Monitoring of chlorinated hydrocarbon compounds residues in surface water and bed sediment samples from El-Rahawy drain, Egypt

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doi:10.6088/ijessi.00107020048

ABSTRACT

The concentrations of organochlorine pesticides and polychlorinated biphenyls were determined in surface water and bed sediments from El Rahawy drain in the southwestern part of Nile Delta. Results obtained show that the concentration of ΣDDT compounds in surface water range from 0.008 to 0.239 μg L⁻¹ and from 0.011 to 3.10 μg kg⁻¹ (dry weight) in bed sediments during wet and dry seasons. Hexachlорocyclohexanes (HCHs) have also been widely used in the region but the current environmental concentrations are slightly higher than those of DDT’s, which is due to the less persistence of those compounds. Cyclodiienes (Cds) were measured, for example as endosulfan II, in concentrations range from 0.021 to 0.823 μg L⁻¹ and 0.09 to 1.73 μg kg⁻¹ (dry weight) in surface water and bed sediments, respectively. Polychlorinated biphenyls including Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260 were not detected in any of surface water and bed sediments samples due to low funding limitations. The investigation of chlorinated hydrocarbon compounds in the surface water and sediments are still within safety margins compared to Canadian guidelines.

Keywords: Organochlorine pesticides, Polychlorinated biphenyls, El Rahawy drain, water, sediments, Canadian guidelines.

1. Introduction

Organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) are two main categories of chlorinated organic compounds present as contaminants in the environment. A large number of man-made chemicals, organochlorines pesticides (OCPs) such as dichlorodiphenyl ethane (eg, DDT, DDD and DDE), cyclodiene (example: aldrin, dieldrin, heptachlor and endosulfan), and chlorocyclohexane (eg, α, β, γ and δ-HCH) are of great concern due to their highly persistent nature and global occurrence (Glynn et al., 1995). These chemicals are bioaccumulative in nature and induce various toxic effects in aquatic environment (Guruge and Tanabe, 2001). On the other side, PCBs are mixtures of aromatic chemicals, manufactured by the chlorination of biphenyl in presence of a suitable catalyst. The empirical formula for PCBs is C₁₂H₁₀⁻nClₙ where n may be any value from 1 to 10. PCBs with 5 or more chlorine atoms per molecule are referred to as higher chloro biphenyls and are relatively more persistent in the environment than lower chloro biphenyls which have four or fewer chlorine atoms (El-Kady et al., 2007). PCBs consist of a large number of homologues and isomers; seven of the commonly occurring Aroclor mixtures (Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260) are possible. PCBs are used as industrial chemicals and have no known or identified use in agricultural production. The main source of PCB in the watershed is thought to be from electrical transformers; electrical power lines, cross the study area, although each region does have transformers for step-down conversion of electrical energy.
Assessment of Organochlorine Pesticide in water and sediment samples collected from El-Rahawy drain, Egypt

El Bouraie M, El Barbary A, Yehia M
International Journal of Environmental Sciences Volume 1 No. 7, 2011

The presence of OCPs in the environment has been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans. Despite the ban and restriction on the usage of OCPs in developed countries during the 1970s and 1990s, some developed countries are still using them for agricultural and public purposes because of their effectiveness in controlling various insects (Tanabe et al., 1997).

Some OCPs are highly resistant to degradation by biological, photochemical or chemical means. They are also liable to bioaccumulation and are prone to long range transport (Tanabe et al., 1994). Many of these compounds have already been listed as top-priority pollutants owing to their carcinogenic, hepatoxic and mutagenic effects (WHO, 1989). These compounds are also typically characterised as having low water solubility and high lipid solubility.

