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Original Article

Determination of Safety Organochlorine and Organophosphorus Residual Levels Using Gas Chromatography in Tomato from Different Governorates in Upper Egypt

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Abstract

High persistent organochlorine (OC) insecticides are banned to be used in indoor. In some developing countries, they used for controlling vectors insects. Organophosphorus (OP) insecticides widely utilized to control which replaced OC occasionally. On the contrary, organophosphorus pesticides are widely used in the control of various insect pests of agricultural crops and fodder for animal production. In comparison with OC group, OP has highly toxic hazards and short-term environmental degradation. Herein, we determine the organochlorine pesticide residues in tomato samples from various governorates in Upper Egypt. As a result, heptachlor-epoxide, dieldrin, aldrin, p, p'-DDE, and p, p'-DDT had the lowest residues in all tomato samples, with values of (0.61, 0.93, 1.38, 1.7, and 1.74 µg/ kg) for each pesticide residue, respectively, based on results of gas chromatography in tomato samples using the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method. Further, heptachlor and methoxychlor was found to be the highest levels among the pesticide residues that detected (13.9 and 10.42 µg/ kg) respectively. For the OP insecticide residues, the collected samples of tomatoes from Assiut, New Valley, El-Minia and Sohag were no residues to be found. Further studies of continues monitoring OC and OP residues of pesticides in different ecosystems septically in table vegetables and fruit should be applied.

Keywords: *Detecting, Tomato, Health Risk, Organochlorine, Organophosphorus, Residual Insecticides.*

Introduction

Pesticides are used by farmers all over the world as an essential tool against crop loss caused by pests and diseases (Bemphah *et al,* 2011). However, the unwise use of pesticides leads to residue impacts. Thus, monitoring residues of pesticides in vegetables for a comprehensive assessment pesticide research aims to improve the quality of vegetables as a primary goal because it causes potential risks for human health. To identify the residues of these chemicals in a range of food

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matrices, very sensitive and selective analytical methods must be applied. Many volatile pesticides have been successfully analyzed using gas chromatography (GC) with mass spectroscopy (MS) detection technologies, which give a quantitative and analytical estimation for a large number of pesticides, great separation efficiency, high analysis speed, and a wide range of device sensitivity. By using GC-MS, it is possible to use selective detection Several multi-residue methods for determining organic phosphorus and organochlorine to protect consumer health in several countries where legal guidance has been developed to control pesticide levels in food and organic nitrogen pesticides in crops using gas chromatography for individual compound separation followed by detection using selective and sensitive reagents by reducing Maximum Residue Levels (MRLs) by Osman *et al* (2010). The study aims to evaluate organochlorine and organophosphorus insecticide levels in tomato fruits collected from different governorates in Upper Egypt markets to avoid pesticide hazards and reduce risks to human health.

Materials and Methods

Location of collected samples

Tomato samples were selected randomly from 4 markets in Upper Egypt's governorates (Table 1)**.**

Table 1. The selected markets located in Upper Egypt governorate from which the tomato samples obtained

Location of Market	Governorates
Naela Khatoon	Assiut
Der-Mowas	El-Minia
El-Kharga	New -Valley
Tahta	Sohag

Collection of tomato samples

The present study was carried out during 2018-2019. A total of 16 samples (four kilograms) were randomly collected from 4 local markets in four cities in Upper Egypt. The collected samples were covered immediately and put in an ice box. Furthermore, the samples were labeled with the name of the market and the city before being transported to the laboratory (Pesticides Laboratory, Department of Plant Protection, Faculty of Agriculture, Assiut University) and kept at -20 °C in the deep freezer until the time limit was reached analytics.

Insecticides residual analysis in tomato

The Central Agricultural Pesticides Laboratory (ARPL) in Dokki, Egypt, analyzed pesticide residues. For identifying pesticide residues in food, a novel QuEChERS method was utilized for extraction and cleaning based on Anastassiades *et al*., (2003) and Abdelhamid (2013).

