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Concentrations and sources of pesticides and PCBs in surficial sediments of the Red Sea coast, Egypt

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Abstract Sixteen surface sediments from the Egyptian coast of the Red Sea were collected and studied for organochlorine contamination. This research was endeavored to study sources, concentrations and risk factors of pesticides and PCBs in the surficial sediments collected from the studied locations. The sediments in the studied areas are predominantly sand. The most abundant PCB congeners detected in the investigated sediment samples of the Red Sea proper were a total of PCB 52 and a total of PCB 138 (225 and 465 ng kg⁻¹ dry wt., respectively). Meanwhile, in the Aqaba Gulf the most abundant PCB congener was a total of PCB 138 (226 ng kg⁻¹ dry wt.). At the Suez Gulf, the most abundant PCB congeners were a total of PCB 180 and 153 (127 and 103 ng kg⁻¹ dry wt., respectively). The input of direct industrial and domestic discharge in most of the contaminated zones of the studied area resulted in a larger concentration of total PCB 52, 138, 153 and 180. The results obtained showed fairly low levels of pesticide residues. The most dominant pollutants were the HCHs and DDTs, high proportions of α -HCH over γ -HCH isomer indicated less recent input of lindane. The α -HCH/ γ -HCH ratios in most of the studied locations are slightly less than those in technical-grade HCH mixture (66.5% α isomer, 11.4% β isomer, 15.2% γ isomer (lindane), 6.4% δ isomer, and 0.5% other isomers) indicating that there was less input of lindane in the past several years. This study clearly indicates that PCB concentrations, DDTs, cyclodienes, HCHs were much lower than those recorded by the international organization.

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Introduction

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and hydrophobic organic compounds (HOC) of anthropogenic origin have been produced and used worldwide

in great quantities over many years since the 1950s. OCPs and PCBs have been introduced into the ecosystem via direct discharge, atmospheric deposition and the runoff from terrestrial sources. OCPs and PCBs, HOCs sorb readily to particles due to their hydrophobicity, therefore PCBs and OCPs can move out of the seawater column to the surface sediment, where they can remain for some time. An analysis of the PCB and OCP distribution in marine sediments is important in the providing of valuable information about their toxicity to organisms in the marine environment. Many PCBs and OCPs were also found to bioaccumulate within the tissues of the aquatic biota.

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Persistence of PCBs and OCPs in the environment and their propensity to bioaccumulate and biomagnificate in living organisms, coupled with their toxic effects, makes them a source of continuing concern to aquatic organisms and human health (El Nemr et al., 2003, 2004; Khaled et al., 2004). In 2004, the Stockholm Convention listed PCBs and DDTs as persistent organic pollutants (POPs) and α -HCH, β -HCH, and γ -HCH (lindane) were added to the list in 2009 (<http://chm.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx>). POPs have a wide range of effects on human health, such as reproductive, carcinogenicity and nervous disorders; they are also suspected to be hormonal disruptors (Van den Berg et al., 2006). OCPs have been used essentially in Egypt to control agricultural pests. Also, PCBs have been used substantially in Egypt in ship painting, electrical equipment, transformers and other industrial uses (Barakat et al., 2002).

The Red Sea has a unique geography with diverse ecosystems including algae, coral reefs and mangrove (Alkershi and Menon, 2011). It has two gulfs, the Aqaba Gulf and the Suez Gulf, near the Red Sea proper. The Gulf of Suez is completely bordered by Egypt, while Egypt, Jordan, Israel and Saudi Arabia border the Aqaba Gulf. The Red Sea proper is bordered by Saudi Arabia, Egypt, Sudan, Eritrea, Djibouti and Yemen. The distribution of pollution among the Red Sea has been reported (El Nemr et al., 2004, 2013, 2016; Khaled et al., 2004). The severity of pollution issues in the Red Sea is increasing due to the small size (458,620 km²) and slow rate of water turnover of the Red Sea as well as the fact that the Red Sea is bordered by eight countries (Medio et al., 2000). The pollution sources in the Red Sea include oceanic sources (petroleum industries, fishing, shipping and marine traffic), land-based sources (urban development, dredging and filling, industrial activities, agriculture activities and tourism) and atmospheric sources (port activities or industries). If this level of pollution becomes severe, it will possibly affect the biological life and may disturb the natural ecosystems of the Red Sea. Therefore, the aim of the present paper is to study the sources, concentrations and hazard levels of pesticides and PCBs in surficial sediments collected from the Suez Gulf, the Aqaba Gulf and the Red Sea proper.

Material and methods

Grain size analysis

The grain size analysis was made following the method reported by Folk (1974) as following. The air dried samples, each of about 50 g, were washed by distilled water and dried at 50 °C and then stored in clean stopper jars ready for mechanical analysis. Samples containing >90% of the coarser fractions (> 4 phi, 0.063 mm) were subjected to dry sieving and the remaining containing >10% of finer fraction (< 4 phi) underwent pipette analysis.

