (Japan) GC-MS device with RTX-5MS Capillary column (30 m; 0.25 mm; 0.25 μm) in this laboratory was used in the analysis. The carrier gas is Helium, the injection temperature is 280 ˚C, the injection mode is splitless, and the injection volume is 2 µL. The oven temperature programming is in the form of 5 minutes of waiting at 60˚C, then reaching from 60˚C to 280˚C with an increase of 5˚C/min and waiting for 6 minutes at 280˚C, and the total analysis time is 55 minutes.

Moisture, ash and pH analyzes

Moisture, ash and pH analyzes were performed according to AOAC 985.26, TS EN 1135 and TS 1728 ISO 1842, respectively.

Quality assurance

OCP Mix Standard was diluted with n-hexane from Pesticide-Mix 71 standard mixture and a calibration solution was created at 6 different concentrations in the range of 5-200 ng mL^{-1} and a calibration curve was created. The correlation coefficients (R^2) for each pesticides were greater than 0.99 with good linearity. The limit of quantification (LOQ), precision, and accuracy of the method, were evaluated by recovery studies. LOQ of the methods were expressed as the lowest spike level of the validation according to the SANTE guidance document (2018) and in the range of 0.59–4.95 ng mL^{-1}. Acceptable mean recoveries obtained in our validation process are those within the range 70%–120% and RSD ≤ 20% according to the criteria of the SANTE's guidance document (2018), for all pesticides investigated in this study.

Statistical analysis

SPSS 22 program provided by Kastamonu University was used in the analysis. The normality and homogeneity of the groups were checked with the Shapiro-Wilk test and Levene's test, respectively. According to the test results, although the majority of the groups were homogeneous, they did not show normal distribution, so Kruskal Wallis test, one of the non-parametric tests, was used to compare the results of the analysis parameters of the groups. The non-parametric

Spearman correlation test was also used to investigate whether there is a relationship between the residue amounts of the analyzed pesticide types.

Results and Discussion

The average moisture, ash and pH levels of 23 garlic samples were to be 62.18 ± 1.75 (% w/w), 0.89 ± 0.15 (% w/w) and 5.86 ± 0.11 respectively. The OCP residues analysis results of garlic samples are given in Table 1. In our study, at least one OCP was detected in 14 of 23 samples, while no OCP residues were found in 9 samples (see Table 1). 20 of the 23 OCPs we examined in our study, were detected in at least one sample. The most common pesticide residues were p,p'-DDT, o,p'-DDT, o,p'-DDE, p,p'-DDE and o,p'-DDD, which were detected in 5 of 23 samples. They are followed by p,p'-DDD in 4 sample, and dieldrin seen in 3 samples. While cis-chlordane residue was found in only 2 samples, alpha-endosulfan, beta-endosulfan, alpha-HCH, beta-HCH, gamma-HCH, heptachlor, heptachlor endo-epoxide, methoxychlor, trans-chlordane, aldrin, endrin and quintozen were determined in only 1 sample. Technazene, hexachlorobenzene and heptachlor exo-epoxide were not detected in any of the samples.

As can be seen, the most frequently detected OCP residue in garlic is DDT and its metabolites. 18 of the OCPs we examined in our study, were determined in sample 16 and 14 of them had very high concentrations. Although pesticide residue levels were detected in quite high amounts in this garlic sample, in general, the residue amounts of the other samples were at low levels (between 0.07-4.89 µg kg^{-1}).

Table 1. The OCP residue concentrations (mean ± SD; µg kg^{-1}) of garlic samples.

