



FULL LENGTH ARTICLE

Assessment of pesticides and polychlorinated biphenyls (PCBs) in sediments of the Egyptian Mediterranean Coast

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Abstract In an attempt to evaluate the toxicological condition of the Egyptian Mediterranean Sea from El-Sallum to El-Arish, 10 surficial sediment samples were collected from different locations covering the region that receives the majority of the industrial, agricultural and urban effluents (land-based activities), and thus is expected to be contaminated with different degrees of pollution. Sediment samples were analyzed for PCBs (PCB 18, 28, 44, 52, 101, 118, 138, 153, 180 and 194), and organochlorine pesticides (α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, methoxychlor, heptachlor-epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, γ -chlordane, α -endosulfane, β -endosulfane, p,p' -DDE, p,p' -DDD, p,p' -DDT). The investigated sediments were dominated by the sand fraction, except Rosetta station. The concentration of organic pollutants in sediments followed the order: Total cyclodienes > PCBs > DDTs > HCHs. Sediments were dominated by the metabolites of DDT (DDD and DDE) indicating that the detected DDTs in the bay sediments are not recently introduced into the bay. At the same time, DDE concentrations were higher than DDD in all the sediment samples (except El-Sallum and Sidi-Kreer) indicating oxic conditions. The risk assessment for organic pollutants were studied, indicating a greater possibility of the occurrence of toxic adverse ecological effects with respect to all investigated organic pollutants and frequent toxic effect is expected for lindane and p,p' -DDT.

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Introduction

The use of pesticides increased significantly in many countries of the world, including Egypt during the last two decades of the twentieth century. The usage of PCBs in Egypt is not well established, but the use of PCBs in transformers, electrical equipment, and other industries is common and owing to their persistence, PCB contaminations are widespread at the Alexandria Harbor (Barakat et al., 2002). As one class of the

ubiquitous persistent organic pollutants (POPs), organochlorine pesticides (OCPs) have been a major environmental issue, drawing extensive attention to environmental scientists and the public (Jiang et al., 2009; El Nemr et al., 2003; El Nemr, 2005, 2011, 2012, 2013). They were the most widely used pesticides around the world before the 1970s (Wong et al., 2005). Organochlorine pesticides in the environment are characterized by high chemical stability, poor water solubility and low vapor pressures (Bouwman, 2004). Consequently they are commonly referred to as persistent organic pollutants (Darko et al., 2008). As such, out of the 21 POPs that have been earmarked for phase-out and elimination, 14 are organochlorine pesticides, dichlorodiphenyltrichloroethane (DDT), aldrin, endrin, dieldrin, chlordane, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, chlordecone, lindane and pentachlorobenzene (Stockholm Convention, 2001, 2009), despite bans on their production and usage (Guruge and Tanabe, 2001; Iwata et al., 1994). Many of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of humans and wildlife (Colborn and Smolen, 1996). OCPs were found widespread in the environmental media, such as soil, water, suspended particulate matter, sediment, atmosphere and organisms (Cai et al., 2010; Liu et al., 2008). The OCPs could spread into aquatic environments through runoffs from non-point soil sources. With low-water solubility and high hydrophobicity, OCPs are readily sorbed onto suspended particulate matter and subsequently deposit into river and marine sediments (Yang et al., 2005). Soil and sediments play an important role in the global distribution and fate of POPs. They not only have a large retention capacity but also re-emit into the environment as a secondary source and release bound-OCPs from particles into the water under favorable conditions (Barra et al., 2005; Zheng et al., 2009). Through the interaction between sediments and water, the transfer of OCPs from sediments to organisms is now regarded as a major route of exposure for many species (Zoumis et al., 2001). In the aquatic environment, a low dose of OCPs might still cause biologically toxic effects on ecosystems (Crisp et al., 1998) and the contamination might even hazard the human beings through aquatic food. Studies have suggested that OCPs may affect the normal function of the endocrine system of humans and wildlife (Colborn and Smolen, 1996; Xue et al., 2005). Some of the most known POPs are the polychlorinated biphenyls (PCBs), which are a class of 209 congeners, each of which consists of two benzene rings and one to ten chlorine atoms (Hutzinger et al., 1974). The PCBs are highly lipophilic, thermally stable and have low flammability (De Voogt and Brinkman, 1989). The degree of lipophilicity increases with the increase in chlorination where the log K_{ow} increases from 4.46 to 8.18, respectively, from PCB1 to PCB 209 (Hawker and Connell, 1988). The PCBs have been detected in various environmental compartments worldwide, and they have been shown to bioaccumulate within food chains (Lundgren et al., 2002). It is well known that over one hundred PCBs were identified in the technical PCBs mixtures. However, only a part of them could be detected at significant levels in nature. Moreover, it is highly cost-effective to monitor fewer congeners, especially since it may be possible to acquire nearly all desired information from a reduced set of measurements, due to the high correlation of many PCB congeners.

The Mediterranean Coast of Egypt extends for about 1050 km from Rafah in the east on the Sinai Peninsula to

Sallum in the west. It is one of the longest Mediterranean shores in North Africa. The Mediterranean Sea appears to suffer from high anthropogenic pressure due to inputs from; industrial, sewage effluents, storm water drains, shipping activities, spillage, rivers, atmospheric-fallout, coastal activities and natural oil seeps (UNEP, 1984). It is also characterized by the occurrence of Egypt's four northernmost lakes.

In this study, concentrations of polychlorinated biphenyls and organochlorine pesticides in surface sediments have been determined to study the horizontal distribution of these compounds along the Egyptian Mediterranean Coast from El-Sallum to El-Arish and to evaluate their potential effects on aquatic organisms.

Materials and methods

The Egyptian Mediterranean Coast is extending from El-Sallum in the West to El-Arish in the East. Ten stations were selected where Sidi-Kereer is affected by SUMED oil Production Company, El-Mex Bay is affected by industrial wastes, in addition to huge amounts of drainage waters mixed with remains of pesticides and fertilizers from the agricultural wastes (Shriadah and Emar, 1991). Eastern Harbor, semi closed basin is affected by untreated sewage beside its ship-yard waste disposal (Shriadah and Emar, 1991) while Abu-Qir Bay is exposed to industrial and agricultural wastes (El-Tawil and Khalil, 1983). El-Jamil and Port Said which are nearby Lake Manzallah suffer from industrial and agricultural wastes while El-Arish is located near Lake Bardawill.