Total carbonates, total organic carbonates and total organic matter

Total carbonates (TCO₃) were estimated using the method reported by Molnia (1974). Dry sample (500 mg) was weighted in a clean dry beaker and 3 N HCl (25 ml) was added and

heated to 50 °C. After the completion of the reaction, it was filtered through glass filter paper, washed with distilled water before dried in an oven (40 °C) and reweighed until constant weight. The residue was recorded as the non-carbonate (silicate) and the difference in weight was recorded as the carbonate weight. The TOC% was obtained by using the following method (Walkely and Black, 1934).

$$\text{TOM\%} = 1.8 \times \text{TOC\%}$$

Total phosphorus (TP), organic phosphorus (OP) and inorganic phosphorus (IP)

The total phosphorus (TP) content was obtained by the method reported by Aspila et al. (1976). 0.5 g of the sediment sample was put into a crucible and heated in air at 550 °C for 2 h. It was then cooled and transferred into measuring flasks (100 ml) using 1 N HCl (50 ml). Later, the measuring flask was shaken for 18 h. After the extraction, the ignited solutions were centrifuged for 5 min at 2000 rpm. Clarified extract was analyzed for TP. IP and OP (Murphy and Riley, 1962).

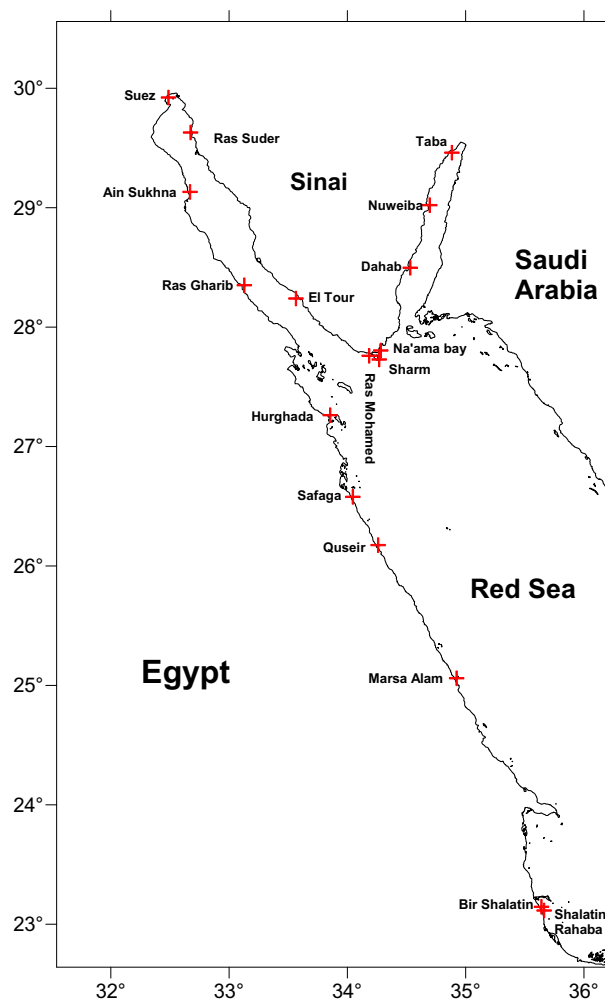


Figure 1 Map of the sediment samples location along the Suez Gulf, the Aqaba Gulf and the Red Sea proper.

Determination of PCB's and pesticides

Stainless-steel Grab Sampler was used to collect surface sediments from sixteen different locations covering the Suez Gulf, the Aqaba Gulf and the Red Sea proper during August, 2011 (Fig. 1). The top 5 cm of the six grabs that were taken from each station were put into pre-cleaned glass bottles with wide-mouth, then frozen and stored in the laboratory at -20°C until analysis. The method used for extracting the PCBs and pesticides from surface sediments was modified from the US EPA Method (USEPA, 1996). Sediment (30 g) (triplicates were made for each sample) was extracted for 8 h using the Soxhlet instrument with 200 ml (1:1) of *n*-hexane- CH_2Cl_2 . The extract was later desulfurized using activated copper powder, then filtered and evaporated in a rotary evaporator at temperature ($<40^{\circ}\text{C}$) to a few milliliters followed by a concentrated under flow of N_2 gas down to a volume of 1 ml. The remaining 1 ml was fractionated using a glass column (50 ml) packed with Florisil (20 g) eluted with 70 ml of *n*-hexane for PCB fraction (F1). It was then eluted with 50 ml of mixture of 30% CH_2Cl_2 and 70% *n*-hexane for the pesticide fraction (F2). Each fraction was concentrated to 1 ml and injected into a GC-MS (El Nemr and El-Sadaawy, 2016).

Quality assurance and quality control

To control the analytical accuracy and assure the method efficiency, six analyses were made on the reference material (IAEA-408) provided by International Atomic Energy Agency (IAEA). The detection limits of OCPs were defined as three times the signal-to-noise ratio (S/N). The results obtained showed that recovery efficiency ranged from 91.93% to 104.15% for all OCPs and PCBs.

Results and discussion*Geological study*

The grain size analysis and sediment analysis for TOM%, TOC%, $\text{TCO}_3\%$, $\text{TSiO}_3\%$, IP, TP and OP results of the sixteen sediment samples are presented in Tables 1 and 2. The average percentage of the sediment analyses for TOC%, TOM%, $\text{TCO}_3\%$, $\text{TSiO}_3\%$, of Suez Gulf sediments (Suez, Ein Sukhna, Ras Suder and El-Tour) represented 0.28%, 0.50%, 88.30%, and 11.70%, respectively (Table 1). Meanwhile, the average concentrations of OP, IP and TP at the same locations were 391.35, 252.82, and 138.52 mg kg^{-1} , respectively. In Aqaba

Table 1 Sediment analysis for TOC%, TOM%, $\text{TCO}_3\%$, $\text{TSiO}_3\%$, TP, IP, and OP.