Studies conducted on OCPs and PCBs in aquatic environments in Egypt (Barakat et al., 2002; Said and Hamed, 2006; Barbary et al., 2008), Africa (Fatoki and Awofolu, 2003; Okonkwo et al., 2007), Europe (Blair et al., 1997; Fernandez-Alba et al., 1998), Asia (Iwata et al., 1994; Xue et al., 2006) and America (Dorothea and Muir, 1991; Guillette et al., 1998) have shown a widespread occurrence of residues of these pesticides in environmental aquatic systems, despite the fact that they have been banned for decades. In developing countries such as Egypt, Technical HCH and DDT were the most extensively used pesticides in Egypt, resulting in widespread contamination in various environmental compartments. These chemicals can enter aquatic environment through several ways such as effluents release, agricultural runoff, atmospheric deposition and other means. Due to the low water solubility, OCPs have a strong affinity for suspended particulates and subsequently settle down to sediments. It is believed that some group of OCPs may still be in use clandestinely under unknown trade names in agriculture due to their low cost and effectiveness for pest control.

In Egypt, El Rahawy drain is one of the most severely contaminated areas by OCPs and PCBs because of its long-term usage and wastewater discharge from local domestic of El-Rahway village in addition to all sewage of El-Gieza governorate. Although the production of OCPs was officially banned in Egypt since late 1990, OCPs are still using for agricultural and public health purposes because of their low cost, easy to use and versatility against various insects (Jahin et al., 2008).

The original objectives of this study were to determine the remaining residues of chlorinated hydrocarbon compounds in surface water and sediments in water body of El Rahawy drain. Another purpose was to study the composition and distribution of OCPs and PCBs residues in surface water and sediments from El Rahawy drain. Furthermore, the temporal changes and the environmental fate of OCPs were discussed.

2. Materials and Method

2.1 Reagents and Standards

All used solvents were of the grade "for Pesticides Residue Analysis". The anhydrous sodium sulfate was heated for at least 5 h at 550 ºC, cooled and stored in a closed container. The Florisil was activated overnight at 550 ºC, cooled and stored in a closed container. The
needed amount of Florisil was heated once again at 110 °C for another 8 h, cooled and mixed with de-ionized distilled water to give a 7% (w/w) mixture. This mixture was shaken for 30 min and kept for 24 h in a closed container, prior to use. Other materials used throughout the experimental procedure, such as cotton wool and filter paper, were extracted using a 1/1 acetone/dichloromethane mixture in a Dionex (ASE 200) apparatus, prior to use. All primary standards of OCPs and PCB Aroclors (98.2-99.9% purity) were purchased from SUPELCO (PA, USA). A standard solution of each OCP and PCB was prepared in a proper way depending on being solid or liquid, to give a 100 µg mL⁻¹ stock solution in n-hexane, which was stored at -20 °C. Dilutions were prepared from the stock solutions and stored in the refrigerator at +4 °C. A standard mixture solution containing all 18 OCPs and 7 PCB Aroclors were prepared with the appropriate concentrations of each compound, and stored at -20 °C.

2.2 Study area and sampling

Samples of surface water and sediment were collected in wet and dry seasons from January to June 2010. Two sampling sites along El Rahawy drain were selected. The locations of these sampling sites are located in the southwestern part of Nile Delta, about 30 km north-west of Cairo at El-Kanater El-Kahyria area, Egypt as shown in Fig. 1 and tabulated in Table 1. El-Rahawy drain lies between latitudes 30º 10' N to 30º 12' N and longitudes 31º 2' E to 31º 3' E passes through El-Rahway village and many villages dotted along it receiving agricultural and domestic wastes in addition to sewage of El-Gieza governorate and discharged these wastes directly without treatment into the Nile (Rosetta Branch).

Figure 1: Map of the study area and sampling sites.
Table 1: Locations and description of the surface water and bed sediment samples collected.

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Site Name</th>
<th>Code</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>El-Rahawy drain at 3 km from Rosetta branch</td>
<td>SW1</td>
<td>SD1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Latitude (˚N)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30˚ 11’ 13.26”</td>
</tr>
<tr>
<td>2</td>
<td>El-Rahawy drain at 0.5 km from Rosetta branch</td>
<td>SW2</td>
<td>SD2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Latitude (˚N)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30˚ 12’ 15.76”</td>
</tr>
</tbody>
</table>

SW: surface water sample, SD: bed sediment sample.

