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Persistent Organic Pollutants (POPs) in Egyptian Aquatic Environment

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Abstract: The concentration of organochlorine pesticides (OCPs) and polychlorinated biphenyl (PCBs) in aquatic environment at El Menofiya Governorate were assessed to explore the effect of sampling area and different matrix. Water, sediment and fish samples were collected from El Menofiya, canal water supplies (El Sarsawia, El Bagoria and Bahr Shebin), in addition to El Embaby, El Menofi and Miet Rabiha drainage canals each two month during periods of 16 month, June 2007-Septemper 2008. The samples were analyzed by gas chromatography with electron capture detector (GC-ECD) and confirmed by GC with mass spectrometry. The concentration of pesticides residue in the analysed water samples followed the following descending order p,p'-DDE > p,p'-DDD > endosulfan > endrin > heptachlor epoxide > aldrin > γ-HCH > ß-HCH > γ-chlordane > heptachlor > p,p'-DDT. DDT and its metabolites P,P'-DDD, P,P'-DDE, P,P'-DDT (mean concentrations 29.79, 32.506 and 11.067 ng g^{-1} dry weight) were detect at high levels in sediment sample. The P,P'-DDE residue were the most abundant in fish sample. The highest concentration of total PCBs in water samples was 67.89 ng l^{-1}, while in sediment samples was 108.118 ng g^{-1} dry weight basis. This study provides the first record of residues of PCB congener in the studied area.

Key words: Organochlorine pesticides, Polychlorinated biphenyl, Water supplies, Drainage water, Sediment, Fish.

INTRODUCTION

Egypt is a typical third world country as well as being mainly an agricultural economy. It has relied heavily on pesticides to fight pests harmful, mainly, to cotton, maize, corn, sugarcane and rice as well as many different varieties of vegetable and fruit crops.

The human population is exposed to pesticides both through the drinking water and via the food supply. Attention is usually focused on contamination by OCPs, because of a number of disadvantages including environmental persistence, bioaccumulation and their toxic action upon the nervous systems[1-3]. Furthermore, OCPs may act as environmental oestrogens by disrupting the normal functioning of hormones and may cause breast cancer in humans, posing a significant threat to the ecosystems[4]. The reported major OCPs used in Egypt during a 50-year period were toxaphene (1955-1961), Endrin (1961-1981), DDT (1952-1971) and lindane (1952-1978) the continuous shifting from one compound to another was mainly attributed to the development of resistance of cotton leaf worm[5].

Some developing countries are still using these compounds because of their low coast and versatility in industry, agriculture and public health[6]. Usage of OCPs has been prohibited since 1980 in Egypt by the ministry of agricultural. Although most OCPs are no in longer use, they are still being found as residues and they are occurring in food now as a result of environmental contamination. Medical reports assert that liver and kidney diseases have increased in the past few years in Egypt. However, the widespread use of pesticides during the last twenty years in Egypt has created serious problems following chronic exposure to trace residues.

PCBs represent an important group of POPs, which are believed to be possible carcinogens or mutagens as well as endocrine disruptors[7,8]. PCBs are used in many industrial processes, for example, in dielectric fluids for transformers and capacitors[9]. River run off is thought to be one of the major sources of PCBs to the marine environment. Due to their hydrophobic nature, PCBs have strong affinity for particulate material in aquatic ecosystem. The present work aimed to monitor the residue level of PCBs and OCPs in the aquatic

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environment at Menofiya governorate in Egypt during June 2007 to September 2008.

MATERIAL AND METHODS

Reagent: n-Hexane, acetone and methylene chloride were purchased from Alliance Bio, USA. All solvents were Pesticide Residue (PR) grade (guaranteed for purity by GC-ECD after 300-fold concentration). Florisil, 60-100 mesh, PR grade (Sigma, USA). Florisil was activated in an oven at 130ºC for 24 hours. Prior to actual use in a column, it was cooled in a dessicator and subjected to appropriate deactivation with water (0.5% by weight to Florisil). Sodium sulfate anhydrate were analytical grade, and purchased from El Naser Pharmaceutical Chemical Co., Egypt. Copper granules (20-40 mesh) were obtained from Sigma, USA.

Cleaning of Glassware: Before use all, the glassware was wash with tap water and detergent, hot water, distilled water, and rinsed with acetone then with n-hexane. All glassware used had glass or Teflon stoppers.

Description of Sampling Area: Water, sediment and fish samples were collected each two month, during the period from June 2007 to September 2008 from six sites as shown on the map (Fig. 1). The sampled site for the study was selected in El Menofiya governorate. Samples were taken from El-Sarsawia, El-Bagoria, Bahr Shebin canals, in addition to three drainage canal sites El-Embaby, El-Menofi and Miet Rabiha drain. Three of the study sites are used as water canals with which to irrigate fruit and vegetable gardens. One of this sites (El-Bagoria) are at the inlet of Menof water purification station. Farmer at such sites always uses this water for domestic as well as agricultural purposes. Some fishermen in El Menofiya governorate depend on theses canals for fishing and small-scale fish culture.

Sample Collection:

Water: Water samples (2.5-L) were collected in glass bottles at the water surface and 50 cm below water level from the six different sites each two month during a periods of 16 month, June 2007- September 2008. The bottles were covered with screw caps and the samples were immediately transported to the laboratory for analysis. Water samples were filtered to remove sand and debris.

Sediment: Sediment samples (about 2 kg each) were taken from the same locations and time for water sampling at a depth 5 cm of sediment surface. The water was removed from the sediments by decantation and then transferred to the laboratory. Samples were air dried in dark for 48 hours before analysis.

Fish: Healthy and vigorous fish (*Tilapia Nilotica*) were caught by fishermen about 2-2.5 kg from the different sites at the same times as water and sediment sampling. They were transport without sexing to the laboratory. The soft parts of fish samples be removed and a muscle tissue sample (10 g) was taken from the dorsal muscle in aluminium foil and kept in deep freezer until analysis.

