

# MONITORING OF ORGANOCHLORINE AND ORGANOPHOSPHOROUS RESIDUE IN SEDIMENTS OF RIVER NILE, EGYPT

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## ABSTRACT

Several hundred pesticides of different chemical nature are currently used in large quantities especially in developing countries for the control of agricultural pests. Because of their widespread use, they are detected in various environmental matrices, such as soil, water, and air. The aim of this study is to determine aspects of sediment quality in different sites along the River Nile, by analyzing their content of organochlorine and organophosphorus pesticides residues. Surface samples from 27 sites were collected from different locations of River Nile from Aswan to Damietta Governorate during December 2004 to January 2005. The obtained results showed that thirty-two different pesticide residues were monitored in sediment samples and most of the analyzed sediment samples contained detectable levels of pesticide residues, according to sampling location. Organochlorine pesticides were the main contaminations of sediment samples, while the existences of organophosphorous pesticide were the negligible in the same selected sites. BHC isomers i.e.,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ; cyclodine i.e., heptachlor, heptachlor epoxide,  $\gamma$ -chlordane, aldrin, dieldrin, endrin and diphenyl trichloro ethan i.e.,  $\rho$ ,  $\rho$ -DDE,  $o$ ,  $\rho$ -DDT,  $\rho$ ,  $\rho$ -DDD and  $\rho$ ,  $\rho$ -DDT were detected at significantly greater concentrations than other pesticides. The geographic distribution of pesticide concentration generally follows regional patterns in agricultural use and the influence of urban area. Upper Egypt Governorates recorded higher concentration of organochlorine pesticide residues than North Egypt Governorates; on the other hand, North Egypt Governorates recorded high concentration of organophosphorous pesticide residues than detected in Upper Egypt Governorates. In general, it was found that the detected amounts of organochlorine pesticide residues always same residue content in sediments from other rivers in the world. However, the detected content of pesticide residues in the studied sediments are in the permissible limits.

**Keywords:** Monitoring, Organochlorine; organophosphorous; residues; sediment.

## INTRODUCTION

The River Nile receives its water from the tropical headwaters in central Africa and Ethiopia. Egypt, the downstream country, is located in an arid climatic zone and it depends absolutely on water from a single source, the Nile water. Most of the populated centers and industries activity, agricultural activity are located directly on both sides of the Nile. Consequently, the Nile currently receives enormous amounts of agricultural wastewater that carry various chemical pollutants related to the widespread use of fertilizers and pesticides. Besides, great quantities of industrial, municipal and domestic wastes and storm water runoff are drained directly or indirectly into the Nile (Omer, 2003). Pesticides are divided to many classes, of which the most important are organochlorine and organophosphorous compounds. Organochlorine compounds, i.e. hexachlorocyclohexanes (HCHs), DDT and its metabolites, and endosulfan,

endosulfan sulfate are ubiquitous, persistent, toxic and bioaccumulation in nature. The unique properties of such compounds make them environmentally persistent with a global distribution and they are, thus exerting chronic toxic effects on wildlife and humans (Loganathan and Kannan, 1994). Organochlorine pesticides are still used in the countries from which water comes to, river Nile such as Ethiopian and Sudan. Therefore, they consider as important component of the chemical pollutants found in all parts of the global marine environment. They are potentially hazardous to living systems because of their inclination to bioaccumulate in the lipid component of biological species and their resistance to degradation (GESAMP, 1989). Organophosphorous pesticides, on the other hand, are known to be highly soluble in water and relatively short lived in the environment, because of their rapidly degradation depending on their formulation, method of application, climate and growing stage of plant. These types of pesticides generally may cause short-term problems when present at high concentration.

Chemicals and pesticide residues are often scavenged from the water through sorption onto suspended material that later is deposited on the bottom upon reducing flow rates of the water stream to become part of the bottom substrate. Consequently, bottom sediments often become reservoirs of pesticides in the environment (Khan, 1977). Miliadis (1994) stated that pesticides residues reach the aquatic environment through direct run off, leaching, careless disposal of empty containers, equipment washings, etc. The sediment component of aquatic ecosystems can be an ultimate sink of pesticides; suspended particulate entering slower moving waters such as larger water bodies settle out, and their associated pesticides are added to the sediment component (Chau and Afgan, 1982). Therefore, chemical analysis of such sediments is important to evaluate the pollution status of streams, and the local sources of pollution can be detected.

