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Determination of persistent organic pollutants in sediment and fish of the western coast of Alexandria, Egypt

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Persistent organic pollutants (POPs) were recorded in sediment and fish samples collected from the western coast of Alexandria. Total hydrocarbons (aliphatic + PAHs) in sediment ranged from 683.8 to 34670.1 ng g⁻¹ with an average of 9286.9 ng g⁻¹. The sum of C16–C34 of aliphatic fractions was <4000 ng g⁻¹, indicating the presence of a fresh petroleum source. For all sediments, the anthracene/phenanthrene ratio was >0.1, suggesting the dominance of a pyrolytic source. Total aliphatics in different fish species ranged from 253 to 11 132 ng g⁻¹, while total PAHs ranged from 3862 to 35 746 ng g⁻¹ wet weight. Benzo[a]pyrene was the most dominant PAH fraction ranged from 1902.7 to 32 905.5 with an average of 9464.5 ng g⁻¹ wet weight in all fish species. Concentrations of polychlorinated biphenyls (PCBs) ranged from 0.79 to 64.9 ng g⁻¹ with an average 12.14 ng g⁻¹ wet weight. The concentrations of organochlorines in fish species (*Euthymus alleferatus*, *Scomberomorus commerson*, *Sphyræna Sphyræna*, *Diplodus vulgaris*, and *Alepes djedaba*) decreased following the order: PCBs > DDTs > HCHs > total cyclodienes. Concentrations of DDTs in fish tissues ranged from 4.89 to 36.37 ng g⁻¹ with an average of 16.4 ng g⁻¹ wet weight. The concentrations of total HCHs ranged from 0.3 to 65.7 ng g⁻¹ with an average of 16.35 ng g⁻¹. The present study indicates: (1) fresh petroleum input where Pr/Ph > 1; (2) PAHs in sediment <4000 ng g⁻¹; (3) BaP concentration exceeded the permissible levels in *Alepes djedaba* species; (4) DDTs in sediment were below the effective range low level; (5) PCBs > effective range low and < effective range medium; and (6) pesticides and PCBs in all fishes were below the acceptable limit.

Keywords: POPs; Sediment; Fish; Alexandria; Egypt

1. Introduction

The Mediterranean Sea receives substantial point and non-point discharges from a variety of sources including industrial and sewage wastes, ship loading/unloading operations at harbours, river and lake outfalls, and accidental petroleum spills. The inputs of these different sources amount to some 750 000 tonnes discharged into the Mediterranean Sea [1]. Estuaries and coastal areas have traditionally been sites of industrial activity because of the ease of transport and because the sea offers a convenient place for the disposal of waste substances [2]. It has been estimated that at least 40% of all marine contaminants come from land-based sources [3]. The coastal sea area of Alexandria, which comprises the largest and main harbours in the country, in

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addition to the most industrialized zones, receives considerable amounts of petroleum and its products. Part of this is the SUMED pipeline that transports more than 100 million tonnes per year from crude petroleum of the Arabian Gulf countries. It was opened in December 1976 with its terminal at about 35 km west of Alexandria. Another important source of oil contamination in the area is the discharge of huge amounts of land drainage water from the highly polluted Lake Mariut and the sewage water; they may include the wastes of lubricants and other mineral oils. There is a tremendous lack of information regarding the petroleum-contamination problem in the coastal region of Alexandria [4–6].

The present investigation was carried out along the western coast of Alexandria at two sites: El-Max Bay and tourist villages distributed along the western part of Alexandria. The area includes the newly constructed El-Dekhela Harbour. The south-western part of the region is El-Max Bay, which represents a semi-closed shallow basin with an average depth of about 9.0 m bordered from its north-eastern side by the Western Harbour outlet and by El-Dekhela Harbour at the north-west. El-Max Bay, which extends about 15 km between El-Agamy headland to the west and from the Western Harbor to the east and from the coast to a depth line of about 15 m, has a mean depth of 10 m (figure 1). It receives a heavy load of wastewater both directly from industrial outfalls and indirectly from Lake Maryut via El-Max pumping station [7]. The main outfalls are Misr Chemical Industries effluent, the combined wastewater effluent from the tanneries and slaughter House, the Nobariya canal and El-Mahmoudiya canal. El-Max pumping station lies about 1 km upstream on El-Umum Drain and pumps about $2.8 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$. This is agricultural drainage water collected by El Umum Drain but also comprises the overflow from Lake Maryut. Lake Maryut receives wastewater from the three Sources in its eastern section, consisting of domestic, industrial, and agricultural wastes. These wastes fill the Lake and overflow west to El Umum drain to be discharged to the sea via El-Max pumping station. El Umum canal drains the south-western part of El Beheira Governorate, which is about 45.8 km long with a bottom depth of 20 m and an average depth of 3–4 m. It receives water from several pumping stations located at El Delengate, El Sher-shera,

