J. Plant Prot. and Path., Mansoura Univ., Vol.10 (7): 387 – 390, 2019

Levels of 15 Organochlorine Pesticide in Freshwater during Several Seasons along the Nile River, Egypt

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ABSTRACT

The object of this study was determination of organochlorine pesticide residues in freshwater samples collected along the Nile River at the Rosetta branch at Shubra Khait region El-Behera Governorate and Kufr EL-Zayat region, EL- Gharbia Governorate from two sites in different seasons during 2016-2017. The determination of organochlorine pesticide residues (PP-DDT, endosulfan, endrin, PP-DDD, OP-DDE, OP-DDD, Aldrin, Heptachlor- epoxide, heptachlor, d-HCH, a-HCH, g-HCH, dieldrin, PP-DDE, and methoxychlor) carried out by GC-µECD. The results indicated that the concentrations of pesticide residues monitored was below the permissible limits according to the World Health Organization (2011). Therefore, it is recommended to preserve the water of the Nile River by not dumpling sewage, agricultural and industrial waste without treatment in the Nile water and using pesticides in good way.

INTRODUCTION

Pesticides used in agriculture around the world to improve food production and crop yields, Rashi *et al.* (2012). Organochlorine pesticides (OCPs) are a group of the Persistence of Organic Pesticides (POPs). Organochlorine pesticides have an international measure persistence, and bioaccumulation, which have continuing resides in the environment. Organochlorine pesticides used in controlling pests until the Stockholm convention on persistent organic pollutants (POPs) was applied in 2005, Wittayanan *et al.* (2017).

These compounds arrive to the ecosystem usually by uncaring discarding of empty bottles, washing the equipment, surface runoff, and release from surface pesticides treatments that are hazardous for the safety of human health and environmental management, Wang *et al.* (2008); Lu *et al.* (2011) and Abd El-Gawad (2016). Monitoring of pesticide residues such as Organochlorines is vital features in evaluating harmful ecological influences, probable risks to human healthiness and guide of pesticides acceptable use approving public health necessities, Hrouzková *et al.* (2013) and Omwenga *et al.* (2016). Greatest commonly detected pollutants in surface water were organochlorines Nesser *et al.* (2016). Also, these chemicals generally persist in the environment and transfer from contaminated soil to plants, Taha *et al.* (2013). As of their high perseverance, they can be accrued in the human body by regular consumption of plant crops and drinking water, Dipo *et al.* (1999). Also, High toxicity of OCPS, possess important fears to human health and aquatic organisms, assess the OCPs impact on aquatic ecosystem and human health instantly essential, Bai *et al.* (2018). Kafr El-Zayat district is an agricultural and industrial area, it has a major pesticide factory in Egypt, in addition, there is the company of salt and soda and America, Oil and Soap company also financial company to production superphosphate. In addition to sanitation and agricultural drainage all that consider sources of contamination in Nile River at Rosetta Branche of Kafr EL-Zayat region. The object of the research is to quantitate the residues of organochlorine pesticide in freshwater the Nile River during the four seasons of 2016-2017 in two sites in Kafr EL-Zayat region, EL-Gharbia Governorate and two sites in Shubra Khait region, EL-Beheira Governorate.

MATERIALS AND METHODS

1. Chemicals and reagents

The standards of tested pesticide were purchased from Riedel-de Haen (Seelze, Germany) and Dr. Ehrenstorfer (Augsburg, Germany). Stock solutions of 100 µg/ml for pesticides were prepared individually with acetone, n-hexane and ethyl acetate according to their polarity and solubility. Stock solutions were mixed well and then serially diluted with the appropriate solvent. All standard solutions were stored in the dark at 4ºC.

Organic solvents, (acetone, n-hexane, ethyl acetate and dichloromethane), all residue analysis chemicals were purchased from S.D.S. (France). Anhydrous sodium sulphate was purchased from El-Nasr Pharmaceutical Chemicals Company (Egypt) and before it used, it was activated by heating.

2. Sample collection

Forty-eight water samples (2L) were collected in glass bottles from the water course with 50 cm below water surface level from the selected sites during the four seasons 2016-2017 along the Nile River at Rosetta branches of Kafr- EL-Zayat region, EL-Gharbia Governorate and Shubra Khait region EL-Beheira Governorate. All samples were filtrated through pad of cotton to remove impurities.