Sampling

Surface sediment samples (0–5 cm) were collected along the Egyptian Mediterranean Coast, from El-Sallum to El-Arish (Fig. 1) using a van Veen grab sampler. Immediately after collection, samples were placed in aluminum bags, frozen and transported to the laboratory for analysis. Sediment samples were dried in a vacuum oven (Medline, OV-12) at 40 °C for 3–4 days until constant weight, sieved to separate shells and stone, lightly ground in an agate mortar for homogenization and prepared for analysis after separation of shells and stones from each sample.

Grain size analysis

Sediment samples were dried in an oven at 105 °C to constant weight. The grain size analysis of samples was performed using the sieving technique according to Folk (1974).

The total organic carbon

Total organic carbon (TOC) content was determined by oxidation with 1 N $K_2Cr_2O_7$ acidified with concentrated H_2SO_4 and titration with 0.5 N $[Fe(NH_4)_2(SO_4)_2]$ (Loring and Rantala, 1992).

Total organic matter

Total organic matter (TOM) was calculated by the equation:

$$TOM\% = TOC\% \times 1.8$$

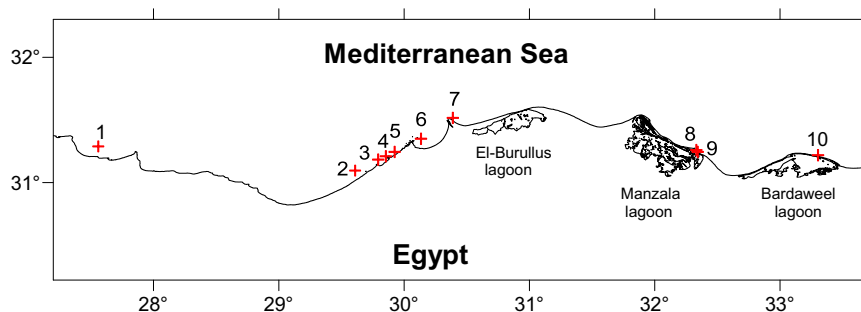


Figure 1 Sampling locations map, 1: El-Sallum, 2: Sidi-Kereer, 3: El-Mex, 4: Eastern Harbor, 5: El-Shatby, 6: Abu-Quir, 7: Rosetta, 8: El-Jamil, 9: Port Said, 10: El-Arish.

The total phosphorus

The total phosphorus (TP) content was determined according to [Aspila et al. \(1976\)](#). 0.2–0.5 g of the sample is transferred into uncovered crucible and ignited in muffle furnace at 550 °C for 2 h and left to cool, then transferred to 100 ml measuring flasks with the help of about 50 ml of 1 N HCl. Then the flask was shaken for 14–18 h on an electric horizontal shaker. After the extraction, aliquots of the ignited solutions were transferred into a 15 ml test tube and centrifuged at 2000 rpm for about 5 min. Then clarified extracts are finally diluted and analyzed for total-P using the modified single solution method described by [Murphy and Riley \(1962\)](#).

The inorganic phosphorus

The inorganic phosphorus (IP) was determined using the same method for TP omitting ignition.

The organic phosphorus

The organic phosphorus (OP) was estimated by subtracting the value of IP from that of TP for the same sample.

Total carbonates

Total carbonates were estimated as described by [Molnia \(1974\)](#).

Extraction and cleanup

Homogenized subsamples were extracted with Soxhlet apparatus; 15 g sediment was placed into a thimble filter and extracted with 250 ml *n*-hexane for 8 h at a rate of 4–6 cycles/h. The sample extract was then pre-concentrated to 2–3 ml on a rotary evaporator. Activated copper powder was used to remove sulfur compounds from the extract, ([Doong et al., 1999](#); [UNEP, 1991](#)). The final extracted volume (1 ml) was transferred to the top of a glass column packing with 20 g of florisil followed by 1 g of anhydrous sodium sulfate. Elution was performed using 70 ml of *n*-hexane for PCB fractions (F_1), then 50 ml mixture (70% hexane and 30% dichloromethane) for pesticide fractions (F_2). The eluted solvents were concentrated to about 1–2 ml on a rotary evaporator and then transferred to 10 ml

glass tubes with small amounts of *n*-hexane. The solvent in the glass tube was evaporated almost completely under a gentle stream of nitrogen and the precipitates were re-dissolved in 1 ml hexane. The concentrations of organochlorine pesticides in the extracts were monitored with Hewlett Packard 5890 series II GC gas chromatograph equipped with ^{63}Ni -electron capture detector (ECD). A fused-silica capillary column (30 m \times 0.32 mm \times 0.52 μm) coated with DB-1 (5% diphenyl and 95% dimethyl polysiloxane) was used for the quantification. The oven temperature was programmed from an initial temperature of 70 °C (2 min hold) to 280 °C at a rate of 5 °C min^{-1} and was then maintained at 280 °C for 20 min. Injector and detector temperatures were maintained at 270 and 300 °C, respectively. Helium was used as the carrier (1.5 ml min^{-1}) and nitrogen as the make-up (60 ml min^{-1}) gas. Concentrations of individually resolved peaks were summed to obtain the total PCB concentration. Compound identification was confirmed by GC coupled to mass spectrometry in the chemical ionization mode and negative ion recording (Trace DSQ II Ms with capillary column; Thermo TR-35 MS Mass Selective Detector). Ion repeller was 1.5 V. Data were scanned from m/z 50 to 450 at 1 s per decade. Data were also acquired in selected ion monitoring mode with dwell time and span of 0.06 s and 0.10 a.m.u., respectively.

The whole analytical procedure was validated by analyzing sediment reference materials IAEA-408 provided by International Atomic Energy Agency (IAEA). The results of analyzing the reference materials fell within the range of the certificated value for almost all of the investigated organic pollutants as shown in [Table 1](#).