Sample no	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	Methoxychlor	Dieldrin	alpha-endosulfan	beta-endosulfan
1	0.74 ± 0.01	ND	ND	ND	ND	4.59 ± 0.04	ND	ND	ND	ND
2	0.81 ± 0.00	0.15 ± 0.00	1.12 ± 0.06	1.78 ± 0.04	3.09 ± 0.02	ND	ND	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	0.14 ± 0.03	ND	1.83 ± 0.03	3.16 ± 0.01	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7	ND	ND	ND	ND	ND	3.64 ± 0.08	ND	ND	ND	ND
8	0.69 ± 0.00	0.07 ± 0.01	ND	2.22 ± 0.05	3.67 ± 0.01	ND	ND	4.89 ± 0.02	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	0.22 ± 0.00	ND	ND	2.91 ± 0.02	ND	ND	ND	ND	ND
11	ND	ND	0.92 ± 0.05	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	0.66 ± 0.01	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	1.00 ± 0.01	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	0.87 ± 0.03	772.45 ± 1.02	1.16 ± 0.02	663.75 ± 1.99	12.16 ± 0.07	801.76 ± 2.93	556.3 ± 0.87	691.95 ± 1.21	459.35 ± 0.99	532.40 ± 2.00
17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	0.69 ± 0.10	ND	ND	ND	ND	3.94 ± 0.09	ND	ND	ND	ND
19	ND	ND	ND	ND	ND	ND	ND	3.49 ± 0.03	ND	ND
20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
22	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
23	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample no	alpha-HCH	beta-HCH	gama-HCH	Heptachlor	Heptachlor endo-epoxide	cis-chlordane	trans-chlordane	Aldrin	Endrin	Quintozen
16	280.55 ± 0.55	617.95 ± 1.18	364.5 ± 0.89	484.80 ± 1.34	703.5 ± 1.97	2.30 ± 0.07	ND	203.35 ± 0.61	729.25 ± 0.94	ND
18	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.57 ± 0.12
21	ND	ND	ND	ND	ND	0.48 ± 0.00	ND	ND	ND	ND
22	ND	ND	ND	ND	ND	ND	0.62 ± 0.06	ND	ND	ND

SD: Standart deviation; ND: Not detectable

The non-parametric Spearman correlation test was applied to investigate whether there is a statistically significant relationship between the moisture, ash, pH, and residual amounts of detectable pesticides. According to the correlation results, there is a significant positive correlation ($p<0.05$) between o,p'DDE and o,p'DDD, p,p'DDD, o,p'DDT and p,p'DDT. Since these pesticides are already DDT and its metabolites, the correlation between them is understandable. It was determined that there was a positive correlation ($p<0.05$) between dieldrin and DDT and its metabolites. Since DDT and its derivatives and dieldrin were used extensively at the same time, a correlation between them is an expected result.

All OCP residues detected in garlic samples in our study are banned pesticides that should never be present in any vegetable samples. However, in order to make a risk assessment, the results of our study were compared with the MRL in the European Union regulations (Reg (EC) No 396/2005). The residue levels of all garlic samples were below their MRLs, except for sample 16. The 18 OCP residues detected in sample 16 and their MRL levels are compared in Table 2. In this sample, the residual amounts of ∑DDT, aldrin + dieldrin, alpha + beta endosulfan and heptachlor + heptachlor epoxides were found to be 45, 90, 99 and 119 times higher than the respective MRL values, respectively.

Table 2. Comparison of residue amounts of pesticides in Sample 16 and MRL, ADI and EDI values of pesticides detected in this study

Pesticide	Mean residue levels in sample 16 (mg kg^{-1})	MRL (mg kg^{-1})	ADI (mg kg^{-1} body weight/day)	EDI (mg kg^{-1} body weight/day)
∑DDT (p,p'DDT + o,p'DDT + p,p'-DDE + p,p'-DDD)	**2.25**	0.05	0.01	0.0002
Dieldrin (Aldrin + Dieldrin)	**0.90**	0.01	0.0001	0.00006
Endosulfan (alpha + beta endosulfan)	**0.99**	0.1	0.006	0.00007
Methoxychlor	**0.56**	0.01	0.1	0.00004
Alpha-HCH	**0.28**	0.01	-	0.00002
Beta-HCH	**0.62**	0.01	-	0.00004
Gama-HCH	**0.37**	0.01	0.005	0.00003
Heptachlor (heptachlor + heptachlor epoxides)	**1.19**	0.01	0.0001	0.00009
Chlordane (cis + trans chlordane)	**0.0023**	0.01	0.0005	1.6×10^{-7}
Endrin	**0.73**	0.01	0.0002	0.00005

