Some Anthropogenic Driven Toxic Pollutants in El-Mex Bay and its Neighbourhood, Alexandria, Egypt

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Abstract: Persistent organic pollutants (POPs) continue to receive widespread attention as harmful contaminants in the global environment. Thirteen samples of marine surface sediment were collected from El-Mex Bay and its neighbourhood during October 2010 to determine the prevailing concentrations of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) and their impact on Mediterranean Seawaters. These compounds demonstrated markedly different distribution patterns, reflecting different domestic, agricultural and industrial usage in the area. DDTs were the major pollutant, that exhibited values <0.60-228.60 ng/g, representing 95.8% of OCPs, but their individual metabolites showed different contributions. Ratios of DDT/(DDE + DDD) in sediments indicate recent inputs of DDT into El-Mex marine environment. PCBs exhibited values <1.0-216.6 ng/g, showing high concentrations at sample locations closer to industrial areas with intensive shipping activities. Sediment Toxicity Reference Values of OCPs and PCBs are higher than those recorded in the present study. Results of correlation and factor analysis show low positive and negative correlations among HCHs, cyclodienes, PCBs, sand, silt and clay, indicating that these compounds have different anthropogenic sources, in addition sorting the sediment and adsorption processes are the fundamental influence affecting the spatial distribution of cyclodienes, while sand acts as adilutant.

Key words: Pesticides · PCBs · Sediment · GC-MS · Alexandria · Egypt

INTRODUCTION

Persistent organic pollutants (POPs) such as organochlorine pesticides and PCBs have been of great concern due to their occurrence in high concentrations even in remote ecosystems, despite bans on production and usage [1-2]. Many of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of humans and wildlife [3]. Some developing countries are still using these compounds because of their low cost and versatility in industry, agriculture and public health [4].

The use of organochlorine insecticides in Egypt began in the 1950s and were extensively used until 1981 to protect crops from insects, disease fungi and weeds, to remove unwanted vegetation and to control insects by the general public. DDT had still a limited use in the country as a rodenticide and termiticide. Based on the reports of their harmful effects to wildlife and humans, many organochlorine pesticides were banned or restricted from use or trade since 1988 by the Ministry of Agriculture. In 1996, a Ministerial Decree prohibited the import and use of 80 pesticides including aldrin, dieldrin, endrin, DDT. Due to the great concern in protecting the human health and environment from POPs, Egypt signed the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2002 and ratified it in 2003. Nonetheless, many of the pesticides banned or withdrawn from developed markets are still produced and sold in developing country markets [5]. Similar to many countries in the Mediterranean Region, there are no emission inventories of sources or release of organic and inorganic pollutants in the Egyptian environment, or any official data on stockpiles and disposal [6].
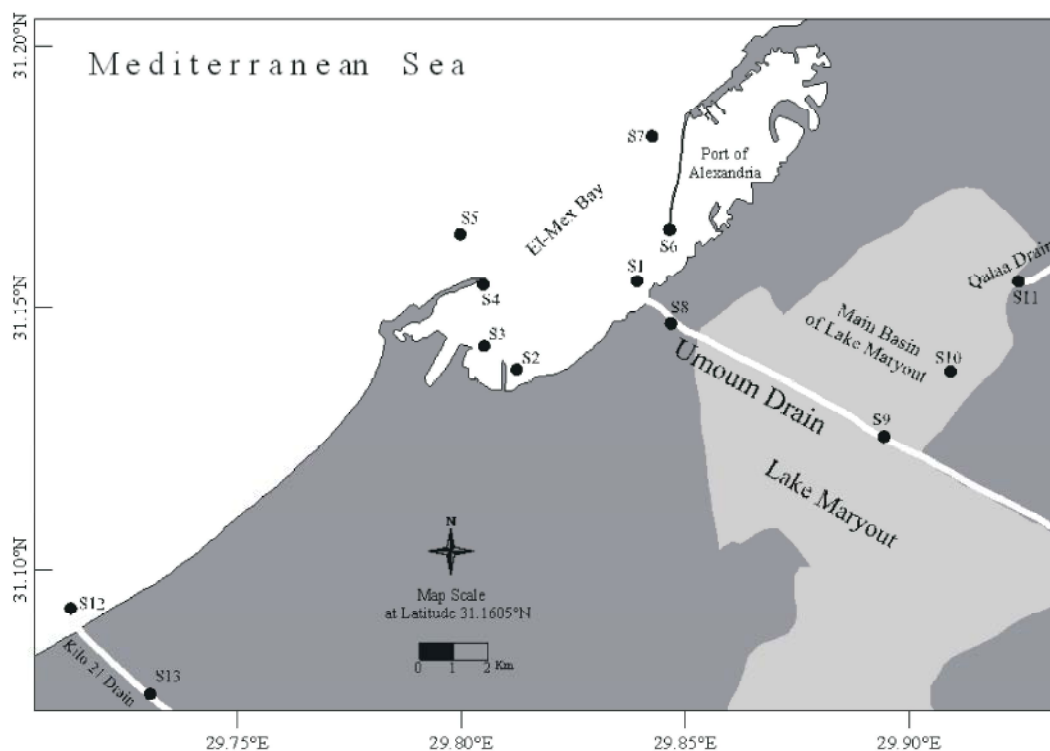
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Fig. 1: Sampling sites in El-Mex Bay, El-Umoum drain, El-Qalaa drain, Main Basin of Lake Maryout and Kilo 21st drain during 2010