Statistical analysis

Principal component analysis (PCA), cluster analysis (CA) and Spearman (non-parametric) rank order correlations are the most common multivariate statistical methods used in environmental studies ([Bakaç, 2000](#); [El Nembr and Abd-Alla, 2004](#); [El Nembr et al., 2006, 2007, 2012a,b,c, 2013](#)). In the present study, SPSS for Windows, Version 15, was utilized for the multivariate analysis and for correlation analysis.

Principal component analysis

Multivariate analysis (Principal component analysis, PCA) has been applied on the data set for ten sediment samples and four variables (HCHs, TC, DDTs and PCBs). R-mode factor

Table 1 Results obtained (ng/g dry wt) for reference IAEA - 408 sediment materials.

Organochlorines	Required	Found	Recovery%
PCB 18	0.74	0.73	98.65
PCB 28	0.79	0.77	97.47
PCB 44	0.47	0.47	100.00
PCB 52	0.60	0.63	105.00
PCB 101	1.20	1.19	99.17
PCB 118	1.20	1.36	113.33
PCB 138	1.60	1.69	105.63
PCB 153	1.90	1.92	101.05
PCB 180	1.10	1.07	97.27
PCB 194	0.20	0.20	100.00
α -HCH	0.61	0.62	101.64
β -HCH	0.55	0.57	103.64
γ -HCH	0.19	0.18	94.74
<i>p,p'</i> -DDE	1.40	1.33	95.00
<i>p,p'</i> -DDD	0.87	0.85	97.70
<i>p,p'</i> -DDT	0.67	0.65	97.01
Aldrin	0.41	0.38	92.68
Dieldrin	0.30	0.27	90.00
Endrin	0.57	0.58	101.75
Heptachlor	0.42	0.39	92.86
Heptachloro epoxide	0.64	0.64	100.00
γ -chlordane	0.27	0.28	103.70
Endosulfan (alpha)	1.60	1.50	93.75
Endosulfan sulfate	1.60	1.59	99.38

analysis with VARIMAX rotation with Kaiser Normalization, as well as the Eigen values was applied to the previous organic pollutants in the sediment samples.

Cluster analysis

Hierarchical cluster analysis (HCA) was carried out using the average linkage clustering which was applied on the Pearson correlation for the four groups of pollutants under investigation. This dendrogram was confirmed by applying two other clustering methods: (1) single linkage, using the cluster method nearest neighbor with interval Pearson correlation, (2) complete linkage, using the further neighbor with the interval Pearson correlation.

Risk assessment

The effect characterization was based on several sets of sediment quality guidelines (SQGs) reported in texts. These SQGs have been calculated using different theoretical and empirical approaches; the effects range approach including the effect range low (ERL) and the effect range medium (ERM) (Long et al., 1995), the effects level approach (ELA) including the threshold effect level (TEL) and the probable effect level (PEL) (MacDonald et al., 1996). In most of the developed sediment quality guidelines, more than one value is available, one representing the low level of adverse ecological effects (ERL, TEL and T20) and the other representing the higher level of adverse ecological effects (ERM, PEL, and T50). As a result of the different approaches mentioned above in the section, SQGs reported for different pollutants exhibit a great variability, so that some authors have developed the consensus based approach trying to harmonize the existing values (Swartz,

1999; MacDonald et al., 2000a,b), which was used in the present study for the risk calculations and for pointing out the presence of any hot spots along the Egyptian Mediterranean Sea. Because consensus based marine SQGs were not available for all the target pollutants, with the exception of PCBs (MacDonald et al., 2000a), values were calculated for all the target pollutants in the present study following the methodology described by MacDonald et al., 2000a,b). Following classification of the existing SQGs, consensus-based TECs were calculated by determining the geometric mean of the SQGs that are included in this category. Likewise, consensus-based PECs were calculated by determining the geometric mean of the PEC-type values. The geometric mean, rather than the arithmetic mean, was calculated because it provides an estimate of central tendency that is not unduly affected by outliers and because the SQGs may not be normally distributed. Consensus-based TECs or PECs are calculated only if three or more published SQGs are available for a chemical substance or group of substances (MacDonald et al., 2000a,b). In the present study, the risk was characterized by comparing the maximum concentration of each pollutant with its corresponding sediment quality guideline. The selected approach was the hazard quotient (HQ). Two HQs were calculated for each pollutant; *TEC HQ* which was calculated by dividing the maximum concentration of each pollutant by the calculated consensus-based TEC ($CBSQG_{TEC}$) and the *PEC HQ*, which was calculated by dividing the maximum concentration of each pollutant by the calculated consensus-based PEC ($CBSQG_{PEC}$). When *TEC HQ* < 1 for a given pollutant, rare adverse ecological effects are expected to occur with respect to this pollutant, when *PEC HQ* > 1, frequent adverse ecological effects are expected to occur and when *TEC HQ* > 1 > *PEC HQ*, adverse ecological effects are possible but less frequent than the previous level.

$$TECHQ = \frac{\text{Concentration of the pollutant}}{CBSQG_{TEC}}$$

$$PECHQ = \frac{\text{Concentration of the pollutant}}{CBSQG_{PEC}}$$

Results and discussion

The grain size analysis, total phosphate, total organic carbon, total organic matter, total carbonate and total silicate are illustrated in Table 2. All sediment samples were sand except El-Sallum and Rosetta stations which had 91.54% and 56.03% of sand. Total phosphate fluctuated from 56.32 at El-Mex station to 345.54 $\mu\text{g/g}$ at El-Jamil station. Stations Sidi-Kreer, El-Mex, El-Shatby, El-Arish are moderately sorted, while stations El-Sallum, Eastern Harbor, Abu-Qir, El-Jamil and Port-Said are poorly sorted and Rosetta is extremely poorly sorted. Total organic carbon and total organic matter recorded their lowest values at Port-Said station (0.12% and 0.22% respectively), while the highest levels were recorded at Rosetta station (1.46% and 2.64% respectively). El-Arish station recorded the highest value for total carbonate whereas the highest value of total silicate was recorded at El-Shatby station (80.37% and 98.30% respectively). On the other hand, the opposite trend was obtained, where the lowest value of silicate was recorded at El-Arish station, while El-Shatby recorded the lowest value for total carbonate (19.63% and 1.70% respectively).