3. Extraction procedure.

Liquid-liquid extraction of organochlorine pesticide residues in water samples was carried out using a liter of water sample and it was extracted with 50 ml dichloromethane in a separatory funnel (2-L). The mixture was shaken for 5 min manually, then the lower organic layer was collected. It extracted twice each time with 50 ml dichloromethane. The collective dichloromethane extracts (150 ml organic layer) is separated and filtered through a glass funnel containing 30 g of anhydrous sodium sulphate. The collected organic layer was evaporated to dryness using a rotary evaporator. Then it dissolved into 1 ml n-hexane for GC analysis.

4. Determination using GC-µECD

The gas chromatograph (HP6890) equipped with an auto-sampler (HP7673), a micro electron-capture detector. A 30 m x 0.32 mm capillary column coated with a 0.25 µm thick film of 5% phenylmethyl polysiloxane (HP-5) from Hewlett and Packard was used in combination with the following oven temperature program:

Initial temperature 190 ºC for 5 min, 5 ºC / min up to 220 ºC and held for 5 min, 5 ºC/min up to 240 ºC and held for 5 min, 10 ºC/min up to 260 ºC and held for 5 min, 10 ºC/ min up to 280 ºC and held for 5 min. The carrier gas (N_2) flow rate was 3 ml/min., splitless injection of a 1µl volume was carried out, detector and injector temperatures were 300 ºC and 280 ºC, respectively.

RESULTS AND DISCUSSION

Data is a table (1) showed that, the quantities of OC compounds which found in the samples collected from the Nile river at Kafr El-Zayat region. The existence concentrations of DDT and its isomers were lower than the permissible limit according to WHO (2011) 1 µg/L in all seasons in the first and the second site at Kafr EL-Zayat. Also, the results of Endosulfan with concentration levels were lower than the permissible limit according to WHO (2011) 20 µg/L which were 0.09 µg/L in summer season in the first site and (0.018 and 0.031 µg/L) in summer and autumn seasons in second site while the other seasons summer, autumn, winter in the first site and spring and winter in the second site contain residues below the detection limits. The results showed that all samples were had concentration levels of endrin lower than the permissible limits according to WHO (2011) 0.6 µg/L which were (0.096 and 0.081 /µg/L) in autumn and winter in the first site and (0.089, 0.094, 0.143 and 0.122 µg/L) in spring, summer, autumn and winter in second site at Kafr El –Zayat region. All samples of water had concentrations of aldrin exceeded the permissible limit according to WHO (2011) 0.03 µg/L except the samples which collected during the spring seasons in the first site. The water samples in all seasons except the summer in the first site and the spring and the summer seasons in the second site in Kafr El-Zayat region had concentrations of heptachlor and heptachlor-episode higher than the permissible limit according to WHO (2011) 0.03 µg/L. The HCH and its isomers concentrations in all water samples were lower than the in Kafr EL-Zayat region. All dieldrin concentration levels in all water samples were lower than the acceptable limit according WHO (2011) 0.03 µg/L during all seasons in the first and the second site at Kafr EL-Zayat region. Finally methoxychlor concentrations which detected in all samples were lower than the permissible limit according to WHO (2011) and the samples contained residues of methoxychlor with (0.015, 00.009, and 0.009 µg/L) in spring, summer and autumn, respectively in the first site and (0.021, 0.081 and 0.007 µg/L), respectively in spring autumn and winter in the second site at Kafr EL-Zayat region.

Table 1. Organochlorine residues in water samples collected from Kafr El-Zayat region.

pesticides	MRL (µg/L) WHO (2011)	Pesticide residue amount (Ug/L)							
		First site				Second site			
		Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
pp-DDT	1	ND	0.032	0.276	0.067	ND	0.093	0.117	0.096
Endosulfan	20	0.090	ND	ND	ND	ND	0.018	0.031	ND
Endrin	0.6	ND	ND	0.096	0.081	0.089	0.094	0.143	0.122
pp-DDD	1	0.1	0.090	0.091	0.083	ND	0.094	0.158	0.118
op-DDE	1	0.061	0.093	0.117	0.106	0.055	0.114	0.125	0.150
op-DDD	1	ND	0.051	0.095	0.082	0.029	0.096	0.143	0.121
Aldrine	0.03	0.010	0.077	0.084	0.067	0.095	0.081	0.035	0.104
Heptachlor-epoxide	0.03	0.081	ND	0.092	0.082	0.085	ND	0.124	0.117
Heptachlor	0.03	0.066	0.057	0.097	0.077	ND	0.091	0.163	0.119
d-HCH	0.03	0.0127	0.0210	0.0125	0.0106	ND	0.0121	0.0223	0.0157
a-HCH	0.03	0.005	0.010	0.009	ND	ND	0.006	ND	ND
g-HCH	0.03	0.007	ND	0.009	ND	ND	ND	ND	0.009
Dieldrin	0.03	ND	0.007	ND	ND	ND	0.006	ND	0.009
pp-DDE	1	0.015	0.009	0.009	ND	0.021	ND	0.091	0.007
Methoxychlor	20	ND	0.009	0.005	0.013	0.011	0.008	ND	ND

ND: Not detectable.