According to the literature review, no study conducted in our country and examining OCP residues in garlic has been found before. However, when studies examining OCP residues in agricultural products in our country are taking into account, it is seen that in a study conducted in Konya region by Dağlı (2008), OCP contamination in wheat was investigated by gas chromatographic method and aldrin, trans-chlordane and methoxychlor in 1 sample and oxy-chlordan in 8 samples, were detected above MRL levels. In addition, cis-chlordane and methoxychlor residues were found in all of the wheat samples. Intensive agriculture and the high use of pesticides from past to present in the Konya region can be considered as the reason for the presence of residues above MRLs in many samples. In the study conducted by Özcan (2016), in Kırklareli, OCP residue levels in zucchini, cherry, tomato, banana, pepper, lettuce, purslane, green bean, cucumber and onion samples were analyzed by GC-MS combined with QuEChERS extraction method as in our study. The analyzes showed that the concentrations of ΣHCH, aldrin, heptachlor, dieldrin, endosulfan, methoxychlor and ΣDDT were in compliance with the LOD and LOQ limits. Residual concentrations of pesticides ranged from undetectable to 73.6 µg kg^{-1} in all vegetable samples examined. Endrin concentrations in all samples were 1.2 to 7.4 times higher than the its MRL value. Özcan and Balkan (2017) investigated the usage levels of OCPs in tomato, eggplant and cucumber production in Kırklareli. 18 OCPs were detected in vegetable samples. Pesticide concentrations were shown to

be in the range of undetectable to 123 µg kg^{-1} in all vegetables studied, and endrin and methoxychlor levels were above the MRLs, while other pesticides were below the legal limit. Looking at the foreign literature, there are a few studies investigating OCP residue amounts in garlic. 213 pesticides were investigated in 8 leek and 8 garlic samples based on QuEChERS procedure combined with GC-MS/MS by He et al., (2015). Altough, 17 pesticides were detected in leek samples, no pesticide was detected in the garlic samples, in their study. Ali et al., (2019) investigated the residual amounts of 30 endocrine disrupting pesticides (EDPs), including OCPs in Pakistan. The concentrations of the selected EDPs in 6 vegetable species (radish, spinach, lettuce, turnip, onion, garlic. The mean concentration levels of Σ30 EDPs were in the order of lettuce>radish>spinach>onion>turnip>garlic and were below the MRLs. Carrot, Onion, Cabbage, Garlic and Ginger (ten samples each) were investigated in respect of OCP residues in Nigeria by Olutona et al., (2021). The OCPs were detected at varying concentrations in all the vegetable samples except onions, in their study. Mean concentrations of dieldrin, endrin, alpha-endosulfan, beta-endosulfan, heptachlor epoxide, p,p'-DDT, p,p'-DDE and methoxychlor were detected to be 0.03, 0.2, 3.9, 0.14, 0.32, 0.44 and 0.05 mg kg^{-1}, in garlic samples, respectively, and all of these residue amounts higher than the their MRL values. The results of this study show that, as in our study, banned OCPs with historical use can still be detected in garlic and pose a threat to human health. However, residues of OCPs were found in all garlics in Nigeria and their mean values were determined above their MRLs. In our study, however, no pesticide was detected in 9 samples and residue levels exceeding MRLs were found in only one sample, which indicates that there is less residual pollution in Kastamonu province. The reason why various OCPs residues were detected well above the MRLs in sample 16 examined in our study may be that the area where the sample was produced, was heavily contaminated in the past. Another strong possibility is that this area is an area where these pesticides were destroyed by unlawful burial after the ban.

In addition, estimated daily intake levels (EDI) of all samples were calculated to determine whether the acceptable daily intake (ADI) levels were exceeded in order to make a risk assessment. The following formula was used to make this calculation.