Two water samples (SW1 and SW2) were collected from the surface using clean glass containers (1.5 liter capacity), stored in the refrigerator at + 4 °C and extracted within 24 hours. The collected water samples were filtered through 0.45 µm glass fibre (Whatman) to eliminate particulate matter.

Two bed sediment samples (SW1 and SW2) were collected using an Eckman sampling device (0-10 cm) in areas of low flow velocity (<0.3 m s⁻¹). The samples were put in glass-bottles which were kept cool in the field (4 °C). Immediately after collection sediments were preserved in deep freeze in order to avoid degradation. After transportation into the laboratory they were lyophilized and grounded using a ball mill. The grinding stock was passed through a 75 µm and stainless steel sieve.

2.3. Sample preparation

One liter of each water sample was extracted with 60 ml dichloromethane in a 2-L separatory funnel (APHA, 2005). The mixture was shaken manually for 5 min, followed by collection of the lower organic layer. The extraction was repeated twice each time with 50 ml dichloromethane. The pooled 180 ml dichloromethane extracts were dried over anhydrous sodium sulfate and filtered. The solvent was evaporated to dryness under vacuum at ≤ 40 °C and 350 mbar. The residues were dissolved in 1 ml n-hexane containing 1 mg L⁻¹ aldrin as internal standard. For qualitative and quantitative interpretation of results, a concentration of 1.0 ppm aldrin was used as internal standard for OCPs and PCBs standard mixture and in the real sample final solutions (Haynes et al., 2000).

Homogenized bed sediment samples (10 g) were extracted by pressurized solvent extraction (PSE), using a Dionex ASE 200 Accelerated Solvent Extractor (ASE) (Dionex, Sunnyvale, USA) in combination with a solvent controller (Dionex) was used for extraction of the sediment samples. The ASE 200 conditions were: oven temperature 100 °C, oven heat-up time 5 min, static time 5 min, flush volume 60 % of the extraction cell volume (11 ml), extraction pressure 10 MPa and as extraction solvent a mixture of n-hexane/acetone (1:1, v/v) was used. The obtained extracts were concentrated under reduced pressure to a volume of 5.0 ml hexane (You et al., 2004).

The residue of the extraction step of each sediment sample was transferred to a Florisil minicolumn (8 mm ID, filled with 3.5g of 7% deactivated Florisil with distilled water, and a 1 cm layer of anhydrous sodium sulfate used to cup the Florisil from both sides). The Florisil column was washed with 20 ml n-hexane before use. The sample was eluted from the column first with 20 ml of hexane followed by 20 ml of an acetone/hexane mixture (1+99, v/v). After the solvent of the eluate was evaporated at ≤40 °C and 350 mbar, the final residues were dissolved in 1 ml n-hexane containing 1 mg L⁻¹ aldrin as internal standard. 20. 2.0 µl of each final residue solution were injected onto the GC column under the above mentioned conditions.
Based on a signal-to-noise ratio of 3:1, the calculated detection limits were as follows: The detection limits of the methods for OCPs residue in water and sediment. Based on a signal-to-noise ratio of 3:1, the calculated detection limits is 0.01 ng L\(^{-1}\) for water and 0.01 ng kg\(^{-1}\) for sediment samples as reported by (Sibali et al., 2008).

2.4. Instrumental and operating conditions

Each final residue solution of the sediment and water samples was prepared and analyzed in duplicate throughout the described analytical procedure (GC capillary column under optimized chromatographic conditions and detection with the \(^{63}\)Ni-ECD).