Data in the table (2) showed that the existence of organochlorine pesticide residues in different seasons and the quantities of these compound were detected in various amounts depending upon the location of sites and time of collected samples in Rosetta branch along the Nile river at Shubra Khait region. The residues of DDT and its isomers with concentration levels lower than the permissible limit according to WHO (2011) 1 µg/L in all collected samples in the two sites during all seasons. Also, endrin residues in all water samples had concentration levels lower the permissible limits WHO (2011) 0.6 µg/L which were (0.097, 0.095, 0.094 and 0.103 µg/L) in spring, summer, autumn and winter seasons, respectively in the first site and (0.076, 0.089, 0.095 and 0.110 µg/L) in spring, summer, autumn and winter seasons, respectively in the second site at Nile river at Shubra Kahit region. The residues of dieldrin in the water samples were below the detection limit except the samples which collected during the winter season but also these residues below the permissible limit which set according to WHO (2011) 0.03 µg/L. On the other hand concentrations of aldrin detected in all collected samples were lower than the permissible limit according to WHO (2011) 0.03 ug/L except the samples which collected during the winter and the spring in the first site and during the winter in the second site which were (0.038, 0.066 and 0.042 µg/L), respectively. All samples contained residues of heptachlor exceeded the permissible limit of WHO (2011) 0.03 µg/L which were (0.121, 0.135, 0.138 and 0.150 µg/L) in the spring, autumn and winter in the first site and (0.073, 0.095, 0.098 and 0.133 µg/L) in the summer, autumn and winter in the second site Shubra Khait region, also, heptachlor concentrations that detected in the samples were exceeded the permissible limit by WHO (2011) 0.03 µg/L except the samples which

collected during the spring in the first site and the summer in the second site at shubra khite region, HCH and its isomers residues in all samples were lower than the permissible limit WHO (2011) 0.03 µg/L in the first and the second site in shubra Khait region during all seasons. Finally, methoxychlor and endosulfan with the permissible limit 20 µg/L for both compounds, so the samples had concentrations of the both compounds below the permissible limit in the first and the second site in shubra Khait on along Rosetta branch Nile river.

Our results were agreed with Bouraia *et al*. (2011) who investigated the pollution of organochlorine pesticides (OCPs) from the designated sites in EL Rahway area to evaluate the existing station of contamination in groundwater and surface water. He found that groundwater was polluted with OCPs less than surface water, specially endosulfan that was distinguished in the wide range concentration of 0.021 to 0.375 µg/L and 0.083 to 0.823 ug/L through summer and winter seasons, respectively.

Table 2. Organochlorine residues in water samples collected from Shubra Khait region.

pesticides	MRL (µg/L) WHO (2011)	Pesticide residue amount (µg/L)							
		First site				Second site			
		Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
pp-DDT	1	ND	0.051	0.071	0.089	0.046	0.016	0.085	0.110
Endosulfan	20	0.072	0.056	ND	ND	0.053	0.066	ND	ND
Endrin	0.6	0.097	0.095	0.094	0.103	0.076	0.088	0.095	0.110
pp-DDD	1	0.113	0.078	0.107	0.098	0.064	0.111	0.095	0.114
op-DDE	1	0.086	0.012	0.090	0.106	0.094	0.073	0.097	0.099
op-DDD	1	0.031	ND	0.114	0.93	0.079	ND	0.094	0.109
Aldrine	0.03	ND	0.018	0.029	0.038	0.066	ND	0.015	0.042
Heptachlor-epoxide	0.03	0.121	0.135	0.138	0.150	0.073	0.095	0.098	0.133
Heptachlor	0.03	ND	0.091	0.122	0.117	0.073	ND	0.118	0.134
d-HCH	0.03	ND	0.029	0.017	0.02	0.011	0.016	0.012	0.014
a-HCH	0.03	ND	0.004	ND	0.012	0.02	0.009	0.022	ND
g-HCH	0.03	0.005	ND	ND	0.008	ND	ND	ND	0.005
Dieldrin	0.03	ND	ND	ND	ND	ND	ND	ND	0.005
pp-DDE	1	0.007	0.005	ND	ND	0.010	0.009	ND	0.033
Methoxychlor	20	0.005	0.006	0.010	ND	0.005	0.007	ND	ND

ND: Not detectable

The OCP concentrations were exceeded the quality guidelines of Canada for the protection of agriculture water uses (CWQGS) in all water samples.