Chemical Analysis:

Extraction:

Water: 1 L of water sample was extracted twice with 60 ml of 15% methylene chloride in n-hexane. The combined extracts were dried over anhydrous sodium sulfate and concentrated to about 1 ml in a rotating evaporator.

Sediment: 50 g of air-dried sediment were weighted, and homogenized in ceramic mortar with 20 g anhydrous sodium sulfate. The homogenized samples were placed in conical flask then orbital shaker was used for shaking samples two hours with 130 ml mixture of 30% acetone in n-hexane as modification instead of n-hexane only to be suitable in sediment extraction then extract was dried through 50 g of anhydrous sodium sulfate. The obtained organic phase was treated with acid activated copper granules to remove sulfur. The extract was evaporated to about 1ml using rotary evaporator.

Fish: 10 g tissue samples were analyzed for PCB congeners and pesticides following well-established techniques[10-12].

Fish sample (10 g of wet weight) was placed in ceramic mortar, anhydrous sodium sulfate (30 g) was added, and the mixture was well homogenized. The mixture was transferred to a pre-cleaned extraction thimble and the dehydrated tissue was extracted with 200 ml of 50% methylene chloride in n-hexane for 8 hours in a Soxhlet apparatus cycling 5-6 times per hour. The extracted solvents were concentrated with rotary evaporator to about 1 ml.

Clean Up: Water, sediment and fish extracts were cleaned and fractionating using 20 g of 0.5% deactivated florisil topped with 1 g anhydrous sodium sulfate in order to avoid ressuspention of the top layer when pouring solvents into the column then the column washed with 50 ml n-hexane, before the sample loaded. The first fraction (F1) eluted by 70 ml of n-hexane contained PCBs congeners. The second fraction (F2) was eluted with 60 ml of 30% methylene chloride in n-hexane which contain HCH, P,P'-DDD and P,P'-DDE.

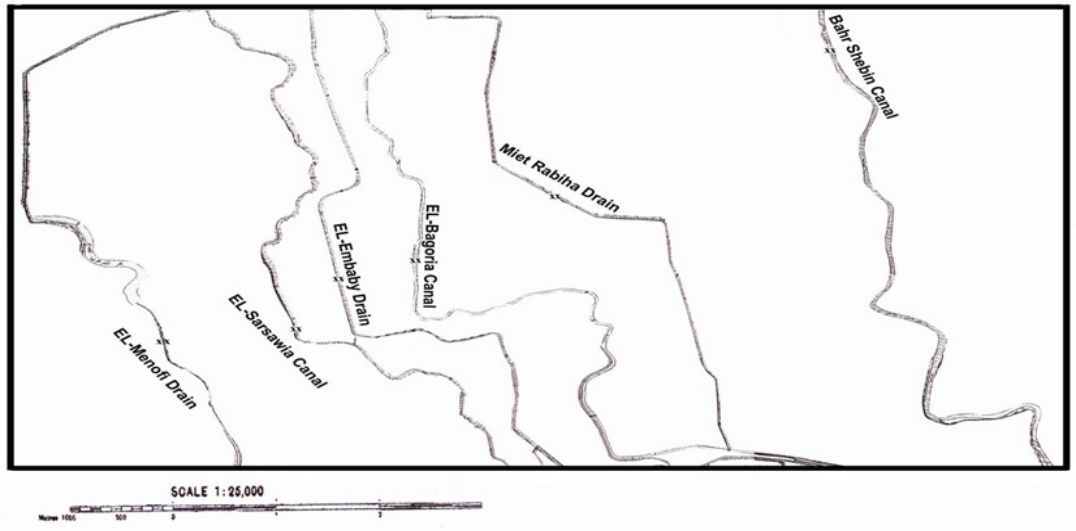

Fig. 1: Location of sampling sites

Then the column eluted with 40ml of methylene chloride (F3) which contain dieldrin and endrin. Each fraction was transferred to rotary vacuum evaporator adjusted at 35ºC and evaporated until the volume reached 2-3 ml. The final extract was transferred quantitatively by rinsing with aliquot of the organic solvent into a concentrator tube and evaporated to dryness. The residue was dissolved in 2 ml of n-hexane and transferred into autosampler vial for GC-ECD.

Preparation of Blank Solution: The same volume of solvents and anhydrous sodium sulfate, which used in extraction of OCPs and PCBs from water, sediment and fish samples were subjected to the same procedures as the examined samples to detect any possible traces of the studies pesticides or PCBs and its value was subtracted from the results.

Quantitative Determination of OCPs and PCBs: The extracts were concentrated and injected into GC (Aglient 6890) equipped with a ^{63}Ni ECD, a split/splitless injection inlet, capillary column capability, and a 7683A autosampler. Chemistation software was used for instrument control. GC analysis was conducted on a HP-5MS (Aglient, Folsom, CA) capillary column of 30 m, 0.25 mm id., 0.25 µm film thickness. The oven temperature was programmed from an initial temperature 160 (2 min hold) to 240 ºC at a rate of 5º C min^{-1} and was maintained at 240 ºC for 20 min. Injector and detector temperature were maintained at 260 and 320 ºC, respectively. Nitrogen was used as a carrier at flow rate of 3 ml min^{-1}.

All OCPs and PCBs congener's reference standards were obtained from Dr.Ehrenstorfer, Augsburg in Germany. Method sensitivity and recovery were determined by using samples spiked with the tested compounds and congeners. Before analysis, relevant standards were run to check column performance, peak height, resolution, and limits of detection. Peak was identified by comparison of sample retention time value with those of the corresponding of pure standard compounds. With each set of samples to be analysed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. The average recovery percentages of OCPs and PCBs for fortified samples at different levels were determined and calculated for all tested compounds in each aquatic system compartment. The average recovery percentages of OCPs and PCBs for fortified samples at different levels were determined and calculated for all tested compounds in each aquatic system compartment. Mean Recovery of organochlorine pollutants were 86.85±5.4, 83.50±5.12 and 84.71±5.68 in water, sediment and fish sample, respectively (Table1).