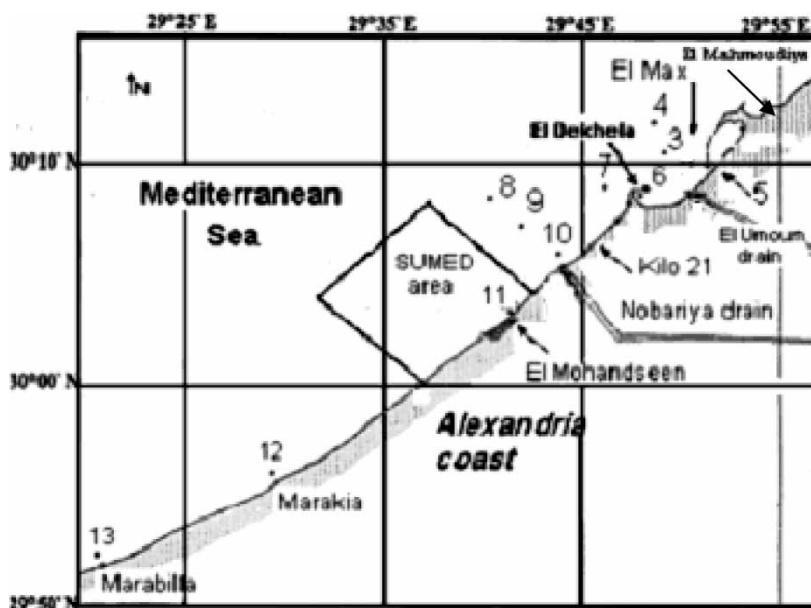


Figure 1. Study area and sampling stations: stations 3–6 (El Max), station 7 (El Dekhela harbour), stations 8–10 (SUMED area for petroleum activity), stations 11–13 (tourist villages), and station 14 (Noubariya drain).

Farough, El Qualaa, El Deshoudy, Hares, and Maryut. The drain level is maintained between 2.6 and 2.9 m below sea level by the action of El Max pumping [8].

Untreated domestic wastewaters with agricultural and industrial wastes release through a number of drainages and outfalls along the coastal area of study. Persistent organic pollutants (POPs) have a wide range of industrial, anthropogenic, and agricultural applications. They include pesticides such as DDT (dichlorodiphenyltrichloroethane) and lindane (γ -HCH), in addition to petroleum hydrocarbons which are organic chemicals composed of fused benzene rings formed during incomplete combustion of coal, oil, petrol, and wood [9, 10]. Svobodova *et al.* [11] stated that organochlorine pesticides act as nerve poisons and are highly toxic to fish ($48\text{-h LC}_{50} < 1 \text{ mg l}^{-1}$); their use is now strictly controlled or banned [12]. On the other hand, several polycyclic aromatic hydrocarbons (PAHs) are known to be potential human carcinogens these include; benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene [13].

A baseline study was aimed to determine the occurrence of POPs in sediment and fish samples collected from the western coast of Alexandria. The lack of investigation and available data on these pollutants in Alexandria coast give priority to follow-up and evaluate the present condition of contamination. In addition, our objective was to obtain more information on the origin of different hydrocarbon fractions considering anthropogenic sources.