Station	TOC%	TOM%	$\text{TCO}_3\%$	$\text{TSiO}_3\%$	TP (mg kg^{-1})	IP (mg kg^{-1})	OP (mg kg^{-1})
<i>The Suez Gulf</i>							
Suez	0.66	1.18	86.88	13.12	215.48	158.11	57.37
Ein Sukhna	0.26	0.47	89.52	10.48	195.12	154.46	40.66
Ras Suder	0.14	0.24	96.45	3.55	652.87	446.11	206.76
El-Tour	0.06	0.10	80.35	19.65	501.91	252.61	249.3
Min	0.06	0.10	80.35	3.55	195.12	154.46	40.66
Max	0.66	1.18	96.45	19.65	652.87	446.11	249.30
Average	0.28	0.50	88.30	11.70	391.35	252.82	138.52
<i>The Aqaba Gulf</i>							
Nuweiba	0.19	0.35	78.59	21.41	452.27	279.02	173.25
Dahab	0.14	0.24	82.08	17.92	606.73	381.03	225.7
Sharm	0.24	0.43	71.29	28.71	344.11	230.83	113.28
Ras Mohamed	0.17	0.31	83.68	16.32	339.31	213.69	125.62
Na'ama Bay	0.49	0.89	30.81	69.19	409.24	161.46	247.78
Min	0.14	0.24	30.81	16.32	339.31	161.46	113.28
Max	0.49	0.89	83.68	69.19	606.73	381.03	247.78
Average	0.25	0.44	69.29	30.71	430.33	253.21	177.13
<i>Red Sea proper</i>							
Hurghada-NIOF	0.42	0.76	84.16	15.83	735.69	360.15	375.54
Hurghada-Sheraton	0.73	1.31	73.86	26.14	694.23	627.84	66.39
Safaga	0.31	0.56	55.60	44.4	2634.97	2143.25	491.72
Quseir	0.20	0.37	43.88	56.12	1444.12	1202.26	241.86
Marsa Alam	0.23	0.42	24.58	75.42	1085.1	747.97	337.13
Shalatin El-Rahaba	0.37	0.66	98.93	1.07	554.97	344.07	210.9
Bir Shalatin	0.35	0.63	80.27	19.73	971.41	427.79	543.62
Min	0.20	0.37	24.58	1.07	554.97	344.07	66.39
Max	0.73	1.31	98.93	75.42	2634.97	2143.25	543.62
Average	0.37	0.67	65.90	34.10	1160.07	836.19	323.88

TOC: total organic carbon; TOM: total organic matters; TCO_3 : total carbonates; TSiO_3 : total silicates; TP: Total phosphorus; IP: inorganic phosphorus; OP: organic phosphorus.

Table 2 Water contents and grain size parameters in sediments samples collected along the Egyptian Red Sea Coast.

Station	Water content	Mean (\emptyset)	Sorting (\emptyset)	Skewness	Kurtosis
<i>The Suez Gulf</i>					
Suez	2.09	1.96 (MS)	2.12 (VPS)	0.19 (CSK)	0.58 (VP)
Ein Sukhna	2.01	2.49 (FS)	0.46 (WS)	-0.06 (NS)	1.21 (L)
Ras Suder	1.29	3.11 (VFS)	0.92 (MS)	-0.49 (CSK)	1.58 (VL)
El Tour	1.75	-0.63 (VCS)	1.52 (PS)	0.65 (SFS)	1.35 (L)
Min	1.29	-0.63	0.46	-0.49	0.58
Max	2.09	3.11	2.12	0.65	1.58
<i>The Aqaba Gulf</i>					
Nuweiba	3.99	2.09 (FS)	1.5 (PS)	-0.41 (SCS)	1.36 (L)
Dahab	3.91	1.7 (MS)	1.01 (PS)	-0.15 (CSK)	0.73 (P)
Sharm	3.02	-0.45 (VCS)	1.0 (MS)	0.83 (SFS)	0.68 (P)
Ras Mohamed	4.01	2.71 (FS)	0.76 (MS)	0.02 (NS)	1.16 (L)
Na'ama Bay	2.92	-0.04 (VCS)	0.79 (MS)	-0.26 (CSK)	0.88 (P)
Min	2.92	-0.45	0.76	-0.41	0.68
Max	4.01	2.71	1.50	0.83	1.36
<i>The Red Sea proper</i>					
Hurghada-NIOF	1.15	2.22 (FS)	1.27 (PS)	-0.24 (CSK)	0.87 (P)
Hurghada-Sheraton	0.92	2.22 (FS)	1.70 (PS)	-0.16 (CSK)	0.88 (P)
Safaga	1.08	3.08 (VFS)	0.82 (MS)	-0.41 (CSK)	1.17 (L)
Quseir	0.96	3.11 (VFS)	1.10 (PS)	-0.42 (CSK)	1.69 (VL)
Marsa Alam	1.33	0.26 (CS)	0.93 (MS)	-0.43 (FSK)	0.68 (P)
Shalatin El-Rahaba	1.68	2.71 (FS)	0.84 (MS)	-0.04 (NS)	1.37 (L)
Bir Shalatin	1.75	2.31 (FS)	1.77 (PS)	-0.44 (CSK)	0.76 (P)
Min	0.92	0.26	0.82	-0.44	0.68
Max	1.75	3.08	1.77	-0.04	1.69

MS: medium sand; FS: fine sand; VFS: very fine sand; VCS: very coarse sand, CS: coarse sand; VPS: very poorly sorted; WS: well sorted; MS: moderately sorted; PS: poorly sorted; CSK: coarse skewed; FSK: fine skewed; NS: near symmetrical; SFS: strongly fine skewed; SCS: strongly coarse skewed; VP: very platykurtic; L: leptokurtic; VL: very leptokurtic; P: platykurtic.