Confirmation: Selected samples were analysed by full-scan GC-MS to confirm the GC-ECD results. The column used was HP-5MS (Aglient, Folsom, CA) capillary column of 30 m, 0.25 mm id., 0.25 µm film thickness. The carrier gas was helium at a flow rate of 0.5 ml min^{-1}. Inlet temperature was 225ºC with injection volume of 2µl (splitless injector). The column temperature was set at 70ºC for 1min and then programmed at 10ºC min^{-1} to reach 200ºC. GC-MS interface was 280ºC. Chemistation software was used for instrument control and data analysis.

Table 1: Recovery percentage, relative standard deviation and method detection limits.

Pesticide	Water			Sediment			Fish		
	Recovery	RSD (%)	LD (ng l^{-1})	Recovery	RSD (%)	LD (ng g^{-1})	Recovery	RSD (%)	LD(ng g^{-1})
α-HCH	88	7	0.05	83	8	0.05	89	8	0.03
ß-HCH	81	8	0.04	80	4	0.05	82	5	0.03
γ-HCH	86	5	0.05	83	10	0.05	80	13	0.05
ə -HCH	85	7	0.02	84	12	0.05	85	4	0.06
Heptachlor	87	9	0.01	84	6	0.06	85	6	0.07
Aldrin	83	7	0.06	86	11	0.03	84	9	0.06
Heptachlor epoxide	79	10	0.03	78	8	0.04	79	4	0.03
γ-chlordane	91	6	0.03	80	10	0.02	81	7	0.02
Endosulfane	87	6	0.03	81	3	0.02	83	7	0.07
Dieldrin	89	5	0.03	80	12	0.02	79	5	0.02
P,P'-DDE	78	8	0.02	76	4	0.01	78	5	0.06
Endrin	93	3	0.01	95	8	0.05	94	9	0.02
P,P'-DDD	92	4	0.01	89	7	0.02	92	11	0.02
P,P'-DDT	97	5	0.01	90	5	0.02	95	8	0.03

RESULTS AND DISCUSSION

In spite of use of all OCPs has been prohibitated in Egypt in 1980s; many OCPs and their degradation products were detected at certain levels in water, sediment and fish samples[13-15]. In Egypt there are no regular monitoring programmes concerning the identification and determination of different pesticides in the environment. A few studies were carried out to measure the concentration of OCPs in the aquatic environment.

The level of OCPs residues in water samples are shown in Table (2). The highest average amounts of extractable ß-HCH, heptachlor epoxide and endrin were 1.668, 2.098 and 4.66 ng l^{-1}, respectively in water samples from El-Sarsawia canal. The highest average amounts of aldrin and endosulfan were 2.149 and 5.746 ng l^{-1}, respectively, which were found in El-Embaby drain. In addition, the highest average amount of γ-HCH (1.815 ng l^{-1}), heptachlor (1.232 ng l^{-1}), dieldrin (1.199 ng l^{-1}) and γ-chlordane (1.569 ng l^{-1}) were found in water sample taken from El-Menofi drain, El-Embaby drain, Bahr Shebin canal and Miet Rabiha drain, respectively. The highest average amount of DDT and its metabolites p,p'-DDE (15.106 ng l^{-1}), p,p'-DDD (8.150 ng l^{-1}) were found in El-Menofi drain and p,p'-DDT (0.894 ng l^{-1}) was found in Miet Rabiha drain, respectively, in water sample (Fig 2-A). α-HCH was not found in any water sample analysed. The data showed that the concentration of pesticides residue in the analysed samples followed the following descending order p,p'-DDE > p,p'-DDD > endosulfan > endrin > heptachlor epoxide > aldrin > γ-HCH > ß-HCH > γ-chlordane > heptachlor > p,p'-DDT.

In water samples Table (2) it was notable that the residue of organochlorine pesticide varied between different locations, e.g., OCPs residue level (especially Aldrin, Endrin, Dieldrin, Heptachlor, Heptachlor epoxide, Endosulfan, p,p'-DDE, p,p'-DDD, p,p'-DDT) detected in the drainage canals water were the highest residues values, while the drainage water has been exposed to much industrial and sewage pollution. Table (2) confirms the presences of OCPs in the water canals (El-Sarsawia, El-Bagoria and Bahr Shebin) with low concentration that must directed our attention to stop discharging the waste into the water supplies. Toxic substances, which occur at such low concentrations in water at to pose no threat through direct toxicity, may, if absorbed, be accumulated in food chains, affect aquatic organisms, and their predators[16]. Numerous investigators have reported the occurrence of OCPS in water. The levels of some OCPs in the aquatic environment of the drainage canal surrounding a pesticide factory at Damietta Governorate were studied[17]. Residue of BHC, lindane, endrine, DDT and its analogues were detected in all water samples. Also, the occurrence of OCPs residues were reported in water sample collected from El-Haram Giza, canal