El-Mex bay situated along the Egyptian Mediterranean Sea coasts extends for about 15 km between El-Agami headland and the Western Harbour (Figure 1). It has a mean depth of 10 m, a surface area of about 19.4 km^2 and a volume of 190.3 x 10^6 m^3 [7]. It receives huge amounts of drainage water from El-Umoum drain as well as mixed wastes from Lake Maryout *via* El-Mex pumping station which lies about one kilometre up stream on El-Umoum drain canal [8]. It is one of the most important industrial and trade regions of Alexandria city, where it is surrounded by several industrial plants that discharge their effluents into it, such as Misr Petroleum Company, Cement factory and tanneries, Alexandria Petroleum Company, Misr Chemicals Industries Company and Alexandria Iron and Steel Factory. In addition to that more than 75% of the Egyptian external trade and shipping activities are handled through Alexandria Western Harbour and El-Dekheilah Port [9].

Lake Maryout is one of the four shallow northern Nile Delta lakes. It has been partitioned into five basins (the fishery, the northwest, the southwest, the west and the main basins) with several barriers. The main basin (MB) is the most polluted part of the lake. It receives most of its water from a heavily polluted drain (El-Qalaa drain), which is the main drain carrying effluent from the East

Treatment Plant, raw wastewater and irrigation drainage and agriculture runoff [10]. This drain is very anoxic and disposes about 920 x 10^3 m^3 wastewater per day in the main basin of Lake Maryout [11].

El-Umoum drain transports the agricultural drainage water from El-Beheira Governorate as well as mixed wastes from the Lake Maryout and discharges them into El-Mex bay ((Figure 1). The volume of the discharged water from El-Umoum drain to El-Mex bay during 2003-2004 by Mohamoud and Fahmy [8] was about three times more than that discharged during 1988-1989 by Said *et al*. [7].

Kilo 21st drain, that carries the agricultural drainages from El-Noubariya farms and discharges them into the sea, is located west of Alexandria city at Lat. 31.09267 and Long. 29.71267 (Figure 1).

The objective of this paper is to study the occurrences and distribution of chlorinated pesticides and polychlorinated biphenyls in sediment and the effect of different drains on the distribution of different organic pollutants.

MATERIALS AND METHODS

Collection of Samples: Surface sediment samples were collected at thirteen stations shown in Fig. 1, during

Table 1: Factor analysis of sediments of El-Mex Bay and its neighborhood loading

Variable	Factor 1	Factor 2
Sand	-.942	-.128
Silt	.914	.157
Clay	.820	-.110
HCHs[a]	-.186	.815
TC[b]	.740	.059
DDTs[c]	.139	.872
PCBs[d]	.620	.506
% Variance	48.949	22.422

[a]Hexa-chlorocyclo hexane

[b]cyclodienes

[c]dichloro-diphenyl trichloro-ethane

[d]poly-chloronated biphenyl

October 2010 from the study area using a stainless steel grab sampler, covering the sites that are expected to be polluted with industrial, agricultural and anthropogenic wastes. The depths of sampling sites vary from 1.8 to 24 m (Table 1 and Figure 1).

Samples were preserved in an icebox and moved to the laboratory, where they were stored at -20°C [12]. Representative sediment samples were split, oven dried at 40°C and the grain size analysis was carried out according to the method described by Sweet *et al*. [13].