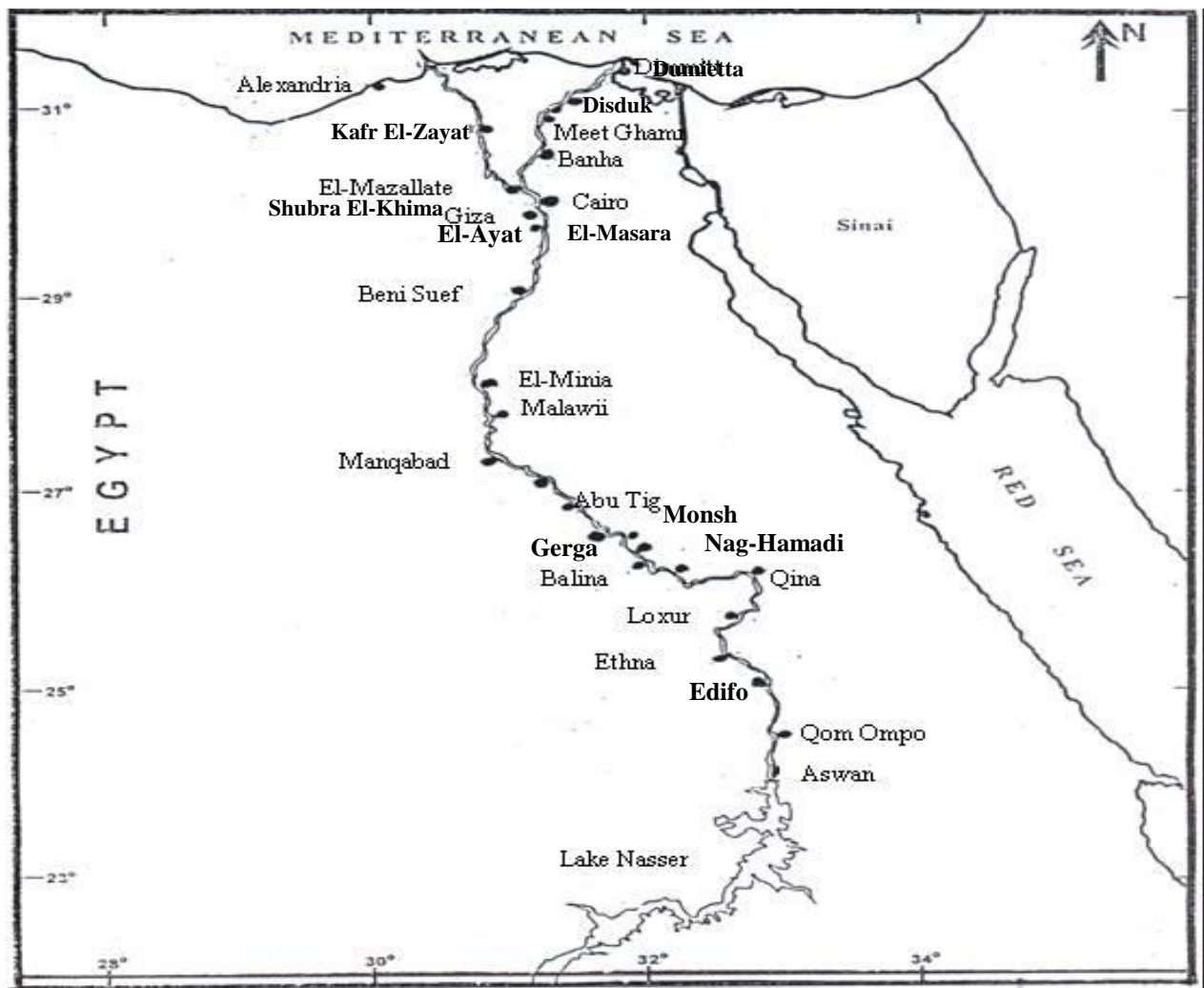
Pesticide residues mainly organochlorine and organophosphorous compounds in various aquatic ecosystem have been studied by several investigator such as, Allen Gil *et al* (1997).; Pandit, *et al* (2001).; Bhattacharya *et al* (2003).; Bakan and Ariman (2004); and Sankaramakrishnan *et al* (2005). In Egypt, Badawy *et al* (1997).; Abbassy (2000).; Zidan *et al* (2002).; and Abbassy *et al* (2003).

The objective of our study was to assess environmental concentrations of used pesticides especially organochlorine and organophosphorous in sediment from several areas along the River Nile, Egypt.

## **MATERIALS AND METHODS**

### **Study site**

During winter drought when the level of the Nile water is significantly dwindled. (December 2004 to January 2005), 27 samples of surface sediments were collected along the Nile banks in Egypt from Aswan to north branches (Damietta and Rosetta) **Fig (1)**. Accordingly, the surface bottom sediments along the Nile banks become very shallow and accessible to be sampled correctly. At each sampling point the top sediment layer was taken from river positions where an accumulation of fine-textured substrate mostly at water depth of few centimeters. Sediment samples were composited from separate grabs collected from a 10 m<sup>2</sup> area, homogenized, and wrapped in aluminum foil. Samples were immediately stored on ice after collection and stored at -20 °C in the laboratory until analysis. In the laboratory, samples were passed through 1 mm plastic sieve to remove the coarse materials. Sub samples were then lightly ground in mortar and pestle break to fine fraction (< 60µm).



**Fig 1. Map shown the location of sampling sites of River Nile, Egypt**

Physiochemical characteristics, i.e.; organic carbon; calcium carbonate; sand; silt; and clay for studied sediments were determined by method of Dewis and Freitas (1970), and then the sediment textures were calculated according to USDA (1996). Total Fe and Mn in the collected samples were determined by Buck Scientific 210-Atomic Absorption after digestion according the method described by Ure (1990)

## **Analytical procedure**

### **Extraction**

Twenty grams of sediment were weighed, in triplicate, mixed separately with 20 g. of anhydrous sodium sulphate and homogenized in a mortar with pestle. The homogenized samples were placed in round bottom flask (250 ml) with 100 ml n- hexane and shaking for 3 hours. The extract was filtrated through a funnel with plug cotton into a 250 ml round bottom flask and the funnel was rinsed with 50 ml n-hexane. The extracts were concentrated in a rotary evaporator to about 2 ml at 50 °C

## Clean up

The clean up and fractionation procedure was carried out according to the methods reported by Lappe *et al* (1983). The extract passing through a florisil (17 g) column, which had been activated at 130 °C for 12 h. and partially deactivated with 0.5 % water. From this column, three fractions were collected: the first fraction with 70 ml of n- hexane; the second fraction with 50 ml of n- hexane / dichloromethane (70: 30) and then a third fraction with 40 ml of dichloromethane and n- hexane. All of the fractions were concentrated to about 1 ml by rotary evaporator, and kept under refrigeration until determination.