Table 2: Concentration (ng L^{-1}) of organochlorine pesticides in water samples

Pesticides Name	El-Sarsawia canal		El-Bagoria canal		Bahr Shebin canal		El-Embaby drain		El- Menofi drain		Meit-Rabiha drain	
	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)
α-HCH	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
ß-HCH	ND-1.668 1.66	12.5	ND	0.0	ND-0.571 0.571	12.5	ND	0.0	ND	0.0	ND-0.910 0.515	25
γ-HCH	ND	0.0	ND	0.0	ND-1.152 0.736	25	ND	0.0	ND-1.815 1.815	12.5	ND	0.0
ə -HCH	ND-0.242 0.242	12.5	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
Heptachlor	ND-0.536 0.392	25	ND-0.592 0.592	12.5	ND	0.0	ND-1.232 1.232	12.5	ND-0.951 0.720	25	ND-0.682 0.673	25
Heptachlor epoxide	ND-2.835 2.098	37.5	ND-2.721 1.81	37.5	ND	0.0	ND-2.084 2.084	12.5	ND-1.510 0.855	25	ND-1.021 1.021	12.5
γ-chlordane	ND	0.0	ND	0.0	ND-0.515 0.515	12.5	ND	0.0	ND	0.0	ND-1.569 1.569	12.5
Aldrin	ND-0.359 0.231	12.5	ND-2.089 2.089	12.5	ND-1.240 0.884	37.5	ND-3.342 2.149	37.5	ND-1.625 1.123	37.5	ND-1.890 1.890	12.5
Endrin	ND-11.68 4.66	50	ND-4.657 2.528	37.5	ND-0.794 1.854	37.5	ND-5.744 2.839	62.5	ND-4.282 1.136	62.5	ND-5.360 2.156	62.5
Dieldrin	ND	0.0	ND-0.465 0.369	37.5	ND-1.920 1.199	25	ND-1.042 0.836	25	ND-0.120 0.114	25	ND-0.111 0.111	12.5
Endosulfane	ND-1.325 1.32	12.5	ND-0.936 0.785	12.5	ND	0.0	ND-12.790 5.746	37.5	ND-3.703 2.234	37.5	ND-2.466 2.466	12.5
P,P'-DDD	ND-0.948 0.638	37.5	ND-0.393 0.254	12.5	ND	0.0	ND-2.349 1.466	37.5	ND-11.15 8.150	37.5	ND-3.736 2.069	25
P,P'-DDE	ND-18.74 1.79	62.5	ND-2.988 1.855	12.5	ND-2.618 1.471	50	ND-1.042 0.640	37.5	ND-29.80 15.106	50	ND-7.393 2.597	50
P,P'-DDT	ND-0.892 0.533	12.5	ND	37.5	ND-0.206 0.174	25	ND-0.297 0.227	37.5	ND-1.214 0.733	25	ND-1.214 0.894	25

n: number of sample.
Nd: Not Detectable

water supplies (El-Zomor, Abd-el-all land, Seaside and El-Mansorya), in addition to El-Moheat drainage water[14]. Sixteen OCPs were detected in most of the water samples and the percent of positive samples followed the order drins > total BHC >total DDT > endosulfan > heptachlor epoxide > heptachlor.

The residue levels of OCPs in sediment samples collected from different location are presented in Table (3). The highest average concentration of extractable α-HCH (21.234 ng g^{-1} dry weight basis) was found in sediment sample of El-Bagoria canal. The highest average residue level of ß-HCH (7.815 ng g^{-1} dry weight basis) was found in El-Embaby drain. In addition, the highest amount of extractable γ-HCH (57.471 ng g^{-1} dry weight mean in El Menofi drain), δ-HCH (27.08 ng g^{-1} dry weight mean in Miet-Rabiha drain), heptachlor (16.56 ng g^{-1} dry weight mean in El-Menofi drain), heptachlor epoxide (66.010 ng g^{-1} dry weight mean in Miet-Rabiha drain) and Endosulfane (32.942 ng g^{-1} dry weight mean in El-Menofi drain) were detected in sediment samples. DDT and its metabolites P,P'-DDD, P,P'-DDE, P,P'-DDT (mean concentrations 29.79, 32.506 and 11.067 ng g^{-1} dry weight, respectively, in El-Menofi drain) were detect at high levels in sediment sample (Fig 2-B). Metabolic transformation of DDT under oxidative conditions leads to P,P'-DDE, whereas under anaerobic conditions P,P'-DDD is formed.

Sediment samples had higher concentrations of pesticide residues than water and fish samples. This trend reflects its great capacity to adsorb and accumulate such pollutants[18]. In addition, the concentration of OCPs are unlikely to occur in large quantities in water because they are relatively insoluble[19]. On the other hand, Fay and Newland reported that no such relationship existed between the insecticide present in water and those in the sediments[20]. Variation in the value of the pesticide concentrations in sediment sample reflects the effects of the ongoing processes of adsorption-desorption and uptake by living organisms.

The detection of OCPs in ecosystem is higher in the developing countries than in more developed ones. In Benin, the sediment samples collected from Queme River were contaminated by a variety of persistent OCPs and in several cases, pesticides concentration exceeded sediment quality guidelines[21]. In addition, DDT and its metabolites were detected at higher concentration in the sediment collected from Msimbazi River in Tanzania[22]. γ-HCH was found in higher concentration in the sediment sample collected from Sabaki River in Kenya[23].

Table 3: Concentration (ng g^{-1} dry weight) of organochlorine pesticides in sediment samples