Determination of organochlorine insecticides

Hewlett Packard GC Model 6890 equipped with an Ni^{63} -electron capture detector as chromatography (GC) conditions: DB-17(J& W Scientific) capillary column (30 m length 32 mm internal diameter (id)x 0.25m film thickness), carrier

gas N2, at a rate of 4 ml/min; injector and detector temperatures were 300°C and 320°C, respectively. The starting column temperature was 160°C for two minutes, then elevated to 200°C at a rate of 5°C/min before being held at 200°C for another two minutes.

Determination of organophosphorus insecticides

A flame photometric detector (FPD) with a phosphorus filter is included in the Agilent 6890 gas chromatograph. A capillary made of fused silica (PAS-1701). It was used to separate in the GC with a column containing 14 percent cyanopropilsyloxane as the stationary phase (30m length x 032mm internal diameter (id) x 0.25pm film thickness). The following were the GC's operational conditions: Injector and detector temperatures were 240 and 250 degrees Celsius, respectively; starting oven temperature was 160 degrees Celsius for two minutes, and then escalated at a rate of 5 degrees Celsius per minute until being held at 240 degrees Celsius for two minutes. The carrier gas was nitrogen at 3 ml/min, while the combustion gas was hydrogen at 75 ml/min and air at 100 ml/min, respectively.

Limits of detection (LOD) and quantification (LOQ) were 0.01 µg/ kg and 0.03 µg/ kg, respectively for organochlorine and organophosphorus. Figures (1 and 3) show the standard chromatogram used for detecting OC and OP.

Determination of the health risk levels of OP and OC

The Estimated Daily Intake (EDI) for pesticide residue was determined using international criteria, and is expressed as micrograms of insecticides per kilogram of body weight per day (g kg b.wt., day) and computed using the equation:

$$EDI = \sum \frac{C \times F}{D \times W}$$

where **C:** represents total pesticide concentration (µg/Kg) at each location, **F:** represents average yearly food intake per person, **D:** represents the number of days in a year (365 days), and **W:** represents average body weight (80 kg). Egypt's yearly tomato consumption per capita is 45.5 kg/person/year. The health risk index (HRI) is the daily ratio of expected daily intake (EDI) to acceptable daily intake (ADI) for the rest of one's life **(EU, 2009)** An HRI value acquired from the EU that is higher than one considered dangerous to human health**.** If the calculated amount of pesticide residue is greater than the quantity of pesticides that can be consumed, HRI is set to 1.

Results and Discussion

Determination of organochlorine insecticide residue in tomatoes

The organochlorine residues were detected using GC-ECD (Tables 2 and 3). Aldrin concentration was revealed in two different markets: Sohag (0.69 µg/kg), and El-Minia (0.69 µg/kg). Heptachlor-epoxide concentration was demonstrated in a single market: Sohag (0.61 µg/kg). P, P'-DDE concentration was detected in two markets: Sohag (0.70 µg/kg), and Assiut (1 µg/kg). P, P'-DDT concentration

was found in the New-Valley market (1.74 µg/kg). Methoxychlor concentration was stated in two different markets: New-Valley (5.41 µg/ kg), Assiut (5.01 µg /kg). Heptachlor concentration was found in two different markets: El-Minia (6.84 µg/ kg), Assiut (7.06 µg /kg). Dieldrin concentration has been detected in two different markets: El-Minia (0.44 µg/ kg), Assiut (0.49 µg/kg). Aldrin level, heptachlor-epoxide, p, p'-DDE, p, p'-DDT, methoxychlor, heptachlor, dieldrin was found non-exceeded the MRL developed by the European Union Database of Insecticides.