Gulf (Noweiba, Dahab, Sharm, Ras Mohamed, Na'ama Bay) the average percentage of TOC%, TOM%, TCO₃%, and TSiO₃% obtained were 0.25%, 0.44%, 69.29%, and 30.71%, respectively. The concentration of TP, IP and OP recorded at the same stations were 430.33, 253.21, and 177.13 mg kg⁻¹, respectively. In the same manner the average percentage of TOC%, TOM%, TCO₃%, and TSiO₃% reported in the Red Sea proper stations (Hurghada-NIOF, Hurghada-Sheraton, Safaga, Quseir, Marsa Alam, Shalatin El-Rahaba, and Bir Shalatin) were 0.37, 0.67, 65.9, and 34.10, respectively, as well as, the TP, IP, and OP at the same locations were 1160.07, 836.19, and 323.88 mg kg⁻¹, respectively.

The organic matter content in sediments is attributed to the decomposition of organisms and plants by bacteria, in addition to organic matter derived from terrigenous deposition. Organic matter is composed generally from lightweight materials, which has sedimentation method following the same laws as those of fine particles accumulating in calm zones. The organic matter distribution in sediments is dependent on the organic material moved out to the coast by waves, on the rate of organic matter oxidation and on the hydrodynamic regime (El-Askary et al., 1988). In the present study, all studied sediment samples have low TOM (Table 1), which is an indication to the effect of hydrodynamic factors that provoked winnowing any less dense materials than shells. Also, the low TOM value may be attributed to the sampling position from the terrestrial discharge that is regarded as the main contributor of the organic detritus. This may indicate the dominance of oxidizing conditions due to low sedimentation and permanent

sediment reworking. The carbonate content is an important factor in the marine environment. In general, the carbonate content shows fluctuation between high and low level. The highest value was obtained due to the increase in the number of shells; this led to richness in carbonate content due to the materials derived from terrestrial origin. Also, the distribution of the carbonate is affected by the movements of the shells over the bottom. On the other hand, the areas subjected to direct winnowing of water showed lower carbonate contents. This can also be attributed to the inverse relationship between carbonate's content and the amount of terrigenous mud. In this study, the carbonate sources in marine sediments are residual from terrestrial and biogenic from skeletal parts and weathering of limestone rock. The most studied samples of sediment belong to terrigenous sediments; sediments of Shalatin Al-Rahaba station contain a high carbonate value (98.93%), while sediments with lower contents (Marsa Alam, 24.58%) are reported in areas that are subjected to the direct winnowing effects of water.

Particulate and dissolved forms are the form of phosphorus to enter aquatic systems. The dissolved forms latter may become associated with suspended particles as they settle out of the water column (Bloesch et al., 1988). During weathering, phosphorus is liberated from minerals in large quantities. In addition, some researchers proposed that the phosphate distribution may reflect the equilibrium occurred, via chemical mechanisms, with sedimentary minerals (Liss, 1976). The phosphorus distribution among sediments is mainly controlled by its content in the minerogenous source material and the

Table 3 Concentration (ng kg⁻¹) of pesticides in sediment samples collected from the Egyptian Red Sea Coast.

	α - HCH	β - HCH	γ - HCH	Aldrin	<i>o,p</i> - DDE	Dieldrin	<i>p,p'</i> - DDE	<i>o,p</i> - DDD	Endrin	<i>p,p'</i> - DDD	<i>o,p</i> - DDT	<i>p,p'</i> - DDT	Σ pesticides
<i>The Suez Gulf</i>													
Suez	6	3	3	1	1	1	38	1	2	ND	10	25	89
Ein Sukhna	10	1	4	1	ND	1	63	1	3	ND	18	3	106
Ras Suder	1	4	1	ND	1	ND	13	1	1	ND	1	47	71
El Tour	6	3	3	1	1	1	38	1	2	ND	10	25	89
Total	23	11	11	3	3	3	152	4	8	ND	39	100	355
<i>The Aqaba Gulf</i>													
Nuweiba	5	2	1	1	ND	ND	9	1	ND	ND	2	1	22
Dahab	4	1	ND	ND	ND	1	1	ND	ND	ND	2	10	21
Sharm	5	1	1	1	3	1	1	1	ND	ND	3	14	32
Ras Mohamed	10	1	4	1	ND	1	63	1	3	ND	18	3	106
Na'ama Bay	6	ND	ND	1	ND	2	1	ND	ND	1	3	6	021
Total	30	5	6	4	3	5	75	3	3	1	28	34	202
<i>The Red Sea proper</i>													
Hurghada- NIOF	4	1	1	ND	ND	1	31	ND	2	2	2	20	64
Hurghada- Sheraton	3	ND	7	ND	1	1	5	ND	6	3	2	35	66
Safaga	1	ND	1	ND	ND	ND	1	1	ND	1	4	6	16
Quseir	6	1	3	2	ND	1	2	ND	ND	1	6	10	34
Marsa Alam	7	1	3	ND	1	ND	21	1	1	ND	4	4	43
Shalatin El- Rahaba	12	1	1	1	1	2	42	ND	1	1	4	9	73
Bir Shalatin	3	1	ND	1	1	ND	2	1	1	1	3	7	19
Total	36	5	16	4	4	5	104	3	11	9	25	91	315