Chemical Analysis: Before chemical treatment, individual samples were removed from the refrigerator and allowed to thaw at room temperature for about 5h. Pesticides in the freeze-dried samples were extracted according to USEPA [12]. About 10 g of each freeze-dried sediment sample were extracted with dichloromethane. The extracted solvents were concentrated with a rotary evaporator down to about 15 ml (Meximum temperature: 35°C), transferred to a Kuderna-Danish concentrator and concentrated to 1 ml under a gentle stream of pure nitrogen gas. The remaining extract was transferred to the top of a glass column (50 ml) packed with 20 g Florisil followed by elution with 70 ml of hexane for PCBs congeners fraction (F1). Then the column was eluted with 60 ml of mixture containing 70% of hexane and 30% of dichloromethane for the pesticide fraction (F2). Activation of the Florisil was achieved by heating at 130°C for 12 h, followed by partial deactivation with 0.5% water by weight and stored in a tightly sealed glass jar with ground glass stopper and the mixture were allowed to equilibrate for one day before use. Each fraction was concentrated to 1 ml under a gentle stream of pure nitrogen gas before analysis.

The chromatographic analysis was performed by Gas Chromatography-Mass Spectrometer; GC-MS (Trace DSQ II MS) equipped with a fused-silica capillary column; Thermo TR-35 MS (30m, 0.25mm, 0.25ìm) with 35% phenyl polysilphenylene-siloxane. Helium was used as carrier gas at 2 ml min^{-1}. The temperature was programmed from 90-140°C with rate of 5°C min^{-1}, then holed at 140°C for 1 min and from 140-250°C with rate of 3 °C min^{-1} and was holed at 250°C for 1 min and from 250-300°C with rate of 20°C min^{-1} and was holed at 300°C for 1 min. The injector, ion source and detector temperatures were set at 280°C, 250°C and 310°C, respectively. 2 ìl volume of each sample was injected in the split less mode and the purge time was 1 min. Recoveries of organochlorines through analytical procedure ranged from 97% to 110% for pesticides and 92-109% for PCBs with a coefficient of variation of 15-20% for all congeners. A standard reference material SRM 2974 provided by EIMP-IAEA was analyzed simultaneously for selected PCB congeners and OCPs and the results were in agreement with the certified values. The limit of detection in the present study was estimated to be 0.2 ng/g dry weight for PCBs and 0.3 ng/g dry weight for pesticides. All solvents were pesticide-grade purchased from Merck and appropriate blanks (1000-fold concentrates) were analyzed.