2. Materials and methods

2.1 Sampling

A total of 11 surface sediment samples were collected during March 2005 at sites distributed along the western coast of Alexandria lying between longitude of $29^{\circ} 20'$ and $29^{\circ} 50'$ E and latitude of $29^{\circ} 50'$ and $30^{\circ} 12'$ N (figure 1). The locations were selected, taking into consideration the expected polluted area due to industrial and human activities. Sediments were collected utilizing a stainless-steel grab. Six grabs were taken from each location from which the top 3 cm were scooped into pre-cleaned wide-mouth glass bottles, frozen, transported to the laboratory, and stored at -20°C until analysis. The boat was moved up to 4–6 m between grabs so that the samples would be representative of the area from which they were taken. The samples were analysed for aliphatic and aromatic hydrocarbons following well-established techniques [14, 15]. About 3–4 g of each sample was taken and weighed in an aluminium dish. The sample was oven-dried at 105°C to a constant weight to obtain percentage water content for each sample. In addition, five fish species; *Euthynnus alleferatus*, *Scomberomorus commerson*, *Sphyraena Sphyraena*, *Diplodus vulgaris*, and *Alepes djedaba* were collected during the same period to study the accumulation of organic pollutants. All samples were collected fresh from fishermen working in the area of study, no more than 2 h after catching, and then kept frozen in the laboratory. Biological specimens were dissected, and their tissues were kept frozen until extraction.

2.2 Procedures

Before chemical treatment, individual samples were removed from the refrigerator and allowed to thaw at room temperature for about 5 h. Each sample was then thoroughly mixed, and 30 g of the sediment was mixed with 90 g of anhydrous sodium sulfate. Duplicates were taken from each sediment sample. The sediment sample was then extracted in a Soxhlet extractor with 250 ml of hexane for 8 h and then re-extracted for 8 h into 250 ml of dichloromethane [16]. The extracts were then combined and desulfurized through activated copper powder and then

concentrated to a few millilitres in a rotary evaporator at low temperature (35°C), followed by concentration with a nitrogen gas stream down to a volume 1 ml.

Fish tissue (10 g of wet weight of flesh) was placed in a blender, and 30 g of anhydrous sodium sulfate was added. The fish tissue and sodium sulphate were manually homogenized to determine whether the samples were adequately dried. Samples were blended at high speed until the mixture was well homogenized (2–3 min). The mixture was then transferred to a pre-cleaned extraction thimble, and the dehydrated tissue was extracted with 200 ml (1:1) of *n*-hexane-dichloromethane for 8 h in a Soxhlet apparatus cycling 5–6 times h⁻¹. Anhydrous sodium sulfate (30 g) was extracted in the same fashion as the sample and used as the blank. The extracted solvents were concentrated with a rotary evaporator down to 2 ml (maximum temperature: 35°C), followed by concentration with a pure nitrogen gas stream down to a volume of 2 ml.

Clean-up and fractionation were performed by passing the extract through a silica/alumina column. The first millilitre of the extracted volume (sediment or fish) was passed through the silica column prepared by slurry packing 20 ml (10 g) of silica, followed by 10 ml (10 g) of alumina and finally 1 g of anhydrous sodium sulfate. Elution was performed using 40 ml of hexane (aliphatic fractions), then 40 ml of hexane/dichloromethane (90:10), followed by 20 ml of hexane/dichloromethane (50:50) (which combined contain PAHs). Finally, eluted samples were concentrated under a gentle stream of purified nitrogen to about 0.2 ml, prior to injection into GC/FID for PAHs analysis.

The second millilitre of the extracted volume was passed through florisil column prepared by slurry packing 20 g of florisil, followed by 10 g of alumina and finally 1 g of anhydrous sodium sulfate. Elution was performed using a 50-ml mixture containing 70% hexane and 30% dichloromethane for pesticide fractions. Finally, eluted samples were concentrated under a gentle stream of purified nitrogen to about 0.3 ml, prior to injection into GC/ECD for pesticides analysis. All samples were analysed by a Hewlett Packard 5890 series II GC gas chromatograph equipped with a flame ionization detector (FID) and electron capture detector. For hydrocarbon analysis, the instrument was operated in splitless mode (3 µl splitless injection) with the injection port maintained at 290°C and the detector maintained at 300°C. Samples were analysed on a fused-silica capillary column HP-1; 100% dimethyl polysiloxane (30 m length × 0.32 mm i.d. × 0.17 µm film thickness). The oven temperature was programmed from 60 to 290°C, changing at a rate of 3°C min⁻¹ and maintained at 290°C for 25 min. The carrier gas was nitrogen flowing at 1.2 ml min⁻¹. However, an HP-5 capillary column (50 m × 0.32 mm × 0.52 µm) with ⁶³Ni-electron capture detector (ECD) was used for pesticide analysis. The oven temperature was programmed from 90 to 140°C at rate of 5°C/min, maintained at 140°C for 1 min, then from 140 to 250°C at a rate of 3°C min⁻¹, maintained at 250°C for 1 min, then from 250 to 300°C at a rate of 20°C min⁻¹, and maintained at 300°C for 1 min; the carrier gas was nitrogen flowing at 1.5 ml min⁻¹.