A Hewlett Packard 5890 series II gas chromatograph equipped with an electron capture detector \(^{63}\)Ni-ECD) was used for analysis. GC separations were performed on a fused silica capillary column (DB-XLB; film thickness 0.17 µm; 30 m x 0.32 mm I.D. (J&W, Folsom, USA). The GC operating conditions were: injector temperature 300 °C, detector temperature 320 °C and carrier gas (nitrogen) flow-rate 40 ml min\(^{-1}\). The GC temperature program conditions for the analysis on OCPs and PCBs were: initial oven temperature 110 °C, initial time 0.5 min, heated to 150 °C by a temperature ramp of 25 °C min\(^{-1}\) followed by a second temperature ramp of 12 °C min\(^{-1}\) to a temperature of 260 °C and a third temperature ramp of 15 °C min\(^{-1}\) to an end temperature of 320 °C which was hold for 2 min at 320 °C. The hexane extracts of water and sediment samples were used for OCPs and PCBs analyses by gas chromatography in combination with an electron capture detector (GC-ECD) applying aliquots of 3 µl. Injections were splitted (1:10) without and after column clean-up, respectively (Golfinopoulos et al., 2003). Each sample was analysed twice by GC-ECD. Typical chromatogram of standard sample is presented in Figures 2-9.

![Figure 2: GC/ECD Chromatogram of standard OCPs (0.05µg L\(^{-1}\)).](image)

Calibration curves were prepared from a stock solution of 10.0 mg L\(^{-1}\) OCPs dissolved in n-hexane by serial dilution to reach calibration concentrations of 5, 10, 20, 40 and 50 µg L\(^{-1}\). Each calibration solution was analysed in threefold by GC-ECD. The peak areas of the corresponding analytes were plotted against the calibration concentrations and the regression
Assessment of Organochlorine Pesticide in water and sediment samples collected from El-Rahawy drain, Egypt

El Bouraie M, El Barbary A, Yehia M

International Journal of Environmental Sciences Volume 1 No. 7, 2011

The retention times obtained for the components of the mixture are as follows: α-HCH (11.511 min), γ-HCH (13.288 min), heptachlor (14.514 min), aldrin (16.215 min), β-HCH (16.38 min), δ-HCH (17.311 min), heptachlor epoxide (18.221 min), endosulfan I (19.282 min), p,p'-DDE (20.145 min), dieldrin (20.721 min), endrin (21.523 min), p,p'-DDD (23.112 min), endosulfan II (23.337 min), p,p'-DDT (23.887 min), endrin aldehyde (25.037 min), methoxychlor (26.597 min), endrin ketone (26.786 min) and endosulfan sulfate (28.824 min). The analysis time per injection was 30 min in order to give the best chromatographic separation of PCBs for the quantification of Aroclors (for further explanation, see the supplementary information). A five-point initial calibration for each of the Aroclors (1016, 1221, 1232, 1242, 1248, 1254 and 1260) was determined. This calibration curve ranged from 5 to 100 ppb. The calibration For Aroclors must have an RSD ≤ 20% for the relative response factors and the correlation coefficient R must be >0.99 for linear regression in order for the calibration to be compliant (Albro et al. 1981).

Figure 3: GC/ECD chromatogram of PCB Aroclor 1016

Figure 4: GC/ECD chromatogram of PCB Aroclor 1221
Assessment of Organochlorine Pesticide in water and sediment samples collected from El-Rahawy drain, Egypt

**Figure 5:** GC/ECD chromatogram of PCB Aroclor 1232

**Figure 6:** GC/ECD chromatogram of PCB Aroclor 1242

**Figure 7:** GC/ECD chromatogram of PCB Aroclor 1248
To evaluate the whole analytical procedure, the percent recovery of each OCP and PCB under study was determined for each analytical procedure concerning each sample type. This was performed by spiking with known concentrations of chlorinated compounds’ mixture. The analysis of each sample was performed according to its specific analytical procedure. The recoveries were 92.8-99.5% for the sediment samples, and 89-100% for the water samples.