## Quantitative determination

Organochlorine pesticide residues were determined by gas chromatograph (Hewlett Packard GC Model 6890) equipped with Ni 63 electron capture detector (ECD). This detector allows the detection of contaminants at trace level concentrations in the lower ppb range in the presence of a multitude of compound extracted from the matrix to which these detectors do not response (Table 3). The gas chromatograph condition: DB-17 (J & scientific) capillary column (30 m length × 0.32 mm internal diameter (i.d.) × 0.25 um film thickness). Operating temperatures were: column temperature was programmed 160 °C to 230 °C, at a rate of 3 °C / min. and to 260 °C at a rate 10 °C then hold 10 minutes. Injector temperatures were 300 °C and detector temperature 320 °C with nitrogen carrier gas flow at 4 ml min<sup>-1</sup>. All compounds were identified by their retention times compared to known standards. Peak identical was confirmed by running the samples and standard on a second column. PAS-5 methyl silicon (30 × 0.23 mm i.d. × 0.25 um film thickness).

The organochlorine residues components was identified by comparing their retention times with those of the standards quantified by extrapolation of corresponding sample peak areas with those from standard curves prepared for each pesticide standard. Small variations is corrected by obtaining fresh chromatograms of the standard mixture after every nine injection. Slandered solutions were prepared for each pesticide of concentrations ranging from 0.01 to 0.04 ppm and then 1 µl was injected into the GC. Peak areas of standard solutions were plotted against their concentrations. A line of best fit was drawn through the points and the limits of detection were taken at five times the detector noise level.

Organophosphorous pesticide residues were determined by gas chromatograph, (Hewlett Packard GC. Model 6890) equipped with a flam photometric detector (FPD) with phosphorus filter. A fused silica capillary (PAS-1701), column containing 14 % cyanopropilsyloxane as stationary phase (30 m length × 0.23 mm internal diameter (i.d.) × 0.25 um film thickness), was used for the separation in the GC. While CP-CIL\_13CB 14 % phenyl, 86 % dimethylpolysiloxane as stationary phase (50 m × 0.53 mm i.d. × 1 um film thickness) was used to confirm the detected pesticides.

The following are the operating conditions of GC instrument: Injector and detector temperature were 240 and 250 °C, initial oven temperature, 170 °C for 2 min. , raised at 7 °C / min, and then hold at 230 °C for 2 min, then raised at 10 °C / min to 240 °C and then hold to 2 minutes. The carrier gas was nitrogen at 3 ml / min., and hydrogen, and air were used for the combustion at 75 and 100 ml /min., respectively. All solvents and chemicals used were pesticide residue analytical grade reagents free of interfering residues as tested by Gas chromatography

By using these conditions of separation and determination, obtained retention times and detection limits are shown in **Table (1)** for the tested pesticides.

**Table 1.** Detection limits of organochlorine and organophosphorous in ng g<sup>-1</sup> for ECD and FPD.

Organochlorine	ECD	Rt (min)	Organophosphorous	FPD	Rt (min)
α-BHC	0.002	5.889	Dichlorofos	0.01	1.558
γ-BHC	0.002	7.390	Methamidaphos	0.01	2.018
β-BHC	0.005	7.835	Ethoprophos	0.006	4.481
Heptachlor	0.003	8.652	Cadusafos	0.006	4.878
Δ-BHC	0.005	9.391	Phorate	0.009	5.147
Aldrin	0.004	10.035	Diazinon	0.004	5.698
Heptachlor	0.003	13.465	Di- Syston	0.01	6.350
γ-Chlordane	0.002	13.789	Cyanophos	0.01	6.871
Dieldrin	0.005	16.305	Chlorpyriphos-	0.005	7.888
Pp DDE	0.004	16.511	Pirimiphos-methyl	0.005	8.233
Endrin	0.006	18.207	Chlorpyriphos	0.005	9.047
ρ, ρ-DDD	0.004	19.464	Fenitrothion	0.002	11.829
o, ρ -DDT	0.005	19.665	Phenthioate	0.007	12.471
ρ, ρ-DDT	0.006	21.261	Prothiphos	0.016	13.207
			Profenofos	0.018	14.086
			Fenamiphos	0.09	15.210
			Ethion	0.002	17.066
			Triazophos	0.029	18.660

## RESULTS AND DISSECTION

### Pesticides residue in sediments

#### Organochlorines

The analyzed sediment samples showed the presence of the following organochlorine pesticide residues at concentration above the method of detection limits: BHC isomers i.e., α, β, γ, δ; cyclodine i.e., heptachlor, heptachlor epoxide, γ-chlordane, aldrin, dieldrin, endrin and diphenyl trichloro ethan i.e., ρ, ρ-DDE, o, ρ -DDT, ρ, ρ-DDT, and ρ, ρ-DDD. The results for levels of residues in sediment samples are shown in (Tables 2 and 3). The  $\Sigma$  of four important metabolites of BHC isomers i.e., α, β, γ, δ ranges from ND to 103.20 ng g<sup>-1</sup> with a mean value of 18.40±29.13 whereas the  $\Sigma$  DDT ranges from under detected limit (ND) to 328.9 with a mean value of 80.0 ± 90.6. The β-BHC was observed sharing a major portion of BHC followed by δ BHC, α BHC and γ- BHC, which was below the detection limit in all the samples except west Edfo, Qina and Disuk samples. The concentration of β-BHC isomers is always higher than, α, γ, δ -BHC confirming the characteristics features of more stability and resistance to microbial degradation (Bhattacharya *et al.*, 2003). Rajendran *et al* (2005) stated that, β-isomer is more persistent with respect to microbial degradation and has lowest volatility, which may also account for its higher concentration. Furthermore, both α, γ-HCH are more volatile, leading to long- range transport of these compounds to far regions. Sarkar *et al* (1997) found higher level of α-HCH in west Coast (Arabian sea) sediments, whereas Pandit *et al* (2001) found more of α and γ-HCH in west coast and β-HCH in east coast. In west coast of Srilanka, Guruge and Tanabe (2001) observed the HCH isomers in the following decreasing order: α-HCH > β-HCH > γ-HCH.