RESULTS AND DISCUSSION

The total PCBs (CB-138, CB-153, CB-180, CB-118, CB-101, CB-28, CB-52) concentrations in sediment varied from <1.0 to 216.6 ng/g dry weight, with an average of 46.36±63.0 ng/g dry weight (Figure 2). The geographical distribution of PCB contamination revealed that PCBs contamination spread in the area of study with higher concentrations at station 1: 71.93ng/g dry weight, station 2: 36.43ng/g dry weight, station 5: 101.93, ng/g dry weight, station 9: 216.60ng/g dry weigh, station 10: 92.21ng/g dry weight and station 13: 56.09 ng/g dry weight. An exception was station (8), which showed a low concentration of PCBs (0.93 ng/g dry weight). Estimates for total inputs of PCBs to these locations from municipal wastewater, industrial wastewater, surface runoff, aerial fallout and vessel antifouling paints in El-Mex Bay, constituting virtually all of the latter input. Although antifouling paints presently constitute a completely insignificant mode for PCB input, occasional high PCB concentrations in old paint chips and the correlation of sediment PCB concentrations with antifouling paint usage suggest that this may have been the predominant source
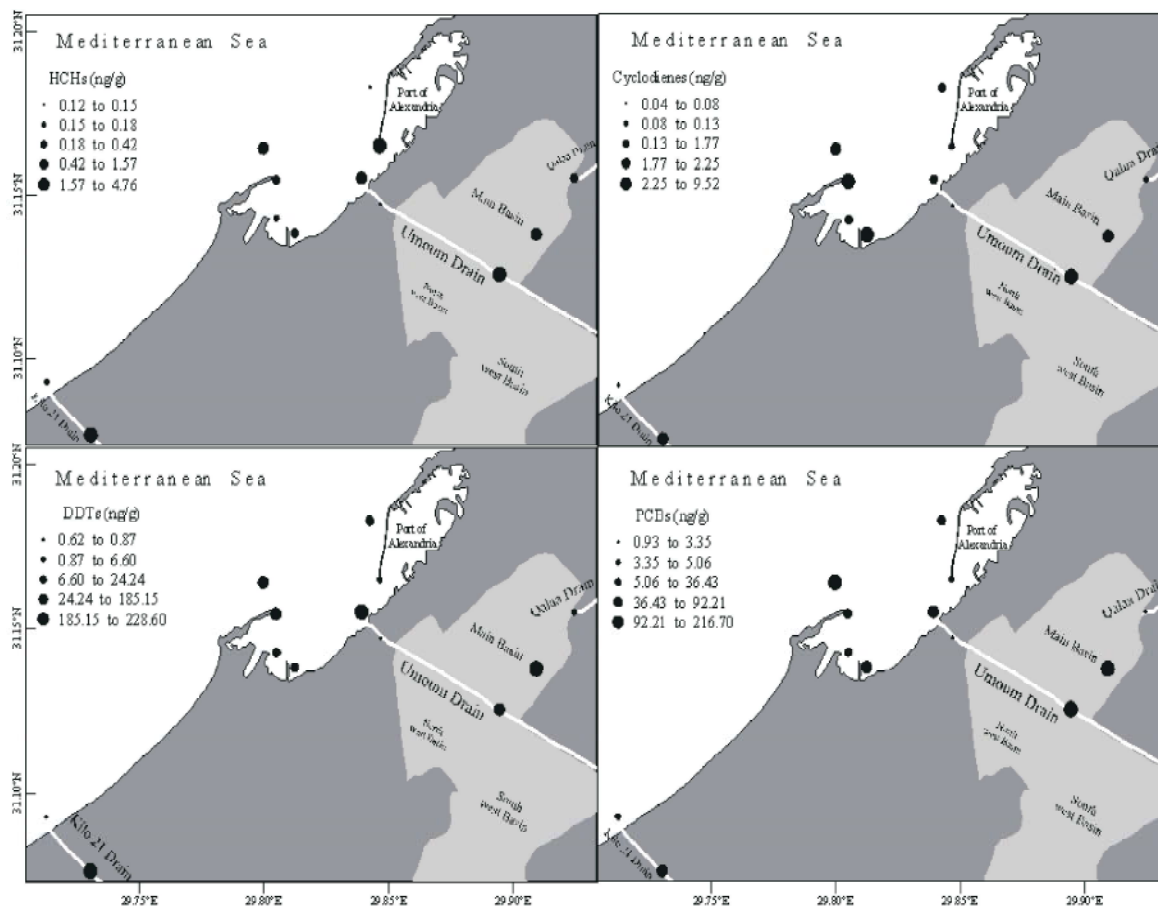
Fig. 2: Spatial distribution of total HCHs, cyclodienes, DDTs and PCBs in sediment of study area during 2010

of PCB to El-Mex Bay and its adjacent areas in recent years. There is also evidence that a part of the PCB contamination in El-Mex sediments has come from marine paints and will continue to do so due to the small, but not insignificant, amounts of PCB that are still incorporated in the coating of older ships. The PCB congeners can be arranged in the following descending order: CB-138 (46.4%) > CB-153 (30.1%) > CB-180 (18.3%) > CB-118 (2.5%) > CB-101 (2.3%) > CB-28 (1.6%) > CB-52 (0.3%). These PCB congeners have low to medium toxicity [14].

This order reveals that low molecular weight PCB compounds were present at relatively low concentrations in comparison to the high molecular weight congeners (hexa-chlorinated biphenyls 138, 153), which predominated in the sediments of El-Mex bay and its adjacent area. The probable reason is that the low molecular compounds are more readily volatilized to the atmosphere, whereas the higher molecular weight compounds can be expected to partition onto the particulate phase and undergo sedimentation [15].

Based on the number of the chlorine atoms in PCBs, Hong *et al.* [16] suggested that, high-chlorinated PCBs with high K_{ow} values are more likely to be adsorbed to suspended particulate material than lower chlorinated PCBs, this is in good agreement with Kennish [17], that stated persistence of PCBs in aquatic sediments might be due to their low rate of degradation and vaporization, low water solubility and partitioning to particles and organic carbon.