Table 2. The levels of organochlorine residue in tomato samples obtained from 4 markets in Upper Egypt

City	Insecticides	MRL (µg/kg)	Concentration of samples (µg/kg)
Sohag	Aldrin	1	0.69
	Heptachlor epoxide	10	0.61
	P, P'-DDE	50	0.70
New- Valley	P, P'-DDT	50	1.74
	Methoxychlor	10	5.41
El-Minia	Heptachlor	10	6.84
	Aldrin	10	0.69
	Dieldrin	10	0.44
Assiut	Heptachlor	10	7.06
	Dieldrin	10	0.49
	P, P'-DDE	50	1
	Methoxychlor	10	5.01

Table 3. Organochlorine residues were found in tomato samples obtained from 4 markets in Upper Egypt

Group	Insecticides	City			
		Sohag	New valley	El-Minia	Assiut
OC	Alfa-BHC	Undetected	Undetected	Undetected	Undetected
	Gama-BHC	Undetected	Undetected	Undetected	Undetected
	Delta-BHC	Undetected	Undetected	Undetected	Undetected
	Heptachlor	Undetected	Undetected	6.844	7.061
	Aldrin	0. 702	Undetected	0. 689	Undetected
	Heptachlor Epoxide	0. 615	Undetected	Undetected	Undetected
	Gama-chlordane	Undetected	Undetected	Undetected	Undetected
	Endosulfan	Undetected	Undetected	Undetected	Undetected
	Dieldrin	Undetected	Undetected	0. 449	0. 494
	Endrin	Undetected	Undetected	Undetected	Undetected
	P, P'-DDE	0. 704	Undetected	Undetected	1.00
	P, P'-DDD	Undetected	Undetected	Undetected	Undetected
	P, P'-DDT	Undetected	1.744	Undetected	Undetected
	Methoxychlor	Undetected	5.418	Undetected	5.010

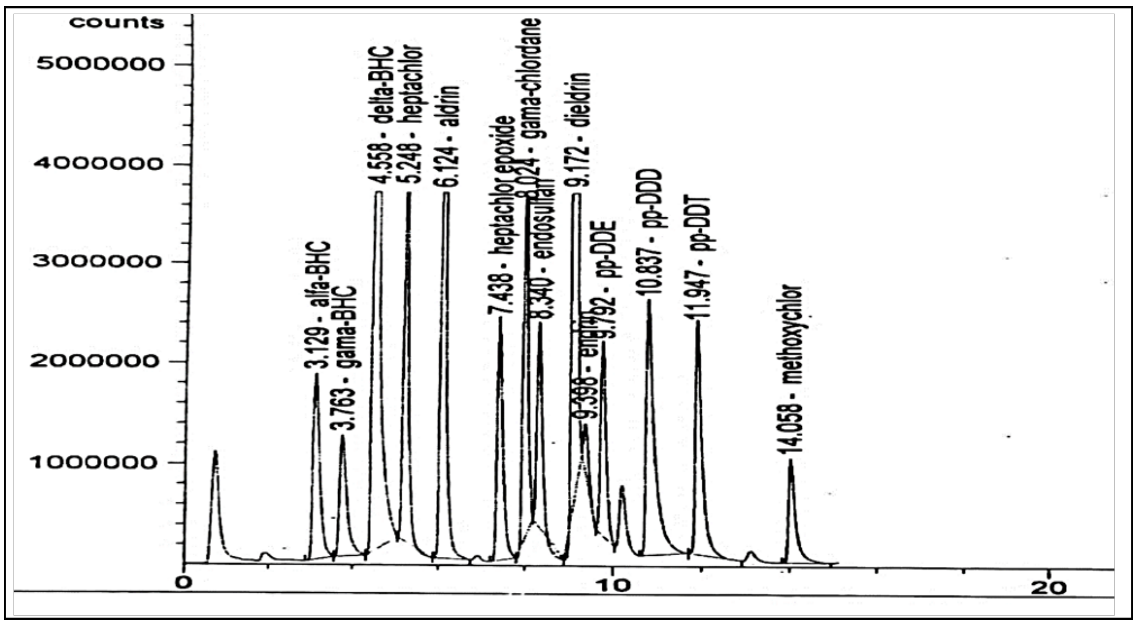

Fig. 1. The standard chromatogram used for detecting OC by GC-ECD (Electron Capture Detectable) in tomato samples.