Table 2 Grain size analysis, the concentration of phosphates, total organic carbon percentage, total organic matter percentage, total carbonate percentage and total silicate percentage.

Sample	Sand (%)	Mud (%)	Mean Sorting (phi)	Skewness (phi)	Kurtosis	TP ($\mu\text{g/g}$)	IP ($\mu\text{g/g}$)	OP ($\mu\text{g/g}$)	TOC (%)	TOM (%)	TCO ₃ (%)	TSiO ₃ (%)	
El-Sallum	91.54	8.46	3.19	1.37	0.11	2.82	160.03	98.25	61.78	0.27	0.49	54.28	45.72
Sidi Kreer	100.00	0.0	3.14	0.89	-0.5	1.85	58.17	26.22	31.95	0.23	0.42	17.48	82.52
El-Mex	100.00	0.0	0.11	0.81	0.31	0.68	56.32	21.50	34.82	0.79	1.43	27.56	72.44
Eastern Harbor	100.00	0.0	0.33	1.01	0.67	0.7	231.38	202.66	28.72	0.91	1.65	3.49	96.50
El-Shatby	100.00	0.0	2.98	0.8	-0.29	1.01	122.62	88.21	34.41	0.13	0.24	1.70	98.30
Abu-Qir	100.00	0.0	1.57	1.64	-0.23	0.48	223.77	72.38	151.39	0.30	0.55	39.41	60.59
Rosetta	56.03	43.97	3.70	3.56	0.07	0.59	273.97	253.46	20.51	1.46	2.64	61.20	38.80
El-Jamil	100.00	0.0	1.25	1.11	0.03	0.80	345.54	232.42	113.12	0.24	0.43	61.88	38.12
Port-Said	100.00	0.0	1.26	1.73	0.09	0.54	151.62	63.04	88.58	0.12	0.22	64.26	35.74
El-Arish	100.00	0.0	1.06	0.91	0.45	0.86	101.16	55.21	45.95	0.16	0.29	80.37	19.63

The concentration of organic pollutants in the present study for sediments followed the order: Total cyclodienes > PCBs > DDTs > HCHs. Despite the ban and restriction on the usage of some organochlorine pollutants (OCPs) (Guruge and Tanabe, 2001; Iwata et al., 1994), the analyzed samples showed the presence of persistent organic pollutants (POPs) in sediments. The POPs detected in sediments include, α -, β -, γ -, δ -HCH, DDTs (*p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT), aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlor, methoxychlor, heptachloro epoxide, γ -chlordane, endosulfan (alpha), endosulfan (beta), endosulfan sulfate and polychlorinated biphenyls (PCBs). The POP residues in surface sediment samples of the Egyptian Mediterranean Coast are summarized in Table 3. Concentrations of total POPs ranged from 30.25 to 155.35 ng g⁻¹ with an average 88.20 ng g⁻¹.

The PCB concentrations in the surface sediments ranged from 7.06 to 75.17 ng g⁻¹ (Table 3). The highest concentrations (75.17 and 55.56 ng g⁻¹) were found in samples collected from El-Mex Bay and Eastern Harbor, respectively. Persistence of PCBs in this area may be due to wastes dumped in these areas; the industrial and shipping activities are intense (Barakat et al., 2002). On the other hand, lower PCB concentration was detected at El-Shatby station (7.06 ng g⁻¹). The most abundant PCB congener detected in the investigated sediment samples was PCB 101 (8.86 ng g⁻¹). The persistence of PCBs in aquatic sediments is due to their low rate of degradation and vaporization, low water solubility, and partitioning to particles and organic carbon (Kennish, 1992). The physico-chemical properties as well as the degradation of PCBs vary widely and depend on the number and position of chlorine atoms in the biphenyl rings (Abramowicz et al., 1993; Rhee et al., 1993). In the present work, the penta, hexa and heptachlorinated biphenyl congeners contributed the most to total PCBs in sediment samples. These findings were in agreement with Lewandowski et al. (1997) and Galanopoulou et al. (2005) who stated that the degradation half-life increases with the increase in the degree of chlorination and ranges between 8 and 365 days. The adsorbed mono-, di-, and tri-chlorobiphenyls have degraded relatively fast. The PCBs with more than 5 chlorine atoms in their molecule are far more stable in biodegradation and as a result they accumulate in higher concentrations. Also, it is suggested that highly chlorinated PCBs with high *K*_{ow} are likely to be adsorbed to suspended particulate material than low chlorinated PCBs. These materials then probably settle onto the bottom sediments near the source

areas. On the other hand, the more water soluble low chlorinated PCBs are probably transported to a further distance from the source than the highly chlorinated PCBs.

After the PCB production was banned in the late 1970s, it had been thought that they would not be found in the environment. The results of the present study, however, showed that this is not the case. It is likely that the PCBs came from the residues from former applications. Due to their resistance to degradation in the environment, PCBs could be continuously detected for many years (Jones and De Voogt, 1999; Zhang et al., 2004).

Two widely used sediment quality guidelines, the effects range-low value (ERL) and effects range-median value (ERM) guidelines (Long et al., 1998, 1995), as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines (CCME, 2002) were applied to evaluate the possible ecotoxicological risks of organic pollutants in the study area. By comparing the PCB level detected in the present study with quality guidelines, all investigated samples exceeded the ERL and TEL whereas 20% of the samples (El-Mex and Eastern Harbor) exceeded ERM and PEL which cause an adverse effect. On the other hand, the rest of the samples (80%) were between ERL and ERM, which suggested that the concentration levels of PCBs at most sites, have a greater possibility in the occurrence of a toxic adverse biological risk.