Also, Behfar *et al.* (2013) determined the levels of organochlorine pesticides residues in the water samples which collected from Karum River at Khuy Zestan area in Iran by gas chromatograph micro electron capture. The highest levels of OCP found in Karum River samples during August to November 2009, it ranged from 71.43 to 89.34 µg/L and the lowest levels were from December 2010 to March 2011 at levels from 22.25 to 22.64 µg/L and the highest and lowest mean concentrations of studied pesticides were endosulfan with 28.5 and and pp-DDT 0.01 µg/L. Also, Modibbo *et al.* (2019) studied the pesticides residue in the water samples collected at the four sampling points in the lake of Njuwa, Adamawa state and detected α-BHC, Endrin, Endosulfan with higher concentration in the surface water which were Endosulfan (0.92 µg/L), Endrin (0.82 µg/L), alpha-BHC (0.57 µg/L). On the other hand, Bai *et al.* (2018) investigated the residues of OCPs along Shaying River in groundwater and surface water, China, at 24 selected sampling sites. The concentration of OCPs were 21.0 - 61.4 ng L^{-1} in groundwater, and 12.3-77.5 ng L^{-1} in surface water.

Fosu-Mensah *et al.,* 2016 determined the residues of organochlorine compounds in drinking water and soils. The residues of lindane were (0.005–0.05 mg/kg), beta-HCH were (<0.01–0.05 mg/kg), dieldrin were (0.005–0.02 mg/kg), and *p,p′*-DDT were (0.005–0.04 mg/kg), with dieldrin occurring commonly in soil samples. Also, the pesticides which detected in the samples of water were lindane, alpha-endosulfan, endosulfan-sulphate, dieldrin and and *p,p′*-DDT and ranged (0.01–0.03 µg/l), (0.01–0.03 µg/l), (0.01–0.04 µg/l), (0.01–0.03 µg/l) (0.01–0.04 µg/l), respectively. while the most occurring pesticide is heptachlor, the organochlorine residues levels were below the MRL of US in soil samples, except for lindane and beta-HCH. While, the organochlorine pesticide residues were below and within the MRLs according to the WHO for drinking water. Alpha-endosulfan, endosulfan-sulfate and heptachlor were above their WHO MRLs. So, these results of OCPs residues in soil and water shows that these chemicals are still being used in this area.

The over dependence of pesticide especially in agriculture has created a serios problem in the environment and the concentration of pesticide residues in the water samples have indicated that the pesticides have been used could result to toxicity at higher level causing an adverse health effect to the general consumer of water in the River Nile.

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مستويات 15 من مبيدات الكلور العضوية في المياه العذبة خلال عدة مواسم على طول نهر النيل ، مصر

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تهدف هذه الدراسة إلى تقدير متبقيات 15 من المبيدات الكلورونية في عينات مياه جمعت من مواقع مختلفة على طول نهر النيل فرع رشيد في منطقة كفر الزيات محافظة الغربية ومنطقة شبراخيت محافظة البحيرة في مواسم مختلفة خلال عامي 2016- 2017 . وتم التقدير باستخدام جهاز الكروماتوجرافي الغازي المزود بكاشف الالتقاط الاليكتروني. اوضحت النتائج ان تركيزات متبقيات المبيدات التى تم رصدها (PP-DDT ، الإندوسلفان ، الإندرين ، PP-DDD، OP-DDE، OP-DDD ، الألدرين ، هيبتاكلور ، هيبتاكلور إيبوكسيد ، ، d-HCH، a-HCH، g-HCH، dieldrin، PP -DDE و methoxychlor) في عينات مياه نهر النيل فرع رشيد من موقعين في منطقة كفر الزيات بمحافظة الغربية ومن موقعين في منطقة شبر اخيت بمحافظة البحيرة أقل من الحدود المسموح بها وفقاً لمنظمة الصحة العالمية (2011). لذلك ننصح بالمحافظة على مياه نهر النيل بعدم إلقاء مخلفات الصرف الصحي والزراعي والصناعي بدون معالجة في مياه النيل بالإضافة إلى ترشيد استخدام المبيدات.