3. Result and discussion

The analysis of OCPs and PCBs present in μg L⁻¹ or μg kg⁻¹ concentrations in environmental samples is not quite easy because often analysis will be disturbed by other matrix compounds also present in the sample extracts (Dong et al., 2002).

Concentrations of OCPs in surface water and bed sediments from El Rahawy drain are shown in Table 2. Compounds identified included hexachlorocyclohexane (α-HCH, β-HCH, γ-HCH, δ-HCH), cyclodiene (aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, endosulfan I, endosulfan II and endosulfan sulfate) and diphenyl aliphatic
(p,p'-DDE, p,p'-DDD, p,p'-DDT and methoxychlor) pesticides. From (Table 2) PCB Aroclors including 1016, 1221, 1232, 1242, 1248, 1254, and 1260 were not detected in any of water samples due to low funding limitations as reported by Palmer et al., 2011. This may be due to ban use of PCBs, which are used in the electrical industry, capacitors, hydraulic systems, the formulation of cutting and lubricating oils, and pesticides, paints, plastics and inks and/or their differences in physicochemical and biological properties, in addition to its low volatility and its resistant to biodegradation and biotransformation.

The results revealed fairly low levels of pesticide residues, mainly organochlorines as shown in Table 2. The concentrations varied between samples of different matrices, with the lowest levels detected, as expected (due to the hydrophobicity of most OCPs) in water samples. However, there was a marked difference in levels between wet and dry seasons, with higher levels in the former. Alarmingly high levels were detected in sediments collected from the same sites. Some pesticides were dominant in many samples while in other samples they were found to be below the method detection limits.

3.1 Chlorinated Hydrocarbon residues in water

Pesticides detected in water were DDT and its metabolites (DDD and DDE), HCH isomers and dieldrin (Table 2). These residues were dominant in the wet season samples while in the dry season most of the residues were below their average method detection limit. The concentrations of ΣOCPs were in the range of 0.07–2.1567μg L⁻¹. Cyclodienes compounds were the most often found OCP compound, followed by DDTs and HCHs. The concentrations were 0.031–1.6837 μg L⁻¹ for cyclodienes, 0.008–0.239 μg L⁻¹ for DDTs and 0.006–0.234 μg L⁻¹ for HCHs.

Relatively high levels of total DDT in environmental samples can be related to past use of the pesticide in agricultural fields. Substantial amounts of pesticides have been reported to be used in agricultural fields along El Rahawy drain in Egypt. DDE and DDT were more dominant in wet season samples from El Rahawy drain indicating some elapse of time from application to sampling. DDE is an aerobic degradation product of DDT, and this degradation is assumed to take place in aerated soils. Thus it is suggested that DDE is transferred from treated soils to water bodies (Mladen, 2000). The p,p'-DDE levels is the most dominant with lower levels of DDT and DDD during wet season, indicating more recent use of the technical pesticide.

Most of the environmental samples showed the domination of γ- and α-HCH isomers implying the use of technical HCH rather than β-HCH > δ-HCH. Despite the fact that technical HCH has been banned from use in many developing countries including Egypt, studies have indicated residual concentrations of these chemicals. Dieldrin, endosulfan II, endosulfan sulfate and endrin aldehyde were detected at low concentrations in surface water samples during both seasons (Nasr et al., 2009). Other pesticides such as δ-HCH, endrin ketone, methoxychlor and aldrin were found to be below the method detection limits (0.1 ng L⁻¹). From the compounds examined endosulfan I, heptachlor, heptachlor epoxide, endrin, γ-HCH, DDT and its metabolites are above Canadian water quality guidelines for irrigation and fresh water(CWQGs, 2005), as shown in Table 2. PCBs for all seven of the commonly occurring Aroclor mixtures (Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260) were below the method detection limits for PCBs of 0.1 ng L⁻¹ in water samples, which suggests that PCB Aroclors compounds are more readily volatilized to the atmosphere, whereas cannot be expected to soluble in water samples at the same sites (Pozo et al., 2007).
### Table 2: Mean levels of chlorinated hydrocarbon compounds observable in surface water samples collected from El Rahawy drain during wet and dry seasons.