The concentrations of total HCHs in the surface sediment samples ranged from 3.20 to 26.71 ng g⁻¹ at Sidi-Kreer and Rosetta, respectively, with an average 7.08 ng g⁻¹ representing about 8% of total organochlorine compounds. A high concentration of β -HCH was observed sharing a major portion of HCH (65% of total HCHs) followed by γ -, δ - and α -HCH. The predominant presence of the β -HCH isomer found in this study can be explained by the lowest water solubility, lowest vapor pressure, highest chemical stability, and the resistance to microbial transformation of β -HCH compared to other isomers (Ramesh et al., 1991). In addition, the transformation of α - and γ -HCH to β -HCH may be the reason for the predominance of β -HCH in sediments (Wu et al., 1997). For the industrial HCHs, the relative proportions of the four components were α -(65–70%) > γ -(12–14%) > δ -(6%) > β -(5–6%), while Lindane consists of 99% γ -HCH. The ratio of α -HCH/ γ -HCH is 4.64–5.83 for industrial HCHs. In the present study, the ratio of α -HCH/ γ -HCH varied from 0.13–1.80 in sediment samples (Table 3), suggesting that the input of HCHs is from a mixture of industrial HCH and Lindane (Iwata et al., 1995).

Table 3 The concentration (ng/g dry wt) of Pesticides and PCBs in sediment collected from El-Sallum to El-Arish along the Egyptian Mediterranean Sea.

Compound	El-Sallum	Sidi-Kreer	El-Mex	Eastern harbor	El-Shatby	Abu-Quir	Rosetta	El-Jamil	Port-Said	El-Arish	Max	Min	Mean	SD
α -HCH	0.52	0.73	0.66	0.23	0.29	0.29	1.21	0.96	0.42	0.53	1.21	0.23	0.58	0.32
β -HCH	2.35	1.99	2.73	4.45	2.37	1.98	21.72	2.03	3.98	2.32	21.72	1.98	4.59	6.08
γ -HCH	0.99	0.40	0.97	0.74	2.20	1.03	2.14	1.35	1.66	1.49	2.20	0.40	1.30	0.58
δ -HCH	0.40	0.09	0.57	0.21	0.56	0.21	1.65	1.32	0.76	0.38	1.65	0.09	0.61	0.50
α -HCH/ δ -HCH	0.52	1.80	0.69	0.31	0.13	0.28	0.57	0.71	0.25	0.35	1.80	0.13	0.56	0.48
HCHs	4.26	3.20	4.93	5.63	5.41	3.50	26.71	5.66	6.82	4.72	26.71	3.20	7.08	6.98
<i>p,p'</i> -DDE	1.18	0.41	4.15	3.47	1.29	5.61	4.28	10.09	2.83	5.96	10.09	0.41	3.93	2.86
<i>p,p'</i> -DDD	6.95	4.37	0.42	2.57	0.38	4.12	2.38	6.57	1.72	2.40	6.95	0.38	3.19	2.29
<i>p,p'</i> -DDT	8.66	5.40	3.00	3.52	3.22	14.96	6.45	13.27	1.10	5.36	14.96	1.10	6.49	4.54
Total DDTs	16.79	10.17	7.56	9.55	4.89	24.70	13.11	29.93	5.66	13.72	29.93	4.89	13.61	8.19
Aldrin	0.35	0.66	10.23	4.78	0.94	0.75	8.03	0.77	2.91	0.54	10.23	0.35	3.00	3.55
Dieldrin	2.21	1.20	1.82	2.32	1.82	1.82	1.38	2.25	2.93	3.46	3.46	1.20	2.12	0.68
Endrin	1.85	0.56	8.17	0.33	1.05	0.51	1.56	0.71	0.94	2.06	8.17	0.33	1.77	2.32
Endrin Aldehyde	1.11	0.54	0.18	0.59	3.80	1.30	0.78	1.50	1.14	0.59	3.80	0.18	1.15	1.01
Endrin Ketone	0.52	0.11	0.45	0.30	0.17	0.97	1.05	5.38	0.06	1.26	5.38	0.06	1.03	1.58
Heptachlor	1.14	0.54	0.50	0.73	0.25	0.60	4.52	4.07	0.24	1.68	4.52	0.24	1.43	1.57
Methoxychlor	0.07	0.03	0.07	0.07	0.09	0.05	0.19	0.08	0.02	0.22	0.22	0.02	0.09	0.07
Heptachloro epoxide	3.89	0.05	1.89	0.07	0.07	0.39	0.09	0.10	0.32	0.14	3.89	0.05	0.70	1.25
γ -chlordane	0.22	0.12	0.34	0.89	0.32	0.99	0.54	0.67	0.42	0.71	0.99	0.12	0.52	0.29
Endosulfan (alpha)	1.42	2.22	0.19	0.84	0.38	2.32	3.35	6.29	2.36	3.22	6.29	0.19	2.26	1.79
Endosulfan (beta)	5.86	5.56	27.71	4.94	1.62	3.28	6.16	5.74	5.75	11.46	27.71	1.62	7.81	7.43
Endosulfan sulfate	8.98	7.48	16.15	14.77	2.39	38.13	15.27	14.94	6.90	16.11	38.13	2.39	14.11	9.70
TCs	27.62	19.07	67.69	30.63	12.89	51.10	42.92	42.49	23.99	41.44	67.69	12.89	35.98	16.38
PCB 18	0.04	0.03	0.18	0.02	0.05	0.33	0.06	0.22	0.12	0.03	0.33	0.02	0.11	0.10
PCB 28	0.72	0.06	2.37	0.07	0.43	0.61	1.08	0.35	0.50	0.10	2.37	0.06	0.63	0.69
PCB 44	0.76	0.00	0.72	0.00	0.01	0.00	0.54	0.01	0.01	0.00	0.76	0.00	0.21	0.33
PCB 52	7.48	0.08	8.52	0.07	0.16	6.25	5.87	1.97	0.38	0.08	8.52	0.07	3.09	3.51
PCB 101	6.09	8.21	25.19	16.61	2.32	5.98	7.54	5.56	4.01	7.07	25.19	2.32	8.86	6.87
PCB 118	0.00	1.68	0.00	3.67	2.16	0.00	0.81	0.00	3.46	3.64	3.67	0.00	1.54	1.60
PCB 138	8.37	6.93	0.00	3.42	0.00	0.00	1.03	6.64	7.16	0.00	8.37	0.00	3.36	3.55
PCB 153	0.00	1.96	35.54	3.01	0.00	4.56	4.91	5.18	0.00	2.70	35.54	0.00	5.79	10.65
PCB 180	11.00	7.42	2.65	28.27	1.66	9.07	9.70	2.11	2.97	1.36	28.27	1.36	7.62	8.14
PCB 194	0.66	0.43	0.00	0.40	0.27	0.00	0.18	0.37	0.42	0.63	0.66	0.00	0.34	0.23
T PCBs	35.12	26.81	75.17	55.56	7.06	26.81	31.71	22.40	19.02	15.61	75.17	7.06	31.53	20.09
TOCs	83.79	59.25	155.35	101.37	30.25	106.11	114.44	100.47	55.48	75.49	155.35	30.25	88.20	35.42
DDE/DDTs	0.07	0.04	0.55	0.36	0.26	0.23	0.33	0.34	0.50	0.43	0.55	0.04	0.31	0.17
DDD/DDTs	0.41	0.43	0.06	0.27	0.08	0.17	0.18	0.22	0.30	0.17	0.43	0.06	0.23	0.13
DDD/DDE	5.90	10.77	0.10	0.74	0.29	0.73	0.56	0.65	0.61	0.40	10.77	0.10	2.07	3.50