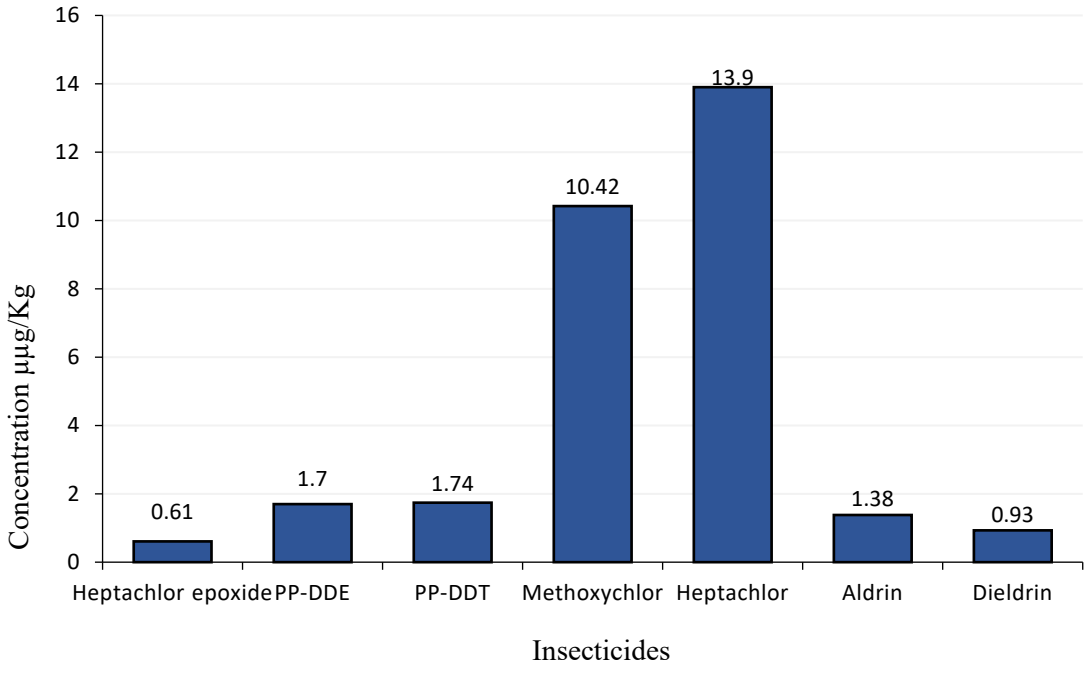

Fig. 2. Total organochlorine insecticide residue levels that detected in tomatoes and collected from different governorates in Upper Egypt markets µg/kg

Result in Fig. (2) shows the heptachlor-epoxide, dieldrin, aldrin, p, p'-DDE, and p, p'-DDT residues were the least determined pesticide residues in all tomato samples, with values of 0.61, 0.93, 1.38, 1.7, and 1.74 µg/Kg for each pesticide residue, respectively. The highest levels of pesticide residue were heptachlor and methoxychlor 13.9 and 10.42 µg/Kg, respectively.

Table 4 displays the pesticide residue estimates for the tomato samples together with the associated health risk score. When the HRI value exceeds 1, it indicates that there may be a health problem for people because the EDI is higher than the ADI values. If the HRI value is less than 1, the ADI is higher than the EDI values and does not pose a threat to human health.

Table 4. Acceptable Daily Intake (ADI), Estimated Daily Intake (EDI), and Health Risk Index (HRI) found in the tomato samples studied.