<table>
<thead>
<tr>
<th>Items</th>
<th>Surface water (µg L⁻¹)</th>
<th>CWQGs (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet season</td>
<td>Dry season</td>
</tr>
<tr>
<td></td>
<td>SW1</td>
<td>SW2</td>
</tr>
<tr>
<td>p,p’- DDT</td>
<td>0.029</td>
<td>0.064</td>
</tr>
<tr>
<td>p,p’- DDE</td>
<td>0.051</td>
<td>0.084</td>
</tr>
<tr>
<td>p,p’- DDD</td>
<td>0.048</td>
<td>0.091</td>
</tr>
<tr>
<td>ΣDDEs</td>
<td>0.128</td>
<td>0.239</td>
</tr>
<tr>
<td>α- HCH</td>
<td>0.0016</td>
<td>0.008</td>
</tr>
<tr>
<td>β- HCH</td>
<td>bdl</td>
<td>0.001</td>
</tr>
<tr>
<td>γ- HCH</td>
<td>0.042</td>
<td>0.225</td>
</tr>
<tr>
<td>δ- HCH</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>ΣHCHs</td>
<td>0.0436</td>
<td>0.234</td>
</tr>
<tr>
<td>Aldrin</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Endrin</td>
<td>0.0038</td>
<td>0.0087</td>
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<tr>
<td>Endrin aldehyde</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Endrin ketone</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>0.018</td>
<td>0.148</td>
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<tr>
<td>Heptachlor epox.</td>
<td>0.06</td>
<td>0.7</td>
</tr>
<tr>
<td>Endosulfan I</td>
<td>0.083</td>
<td>0.823</td>
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<tr>
<td>Endosulfan II</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Endosulfan sulfate</td>
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<td>0.001</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>ΣCyclodienes</td>
<td>0.1688</td>
<td>1.6837</td>
</tr>
<tr>
<td>ΣPCBs</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

CWQGs: Canadian water quality guidelines for the protection of agricultural water uses, bdl: below the detection limit, —: No guideline available, No EQG: No environmental quality guidelines is recommended.

### 3.2. Chlorinated Hydrocarbon residues in bed sediments

Pesticide residues found in bed sediments were the same as those detected in water samples and generally reflected a similar pattern. Endosulfan I and heptachlor epoxide were dominant in the samples, both in dry and wet seasons (Table 3). Higher levels of the residues were found in sediments than in their corresponding water bodies, which is an indication of their hydrophobicity. The results indicated relatively high residue levels at site (SD2) with mean levels were to 0.84 and 0.65 µg kg⁻¹ dry mass of endosulfan I and heptachlor epoxide, respectively, in the dry season (Table 3). The mean levels in the wet season were 1.73 and 2.11 µg kg⁻¹ for endosulfan I and heptachlor epoxide, respectively (Table 3). Surprisingly, very high levels of endosulfan I and heptachlor epoxide were detected in sediments which could probably suggest that endosulfan I and heptachlor epoxide have been massively used in vegetable crops, rather than the “drin” pesticides in the study area. Whereas sediments from El Rahawy drain showed no significant differences in detection frequencies and levels of residues between the two seasons, samples from the study area showed a notable difference.
Some pesticide residues in dry season samples from the study area were generally below the detection limits, but there was a massive enrichment of pesticide-containing sediments run off during the wet season (Table 3). All PCBs data are shown in (Table 3). Aroclors mixtures of PCBs were banned in the 1970s, due to concerns about their toxicity. None of the seven Aroclors were detected in bed sediment samples. The probable reason is that PCB Aroclors compounds are more readily volatilized to the atmosphere, whereas cannot be expected to partition onto the particulate phase and undergo sedimentation (Fagbote and Olanipekun, 2010). Poverty of PCB concentrations in the investigated sediments suggests that the absence of human activities, including fishing, yacht sport, land-based effluents, boat building workshops, recreation and sailing boats anchoring inside the waterway could greatly limit to the sediment contamination with PCBs.