Pesticides Name	El-Sarsawia canal		El-Bagoria canal		Bahr Shebin canal		El-Embaby drain		El- Menofi drain		Meit-Rabiha drain	
	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)
α-HCH	ND	0.0	ND-39.608 21.234	25	ND	0.0	ND	0.0	ND	0.0	ND	0.0
ß-HCH	ND-3.041 1.518	37.5	ND	0.0	ND	0.0	ND-10.419 7.815	25	ND	0.0	ND	0.0
γ-HCH	ND-0.327 0.274	25	ND-31.16 14.682	37.5	ND-32.14 19.053	37.5	ND	0.0	ND-125.1 57.471	37.5	ND-34.3 27.505	25
ə -HCH	ND-0.213 0.177	25	ND-0.846 0.491	37.5	ND-4.510 6.431	37.5	ND-0.404 0.299	25	ND	0.0	ND-29.27 27.08	25
Heptachlor	ND-0.562 0.280	37.5	ND1.863 1.863	12.5	ND-1.508 1.081	25	ND-11.021 5.611	25	ND-20.07 16.56	25	ND	0.0
Heptachlor epoxide	ND	0.0	ND-31.71 28.75	25	ND-3.471 2.185	50	ND-13.051 4.261	50	ND-64.5 54.47	37.5	ND-128.9 66.010	25
γ-chlordane	ND-0.309 0.209	25	ND	0.0	ND	0.0	ND	0.0	ND-0.451 0.383	25	ND	0.0
Aldrin	ND-0.624 0.294	37.5	ND-50.291 10.303	62.5	0.134-36.69 4.953	100	ND-40.44 10.33	50	ND-49.7 22.697	62.5	0.28-123.9 24.803	100
Endrin	ND-2.820 1.565	50	ND-19.512 4.451	62.5	ND-2.682 1.461	75	0.110-2.983 1.017	100	ND-86 52.02	62.5	ND-19.40 18.06	25
Dieldrin	ND	0.0	ND	0.0	ND-2.780 2.60	25	ND-24.497 8.474	37.5	ND	0.0	1.36325	ND-2.613
Endosulfane	ND-14.631 9.312	37.5	ND-1.183 0.927	62.5	ND-14.75 5.381	37.5	ND-34.40 23.75	25	ND-53.5 32.942	50	ND-25.832 9.706	37.5
P,P'-DDD	ND-3.554 1.985	37.5	ND-8.411 3.420	37.5	ND-8.696 3.103	62.5	ND-0.860 0.624	37.5	ND-52.1 29.79	37.5	0.152-32.39 5.129	100
P,P'-DDE	ND-1.749 0.592	62.5	ND-3.121 1.057	75	ND-22.23 4.052	75	0.105-53.8 11.963	100	ND-62.1 32.506	62.5	0.128-18.10 3.128	100
P,P'-DDT	0.184-4.78 1.924	100	0.142-4.473 1.535	87.5	ND-5.662 1.968	75	1.446-0.225 0.857	100	ND-22.74 11.067	62.5	ND-7.354 2.54	100

n: number of sample.
Nd: Not Detectable

Levels of OCPs residues in ng g^{-1} fresh fish weight and their frequency of detection in fish are presented in Table (4). The P,P'-DDE residues were the most abundant residues in fish, and were detected in most samples at relatively higher concentration compared to other residues. The highest average concentration of P,P'-DDE was found in fish samples from El-Bagoria canal (5.957 ng g^{-1} fresh weight) (Fig 2-C). α-HCH residues were only found in fish samples from El-Sarsawia canal and El-Embaby drain at the average concentration of 0.837 and 2.404 ng g^{-1} fresh weight, respectively. ß -HCH was not found in any fish sample analysed. The highest average concentration of heptachlor (2.88 ng g^{-1} fresh weight), heptachlor epoxide (4.541 ng g^{-1} fresh weight), aldrin (1.122 ng g^{-1} fresh weight), endrin (1.75 ng g^{-1} fresh weight), dieldrin (2.123 ng g^{-1} fresh weight), endosulfane (3.836 ng g^{-1} fresh weight) and γ-chlordane (1.650 ng g^{-1} fresh weight) were found in fish from Miet Rabiha drain, Miet Rabiha drain, El-Bagoria canal, El-Embaby drain, El-Bagoria canal, El-Embaby drain and El-Bagoria canal, respectively. The distribution of organochlorine pesticides in the Egyptian aquatic ecosystem (El Malk El Saleh and Manzala Lake) were studied[24]. Data showed that the total DDT followed by heptachlor were predominant in fish sample collected from the River Nile and the same organochlorine were found in water sample collected from Manzala Lake and River Nile.

The minimum, maximum, average concentration and frequency of PCB residues (8, 18, 28, 52, 44, 70, 101, 152, 118, 105, 138, 180, 192 and 194) are summarized in Tables 5, 6 and 7. Total PCBs was defined as the sum of the 14 PCB congeners. Because PCBs component have different structures, each component has its own physical and chemical properties, resulting in differences in marine environment processes. The data in Table (5) showed that most of PCB congeners were detected in water samples, except for PCB congeners no 8, 192 and 194. The highest concentration of total PCBs in water samples was 67.89 ng l^{-1}, which was found in Bahr Shebin canal. Among the congeners, PCB no 44 and 152 represented the most abundant congeners in water samples. Table (6) showed that, most of PCB congeners were detected in sediment samples, except for PCB congener no 8. The highest concentration of total PCBs in sediment samples was 108.118 ng g^{-1} dry weight basis, which was found in El-Embaby drain. Among the congeners, PCB no 44 and 152 represented the most abundant congeners in sediment samples. In

Table 4: Concentration (ng g^{-1} fresh weight) of organochlorine pesticides in fish samples

Pesticides Name	El-Sarsawia canal		El-Bagoria canal		Bahr Shebin canal		El-Embaby drain		El- Menofi drain		Meit-Rabiha drain	
	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)
α-HCH	ND -1.35 0.837	37.5	ND	0.0	ND	0.0	ND -6.8 2.404	37.5	ND	0.0	ND	0.0
ß-HCH	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
γ-HCH	ND	0.0	ND -2.714 1.435	25	ND -0.530 0.393	37.5	ND	0.0	ND -1.31 0.470	50	ND -6.12 3.55	37.5
ə -HCH	ND -0.97 0.31	25	Nd-1.348 0.814	25	ND -0.80 0.74	25	ND -5.06 2.463	37.5	ND -1.5 0.607	37.5	ND -3.4 1.610	37.5
Heptachlor	ND -1.22 0.485	62.5	ND -1.992 0.895	75	ND -0.75 0.39	37.5	ND -2.614 1.938	62.5	ND -.899 0.539	50	Nd-3.91 2.88	37.5
Heptachlor epoxide	ND -1.32 1.015	25	ND -0.502 0.310	37.5	ND -0.592 0.592	12.5	ND -3.76 2.395	25	ND -0.901 0.792	50	ND -6.64 4.541	75
γ-chlordane	ND -0.51 0.358	50	ND -2.266 1.650	37.5	ND -0.954 0.54	25	ND -0.63 0.485	50	ND -0.703 0.430	50	ND -1.486 0.870	37.5
Aldrin	ND -0.928 0.481	50	ND -2.287 1.122	37.5	Nd	0.0	ND -1.62 0.943	37.5	ND	0.0	ND -0.517 0.284	37.5
Endrin	Nd	0.0	ND -2.08 1.47	50	ND	0.0	ND -2.24 1.75	25	ND	0.0	ND	0.0
Dieldrin	ND -1.26 0.723	62.5	ND -3.16 2.123	62.5	ND	0.0	ND -2.44 1.631	87.5	ND -1.7 1.453	25	ND -2.95 1.707	50
Endosulfane	ND -5.77 2.655	75	Nd-7.04 2.907	87.5	ND -2.212 2.13	25	ND -15.44 3.836	75	ND -1.33 0.576	50	ND -5.04 1.785	50
P,P'-DDD	ND -2.18 1.85	37.5	ND -5.06 2.184	87.5	Nd	0.0	ND -4.9 1.237	87.5	ND -9.4 3.263	37.5	ND -6.4 2.621	50
P,P'-DDE	ND -4.3 2.394	62.5	ND -15 5.957	87.5	0.221-4.80 2.437	100	0.12-12 3.99	100	ND -5.6 3.66	100	ND -6.64 3.092	87.5
P,P'-DDT	ND -0.27 0.214	50	ND -1.462 1.016	62.5	ND	0.0	ND -0.762 0.344	62.5	ND -0.413 0.231	37.5	ND -0.72 0.387	37.5