Insecticides	ADI (µg kg^{-1} b.wt., day^{-1})	EDI (µg kg^{-1} b.wt., day^{-1})	HRI (EDI/ADI)	Health risk
Heptachlor epoxide	0.1	0. 00095	0. 009	No
PP-DDE	10	0.0026	0.0002	No
PP-DDT	10	0.0027	0.0002	No
Methoxychlor	0.1	0.019	0.19	No
Heptachlor	0.1	0.021	0.216	No
Aldrin	0.1	0.00215	0.0215	No
Dieldrin	0.1	0.00144	0.014	No

Detection of OP pesticide residues in tomatoes

As demonstrated in Table (5), tomato samples that obtained from Sohag, New Valley, Minya, and Assiut were devoid of any OP pesticide residues

Table 5. Pesticide residue levels (OP) in tomatoes collected from various markets in Upper Egypt governorates.

Group	Insecticides	Governorate			
		Sohag	**New valley**	**El-Minia**	**Assiut**
OP	Ethoprophos	Undetected	Undetected	Undetected	Undetected
	Phorat				
	Diazinon				
	Dimethoate				
	Pirimiphos methyl				
	Chloropyriphos				
	Fenitrothion				
	Quinaliphos				
	Prothiophos				
	Fenamiphos				
	Ethion				
	Triazophos				

The lowest residual pesticide levels were found in all tomatoes obtained from Sohag, New Valley, Minya, and Assiut markets, all of the samples were below the maximum residue values (MRLs). heptachlor-epoxide, Dieldrin, aldrin, p, p'-DDE,

and p, p'-DDT residues were 0.61, 0.93, 1.38, 1.7, and 1.74 g/kg, respectively. The pesticide residues in heptachlor and methoxychlor are the greatest, at 13.9 and 10.42 g/kg, respectively. On the other side, there are no detectable residues of organophosphorus pesticides in market samples. Ahmed *et al*., (2016) In Egypt, pesticide residues were found in tomatoes from random markets. Plus, organochlorine and pyrethroids pesticide residues were higher levels than MRLs. Nonetheless, heptachlor-epoxide, p, p'-DDE, and profenofos were the most often used pesticides, followed by gamma-HCH and pirimiphos-methyl. Further, Gonzalez *et al.,* (2003) demonstrated that banned pesticides such as DDT, heptachlor and dieldrin were found. The levels of OC pesticides in fruit it was less than MRL as considered by the Codex Alimentarius. Proportions of DDE, DDT and HCH refer to the last inputs of DDT and lindane into the environment. The occurrence of OC on farm study, where agricultural chemicals were never used, is a consequence of the atmospheric deposition of those pesticides (Jallow *et al.*2017).