There is little published data available on input of PCBs into El-Mex bay and its neighbourhood [18], however, the use of these substances in ship paints, transformers, electrical equipments and other industries were common and could possibly be the main source of PCBs in study area.

DDTs were detected in 95.8% of OCPs of the investigated sediment samples but their contribution of individual metabolites showed differences. The total DDT concentrations ranged from <0.60 to 228.60 ng/g dry weight with an average of 63.16±88.96ng/g dry weight

(Figure 2). The three highest values that appeared in the investigated area were from Umoum drain mouth (station 1, 228.60 ng/g dry weight), Lake Maryout (station 10, 225.94 ng/g dry weight) and Kilo 21st drain (station 13, 185.15 ng/g dry weight). These highest concentrations were encountered at sites that are influenced by different discharges from different drains (Figure 2).

Basing on the average concentrations, p,p-DDT was the most abundant isomer detected in 83.5% of DDTs, followed by p,p-DDE with 5.2%, o,p-DDT with 5.0%, p,p-DDD with 4.9%, o,p-DDD with 0.9% and finally o,p-DDE with only 0.5% (Figure 2). Accordingly, DDTs are in the following order of predominance: p,p-DDT > p,p-DDE> o,p-DDT > p,p-DDD > o,p-DDD > o,p-DDE.

The composition of organochlorines and their metabolites can provide some information for a better understanding of the origin and transport of these contaminants in the environment, that Peng *et al*. [19] reported a possibility of the continuous illegal use of DDT in China using the ratio of (DDD + DDE)/?DDTs and also DDT undergoes degradation to DDD and DDE in the natural environment by chemical and biological processes [20-21]. In sediments of the present study, Over 70 % of the total DDTs are present as DDT. DDTs are therefore newly released into those locations and were mainly present as DDT (not aged DDTs). Higher contribution of p,p- DDT was recorded which may indicate slow degradation of DDT or recent inputs of fresh DDTs [22-23]. Concentrations of DDTs in sediments of study area are considered as a reflection of the use of DDT in Egypt, especially for agricultural purposes [24]. The high concentrations of total DDTs in these sediments as compared to concentrations worldwide areas indicate that DDT usage was heavy and the bay has received significant inputs of DDTs.

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 was on cotton, which accounted for more than 80% of the use before its ban. Although its usage was banned in 1988, its detection along with the detection of its breakdown products in sediments is expected because the half life of DDTs is from 10 to 20 years as mentioned by Sericano *et al*. [25].

Concentrations of total HCH (α, β and γ) isomers ranged from <DL to 4.76 ng/g dry weight with an average concentration of 0.94±1.32 ng/g dry weight (Figure 2). Higher concentrations of the HCH isomers were observed at stations (1; 1.42 ng/g dry weight, 9; 1.57 ng/g dry weight) which are affected by the wastewater discharged from Umoum drain and in station (13; 4.76 ng/g; dry weight) by Kilo 21st drain. However, beyond the zone of

impact of these discharges, there are some notable exceptions, the concentration drop rapidly in Mex pumping station (station 8), similar to DDTs and PCBs.

β-HCH was the most abundant isomers being detected with 63.7% of HCHs, with higher concentrations in Umoum and Kilo 21st drains, followed by α-HCH (30.2 %) and finally γ-HCH (6.1%). Basing on the average concentrations, the isomers could be arranged in the following descending order: β-HCH > α-HCH> γ-HCH. The α-HCH/γ-HCH ratio can be used to identify the source of HCHs [26].

α-HCH/γ-HCH ratio in areas where lindane has been used typically ranges from 0.2 to 1.0, due to the photochemical transformation of γ-HCH into α-HCH, compared to a range of 4–15 for technical mixtures of HCH [27-28]. These ratios are expected to increase with distance from the source assuming the transformation of γ-HCH to α-HCH [29]. The calculated values of α-HCH/γ-HCH ratio in sediments of El-Mex Bay and adjacent areas ranged from 0.24 to 47.58, indicating that lindane is not the main source of HCHs in the present study, compared to the data given by EL-Sebae [30], that lindane was intensively used in Egypt in the period from 1952 to 1978. About 11300 tons were used in agriculture. No data are available for the use of lindane or HCHs in Egypt after this time period.