Table 4 Comparison of PCB and OCP concentration (ng/g dry wt) in the sediments from other locations.

Location	Year	PCBs	DDTs	Chlordane	HCHs	References
<i>Mediterranean Sea</i>						
Egyptian Mediterranean coast	2010	7.06–75.17	4.89–29.93	0.12–0.99	3.20–26.71	This study
Northwest Basin	1990	1.4–5.8	1.2–5.8	NA	NA	Tolosa et al. (1995)
Open sea	1983	0.8	0.047	NA	0.18a	Burns and Villeneuve (1987)
Coastal Barcelona offshore	1990	4.0–64	4.9–79	NA	NA	Tolosa et al. (1995)
Casco Bay, Maine, USA	1991	0.4–485	<0.2–20	<0.25–4.91	<0.07–0.48a	Kennicutt et al. (1994)
Abu-Quir Bay, Egypt	1989–1991	53–231	44–223	NA	16–82	Abdallah (1992)Abdallah and Abbas (1994)
El-Mex Bay, Egypt	1989–1991	68–164	32.3–87	NA	16–53	Abdallah (1992)Abdallah and Abbas (1994)
<i>Rivers, Lakes, estuaries</i>						
Ebro River, Spain	1995–1996	5.3–1772	0.4–52	NA	0.001–0.038	Fernandez et al. (1999)
Ebro Prodelta, Spain	1990	1.6–39	0.8–93	NA	NA	Tolosa et al. (1995)
Rhone Prodelta, France	1990	38–230	73–704	NA	NA	Tolosa et al. (1995)
Lake Baikal, Russia	1992	0.08–6.1	0.014–2.7	n.d.-0.003	0.019–0.12	Iwata et al. (1995)
Washington, DC, USA	1991	68–3200	7–160	5–153	NA	Wade et al. (1994)
Hong Kong, PRC	1997–1998	0.48–97.9	0.27–14.8	n.d.-11.3	0.1–16.7	Richardson and Zheng (1999)
Chinese river/estuaries systems	1996–1998	0.05–20	0.1–71	NA	0.2–101	Hong et al. (1999)Wu et al. (1999)Yuan et al. (2001)
<i>Harbors</i>						
Victoria harbor, Hong Kong	1992	3.2–27	1.4–30	NA	n.d.-2.3	Connell et al. (1998)
Xiamen harbor, PRC	1993	0.05–7.2	4.5–311	NA	0.14–1.12	Hong et al. (1995)
Manukkau harbor, New Zealand		0.5–14.2	1.2–2.3	0.9–5.3	0.1–2.0	Fox et al. (1988)
Alexandria harbor, Egypt	1998	0.9–1211	<0.25–885	<0.25–44	0.25–6.0	BaraKat et al. (2002)

Note: NA: no data available, n.d.: not detected, a: reported as c-lindane.

The relatively low percentage composition of α -HCH in this study is because this compound has a high vapor pressure and Henry's law constant and therefore is readily lost (Hong et al., 2003). Relatively high levels of β -HCH as the only isomer were also reported in human breast milk in Hanoi City (Minh et al., 2004). δ -HCH was also recorded in this study, which fluctuated between 0.09 and 1.65 ng g⁻¹. All samples in the present study recorded a higher value for γ -HCH than TEL, whereas 60% of samples were higher than PEL causing frequent adverse biological risk.

The total cyclodienes (TC) are detected in the concentration range of 12.89 to 67.69 ng g⁻¹ at El-Shatby and El-Mex, respectively, with an average 35.98 ng g⁻¹. Endosulfan sulfate recorded the highest concentration of (14.11 ng g⁻¹, 39% of total cyclodienes), while the lowest concentration was detected for methoxychlor (0.09 ng g⁻¹, 0.25%). The concentration of aldrin ranged from 0.35 to 10.23 ng g⁻¹ while, dieldrin concentration ranged from 1.20 to 3.46 ng g⁻¹. It is known that aldrin is quickly transformed to the much more toxic and persistent

dieldrin (Falandysz et al., 1998). According to the present study, the concentrations of aldrin and dieldrin indicated the presence of illegal recent inputs of aldrin. The concentration of endrin ranged between 0.33 and 8.17 ng g⁻¹, while the breakdown products endrin aldehyde and endrin ketone (Mohammed et al., 2011) were present in the range of 0.18–3.80 and 0.06–5.38 ng g⁻¹, respectively. The low levels of the endrin ketone may be due to the low photochemical degradation of endrin or to the recent inputs of endrin.

The total DDT concentrations ranged from 4.89 to 29.93 ng g⁻¹ with an average concentration of 13.61 ng g⁻¹ (Table 3). Various approaches based on the ratio of technical DDT and its degradations have been used to assess whether the input of DDT into an area could be considered fresh (Tolosa

Table 5 VARIMAX normalization rotated factor loading for two factors obtained according to pollutants in the sediment samples along the Egyptian Mediterranean Sea from El-Sallum to El-Arish.

Variable	Factor 1	Factor 2
HCHs	0.881	-0.012
DDTs	0.910	0.119
TC	0.259	0.880
PCBs	-0.121	0.908
Variance (%)	42.124	42.124
Cumulative (%)	42.124	82.440

Table 6 VARIMAX normalization rotated factor loading for two factors obtained according to sample location of sediments along the Egyptian Mediterranean Sea from El-Sallum to El-Arish.