**Table 3.** Detection frequency and organochlorine pesticide concentration in sediment samples

Pesticides	Positive detection % of samples	Concentration (ng g <sup>-1</sup> )		
		Minimum	Maximum	Mean of detections
River sediments, sites (n=27)				
α-BHC	22.22	0.20	52.80	2.7
β-BHC	48.15	3.00	41.86	7.5
γ-BHC	11.11	0.47	47.00	1.9
Δ-BHC	44.44	5.00	64.00	6.3
Heptachlor	33.33	5.30	21.00	3.8
Heptachlor epoxide	25.93	0.30	28.00	3.8
γ-Chlordane	18.52	0.57	145.00	6.2
Aldrin	66.67	0.40	174.70	18.4
Dieldrin	62.96	1.00	383.00	41.5
Endrin	37.04	1.00	85.00	10.3
P <sub>p</sub> DDE	59.26	1.30	324.40	53.0
O <sub>p</sub> DDT	22.22	3.60	262.00	17.4
P <sub>p</sub> DDT	29.63	2.70	40.40	7.9
P <sub>p</sub> DDD	29.63	1.00	8.50	1.0

The concentration of BHC isomers i.e., α, β, γ, δ ranged from 0.20 to 52.80; 3.00 to 41.86; 0.47 to 47.00 and 5.00 to 64.00 respectively. These isomers of BHC detected in 22.22; 48.15; 11.11 and 44.44 % from analyzed total samples **Table (3)**. The high concentrations of these pesticides were found in Monshaa, Loxur, west-Edfo and Loxur in Upper Egypt, respectively. Such findings are in agreement with those obtained by Gupta *et al* (2002). They found that, sediment from El- Esmailia Canal ( branch from River Nile) contained α -HCH (47.7 ng g<sup>-1</sup>) and β-HHC (891.6 ng g<sup>-1</sup>), whereas, Barakat *et al* (2002) stated that, hexachlorocyclohexane (HCHs), aldrin, dieldrin, and endrin were below detection limits or detected at low concentrations in most of samples sediment collected from Alexandria Harbor, Egypt.

Among the analyzed organochlorine residues, heptachlor, heptachlor epoxide, γ-chlordane, aldrin, dieldrin, and endrin were detected. at levels ranged from 5.30 to 21.00 for heptachlor, 0.30 to 28.00 for heptachlor epoxide, 0.04 to 145.00 for γ- chlordane, 0.40 to 174.70 for aldrin, 1.00 to 383.00 for dieldrin, and 1.00 to 85.00 for endrin. The highest concentration (383.0 ng g<sup>-1</sup>) was observed for dieldrin in Malawi, 174.70 ng/g for aldrin in Abou-Tig and 145.00 ng g<sup>-1</sup>) for δ-chlordane in Aswan. This finding are harmonized with those of Barakat *et al* (2002) as they found that chlordane(heptachlor and its epoxide, oxy-, γ- and α -chlordane and cis + trans-nonachlor) ranged from < 0.25 to 44 ng g<sup>-1</sup> with the highest concentration found in the Arsenal Basin. Zidan *et al* (2002) found that, in summer, sediment samples from Banha sector contained high amounts of heptachlor (53.67 ng g<sup>-1</sup>), while in soil samples from El- Happy land and El-Mazallat sites, the amounts of heptachlor were 206.33 and 23.67 ng g<sup>-1</sup> respectively. The percentage of contaminated samples reach 33.30, 25.90, 18.50, 66.70, 63.00 and 37.00% for, heptachlor, heptachlor epoxide, γ-chlordane, aldrin, dieldrin, and endrin, respectively.

In this investigation, the concentration of parent compound p, p-DDT (40.40 ng g<sup>-1</sup>) was always lower than p, p-DDE (324.40 ng g<sup>-1</sup>) and o, p -DDT (262.00 ng g<sup>-1</sup>), whereas higher than the p, p-DDD (8.50 ng g<sup>-1</sup>). The occurrence of DDT isomers are predominate in the following order: p, p-DDE > o, p -DDT > p, p-DDT > p, p-DDD. The highest concentration (324.40 ng g<sup>-1</sup>) was observed for p, p-DDE in Girga, 262 ng g<sup>-1</sup> for o, p -DDT in East-Edfo, 40.00 ng g<sup>-1</sup> for p, p-DDT in Manqabad and 8.50 ng g<sup>-1</sup> for p, p-DDD in Bani-Suif, respectively. The results agree with those of Zidan, *et al* (2002) who reported that, sediment samples from El-Mazallat, Happy land and El-Kanater contained high amounts of p, p-DDE (143.67, 317.0 and 325.0 ng g<sup>-1</sup>),