Aldrin, dieldrin and endrin were the investigated cyclodiene pesticides in sediments of the study area, showing concentrations ranged from <DL to 9.51 ng/g dry weight. The Maximum levels were recorded at El-Dekheilah Port (station 4, 9.51 ng/g; dry weigh), that is affected quite significantly by wastewaters from El-Dekheilah Port activities. Low Concentrations of cyclodienes were observed at station 6 (0.08 ng/g dry weigh), station 8 (0.04 ng/g dry weigh) and station 12 (0.05 ng/g dry weigh) (Figure 2), showing the same distribution pattern as PCBs, HCHs and DDTs.

Basing on the calculated average concentrations, cyclodienes can be arranged as follows: endrin (58.3%) > aldrin (33.6%) > dieldrin (8.1%). This reveals that aldrin is rapidly converted to the epoxide form; dieldrin via epoxidation and then rearranged to endrin [31]. Endrin is a stereoisomer of dieldrin and is one of the most toxic of the chlorinated pesticides [32]. Aldrin is more volatile and readily degrades to dieldrin in the environment. Aldrin is estimated to have a half-life in sediment of 1.5-5.2 years, depending on the composition of the sediment. More than 56% of the original weight of aldrin converts to dieldrin; about 19% of the original aldrin weight disappears. This loss has not been accurately accounted for National Oceanic and Atmospheric Administration (NOAA) [33].

The concentrations of organochlorine in sediment of the study area decreased in the order: DDTs > PCBs > cyclodiens > HCHs. The detected concentrations of HCH isomers were much lower than their corresponding DDTs. This could be attributed to the tendency of HCH isomers to metabolize after some years to pentachlorocyclohexane, tetrachlorobenzene and other compounds and/or the higher solubility of HCH isomers compared to DDTs [34], HCH isomers have higher water solubility in seawater (8 mg/l for γ-HCH, [35] and a lower affinity to suspended particulate matter than PCBs and DDTs (0.007 mg/l for both PCB 110 and p,p-DDT, [36]). As a consequence, their removal from the water column by particle association and sedimentation is slower and the concentrations in the water column are expected to be kept at a higher level.

The processes controlling the levels of organo-chlorined pesticides and PCBs in sediment samples are complex. Bulk sediment properties such as grain size; have been shown to account partly for pesticides and PCBs variability in sediments. Law [37] stated that finer particles have a higher adsorptive capacity for organic substances owing to their greater effective surface area. However, concentrations of total cyclodienes and PCBs showed positive relationships with silt (r = 0.74, 5.4) and negative relationship with sand (r = -0.74, -5.6) respectively in sediments of study area. In contrast, relationship between PCBs and clay content (r = 0.69 at p < 0.05) was found in Abu Qir Bay [6], but the studies in Clyde Estuary, UK [38-40] could not identify a strong correlation between PCBs and particle size. Weak or no correlation for the rest of the investigated organic compounds (r < 0.6). Lack of significant correlation of the rest of the investigated organic compounds suggests the introduction of fresh loadings of pesticide and PCBs. Katsoyiannis [41] reported that in an environment where there is continuous introduction of fresh contamination, lack of correlation should be expected, at least until equilibrium is reached. Relatively high concentrations of DDTs recorded in the sediments of El-Mex Bay and its adjacent areas might be an evidence of recent pollution and thus supports the absence of correlation between DDTs concentrations and grain size.

To obtain more reliable information about the relationships among the variables, the statistical technique of factor analysis was applied on the data (Table 1 and Figure 3). The spatial distribution of the measured variables is controlled by two factors:

Factor (1) accounted for 48.95 % of the total variability and is mainly characterized by high positive loadings (>+0.740) for cyclodienes, clay and silt, high negative loadings (-0.942) for Sand, moderate positive

Table 2: Sediment Toxicity Reference Values

Constituent	TRV (mg/kg)*
DDD	0.002
DDE	0.0022
DDT	0.0016
Dieldrin	0.00002
Endrin	0.00002
PCBs	0.023

TRV = toxicity reference value.

* Effects Range - Low [44]

loadings for PCBs (+0.620) and low positive and negative loading for DDTs (+0.139) and HCHs (-0.186), respectively (Figure 3a). This factor represents the interaction of a sorting factor [42], producing an association of cyclodienes with the fine fraction of the sediments and an adsorption processes factor in which cyclodienes adsorb on the surfaces of silts and clays. The inverse association is indicated by the high negative loading on coarse-grained sediment. It denotes that the sorting of the sediment and the adsorption processes are the fundamental influence affecting the spatial distribution of cyclodienes, while sand acts as adilutant.