EDI= (residue concentration in garlic × daily consumption of garlic)/body weight

The consumption amounts of the relevant garlic per person per day were found by dividing the annual garlic production amounts determined according to the plant production statistics and the population of Turkey detected for the year 2020 by TUIK (2020a; 2020b) and 365 days, respectively. The population of Turkey is 83 million 614 thousand 362 people according to TUIK data, and the average body weight is taken as 70 kg in the calculations. TUIK garlic production data and calculated daily garlic consumption amounts per capita are given in Table 3.

Table 3. TUIK garlic production data (2020a) and daily per capita consumption of garlic

Garlic production type	Annual production (ton/year)	Daily consumption per capita (kg)
Dry	28552	0.001
Wet	116840	0.004
Total	145392	0.005

Pesticide residue amounts detected in sample 16, MRL and ADI values of these pesticides and the EDI amounts calculated according to our study results are shown in Table 2. As can be seen from this table, none of the EDI values calculated from the amounts of residues in the sample 16 exceeded the ADI levels.

Conclusion

In our study, at least one OCP was detected in 14 of 23 samples, and the residue levels of none of the samples, except sample 16, did not exceed the legal limits. However, none of the EDI values calculated from residue amounts in the sample 16 exceeded the ADI levels. This is pleasing, but the reason why the EDI values of the OCPs detected in this sample did not exceed the ADIs is that the daily per capita consumption of garlic is extremely low. It should be noted that since we are exposed to pesticide residues from many sources, knowing

the total EDI levels as a result of intake from all sources will reveal the real risks. Furthermore, if the actual consumption of garlic is higher than the consumption amount calculated in our study, it is possible to be exposed to pesticide residues exceeding the ADI amount. As a result, it is extremely important to carry out new studies to determine the residual status of OCPs and their effects from the past to the present, and necessary measures should be taken to eliminate the harmful effects that may arise from these chemicals. Considering the sample 16, the results of this research reveal how important the inspection of agricultural products offered for sale in the bazaars and that the authorities should take the necessary precautions in this regard.

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References

Ali, N., Khan, S., Khan, M.A., Waqas, M. and Yao, H. 2019. Endocrine disrupting pesticides in soil and their health risk through ingestion of vegetables grown in Pakistan. Environmental Science and Pollution Research, 26 (9): 8808-8820.

Anastassiades, M., Lehotay, S.J., Štajnbaher, D. and Schenck, F.J. 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. Journal of AOAC International, 86 (2): 412-431.

Anonymous. 2008. International Institute for Sustainable Development (IISD). In: Summary of the 4th Meeting of the Persistent Organic Pollutants Review Commitiee of the Stockholm Convention: Earth Negotiations Bulletin, vol. 15. pp. 1–17.

Anonymous. Codex Alimentarius. Pesticide Index. FAO-WHO records. https://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/

Anonymous. 2018. Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed. SANTE/11813/2017. Luxembourg, EU: European Commission Directorate General for Health and Food Safety.

Anonymous. 2020a. Crop production statistics. Turkish Statistical Institute (TUIK) Records. https://data.tuik.gov.tr/Bulten/Index?p=Bitkisel-Uretim-Istatistikleri-2020-33737

Anonymous. 2020b. Address based population registration system results. Turkish Statistical Institute (TUIK) Records. https://data.tuik.gov.tr/Bulten/Index?p=Adrese-Dayali-Nufus-Kayit-Sistemi-Sonuclari-2020-37210

Dagli, Z. 2008. Investigation of organic chlorinated pesticide levels in wheat in Konya region. Ph.D. Thesis, Selcuk University, Institute of Science and Technology. Konya.

Eskenazi, B., Marks, A.R., Bradman, A., Harley, K., Barr, D.B., Johnson, C., Morga, N. and Jewell, N.P. 2007. Organophosphate pesticide exposure and neurodevelopment in young Mexican-American children. Environmental Health Perspectives, 115: 792-798.

Eskenazi, B., Rosas, L.G., Marks, A.R., Bradman, A., Harley, K., Holland, N., Johnson, C., Fenster, L., and Barr, D.B. 2008. Pesticide toxicity and the developing brain. Basic and Clinical Pharmacology and Toxicology, 102 (2): 228-236.