Table 3: Mean levels of chlorinated hydrocarbon compounds observable in bed sediment samples collected from El Rahawy drain during wet and dry seasons.

<table>
<thead>
<tr>
<th>Items</th>
<th>Bed sediment (μg kg⁻¹ dry wt)</th>
<th>CSQGs (μg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet season</td>
<td>Dry season</td>
</tr>
<tr>
<td></td>
<td>SD1</td>
<td>SD2</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>0.0113</td>
<td>0.88</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>0.0105</td>
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<tr>
<td>p,p'-DDD</td>
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<td>γ- HCH</td>
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<td>δ- HCH</td>
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<td>0.001</td>
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<tr>
<td>ΣHCHs</td>
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<tr>
<td>Aldrin</td>
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<tr>
<td>Dieldrin</td>
<td>0.0113</td>
<td>0.0165</td>
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<tr>
<td>Endrin</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Endrin aldehyde</td>
<td>0.013</td>
<td>0.37</td>
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<tr>
<td>Heptachlor</td>
<td>0.46</td>
<td>1.16</td>
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<tr>
<td>Heptachlor epox.</td>
<td>0.53</td>
<td>2.11</td>
</tr>
<tr>
<td>Endosulfan I</td>
<td>0.27</td>
<td>1.73</td>
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<tr>
<td>Endosulfan II</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Endosulfan sulfate</td>
<td>0.013</td>
<td>0.37</td>
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<tr>
<td>Methoxychlor</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>ΣCyclodienes</td>
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<td>ΣOCPs</td>
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CSQGs: Canadian sediment quality guidelines for the protection of aquatic life, ISQGs: Interim freshwater sediment quality guidelines, PEL: probable effect levels.

DDTs and HCHs showed high concentrations and were detected in almost all sediment samples. This could be attributed to their high persistency, high stability, and their used in
Egypt for a long time (Nasr et al., 2009). The concentration of DDE and DDD was much higher than that of DDT, which could be attributed to high stability of DDE in the aquatic environment as compared to the parent compound DDT and to other metabolites. Normally, we expect to find more DDD and DDE than DDT; however, here we found that the total DDT levels were higher than that of its metabolites DDD and DDE. This could be explained; that new DDT was measured in the environment is probably not from very recent applications or was previously degraded in soils before entering the aquatic environment. All these findings indicate that the DDT pesticide is currently used in remote villages, especially in the more populated areas. This means that the DDT pesticide has been used not for controlling insect pests in the agriculture fields but for sanitary purposes, to control mosquitoes and flies in the houses.

Concentrations of ΣHCHs in bed sediment samples from El Rahawy drain are slightly higher than concentrations of ΣDDTs (Table 3). At first glance this may seem surprising because the technical mixture of HCHs was largely used years ago in Egypt as well as in most of Middle East, in particular in China, Japan and India, the largest world producers. In later years the world production of technical HCH substantially decreased (Li et al., 1998). There is no quantitative information on the cumulative use of DDT and HCH in El Rahawy area over the years. However, there is no reason to believe that the amount of technical HCH used has been smaller than that of DDT. The most likely explanation for the currently higher concentrations of HCHs in water of El Rahawy drain is related to the relatively short environmental half-lives of HCHs in soils and higher water solubility which is 3 to 4 orders of magnitude higher than that of DDT's (Howard, 1989). Higher concentrations of HCHs in sediments as compared to those of DDTs, is thought to be due to the rapid rate of mineralization and formation of organic volatile compounds of HCHs. Results shown in Table 3, indicate that the proportion of three HCHs, i.e. alpha, beta and gamma isomers in sediments are approximately similar to those of the technical HCH mixture. The levels of OCPs in the study area for bed sediment samples are still within safety margins compared to Canadian sediment quality guidelines for toxic and deleterious substances (CSQGs, 2002), as shown in Table 3.