respectively. Barakat *et al* (2002) found that, total DDT concentration varied from  $< 0.25$  to  $885 \text{ ng g}^{-1}$ . The ratios of DDTs (2,4- and 4,4-DDT)/total DDTs (DDT plus metabolites) in sediment samples from certain sites of Alexandria Harbour, Egypt, were 0.86 or higher, indicating little attenuation or recent input of DDT. The contamination levels of total DDTs and chlordane were in high range compared to other locations worldwide. The largest agricultural use of DDT has been on cotton, which accounted for more than 80% of the use before its ban. Although its usage was banned in 1986, its detection, along with detection of its breakdown products (i.e., DDEs + DDDs), in sediments is expected because the reported environmental half-life of DDTs is estimated as 10-20 years (Woodwell *et al*, 1971). DDTs undergoes degradation to DDDs and DDEs in natural environment by chemical and biological processes (Wedemeyer, 1967).

Data in **Tables (2 and 3)** reveals that concentration of BHCs was lower than DDTs. This may be due to their differences in physicochemical and biological properties, with BHCs having higher water solubility, vapor pressure and biodegradability and lower lipophilicity and particle affinity compared to DDTs.

### **Organophosphorous pesticide residues in sediments**

Concentrations of organophosphorous pesticides in surface sediments from the River Nile, Egypt are shown in **Tables (4 and 5)**. Compounds identified included chlorpyrifos-methyl, chlorpyrifos, Ethion, fenitrothion, prothiophos, pirimiphos-methyl and Phenthiolate pesticides. The concentrations ranged from  $0.81$  to  $5.69 \text{ ng g}^{-1}$  for chlorpyrifos-methyl,  $0.42$  to  $11.0 \text{ ng g}^{-1}$  for chlorpyrifos, N.D. to  $2.31 \text{ ng/g}$  for Ethion  $0.42$  to  $8.78 \text{ ng g}^{-1}$  for fenitrothion, N.D. to  $0.25 \text{ ng/g}$  for prothiophos,  $0.09$  to  $12.0 \text{ ng/g}$  for pirimiphos-methyl and  $0.21$  to  $15.7 \text{ ng g}^{-1}$  for phenthiolate. These pesticides detected in 11.1; 11.1; 3.7; 11.1; 3.7; 14.8 and 11.1 % from the analyzed samples. The high concentrations of these pesticides were found in Kafr El-Zayat, Ethina, Disuk, Talkha and Girga. The same phenomenon took place with Barakat, *et al* (2002) who found that; chlorpyrifos ( $< 0.25$ -  $51 \text{ ng g}^{-1}$ ) was detected in 26% of the samples sediments with highest levels at El- Mahmudiya Quay.

The presence of chlorpyrifos-methyl, chlorpyrifos and fenitrothion, in samples sediments collected from Kafr El-Zayat, could be attributed to the intense agricultural activity in the area (cotton, maize, rice and potatoes planted), chemical application for control of agricultural pests, and industrial area (KZ. company for pesticides and fertilizer). On the other hand, the absence of most organophosphorous pesticides in sediment may be attributed to its rapid degradation depending on their formulation, rate of application, method of application and climatic factors. These compounds are highly soluble in water and relatively short-lived in the environment. In general, the sources of contaminations are closely related to human activities, such as domestic and industrial discharges, agricultural chemical applications and soil erosion.

### **Geographic distribution of pesticide**

The distribution of various organochlorine and organophosphorous pesticides in sediments from 27 sampling stations reveals a wide range of fluctuations, as illustrated in **Tables (2 and 4)**. The distribution of chemical species in a multiphase system is governed by physical and chemical properties such as vapor pressure, water solubility, octanol-water partition coefficients, bio-concentration and hydro geological factors that affect transport from land surface to the water canals.





**Table 5.** Detection frequency and organophosphorous pesticide concentration in sediment samples

Pesticides	Positive detection % of samples	Concentration (ng g <sup>-1</sup> )		
		Minimum	Maximum	Mean of detections
River sediments, sites (n=27)				
Dichlorofos	--	--	--	--
Methamidaphos	--	--	--	--
Ethoprophos	--	--	--	--
Cadusafos	--	--	--	--
Phorate	--	--	--	--
Diazinon	--	--	--	--
Di- Syston	--	--	--	--
Cyanophos	--	--	--	--
Chlorpyriphos-methyl	11.11	0.81	5.69	0.35
Pirimiphos-methyl	14.81	0.09	12.00	0.87
Chlorpyriphos	11.11	0.42	11.00	0.21
Fenitrothion	11.11	0.42	8.78	0.43
Phenthioate	11.11	0.21	15.7	0.62
Prothiphos	3.70	--	0.25	0.01
Profenofos	--	--	--	--
Fenamiphos	--	--	--	--
Ethion	3.70	--	2.31	0.08
Triazophos	--	--	--	--