ND: not detected.

chemical redistribution of biogenous matter through the sediment (Riley and Skirrow, 1965). Table 1 reports the data obtained for organic and inorganic phosphorus contents in the collected sediment samples from the studied sites. The total amount of phosphorus varied from 195.12 mg kg⁻¹ at Ein Sukhna to 2634.97 mg kg⁻¹ at Safaga. The inorganic phosphorus constitute was the dominant form, while the organic phosphorus comprised less constituent of the total estimated phosphorus. Table 2 reports the water contents and grain size parameters in the studied sediment samples. Grain size analysis is an important tool for classifying sedimentary environments, transport and deposition. The grain size analysis can provide important information on the transport history, provenance and depositional condition of the sediments. The parameters applied to describe the grain size distribution are divided into four principal groups: (a) the sorting of the sizes, (b) the average size, (c) the preferential spread or symmetry (skewness) and (d) the concentration degree of the grains relative to the average (kurtosis) (Blott and Pye, 2001). Table 2 shows that the water content in the Suez Gulf sediment ranged from 1.29 at Ras Suder to 2.09 at Suez. Mean sorting (ϕ) ranged from 3.11 at Ras Suder to -0.63 at El-Tour, while sorting of sediment flocculated from 0.46 at Ein Sukhna to 2.12 at Suez. The skewness of sediment was -0.49 at Ras Suder and 0.65 at El-Tour. Also, Kurtosis was 0.58 at Suez and 1.58 at Ras Suder. Meanwhile, the water content in the sediment collected from Aqaba Gulf ranged from 4.01 at Ras Mohamed to 2.92 at Na'ama Bay. The mean sorting (ϕ) differed from 2.71

at Ras Mohamed to -0.45 at Sharm. The sorting of sediment collected from Aqaba Gulf fluctuated from 0.76 at Ras Mohamed to 1.50 at Nuweiba. The skewness of sediment ranged from 0.83 at Sharm to -0.41 at Noweiba and the Kurtosis recorded 1.36 at Noweiba and 0.68 at Sharm. The geological parameter at the Red Sea proper recorded the following, 1.75 at Bir-Shalatin to 0.92 at Hurghada-Sheraton for water content with a mean sorting(ϕ) that ranged from 0.26 at Marsa Alam to 3.11 at Quseir and sorting of 1.77 at Bir-Shalatin and 0.82 at Safaga. On the other side, the skewness and kurtosis ranged from (-0.44 to -0.04) and from (0.68 to 1.69) both at Bir-Shalatin, Shalatin El-Rahaba, Marsa Alam and Quseir respectively. This result shows that sediment in the Suez Gulf ranged from very fine sand to medium sand and with sorting that ranged from very poorly sorted at (Suez) to well sorted at (Ain Sukhna). Meanwhile, sediment in the Aqaba Gulf ranged from fine sand at Noweiba to very coarse sand at Sharm and Na'ama Bay, and sorting ranged from poorly sorted at Noweiba and Dahab to moderately sorted at Sharm, Ras Mohamed and Na'ama Bay. The Red Sea proper sediment ranged from very fine sand at Safaga, Quseir to coarse sand at Marsa Alam with sorting ranging from poorly sorted at Hurghada-NIOF, Hurghada-Sheraton, Quseir and Bir Shalatin to moderately sorted at Safaga, Marsa Alam, Shalatin El-Rahaba. The sediments in the studied areas were found to be predominantly sands. The terrestrial deposit content is the major parameter control determining the mean size of sediment, whether feldspars, quartz or other coarse

sands of silicate constituents. The change in mean grain size may reflect the effects of different erosions, accretions, and shell fragments.

Pesticides and PCB's

Concentrations of OCPs in sediment samples collected from the Suez Gulf, the Aqaba Gulf and the Red sea proper are reported in Table 3. The identified compounds included hexachlorocyclohexane (α -HCH, β -HCH, γ -HCH), cyclodiene (aldrin, dieldrin, endrin) and diphenyl aliphatic (*o,p*-DDE, *p,p'*-DDE, *o,p*-DDD, *p,p'*-DDD, *o,p*-DDT, *p,p'*-DDT). The results obtained are fairly low levels of organochlorines as shown in Table 3. Some pesticides were dominant in many sediment samples. Pesticides can slowly be degraded in the environment by a combination of biological and photochemical processes. The ratio between the degraded compounds and their parent compounds was used as an index of (a) pesticides general environmental decline if its application is discontinued or fairly constant, (b) pesticides dispersion and transport from an intensive use area, and (c) pesticides degradation resistance in the food chain (Otchere, 2005). Thus in environment, one would expect the α -HCH/ γ -HCH ratio can reflect the formulation used and the length of time since its application at the source. The most environmentally stable hexachlorocyclohexane is α -HCH isomer, whereas δ -HCH is easily degraded to α -HCH isomer by microorganisms and by photochemicals. A high γ -HCH concentration was observed sharing a major portion of total HCHs (28.1% of total HCHs) at the Red Sea proper followed by 24.4 in Suez Gulf and 14.6 at the Aqaba