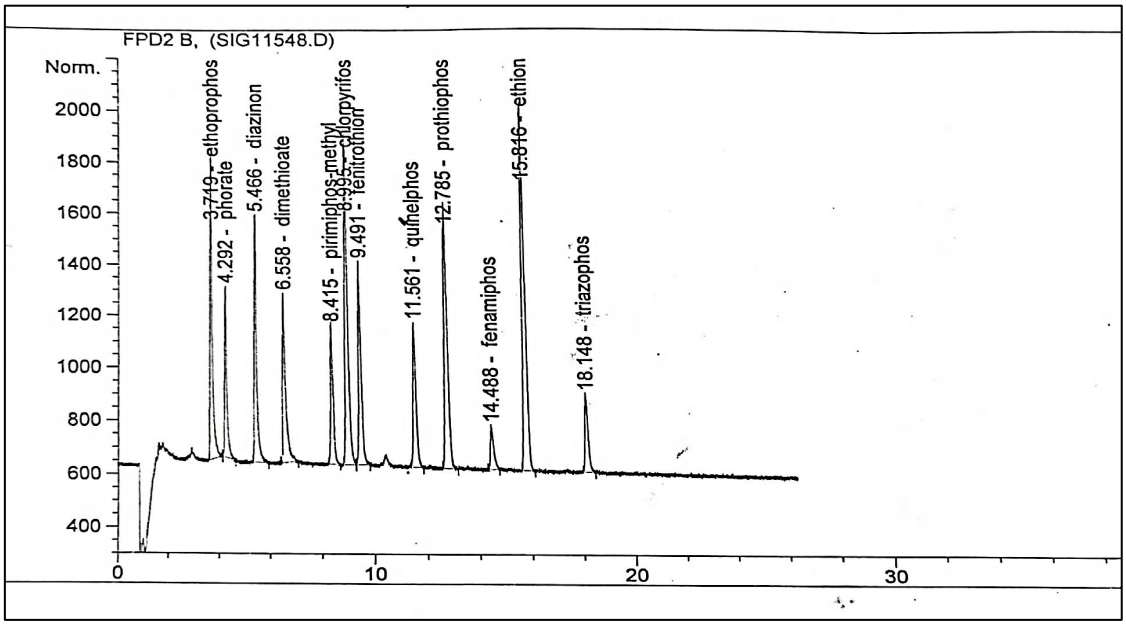

Fig 3. The standard chromatogram used for detecting OP by GC-FPD (Flame Photometric Detector) in tomato samples.

Pesticide residues were measured using gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-tandem mass spectrometry (LC-MS/ MS) in 150 Kuwaiti samples of various vegetables and fruits. Among the pesticides that were tested, 16 pesticides were detected, of which cypermethrin, imidacloprid, malathion, deltamethrin, chlorpyrifos-methyl, monocrotophos diazinon and acetamiprid, were exceeded. Aldrin, an organochlorine insecticide, was found in a single apple sample with amounts that were below the MRL. Bolor *et al* (2018) stated that organic chlorine (OC) residues are found in vegetables, soil and groundwater in Aegia, Ghana. In cabbage, the greatest mean content of 184.10 12.11 µg/Kg methoxychlor was found. Beta-HCH measured the lowest average

content of 0.20 0.00 µg/Kg in cabbage from Ayigya. Cancer risk assessment for aldrin, p, p DDT, and Beta-HCH have been discovered in groundwater >10-6, posing a potentially major carcinogenic risk to consumers.

View aggregate risk index significantly bigger health concerns for children than for adults. Furthermore, the hazard estimates for aldrin were higher than the cut-off value of one, indicating that everyday exposure could be a problem. Bempah *et al*., (2012) reported that organophosphorus pesticide residues were found in 309 samples of fruits and vegetables sold in Ghana's Greater Accra marketplaces between July 2009 and May 2010. Methoxychlor is found in most samples. analyzed, and it exceeded MRLs set by the European Commission. Andarine residues in lettuce and carrots were higher than European Commission MRL, as well as this chlorpyrifos in pineapple.

It is noted that organochlorine insecticides have been banned for 5 decades. However, detecting pesticide residues levels in our study could be explained by the large accumulation of these pesticides in our ecosystem, or these pesticides may be illegally used or deceived. Therefore, based on our recommendation, it is suggested that efforts must be done more thorough investigations to be conducted covering all foodstuffs in Egypt in order to generate reliable data for policy making, develop consumer information laws, and strict the use of some of these pesticides. In this interim, tomatoes collected from the Sohag, New Valley, Minya and Assiut markets recorded the lowest residual levels of pesticides OC (below the MRLs) and no residues of organophosphorus. While heptachlor and methoxychlor detected the highest levels among the pesticide residues detected in the markets of all governorates. The misuse or illegal use of pesticides in the Egyptian market must be avoided. Regular pesticide residue programs must be applied

References

Abd EL-Hamid, R.M. (2013). Effect of formulation type and product source on the residue levels of some pesticides. Ph.D. Thesis, Department of Plant Protection, Faculty of Agriculture, Ain Shams University pp,124.

Ahmed, M.A.I., Abd El Rahman, T.A and Khalid, N.S. (2016). Dietary intake of potential pesticide residues in tomato samples marketed in Egypt. Research Journal of Environmental Toxicology,10 (4): 213-219.

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.