The obtained data showed that organochlorine content in sediment collected from river Nile sites located in Upper and mid Egypt is higher than in sediments collected from Great Cairo and Delta sites. In contrary, organophosphorous residues were found more in North Egypt locations. The high concentration of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -BHC, heptachlor, heptachlor epoxide,  $\gamma$ -chlordane, aldrin, dieldrin, endrin,  $\rho$ ,  $\rho$ -DDE,  $o$ ,  $\rho$ -DDT,  $\rho$ ,  $\rho$ -DDT, and  $\rho$ ,  $\rho$ -DDT were 52.8, 41.9, 47.0, 64.0, 21.0, 28.0, 145.0, 174.7, 383.0, 85.0, 324.4, 262.0, 40.4, and 8.5 ng/g, respectively. The corresponding locations were Loxur, West-Edfo, Monshaa, Aswan, Qina, Aswan, Abou-Tig, Malawii, Loxur, Girga, East-Edfo, Manqabad, and Bani-Suif. (Upper Egypt). On the other hand, locations in North Egypt, reported negligible existence for organochlorine such as,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -BHC which not detected, except site of Desouk (7.2 ng g<sup>-1</sup> of  $\beta$ -HCH) and El-Ayat (0.5 ng g<sup>-1</sup>). The DDT isomers also are not detected, except sites of Meet-Ghamer (3.6 ng g<sup>-1</sup> of  $o$ ,  $\rho$ -DDT) and Desouk (36.0 ng g<sup>-1</sup>) of  $\rho$ ,  $\rho$ -DDT), while  $\rho$ ,  $\rho$ -DDE are detected in high amounts in Damietta, (190.0 ng g<sup>-1</sup>), El-Ayat (179.0 ng g<sup>-1</sup>) and Desouk (83.0 ng g<sup>-1</sup>). Cyclodiene i.e., heptachlor, heptachlor epoxide,  $\gamma$ -chlordane, aldrin, and endrin were in negligible amounts, while dieldrin was observed at high concentration (147.0 ng g<sup>-1</sup>) in Masara. The high concentration of organophosphorous pesticides was found in locations, Kafr El-Zayat, Ethina, Desouk, Talkha and Girga. These locations located in North Egypt, excepted Ethina and Girga from Upper Egypt. Additionally, most locations in Upper Egypt were not detected under the limit of detection.

In our study, the geographic distribution of various pesticide concentrations in sediments samples collected from different locations of River Nile are probably attributed to many factors such as, compound properties, organic matter, agricultural use, urban area, and related to human

intensity/activity. Barakat, *et al* (2002) reported that the geographic distribution of PCBs, total DDTs and total chlordane were similar in sediment samples collected from Alexandria Harbour, Egypt. Doong *et al* (2002) stated that, the hydrological characteristics of Hugli River estuary, such as, tidal effected and seasonal fluctuations of flow rate, could influence the distribution of persistent organic pollutants (POPs) in sediments. The same phenomenon took place with Zidan *et al* (2002) showed that most of the analyzed sediment contained detectable levels of pesticide residues, according to sampling location and to various times.

### **Physiochemical characteristics of sediment in relation to residues content:**

**Table (6)** illustrate the basic physiochemical parameters of the studied sediments. Total Fe and Mn concentrations point to the abundance of both (4.34 to 11.78 % and 0.10 to 0.30 %, respectively). This is attributing to the lithogenic nature of the Nile sediments, which are extremely influenced by the composition of the parent rocks in the hinterlands particularly the Ethiopian basaltic plateau (Omer, 2003). The spatial variability of Fe and Mn along the Nile is influenced by the flow regime, where they are enriched in low-energy sediments, whereas their content are depleted in the high energy sites. The organic carbon of sediments ranged from 0.62 to 8.21 %. The maximum organic carbon of sediment samples was observed at site No 20, which was the heavily polluted by the direct discharge of wastewater of Shubra El-Khima. Sediments with high organic matter are more likely to adsorb lipophilic organochlorine and organophosphorous than those with lower organic carbon levels. Therefore, the sediments from Shubra El-Khima were below detection limits (ND) of organochlorine and organophosphorous pesticide residue. This could be attributed to the high content of the organic carbon they enhanced adsorption of pesticides residue and consequently held it strongly on adsorb sites and prevent its extraction. There is much evidence to indicate that organic matter is the predominate factor controlling the capacity of sediment to bind organochlorine and organophosphorous compounds. There are few reports on the relationship between organic carbon and chlorinated compounds in sediments (Lee *et al* 2001). They found a correlation between total DDT and TOC in sediments of Kyeonggi Bay, Korea, but not between total HCH and TOC. The sediments texture ranged from sand to loam. On the other hand, the clay and total calcium carbonate content range between 2.04 to 34.08 % and 0.78 to 36.60%, respectively.

### **Correlation of organochlorines with other physicochemical parameters**

To find out the correlation of organochlorines with other physicochemical parameters, Pearson correlation matrix was calculated in **Table (7)**. It has been revealed that an overall negative and significant relations exist between organic carbon in sediments with HCHs i.e.  $\alpha$ -,  $\beta$ -  $\gamma$ -  $\delta$ - ( $r = -0.16, -0.12, -0.27$  and  $-0.25$  respectively;  $p < 0.05\%$ ), DDTs i.e. *Pp-DDE*, *Op-DDT*, *Pp-DDT* and *Pp-DDD* ( $r = -0.31, 0.08, -0.07$  and  $-0.04$  respectively;  $p < 0.05\%$ ). Clay content is positively correlated with HCHs i.e.  $\alpha$ -,  $\beta$ -  $\gamma$ -  $\delta$ - ( $r = 0.13, 0.17$  and  $0.33$ ;  $p < 0.05\%$ ), DDTs i.e. *Pp-DDE*, *Op-DDT*, *Pp-DDT* and *Pp-DDD* ( $r = 0.14, 0.37, 0.15$  and  $0.14$ ;  $p < 0.05\%$ ). On the contrary, the correlation values between Calcium carbonate content and other organochlorine residues are insignificant in all cases. Moreover, Fe content is negative correlated with HCHs ( $p < 0.05\%$ ), but positive correlated with DDTs ( $p < 0.05\%$ ). Additionally, Mn content is positive correlated with HCHs ( $r = 0.07, 0.03, 0.06$  and  $0.33$ ;  $p < 0.05\%$ ), and DDTs ( $r = 0.13, 0.13, 0.23$  and  $0.17$ ;  $p < 0.05\%$ ), this results in agreement with those obtained by Bhattacharya *et al* (2003).