Gulf. On the other hand, α -HCH (51% of total HCHs) followed by β -HCH and γ -HCH (24.4%) of the total HCHs reported for sediments of the Suez Gulf and the Aqaba Gulf (Table 4). Meanwhile, among the DDT compounds, *p,p'*-DDE was reported at concentrations frequently higher than those of *p,p'*-DDT, hence suggesting the accumulation from old applications of DDT. The DDT/DDE ratio may be used as a DDT degradation indicator since DDE makes <1% of industrial technical DDT (Larsson and Okla, 1989). A DDT/DDE ratio of >1 to 5 indicates recent exposure to the parent *p,p'*-DDT (Hooper et al., 1997; Salem et al., 2014). In this study, the DDT/DDE ratios in all stations of Suez Gulf were less than (<1) except at Ras Suder which recorded <4. Ratios less than 1 indicate that the *p,p'*-DDT had been biotransformed to DDE under aerobic conditions in most of collected sediment samples (Table 4). The DDT to DDE ratios, of the Aqaba Gulf recorded >5 in Dahab and Na'ama Bay. At the Red Sea proper: Hurghada-NIOF recorded <1, while at Hurghada-Sheraton, Safaga, Quseir >5 (Table 4) In the Western Mediterranean coast (Spain) and in the USA, the ratio is generally between 1:7 and 1:10, respectively, where the use of DDT has been banned in these countries since the mid-seventies (Sole et al., 1994).

Table 5 illustrates the concentration levels of PCB's in the sediment collected from the Suez Gulf, Aqaba Gulf and the Red sea proper. Table 5 reveals that the concentration levels of PCB's are in the order of the Red sea proper > the Suez Gulf > the Aqaba Gulf, in average concentration of (150, 120 and 80 ng kg⁻¹, respectively). The percentage distributions of PCB's are found to be 2% at Suez, 7% at Suez 05, 10% and

Table 4 The HCH isomers to the total HCHs percentage ratio and the DDT to DDE ratio in the sediment collected from the studied locations along the Egyptian Red Sea coast.

	Σ HCHs (ng kg ⁻¹)	α -HCH/ γ - HCHs	α -HCH/ Σ HCHs%	β -HCH/ Σ HCHs%	γ -HCH/ Σ HCHs%	Σ DDE (ng kg ⁻¹)	Σ DDT (ng kg ⁻¹)	DDT/ DDE
<i>The Suez Gulf</i>								
Suez	12	2.091	50.0	25.0	25.0	39	35	0.9
Ein Sukhna	15	2.091	66.7	6.7	26.7	63	21	0.3
Ras Suder	6	2.091	16.7	66.7	16.7	14	48	3.4
El Tour	12	2.091	50.0	25.0	25.0	39	35	0.9
Total	45	2.091	51.1	24.4	24.4	155	139	0.9
<i>The Aqaba Gulf</i>								
Nuweiba	8	5.0	62.5	25.0	12.5	9	3	0.3
Dahab	5	400.0	80.0	20.0	0.0	1	12	12.0
Sharm	7	5.0	71.4	14.3	14.3	4	17	4.3
Ras Mohamed	15	2.5	66.7	6.7	26.7	63	21	0.3
Na'ama Bay	6	600.0	100.0	0.0	0.0	1	9	9.0
Total	41	5.0	73.2	12.2	14.6	78	62	0.8
<i>The Red Sea proper</i>								
Hurghada- NIOF	6	4.0	66.7	16.7	16.7	31	22	0.7
Hurghada- Sheraton	10	0.4	30.0	0.0	70.0	6	37	6.2
Safaga	2	1.0	50.0	0.0	50.0	1	10	10.0
Quseir	10	2.0	60.0	10.0	30.0	2	16	8.0
Marsa Alam	11	2.3	63.6	9.1	27.3	22	8	0.4
Shalatin El- Rahaba	14	12.0	85.7	7.1	7.1	43	13	0.3
Bir Shalatin	4	300.0	75.0	25.0	0.0	3	10	3.3
Total	57	2.3	63.2	8.8	28.1	108	116	1.1

Table 5 Concentration of PCB's (ng kg⁻¹) in sediment collected from the Egyptian Red Sea coast.

	PCB 28	PCB 52	PCB101	PCB 118	PCB 153	PCB 138	PCB 180	ΣPCBs	PCB/ΣPCBs
<i>The Suez Gulf</i>									
Suez	5	ND	4	4	1	2	16	32	2
Ein Sukhna	7	58	3	2	40	7	8	126	7
Ras Suder	2	33	1	2	58	24	21	141	7
El Tour	3	1	5	13	4	48	82	157	8
Total	17	92	13	21	103	81	127	456	24
<i>The Aqaba Gulf</i>									
Nuweiba	2	5	1	4	2	12	21	45	2
Dahab	2	4	1	2	6	10	4	29	2
Sharm El-Maya	1	14	1	4	4	38	11	74	4
Ras Mohamed	21	5	1	4	2	12	21	64	3
Na'ama	2	1	1	1	10	154	30	200	11
Total	28	29	5	15	24	226	87	412	22
<i>The Red Sea proper</i>									
Hurghada-NIOF	4	1	2	2	5	28	39	81	4
Hurghada-Sheraton	1	12	2	3	15	320	13	366	19
Safaga	7	72	16	8	6	9	9	126	7
Quseir	2	14	1	1	10	17	6	52	3
Marsa Alam	26	122	25	26	18	77	25	318	17
Shalatin El-Rahaba	4	2	1	2	2	9	19	37	2
Bir Shalatin	1	2	1	3	10	5	25	48	3
Total	45	225	48	45	66	465	136	1028	54

8% at El-Tour. Meanwhile, their percentage distribution in the Aqaba Gulf and in the Red Sea Proper are Neiwaba (2%), Dahab (2%), Ras Mohamed (3%), Sharm El-Maya (4%), Na'ama (11%), Hurghada-NIOF (4%), Hurghada-Sheraton (19%), Safaga (7%), El Quseir (3%), Marsa Alam (7%), Bir-Shalatin (3%) and Shalatin El-Rahaba (2%).