Variable	Factor 1	Factor 2
ES	0.941	0.231
SK	0.964	0.238
EM	0.883	0.423
EH	0.941	0.312
ESh	0.982	0.416
AQ	0.141	0.960
Ros	0.836	-0.185
EJ	0.696	0.707
PS	0.794	0.506
EA	0.161	0.969
Variance (%)	59.515	59.515
Cumulative (%)	59.515	91.633

et al., 1995; Lee et al., 2001; Hong et al., 2003). The ratio of (DDD + DDE)/DDTs (> 0.5) has often been used to identify aged or weathered technical DDT in the environment (Hites and Day, 1992; Zhang et al., 1999; Doong et al., 2002; Zhou et al., 2006; Gong et al., 2007; El Nemr et al., 2012a,b,c). Sediment samples recorded (DDD + DDE)/DDTs ratio in the range of 0.52–4.13, which suggests that there were little to no fresh inputs of technical DDT into the investigated area (Table 3). Also, whole values of DDD/DDE ratio ranged between 0.10 and 0.74 and were lower than unity, indicating that the eight sediment samples collected from El-Mex to El-Arish stations were dominated by *p,p'*-DDE, the product of aerobic degradation of *p,p'*-DDT. This result showed that the sediments collected from the samples were mainly under oxic conditions (Kucuksezgin and Gonul, 2012). On the other hand, the two stations El-Sallum and Sidi-Kreer recorded the opposite trend where DDD/DDE ratios were 5.90 and 10.77, respectively, which indicated the anoxic condition. DDT was widely used in Egypt on a variety of agricultural crops and for the control of disease vectors. The largest agricultural use of DDT has been on cotton, which accounted for more than 80% of its use before its ban. Although its usage was banned in 1988, its detection, along with the detection of its breakdown products (i.e., DDEs and DDDs), in sediments is expected because the reported environmental half-life of DDTs is estimated at 10–20 years (Woodwell et al., 1971; Sericano et al., 1990).

Concentration levels of *p,p'*-DDE and *p,p'*-DDD were lower than ERL values at 3 sites El-Sallum, Sidi-Kreer, El-Shatby and El-Mex, El-Shatby and Port-Said, respectively. Meanwhile, these compounds were also lower than the TEL value at the same sites for the two compounds except station Port-Said which exceeded in the *p,p'*-DDD only. The level of heptachlor was over the ERL value in 60% of stations under investigation, whereas they were below the ERM and PEL values. For dieldrin, all concentrations were higher than the TEL but still lower than the PEL. This suggested that the concentration levels of heptachlor and dieldrin at most sites

may cause toxic adverse biological risks. For DDTs, all sites in the study area were higher than the ERL value and TEL value, whereas 30% of stations exceeded the PEL and another 30% of stations exceeded the ERM, suggesting that the exposure of DDTs may cause ecological risk on the neighboring benthic organisms. Therefore, DDTs could be the one-main species of OCPs with a more ecotoxicological concern in the area under investigation, while other OCPs in surface sediments would be less possible to cause a toxic adverse biological effect.

Compared to concentrations reported in coastal environments from other parts of the world, PCB concentrations in surface sediments of the investigated area were in agreement with the data recorded by other authors (Table 4). However, the concentration of total PCBs in the severely impacted areas from the US and Spain was higher than the studied area.

Similarly, the concentrations of total DDT in the current study were in agreement with other harbors and riverine/estuary systems except in some severely contaminated locations, such as in the NW Mediterranean sediments from the Rhone Prodelta, France and USA. HCH concentrations in the present study were also higher than those reported from other locations except for the sediments from the Chinese river/estuaries systems.

Statistical analysis

Principal component analysis

By applying the principal component analysis (PCA) on the four pollutants under investigation; two principal components have been extracted by covering 82.44% of the cumulative variance (Table 5). The loading of the variables on the two principal components shows that HCHs, and DDTs were the dominant variables on the PC1 (0.881 and 0.910, respectively), while TC and DDTs (0.880 and 0.908, respectively) were the dominant variables on the PC2. By applying PCA on the sample stations, two principal components have been extracted by covering 91.63% of the cumulative variance (Table 6). The

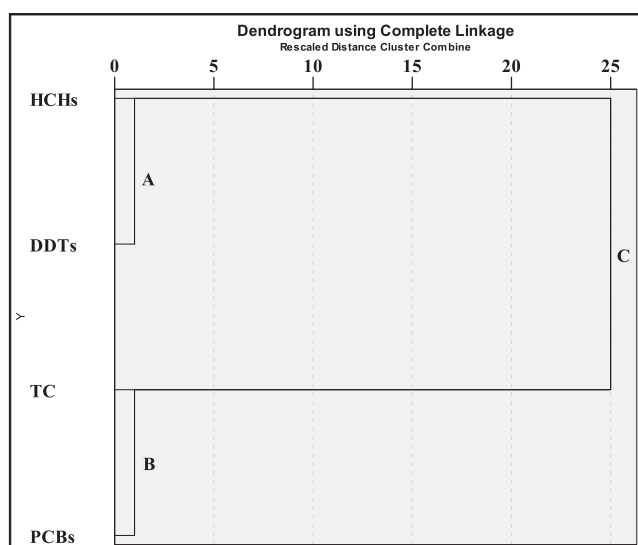


Figure 2 Dendrogram for hierarchical cluster analysis of four groups of pollutant concentrations in collected sediment using complete linkage (between groups).