**Table 6.** The average physicochemical properties of surface sediments collected from the locations of River Nile

No.	Location	Fe	Mn	OC	CaCO <sub>3</sub>	Coarse sand	Fine sand	Silt	Clay	Texture grade
		%								
Upper Egypt										
1	Aswan	7.15	0.15	2.08	4.28	5.76	40.18	46.02	8.04	L
2	Qom-Ompo	8.46	0.18	2.26	3.46	33.04	48.90	10.02	8.04	LS
3	West Edfo	9.70	0.21	0.62	2.32	30.72	19.22	20.02	30.04	SCL
4	East Edfo	7.58	0.15	2.77	4.57	31.30	26.54	8.08	34.08	SCL
5	Ethina	8.93	0.25	1.28	3.87	58.90	31.02	2.04	8.04	S
6	Loxour	6.61	0.20	3.41	3.8	49.30	36.64	6.02	8.04	LS
7	Qina	6.36	0.20	2.97	2.39	67.72	5.22	28.02	2.04	LS
8	Naga-Hamadi	5.11	0.11	2.4	3.24	31.32	52.22	12.40	4.06	LS
9	Balina	8.73	0.31	1.12	5.69	26.92	61.02	2.04	10.02	LS
10	Gerga	5.15	0.22	6.40	36.6	64.72	5.22	28.02	2.04	SL
11	monshaa	5.64	0.26	1.72	5.69	73.02	10.86	2.04	14.08	SL
Mean		7.22	0.20	2.46	6.90	42.97	30.64	14.97	11.68	
Mid Egypt										
12	Abu -Tig	6.32	0.30	2.11	3.24	51.22	24.68	14.08	10.02	SL
13	Manqabad	6.22	0.25	2.08	2.32	35.50	42.42	18.02	4.06	LS
14	Malawii	5.94	0.28	2.8	5.55	28.04	35.88	6.04	30.04	SCL
15	Bany-Suif	5.29	0.15	4.66	3.24	59.80	6.16	18.02	16.02	SL
16	El-Ayat	7.46	0.21	2.38	2.53	8.44	67.32	12.12	12.12	SL
Mean		6.25	0.24	2.81	3.38	36.60	35.29	13.66	14.45	
Great Cairo										
17	El-Maasra	6.35	0.19	2.36	3.24	28.04	35.88	6.04	30.04	SCL
18	Cairo	6.37	0.17	2.55	6.18	12.52	55.40	28.06	4.02	SL
19	El-Mazallate	9.97	0.26	1.73	3.38	59.80	6.16	18.02	16.02	SL
20	Shubra El-Khima	4.34	0.10	8.21	7.24	48.62	45.28	4.06	2.04	S
21	Banha	5.70	0.11	2.95	0.78	11.54	44.39	20.05	24.02	SCL
Mean		6.55	0.17	3.56	4.16	32.10	37.42	15.25	15.23	
Delta										
22	Meet Ghmer	5.91	0.12	2.62	1.83	46.80	37.12	8.04	8.04	LS
23	Kafr El-Zayat	7.96	0.22	3.59	3.73	9.94	57.96	14.08	18.02	SL
24	Desouk	6.43	0.14	1.77	4.64	37.52	38.42	8.04	16.02	SL
25	Talkha	8.25	0.16	2.12	2.89	39.20	14.74	44.02	2.04	SL
26	Mansoura	7.37	0.17	2.01	1.23	23.10	22.00	36.80	18.10	L
27	Damietta	11.78	0.15	2.38	1.9	25.22	52.68	20.05	2.04	SL
Mean		7.95	0.16	2.42	2.70	30.30	37.15	21.84	10.71	



In the **Table (8)** the levels of organochlorine compounds in sediment samples recorded in this study are compared with those of other countries. BHC concentrations were found to be in the range of 0.012 to 40 ng g<sup>-1</sup>. The results of the present study showed that, the concentration of  $\alpha$ -BHC and the other HCH isomers of sites 1, 2, 4, 5, 7, 9, 12, 13, 14, 23 and 24 are comparable to medium to high range values reported from the Romania Coastline by Fillmann *et al* (2002) and from Indian cities by Iwata *et al.* (1994) On the other hand samples from locations No, 7, 10 and 12 had a concentration above the high limit values reported from the samples in various countries, but in complete agreement with the levels of HCH in an Egyptian study on the sediments from El-Esmalia canal reported by (Gupta *et al.* 2002). These indicate usage of BHC as pesticide in this regions. Analysis of sediments showed that the total DDT residue levels from some South Egypt sites were above those of New York (10 ng g<sup>-1</sup>) and California (32 ng g<sup>-1</sup>) sediments quality criteria (Mac Doanld, 1994).

Finely, the results of the present work underscore the need to improved environmental protection measures in order to reduce the bio-accumulative of these compounds through food ingestion. Furthermore, regular monitoring is warranted for the sustainable use of persistent pesticides in agriculture, and to evolve a strategy to mange the environmental hazards due to these pesticides.