The most abundant PCB congeners were detected in the Red Sea Proper samples as PCB 52 and PCB 138 (225 and 465 ng kg⁻¹, respectively). Meanwhile, in the Aqaba Gulf, the most abundant congeners were PCB 138 (226 ng kg⁻¹). At the Suez Gulf, the most abundant congeners were PCB's 180, 153, 52, and 138 (127, 103, 92 and 81 ng kg⁻¹, respectively). There was a direct input of domestic and industrial discharge in the most contaminated zones, the Aqaba Gulf and Suez Gulf, which resulted in a lower proportion of PCB138 in relation to PCB153. PCBs 153 is the main constituent in Aroclor 1260 and PCB 138 is the main constituent in Aroclor 1254 (ATSDR, 2000; Carro et al., 2010). The high concentration levels of PCB congeners are of a particular environmental concern due to their long half life time and easy bioaccumulation in the food chain (Pruel et al., 1993). The predominance of PCB153 was in accordance with many authors and may be attributed to the presence of chlorines at 2, 4 or 5 positions in one or both of the rings. Therefore, the uptake of PCB 153 by particulate matter in sea water is the most important (Green and Knutzen, 2003; Piersanti et al., 2006; Salem et al., 2013). Tolosa et al. (1995) reported that in samples from remote areas, a significant depletion of the higher chlorinated congeners is reported because the less volatile congeners are easier to remove from the atmosphere and cannot be transported to those regions. The report of tetrachlorobiphenyl (PCB 44 and PCB 52), pentachlorobiphenyl (PCB 101 and PCB 118) and hexachlorobiphenyl (PCB 138 and PCB 153)

may suggest a contribution from the PCB commercial mixtures that have been widely used in electrical equipment, transformers and different industries in many countries over the world (Barakat et al., 2002). Generally PCB persistence in the environment is due to their low vaporization, degradation, water solubility and distribution into particles and organic carbon (Kennish, 1992).

Correlation of OCPs and characteristics of sediments

The observed variation in the concentration levels of OCPs in the collected marine sediments can be attributed to the effluent of contaminated water from the agricultural fields, the high rate of influx of contaminants into the marine environment, the abiotic degradation influenced by microbial growths and various sediment physico-chemical characteristics (Sarkar 1991, 1994). Table 2 shows that all the collected sediment samples are sandy, which may explain the low levels of OCPs most of them. Moreover, the distribution of the organochlorine contaminants via the sedimentary layers pore efficiently influences the variation in the concentration of the disparate OCPs found in sediments of different characteristics (Sarkar 1994, El Nemr et al., 2012a,b).

The cluster analysis was used to identify the similarity between different organochlorine sources. Hierarchical cluster analysis (HCA) was carried out using average linkage clustering that was applied on the Pearson correlation for the seven polychlorinated compounds (Fig. 2) and the twelve pesticides (Fig. 3) under investigation. The results of the cluster analysis were confirmed by applying two different clustering methods: (1) complete linkage and (2) single linkage using further neighbor and the nearest neighbor, respectively, with interval Pearson correlation. Similar relations between investigated

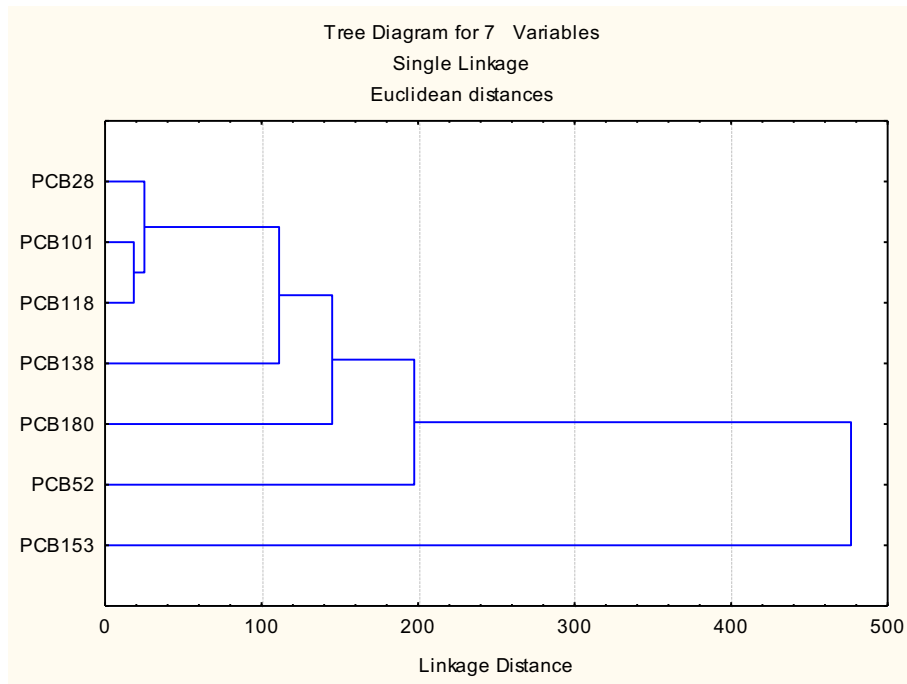


Figure 2 Dendrogram for hierarchical clusters analysis of PCB concentrations in collected sediments using average linkage (between groups).