n: number of sample.
Nd: Not Detectable

Table 5: Concentration ranges (ng L^{-1}) of PCB congeners in water samples

PCBs IUPAC Nos.	El-Sarsawia canal		El-Bagoria canal		Bahr Shebin canal		El-Embaby drain		El- Menofi drain		Meit-Rabiha drain	
	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)
8	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
18	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND-18.62 9.704	25
28	ND	0.0	ND	0.0	ND-23.104 23.104	12.5	ND-2.4 1.697	25	ND-28.1 28.1	12.5	ND	0.0
52	ND	0.0	ND	0.0	ND-23.01 14.33	25	ND	0.0	ND	0.0	ND	0.0
44	ND-0.455 0.455	12.5	ND-0.798 0.798	12.5	ND-9.652 3.662	37.5	ND-0.763 0.608	25	ND-8.108 4.297	25	ND-0.315 0.315	12.5
70	ND	0.0	ND-1.339 1.339	12.5	ND	0.0	ND-1.315 1.315	12.5	ND	0.0	ND	0.0
101	ND-0.447 0.261	37.5	ND-0.520 0.520	12.5	ND	0.0	ND	0.0	ND	0.0	ND	0.0
152	ND-2.495 1.299	25	ND-0.335 0.335	12.5	ND-0.240 0.240	12.5	ND-1.640 0.944	25	ND-684 0.502	25	ND-26.48 8.966	37.5
118	ND-0.301 0.301	12.5	ND	0.0	ND-2.1 2.1	12.5	ND-1.9*31 1.931	12.5	ND	0.0	ND	0.0
105	ND-0.977 0.977	12.5	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
138	ND-1.76 1.181	25	ND	0.0	ND-2.7 2.7	12.5	ND-1.048 1.048	12.5	ND-0.14 0.14	12.5	ND-1.20 1.20	12.5
180	ND	0.0	ND-4.01 1.858	37.5	ND-1.1 1.1	12.5	ND	0.0	ND-0.20 0.20	12.5	ND	0.0
192	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
194	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
Total PCBs	7.478		6.036		67.89		10.77		38.03		47.03	