Concentrations of OCPs in the sediments are considered as a reflection of the applications of pesticide in Egypt, especially for agricultural purposes. The major sources of OCPs in the investigated sediments: exposure to sewage disposal of Greater Cairo pumped into El Rahawy drain, the storm water runoff and residential wastes directly discharged into the drain (El Barbary et al., 2008).

The accumulation of organochlorine compounds in sediment is roughly proportional to the level of the same pesticides in Surface water as tabulated in Tables (2 and 3). There is a statistically significant positive correlation between the concentration of ΣDDTs, ΣHCHs and ΣCyclodienes in sediments and in the Surface water from El Rahawy drain (Fig. 3 and 4). Similarly, a positive correlation exists for DDTs, HCHs and Cyclodienes. These correlations indicate that the reservoir of OCP's in sediments is the main source of these contaminants to water and the high bioconcentration is a direct consequence of the high $K_{ow}$ of organochlorine compounds (Noble, 1993).
Figure 3: Concentrations (μg kg⁻¹ dry weight) of ΣDDTs and ΣHCHs in bed sediments plotted against concentrations in surface water from the same sites during wet and dry seasons. DDTs and HCHs show a positive correlation statistically significant at P < 0.05.

Figure 4: Concentrations (μg kg⁻¹ dry weight) of Cyclodienes in bed sediments plotted against concentrations in surface water from the same sites during wet and dry seasons. The bulk of ΣCds shows a linear positive correlation, statistically significant at P < 0.001.

Finally, the obtained results regarding the water-sediments distribution pattern of the detected compounds reflect the great capacity of the sediments to adsorb and accumulate such compounds. Seasonal variations in the detected pesticide residue levels in water and sediments were observed in almost all sampling sites of the study area with the highest concentrations during wet season and the lowest during dry season. The sediment concentrations have a similar but less marked seasonal trend than the water concentrations. During our monitoring in this study, the presence of organochlorine compounds in a stable level of concentrations in the sediments during the sampling periods could be proved,
indicating that the screened sedimentary reservoir could act as a potential release source of the compounds and consequently sustain aqueous contamination. The concentrations and distribution of the detected OCPs in sediments and water samples from El Rahawy drain reflect this assumption. The measured concentrations of OCPs residues in bed sediments are higher than surface water in both seasons. In comparison with water samples there was less noticeable difference between the sampling sites for sediments.

4. Conclusions

The presence of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are two main categories of chlorinated hydrocarbon compounds in the environment have been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans. Despite the ban and restriction on the usage of OCPs and PCBs in developing countries during the 1970s and 1990s, some developing countries are still using them for agricultural and public purposes because of their effectiveness in controlling various insects. This study documented the composition and distribution of OCPs and PCBs in surface water and bed sediment collected from El Rahawy drain. The investigation OCPs and PCBs concentrations were generally low to medium relative to other areas of the world. The high detection concentration of the biological metabolites, such as endosulfan II, DDE and DDD from the parent OCPs in sediments depict that the OCP contamination was mainly from the aged and weathered agricultural soils as well as, sanitary purposes, to control mosquitoes and flies in the houses. Poverty of PCB concentrations in the investigated area suggests that the absence of human activities, including fishing, land-based effluents, boat building workshops, recreation and sailing boats anchoring inside the waterway could greatly limit to the contamination with PCBs.

Acknowledgement

The authors would like to thank the staff of Central Laboratory for Environmental Quality Monitoring, (CLEQM) for their cooperation during measurements and for making unpublished environmental data available. Authors are thankful to Dr. Faiza Afifi, General Director of Central Water Quality Laboratory, Greater Cairo Water Company for his encouragement and providing all the facilities for extending GC-ECD and carrying out this work.

5. References


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International Journal of Environmental Sciences Volume 1 No.7, 2011