Gasull, M., Porta, M. Pumarega, J., Vioque, J., de Basea, M.B., Puigdomènech, E., Morales, E., and Grimalt, J.O. Malats, N. 2010. The relative influence of diet and serum concentrations of organochlorine compounds on K-ras mutations in exocrine pancreatic cancer. Chemosphere, 79 (7): 686-697.

He, Z., Chen, S., Wang, L., Peng, Y., Luo, M., Wang, W. and Liu, X. 2015. Multiresidue analysis of 213 pesticides in leek and garlic using QuEChERS-based method and gas chromatography-triple quadrupole mass spectrometry. Analytical and Bioanalytical Chemistry, 407 (9): 2637-2643.

Maštovská, K., Lehotay, S.J. and Hajšlová, J. 2001. Optimization and evaluation of low-pressure gas chromatography–mass spectrometry for the fast analysis of multiple pesticide residues in a food commodity. Journal of Chromatography A, 926 (2): 291-308.

Miller, S. and Leschewski, A. 2012. Economic impacts of the IR-4 project and IR-4 project programs. East Lansing: Center for Economic Analysis, Michigan State University.

Roberts, J.R., Karr, C.J., Paulson, J.A., Brock-Utne, A.C., Brumberg, H.L., Campbell, C.C., Lanphear, B.P., Osterhoudt, K.C., Sandel, M.T., Trasande, L. and Wright, R.O. 2012. Pesticide exposure in children. Pediatrics, 130 (6): e1765-e1788.

Serrano, R., Blanes, M.A., Lopez, F.J., 2008. Biomagnification of organochlorine pollutants in farmed and wildgil the adseabream (Sparusaurata) and stable isotope characterization of the trophic chains. Science of the Total Environment. 389: 340-349.

Olutona, G.O., Fakunle, I.A. and Adegbola, R.A. 2021. Detection of organochlorine pesticides residue and trace metals in vegetables obtained from Iwo market, Iwo, Nigeria. International Journal of Environmental Science and Technology, doi: 10.1007/s13762-021-03431-x

Özcan, C. 2016. Determination of organochlorine pesticides in some vegetable samples using GC-MS. Polish Journal of Environmental Studies, 25 (3): 1141-1147.

Özcan, C. and Balkan, S. 2017. Multi-residue determination of organochlorine pesticides in vegetables in Kirklareli, Turkey by gas chromatography–mass spectrometry. Journal of Analytical Chemistry, 72 (7): 761-769.

Tahmas Kahyaoğlu, D. 2021. Comparison of the Antioxidant Activity of Garlic Cloves with Garlic Husk and Stem: Determination of Utilization Potential of Garlic Agricultural Wastes. Turkish Journal of Agriculture and Natural Sciences, 8 (2): 463-469.

Yu, L., Schoen, R., Dunkin, A., Firman, M. and Cushman, H. 1997. Rapid identification and quantitation of diphenylamine, o-phenylphenol, and propargite pesticide residues on apples by gas chromatography/mass spectrometry. Journal of Agricultural and Food Chemistry, 45 (3): 748-752.Thennarasu, K. 1995. On certain non-parametric procedures for studying genotype-environment interactions and yield stability. PhD thesis, PJ School, IARI, New Delhi, India.

Vir, O., Singh, A. K. 2015. Variability and correlation analysis in the germplasm of cluster bean [*Cyamopsis tetragonoloba* (L.) Taub.] in hyper hot arid climate of Western India. *Legume Research-An International Journal*, 38 (1), 37-42.

Wricke, G. 1962. Übereine Methode zur Erfassung der ökologischen Streubreite in Feldversuchen. Zeitschrift für Pflanzenzüchtung, 47: 92-96.

Yan, W. 2014. Crop Variety Trials: Data Management and Analysis John Wiley and Sons, 349.

Załuski, D., Tworkowski, J., Krzyżaniak, M., Stolarski, M. J., Kwiatkowski, J. 2020. The Characterization of 10 Spring Camelina Genotypes Grown in Environmental Conditions in North-Eastern Poland. *Agronomy*, 10 (1), 64, 1-13.