Bempah, C.K., Asomaning, J.K., Ansong, D.A., Boateng, J., and Asabere, S.B. (2012). contamination levels of selected organochlorine and organophosphorus pesticides in Ghanaian fruits and vegetables. Emirates Journal of Food and Agriculture, 24(4): 293-301.

Bempah, C.K., Buah-Kwofie, A., Denutsui, D., Asomaning, J., and Tutu, A.O. (2011). Monitoring of pesticide residues in fruits and vegetables and related health risk assessment in Kumasi Metropolis, Ghana. Research Journal of Environmental and Earth Sciences, 3(6): 761-771.

Bolor, V.K., Boadi, N.O., Borquaye, L.S., and Afful, S. (2018). Human risk assessment of organochlorine pesticide residues in vegetables from Kumasi, Ghana. Journal of Chemistry,1-11.

European Union, (2009). EU pesticides database. Regulation (EC) No 1107/2009. http://ec.europa.eu/food/ plant/pesticides/eu-pesticides-database/public/?event= homepage&language=EN

Gonzalez, M., Miglioranza, K.S., Aizpún de Moreno, J.E., and Moreno, V.J. (2003). Occurrence and distribution of organochlorine pesticides (OCPs) in tomato (*Lycopersicon esculentum*) crops from organic production. Journal of agricultural and food chemistry, 51 (5): 1353-1359.

Jallow, M., Awadh, D., Albaho, M., Devi, V., 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(8): 833.

Osman, K.A., Al-Humaid, A.M., Al-Rehiayani, S.M., and Al-Redhaiman, K.N. (2010). Monitoring of pesticide residues in vegetables marketed in Al-Qassim region, Saudi Arabia. Ecotoxicology and Environmental Safety, 73(6): 1433-1439.

تقدير مستويات امنه لبقايا المبيدات الكلورنية والفسفورية العضوية باستخدام جهاز الكروماتوجرافي الغازي في الطماطم من محافظات مختلفة في صعيد مصر

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الملخص

تم حظر استخدام المبيدات الكلورنية العضوية العالية الثبات وتستخدم على نطاق ضيق ومحدود تحت ظروف خاصة في مكافحة الحشرات النافلة للأمراض في بعض الدول النامية. علي العكس من ذلك تستخدم المبيدات الفوسفورية العضوية على نطاق واسع في مكافحة الآفات الحشرية المختلفة للمحاصيل الزراعية والأعلاف للإنتاج الحيواني. تستخدم المبيدات الحشرية الفسفورية العضوية على نطاق واسع للسيطرة على المبيدات الحشرية التي تحل محل المبيدات الكلورنية العضوية من حين لآخر. بالمقارنة مع مجموعة المبيدات الحشرية الأخرى، فإن المبيدات الفسفورية العضوية لديها مخاطر عالية السمية وتدهور قصير الأجل في البيئة. بالاعتماد على النتائج بجهاز التحليل الكروماتوجرافي الغازي في عينات الطماطم المجهزة بطريقة الكويتشرز وجد ان هبتا كلور - إيبوكسيد، والديلدرين، والألدرين، p,p'-DDE وp,p' -DDT كانت أقل المتبقيات التي تم اكتشافها في جميع عينات الطماطم، كان تواجدها (0.61، 0.93، 1.38، 1.7 و1.74 ميكروجرام / كجم) على التوالي في عينات الطماطم لكل متبقي من مبيدات الآفات. بينما سجلت مبيدات هبتا كلور وميثوكثي كلور أعلى مستويات لمتبقيات المبيدات (13.9 و10.42 ميكروجرام / كجم) على التوالي، كما ان جميع الطماطم التي تم جمعها من سوهاج والوادي الجديد والمنيا وأسيوط كانت خالية من أي متبقيات للمبيدات الحشرية الفوسفورية. ينصح بعمل دراسات تفصيليه مستمرة عن تتبع متبقيات المبيدات الكلور العضوية والفسفور لعضويه في العديد من البيئات خاصه في خضروات وفاكهة المائدة.