n: number of sample.
Nd: Not Detectable

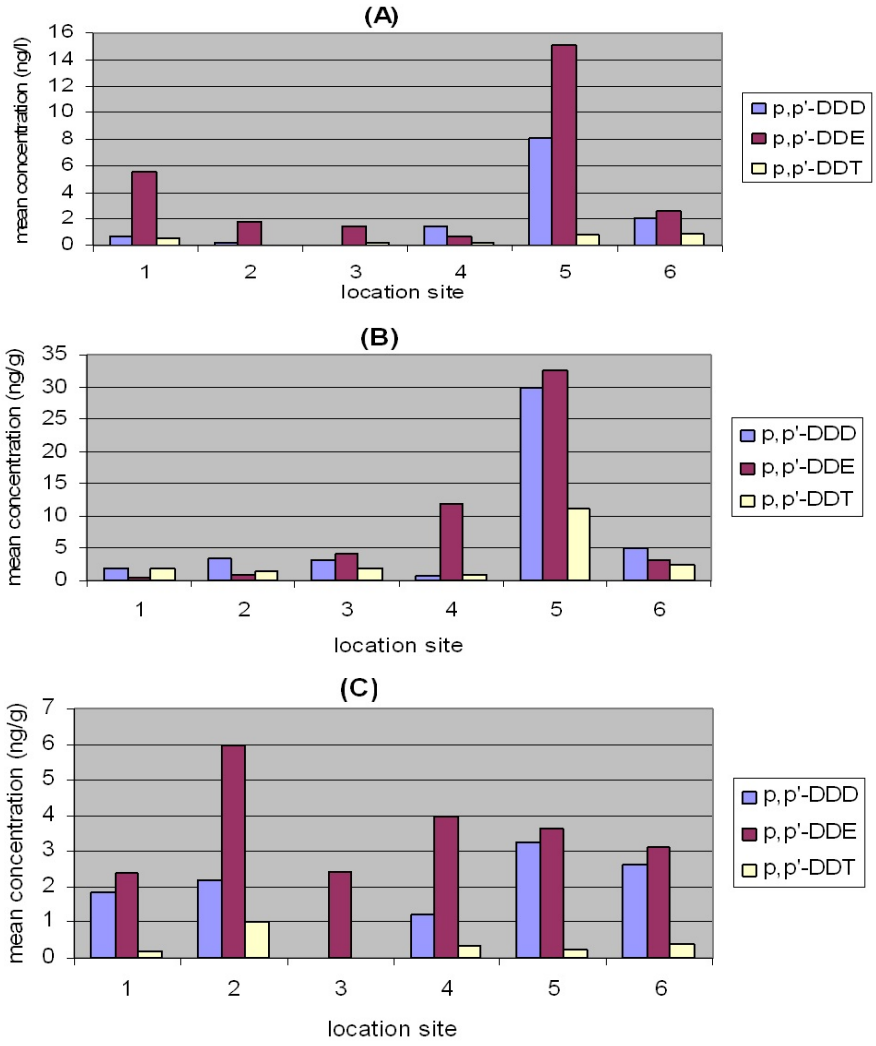

Fig. 2: (A) concentration level of p,p'-DDD, p,p'-DDE and p,p'-DDT in water, (B) concentration level of p,p'-DDD, p,p'-DDE and p,p'-DDT in sediment, (C) concentration level of p,p'-DDD, p,p'-DDE and p,p'-DDT in fish. 1: El-Sarsawia canal; 2: El-Bagoria canal; 3: Bahr Shebin canal; 4: El-Embaby drain; 5: El-Menofi drain; 6: Miet-Rabiha drain

this cocern, the PCB concentrations in the sediments sample collected from Alexandria Harbor, Egypt ranged from 0.9 to 1210 ng g^{-1} dry weight with a median level of 260 ng g^{-1} dry weight basis[9]. The current results indicated that the concentrations of PCBs reported herein were markedly lower than those reported by in Alexandria Harbor.

The results for the concentration levels of the investigated PCB congeners in fish samples in ng g^{-1} on fresh weight basis are depicted in Table (7). These results indicated the presence of PCBs congeners' no. 70, 101, 118, 44, 52 and 180 in fish samples from all different locations. Also, the result illustrated that the most abundant PCBs congeners in fish samples was PCB congener no. 70 which represented 62.5, 87.5, 37.5, 50, 50 and 25% in sample collected from El-Sarsawia canal, El-Bagoria canal, Bahr Shebin canal, El-Embaby drain, El-Menofi drain and Miet Rabiha drain, respectively (Fig 3).

Pollution Levels: The Philippines maximum permissible limit as set for water quality criteria for toxic and deleterious substance in surface fresh water for total DDT, dieldrin and γ-HCH are 50000, 1000 and 4000 ngl^{-1}, respectively[25]. The mean values of DDT, dieldrin and γ-HCH found by this study were therefore below the Philippines limits.

The limits set by EU for drinking water are 100 and 500 ngl^{-1} for individual compounds and total compounds, respectively, for all pesticides[26]. The MRL recommended by WHO for DDT and HCH residues is 1000 ngl^{-1} while for dieldrin is 30 ngl^{-1}[27].

The maximum permissible levels of organochlorine pollutants in fish recommended by the National

Table 6: Concentration ranges (ng g^{-1} dry weight) of PCB congeners in sediment samples

PCBs IUPAC Nos.	El-Sarsawia canal		El-Bagoria canal		Bahr Shebin canal		El-Embaby drain		El- Menofi drain		Meit-Rabiha drain	
	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)
8	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
18	ND	0.0	ND	0.0	ND	0.0	ND-4.014 4.014	12.5	ND	0.0	ND	0.0
28	ND-1.594 1.521	12.5	ND	0.0	ND	0.0	ND-6.710 6.710	12.5	ND	0.0	ND	0.0
52	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND-8.184 8.184	12.5
44	ND-5.981 4.940	25	ND-5.730 3.025	50	ND-5.238 5.238	12.5	ND-9.612 4.569	62.5	ND-8 4.364	50	ND-5.158 3.144	25
70	ND-1.804 1.804	12.5	ND	0.0	ND	0.0	ND-1.75 1.75	12.5	ND	0.0	ND	0.0
101	ND-1.052 1.052	12.5	ND-1.316 1.316	12.5	ND-1.208 1.208	12.5	ND-5.367 4.987	25	ND	0.0	ND	0.0
152	ND-7.730 4.722	37.5	ND-5.41 4.423	50	ND-7.016 4.027	37.5	ND-6.632 3.598	62.5	ND-6.005 4.687	25	ND-5.03 4.65	37.5
118	ND	0.0	ND	0.0	ND	0.0	ND-8.830 4.041	50	ND	0.0	ND	0.0
105	ND-1.70 1.70	12.5	ND-6.340 6.340	12.5	ND-3.419 3.149	12.5	ND-5.04 5.04	12.5	ND-1.656 1.656	12.5	ND-3.859 3.859	12.5
138	ND-1.062 1.062	12.5	ND	0.0	ND-6.896 6.896	12.5	ND-3.609 2.05	37.5	ND	0.0	ND-7.952 5.044	25
180	ND-2.281 2.281	12.5	ND	0.0	ND-4.828 4.828	12.5	ND-2.104 1.912	25	ND	0.0	ND	0.0
192	ND-1.645 1.645	12.5	ND	0.0	ND	0.0	ND-2.630 2.135	25	ND	0.0	ND	0.0
194	ND-5.964 5.964	12.5	ND	0.0	ND-4.864 4.864	12.5	ND-4.730 4.692	25	ND	0.0	ND-9.654 9.654	12.5
Total PCBs	42.638		37.451		38.536		108.118		28.49		51.474	

n: number of sample.
Nd: Not Detectable

Table 7: Concentration ranges (ng g^{-1} fresh weight) of PCB congeners in fish samples