**Table 8.** Organochlorine residue levels (ng g<sup>-1</sup>) in surface sediment collected from different countries

Location	HCHs		DDTs		References
	Range	Mean	Range	Mean	
Victoria Harbour Hong Kong	ND -23.00	0.58	1.38– 25.40	10.20	Hong <i>et al</i> (1995)
Peart River estuary, PRC	0.28 -1.23	0.68	1.36 – 8.99	2.84	Hong <i>et al</i> (1999)
Xiamera Western Bay,PRC	0.14 - 1.12	0.45	4.45 – 31.10	42.80	Hong <i>et al</i> (1995)
Juilong River estuary, PRC	3.70-13.00	9.10	8.70 – 69.00	26.00	Chen <i>et al</i> (1986)
Macao estuary, PRC	-	-	ND- 79.00	-	Zhang <i>et al.</i> ( 1999)
West coast of Sri Lanka	0.086 - 0.33	-	0.09 1.60	-	Guruge and Tandbe ( 2001)
Eastern coast of India	0.008 - 0.02	-	0.10 – 0.097	-	Sakar ( 1994)
Mediterranean	-	0.012		0.047	Burns and Villeneuve( 1987)
Kizilirmk river, Turkey		5.00		ND	Bakan and Ariman(2004)
Yesilirmark river, Turkey		ND		7.00	Bakan and Ariman( 2004)
Cities, India	0.65- 38.00		8.00 – 450.00		Iwata <i>et al</i> (1994)
Romania Coastline	0.20 – 40.00		0.60 – 72.00		Fillmann <i>et al</i> (2002)
Ebro river (Spain)		0.0038		51.80	Fenandez <i>et al.</i> (1998)
River Nile, Egypt	ND – 64.00	15.00	ND – 324.00	56.37	This study

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## رصد متبقيات المبيدات الكلورينية والفسفورية العضوية فى رواسب نهر النيل-مصر

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نتيجة لاستخدام المبيدات على نطاق واسع لمكافحة الحشرات خاصة فى الدول النامية فانه يتبقى منها جزء فى أترابه ثم ما يلبس أن يصل إلى الماء أو الهواء مسببا مشكلات بيئية كبيرة سواء للإنسان أو الحيوان. لذلك استهدفت هذه الدراسة تقدير متبقيات المبيدات فى عينات من رواسب نهر النيل بهدف أيجاد قاعدة بيانات لمدى تلوث النيل بالمبيدات التى قد تصل إليه من الاراضى الزراعية التى تمتد على جانبيه. تم جمع ٢٧ عينة من الرواسب من مناطق عديدة من نهر النيل تمتد من أسوان جنوبا حتى دمياط و رشيد فى الشمال وذلك خلال الفترة التى يكون فيها منسوب المياه فى النيل منخفض (ديسمبر ٢٠٠٤-يناير ٢٠٠٥).

وقد أظهرت نتائج التحليل مايلى

- ◇ وجود متبقيات من المبيدات بصورة واضحة فى معظم العينات و ان موقع العينة له دور هام فى وجود وكمية المتبقيات
- ◇ كانت المبيدات الكلورينية العضوية من أكثر الملوثات الموجودة بالعينات بينما المتبقى من المبيدات الفوسفورية كانت اقل تواجداً وتوجد بكميات ضئيلة
- ◇ تم استكشاف المبيدات التالية بتركيزات ملحوظة عن المبيدات الأخرى:  
BHC isomers i.e.,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ; cyclodine i.e., heptachlor, heptachlor epoxide,  $\gamma$ -chlordane, aldrin, dieldrin, endrin and diphenyl trichloro ethan i.e.,  $p$ ,  $p$ -DDE,  $o$ ,  $p$ -DDT,  $p$ ,  $p$ -DDT, and  $p$ ,  $p$ -DDD.
- ◇ ارتباط التوزيع الجغرافى لتركيزات المبيدات فى العينات المأخوذة من المواقع المختلفة بالاستخدام الزراعى والمناطق الريفية
- ◇ احتوت العينات المأخوذة من مواقع النيل فى محافظات مصر العليا و مصر الوسطى على تركيزات أعلى من متبقيات المبيدات الكلورينية العضوية بالمقارنة من التركيزات التى وجدت فى العينات المأخوذة من محافظات القاهرة الكبرى والدلتا
- ◇ عينات الرواسب المأخوذة من النيل فى محافظات الشمال احتوت على تركيزات عالية من متبقيات المبيدات الفوسفورية مثل chlorpyrifos- methyl, chlorpyrifos, Ethion, fentrothion, prothiophos, pirimiphos-methyl and Phenthiolate pesticide مقارنة بالعينات المأخوذة من محافظات الجنوب.
- ◇ هناك ارتباط سلبي بين محتوى الرواسب من المادة العضوية و المنجنيز والمحتوى من المتبقيات الكلورينية وارتباط موجب بين محتوى الرواسب من الطين والمحتوى من المتبقيات الكلورينية. كما انه لا يوجد ارتباط بين المحتوى من كربونات الكالسيوم والمحتوى من المتبقيات الكلورينية
- ◇ وعلى العموم فانه يمكن القول إن كميات متبقيات المبيدات التى كشف عنها فى رواسب نهر النيل من المناطق المشار إليها سابقا كانت فى مستوى المتبقيات من المبيدات الموجودة فى رواسب انهار أخرى من العالم. ومقارنة بما هو منشور فى الأبحاث العالمية فتن نتائج هذا البحث تتطابق مع مثيلاتها التى تم تقديرها فى هذه الأبحاث.