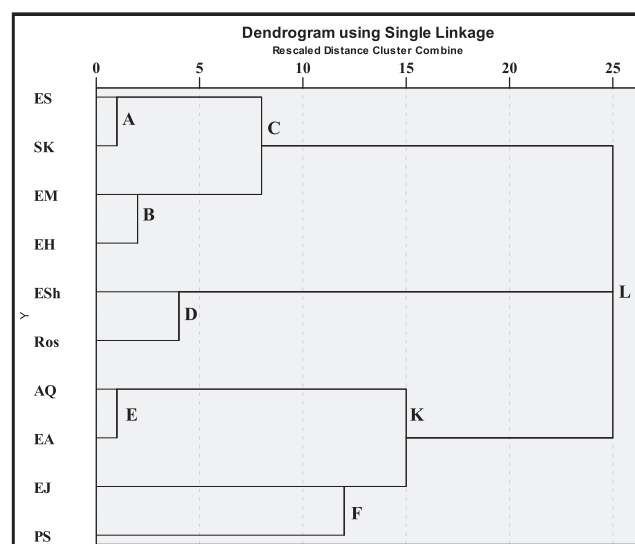


Figure 3 Dendrogram for hierarchical cluster analysis of location samples of collected sediment using single linkage (Nearest neighbor).

loading of the stations on the two principal components shows that El-Sallum, Sidi-Kreer, El-Mex, Eastern Harbor, El-Shatby, Rosetta, and Port-Said stations were the dominant stations on the PC1 (0.941, 964, 0.883, 0.941, 0.782, 0.836 and 0.794, respectively), while stations Abu-Qir, and El-Arish (0.960 and 0.969, respectively) were the dominant stations on the PC2. On the other hand station El-Jamil recorded a similar value in the two principal components (0.696 and 0.707 for PC1 and PC2, respectively) which indicates that each group of stations is subjected to the same source of pollutants.

Cluster analysis

By applying the cluster analysis for both the single and complete linkages similar relations between pollutants were obtained by the two studied clustering methods. The resultant dendrograms (Fig. 2) confirm the results obtained with PCA. Indeed, there were two clusters, which can be identified as follows: the first cluster (A) contains (HCHs and DDTs) at distance 1 (which was well correlated in Factor 1 in PCA); the second cluster (B) contains (TC and PCBs) at distance 1 (which was well correlated in Factor 2 in PCA). At a higher distance (about 25) the two clusters fused formed cluster (C). By applying HCA to the stations; the resultant dendrograms (Fig. 3) confirm the results obtained with PCA. Indeed, there were many clusters, which can be identified as follows: the clusters (C) and (D) which contain (stations Eastern Harbor, Sidi-Kreer, El-Mex, El-Shatby, and Rosetta) at distance 8 and 4, respectively. The second cluster includes the two stations Abu-Qir and El-Arish at distance 1 (which are included in PC2). At distance 12, cluster (F) which contains El-Jamil and Port-Said stations is formed and fused with cluster (E) at distance 15 forming cluster (K). At a higher distance (25), the three clusters (C, D and K) fused and formed cluster (L).

Risk assessment

Calculation of the hazard quotient (*HQs*) for the investigated trace organochlorine pollutants is shown in Fig. 4. It can be seen that all the organochlorine pesticides (γ -HCH, p,p' -DDE, p,p' -DDD, p,p' -DDT, DDTs, dieldrin, chlordane, and PCBs) had *TEC HQ* values lesser than 1; but only γ -HCH, and p,p' -DDT had *PEC HQ* values higher than 1 indicating a greater possibility in the occurrence of adverse ecological effects with respect to these organochlorine pollutants. Frequent toxic adverse effects are expected for lindane and p,p' -DDT.

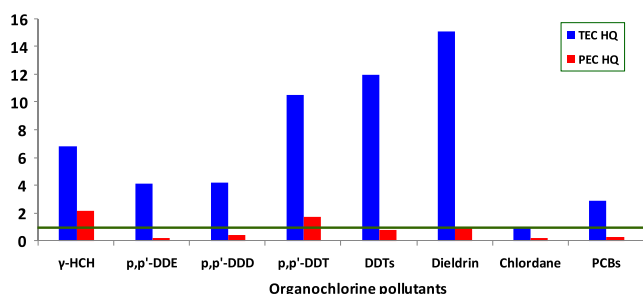


Figure 4 *TEC HQ* and *PEC HQ* for the organochlorine pollutants in sediment collected along the Egyptian Mediterranean Sea.

Conclusions

The measurements of organochlorine pesticides in sediments collected from the Egyptian Mediterranean Sea coast from El-Sallum to El-Arish indicate that HCHs, DDTs and HCB are the main organochlorine pesticides present in the marine environment. The concentration of organochlorine pollutants in sediments followed the order: Total cyclodienes (40.79%) > PCBs (35.74%) > DDTs (15.43%) > HCHs (8.03%). β -HCH, p,p' -DDT, Aldrin, Dieldrin, β -Endosulfan, Endosulfan, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180 were the most abundant compounds in the sediment samples. The increasing trend of these pollutants documented over the last decade in conjunction with an increasing (DDD + DDE)/DDTs ratio indicates little to no fresh inputs of technical DDT into the environment. With regard to PCBs, 80% of sediment samples exceeded the ERM and PEL suggesting the possibility of the occurrence of an adverse effect, while 20% of the samples exceeded the ERM and PEL suggesting the occurrence of frequent adverse effects. All samples in the present study recorded a higher value for γ -HCH than TEL, whereas 60% of samples were higher than PEL causing a frequent adverse biological risk. For DDTs, all sites in the studied area were higher than the ERL value and TEL value, whereas 30% of stations exceeded the PEL and another 30% of stations exceeded the ERM, suggesting that the exposure of DDTs may cause ecological risks on the neighboring benthic organisms. Therefore, DDTs could be the one-main species of OCPs with more ecotoxicological concern in the area under investigation, while other OCPs in surface sediments would be less possible to cause an adverse biological effect. By applying the approach of hazard quotient to study the risk assessment for the marine organisms that survived in the investigated area, it can be concluded that γ -HCH, p,p' -DDE, p,p' -DDD, p,p' -DDT, DDTs, dieldrin, chlordane, and PCBs had a greater possibility in the occurrence of adverse ecological effects and frequent adverse effect is expected for lindane and p,p' -DDT. The concentrations of the organochlorine pesticides fluctuated between the lower limit of guidelines for sediment quality, and very close to the critical value. The obtained results in this study pointed to the urgent needs to establish a program for monitoring organochlorine pollutants, so that any elevation in concentration of pollutants over the environmental quality standards can be detected and appropriate actions can be taken. Further study needs to be conducted on biota organic pollutant contents, in order to identify the sources, behavior, and fate of these pollutants and make the risk assessment of these contaminants on the ecosystems and human health.

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