PCBs IUPAC Nos.	El-Sarsawia canal		El-Bagoria canal		Bahr Shebin canal		El-Embaby drain		El- Menofi drain		Meit-Rabiha drain	
	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)	Min-Max Mean n=8	Frequency (%)
8	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
18	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
28	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
52	ND	0.0	ND-3.906 2.966	25	ND	0.0	ND-5.069 5.069	12.5	ND	0.0	ND-6.245 3.20	25
44	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND-24 10.45	50	ND	0.0
70	ND-25.8 8.53	62.5	ND-12.35 6.184	87.5	ND-5.06 3.67	37.5	ND-7.643 3.667	50	ND-6.26 4.385	50	ND-5.67 3.385	25
101	ND-2.718 1.583	37.5	ND-9.62 4.064	62.5	ND	0.0	ND-2.304 1.462	37.5	ND-3.108 2.402	25	ND-5.86 4.2	25
152	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND-0.696 0.43	25	ND-0.710 0.412	25
118	ND-5.959 5.267	25	ND	0.0	ND	0.0	ND-8.433 8.433	12.5	ND-2.76 2.385	25	ND	0.0
105	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
138	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
180	ND-2.888 2.888	12.5	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
192	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
194	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0	ND	0.0
Total PCBs	60.71		69.367		11.036		32.501		69.914		22.59	

n: number of sample.
Nd: Not Detectable

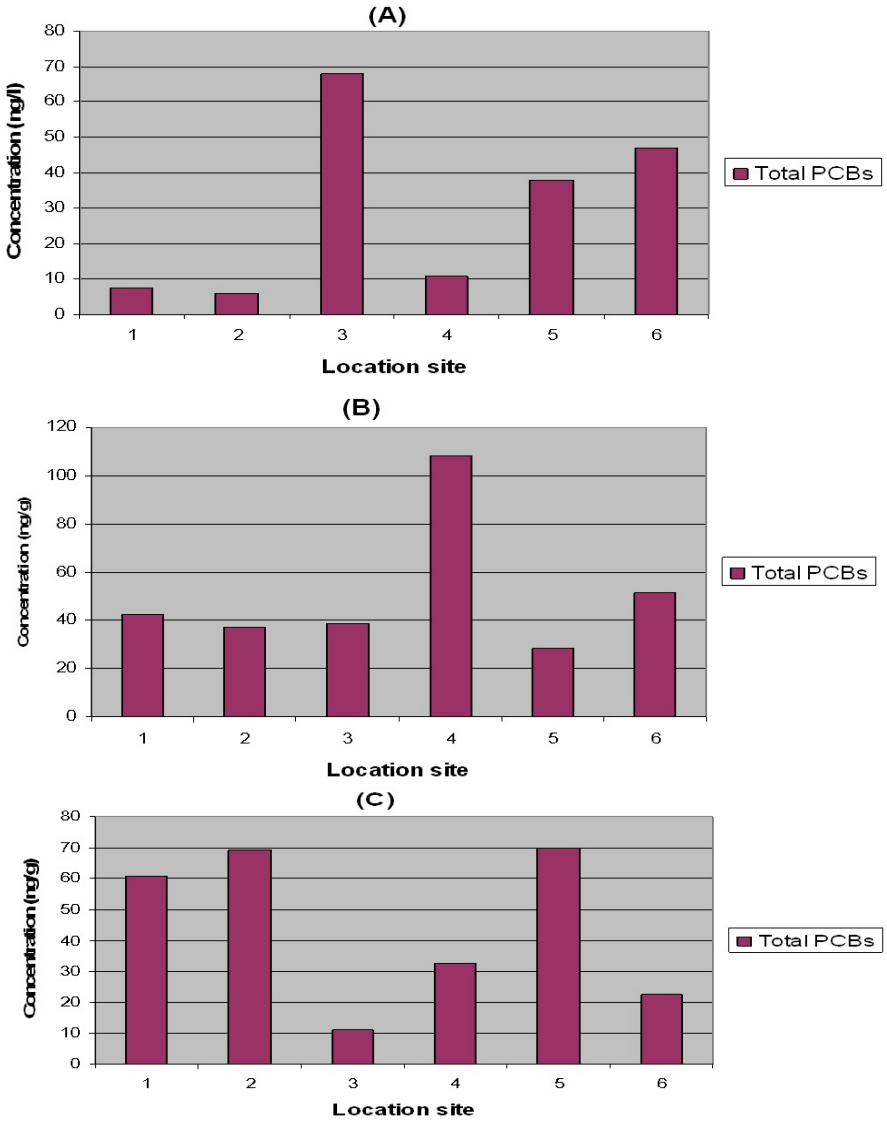

Fig. 3: (A) Concentration level of total PCBs in water, (B) Concentration level of total PCBs in sediment, (C) concentration level of total PCBs in fish. 1: El-Sarsawia canal; 2: El-Bagoria canal; 3: Bahr Shebin canal; 4: El-Embaby drain; 5: El-Menofi drain; 6: Miet-Rabiha drain.

Academy of Sciences and National Academy of Engineering[28] 1000-500 ngg^{-1} for PCBs and 100 ngg^{-1} for cyclodienes (all as weight concentration in whole body tissue). FAO/WHO maximum acceptable limits of total DDT in fish and sea food are 200 ngg^{-1} fresh weight[29] and Canadian maximum allowable limit in fish is 500 ngg^{-1}[30]. The recommended levels by Swedish Food Regulation are 5000 ngg^{-1} for DDTs, 2000 ngg^{-1} for PCBs[31]. The tolerance limit set by US Food and Drug Administration (FDA) for total PCBs in fish and shellfish is 2000 ngg^{-1} wet weight[32,33]. The residue levels of organochlorines pesticides and PCBs in all analyzed fish in this investigation are considerably lower than these tolerance levels.

The Netherlands maximum permissible concentration of organochlorine pesticides in sediment are 58, 98 and 540 ngg^{-1} for p,p'-DDE, total DDT and total HCH, respectively[34]. The Canadian interim sediment quality guidelines (ISQG) and potable effect levels (PEL) for fresh water sediment are 75 and 302 ngg^{-1} for total DDT and 59 and 87 ngg^{-1} for γ-HCH[35].

Conclusions: The OCPs concentration varied between samples of different matrices, with the lowest levels detected, as expected in water samples compared with sediment and fish samples due to hydrophobilicity of most organochlorine compounds. The concentrations of all pesticides under study were higher in sediments than in water and fish. In water samples, it was

notable that the detected concentrations of different OCPs in sample collected from the drainage canal were higher than the water canal supplies. This could be attributed to the drainage canal receives industrial and productive waste-waters.

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