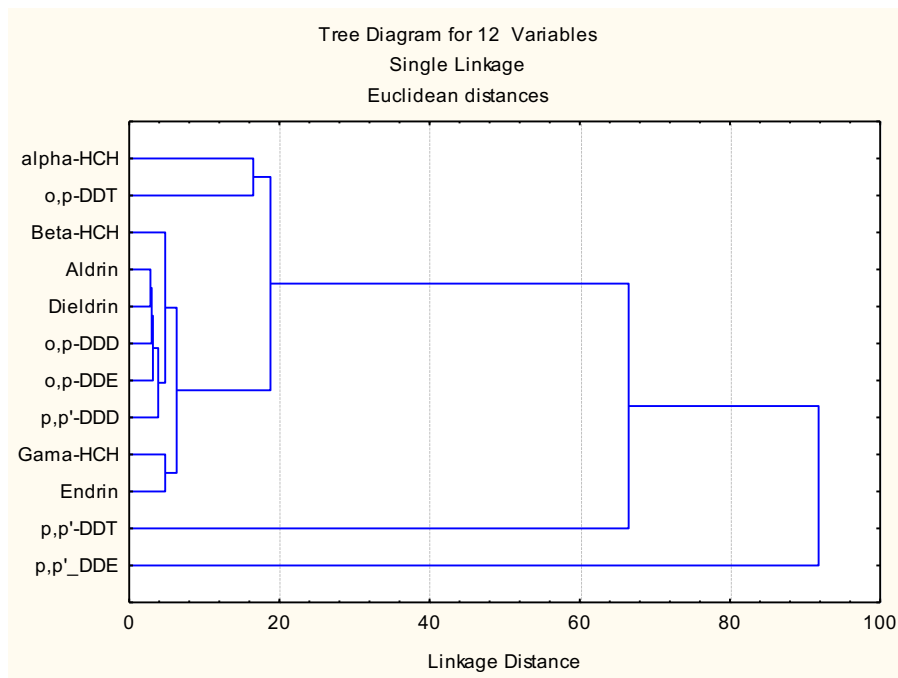


Figure 3 Dendrogram for hierarchical clusters analysis of pesticide concentrations in collected sediments using average linkage (between groups).

pollutants were obtained from the three studied clustering methods. The cluster analysis in Fig. 2 shows that the three PCBs, 28, 101 and 118, may come from similar sources since they have good correlation to each other. PCB 153 on the other hand, reported a very far clustering with the other PCBs

at a distance of 500. The PCBs 52, 138 and 180 are linked to each other at a moderate distance. The source of PCB153 is expected to be different than the rest of the studied PCB sources. Fig. 3 shows the cluster analysis of pesticides, which can be identified as follows: the first cluster contains two pes-

ticides (α -HCH and *o,p*-DDT) at a distance of 17, the second cluster contains eight pesticides (β -HCH, aldrin, dieldrin, *o,p*-DDD, *o,p*-DDE, *p,p'*-DDD, γ -HCH and endrin) at a distance of 7 and fused with the first cluster at distance of 19. At a higher distance (about 67), *p,p'*-DDT formed a cluster with cluster 1 and 2, while the remaining pesticide (*p,p'*-DDE) formed the last cluster with the other pesticides at a distance of 92. The results obtained in Fig. 3 represent how most of the studied pesticides are expected to enter the coast from the same sources.

Hazard levels

The maximum permissible levels of OCPs that are recommended by the National Academy of Engineering and the National Academy of Sciences (NAE-NAS, 1972) are of total PCBs (1000–5000 $\mu\text{g kg}^{-1}$ wet wt.), as for cyclodienes, it is (100 $\mu\text{g kg}^{-1}$ wet wt.). The Swedish Food Regulation recommended levels are 5000 $\mu\text{g kg}^{-1}$ for total DDTs, 2000 $\mu\text{g kg}^{-1}$ for total PCBs and 200 $\mu\text{g kg}^{-1}$ for HCB (SFR, 1983). This study, clearly indicates that the total PCB concentrations, DDTs, cyclodienes, HCHs were much lower than those recorded by the above international organization.

Conclusion

The major conclusions which can be obtained from this study are (i) the most of organochlorine concentrations reported in the collected sediments from the Red Sea proper, Gulf of Aqaba and Suez Gulf coast were either of very low values or below the detection limits (ii) DDTs with low concentrations were reported in some of the examined sediment samples. However, concentrations of DDTs were relatively lower than those reported previously in many areas. (iii) Very low values of PCBs were also found in some samples of the sediment from the Red Sea proper, Gulf of Aqaba and Suez Gulf. The results obtained showed fairly low levels of pesticide residues. High proportions of α -HCH over γ -HCH isomer indicated less recent input of lindane. The ratios of α -HCH/ γ -HCH of most of the studied locations are slightly less than those in technical-grade HCH mixture (66.5% α isomer, 11.4% β isomer, 15.2% lindane, 6.4% δ isomer, and 0.5% other isomers) except at Dahab, Na'ama Bay and Bir Shalatin indicating that there was less input of lindane in the past several years. The source of PCB153 is expected to be different than the rest of the studied PCB sources. Most of the studied pesticides are expected to enter the coast from the same sources. Generally, it is recommended that a continuous monitoring program for the studied areas should be formulated and conducted to ensure that the concentration of DDTs and PCBs are within the acceptable level proposed by the international institute.

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