Factor (2) accounted for 22.42% of the total variance, It is characterized by high positive loadings (>+0.815) on HCHs and DDTs, moderate positive loading (+0.506) on PCBs (Figure 3b). This may be interpreted as inputs of HCHs and DDTs, that these compounds are associated together in agricultural chemicals and wastewater, therefore factor 2 indicates that chemicals with anthropogenic origin.

It can be observed from the obtained values that the behaviour of the pesticides, PCBs was greatly variable and that the grain size of the sediments of El-Mex Bay and its adjacent areas can partly affect the spatial distribution of some of these compounds.

Generally, pesticides and PCBs are hydrophobic and therefore readily bind to the particle fraction in waters. Subsequently, via sedimentation processes, these chemicals are deposited to the bottom. They remain for a very long time in the sediment due to their long half-lives [43]. From the sediment, they can be taken up and retained in benthic organisms and consequently biomagnified through aquatic food chains to higher trophic levels. Humans may be exposed to elevated levels of POPs through ingestion of contaminated fish and shellfish. PCB congeners and pesticides can cause toxic symptoms similar to those caused by dioxin exposure, including developmental abnormalities and growth suppression, disruption of the endocrine system, impairment of immune function and cancer promotion. However the
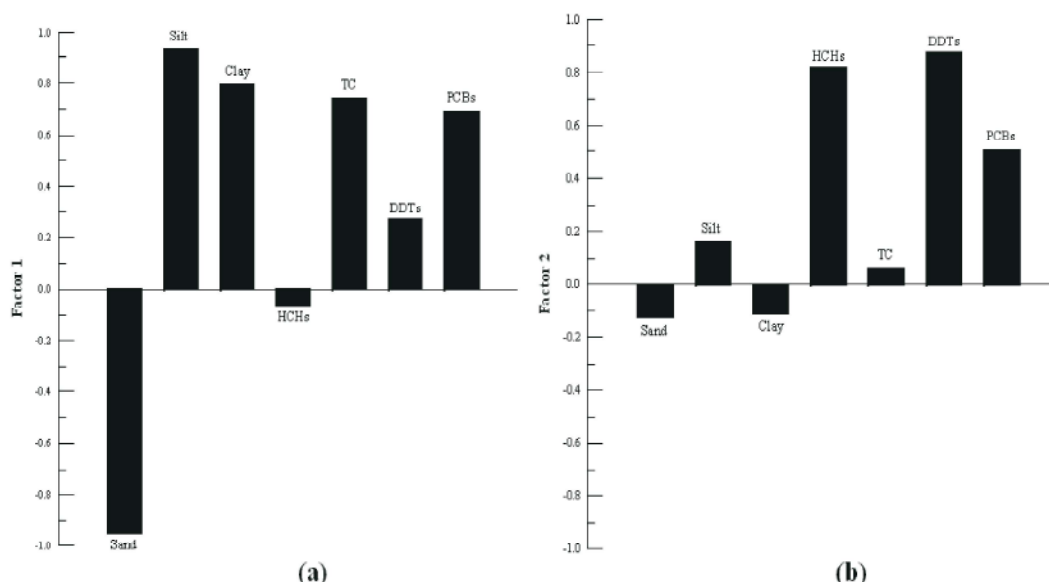
Fig. 3: Results of factor 1 (a) and factor 2 (b) in sediments of El-Mex Bay and its neighborhood areas (a) (b)

concentrations of OCPs and PCBs of the present study were generally low compared to other contaminated coastal sediments in the Mediterranean Sea and oceanic areas and Sediment Toxicity Reference Values (Table 2) are higher than those recorded in the present study with DDT, DDD, DDE, dieldrin, endrin and PCBs, ranging of <DL-219.94, <DL-37.52, <DL-15.67, <DL-0.61, <DL - 9.45, <1.0 - 216.60 ng/g, dry weight, respectively.

This study provides a preliminary assessment of the level of POPs in the Egyptian Mediterranean coast and Alexandria coast, which serves as a baseline study for future comparisons. It may be useful to repeat this study on a large scale in the near future as a quantitative integration of pollution by the most persistent organic pollutants and in identifying the sources of pollution.

ACKNOWLEDGEMENTS

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