A stock solution containing the following PAHs with their alkylated derivatives was used for the quantification of hydrocarbons: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, pyrene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene, and indeno(1,2,3-cd) pyrene by dilution to create a series of calibration standards of PAHs at 0.1, 0.25, 0.5, 0.75, 1.0, 2.0, 5.0, and 10 µg ml⁻¹. The detection limit was 0.04, 0.01, 0.01, 0.01, 0.02, 0.01, 0.03, 0.03, 0.04, 0.04, 0.05, 0.05, 0.05, 0.06, 0.08, and 0.10 µg ml⁻¹ for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, benzo[ghi]perylene, and indeno(1,2,3-cd)pyrene, respectively. For analytical reliability and recovery efficiency, six analyses were conducted on PAH reference materials, HS-5 and 2974 (provided by EIMP-IAEA). The laboratory results showed that the

recovery efficiency ranged from 92 to 111% with a coefficient of variation (CV) of 8–14% for all studied pollutants (16 PAHs fractions with their derivatives).

Organochlorine pesticides were quantified from individually resolved peak areas with the corresponding peak areas of the external standards (POC mixture provided by IAEA). They include: α , β , and γ -hexachlorocyclohexanes, heptachlor, aldrin, heptachloroepoxide, dieldrin, DDT, and its isomer DDE. To control the analytical reliability and ensure recovery efficiency and accuracy, four analyses were conducted on organochlorine compound reference material SRM-1974 provided by EIMP-IAEA. The laboratory results showed a recovery efficiency ranging from 95 to 105% for pesticide reference material no. 2974 with a coefficient of variation of 15–20% for all pesticide congeners. All solvents were pesticide-grade purchased from Merck, and appropriate blanks (1000-fold concentrates) were analysed.

3. Results and discussion

3.1 Aliphatic and aromatic hydrocarbons in sediment and fish

The results represent the concentrations of 19 detectable *n*-alkanes (*n*-C10 to *n*-C34) ranging from 542.87 ng g⁻¹ at El Dekhela harbour (St. 6) to 3265.1 ng g⁻¹ at El Max Bay (St. 3) with an average of 1304.51 ng g⁻¹, as shown in table 1. The presence of *n*-C26 (*n*-hexacosane) in all studied sediment samples suggests possible bacterial contamination [17]. The recorded concentrations of the present study were lower than those recorded for the Black Sea, ranging from 1200 to 24 000 ng g⁻¹ of sediment [18]. Pristane (C19) and phytane (C20) are common isoprenoids detected in coastal marine sediments. They are present in most petroleum products, usually as the major constituents within a much wider range of isoprenoid alkanes and usually considered as good indicators of petroleum contamination [18]. The present study showed that the sum of C16–C34 of aliphatic fractions was <4000 ng g⁻¹, indicating the presence of a fresh petroleum source [16]. In addition, the ratio of pristane/phytane (Pr/Ph) was >1, indicating a fresh petroleum source.

Twenty-six PAH members were identified in the marine sediments where important qualitative differences among the different sampling sites were observed (table 2). The range of PAHs in sediment ranged between a minimum of 38.5 ng g⁻¹ at El Mohandseen village (St. 11) and a maximum of 31 405.0 ng g⁻¹ at El Max Bay (St. 3) with an average of 7921.25 ng g⁻¹. Lower concentrations were detected at the stations of the three tourist villages: El Mohandseen, Marakia, and Marabilla (St. 11–13) with average values of 125.87 ng g⁻¹. These values are higher than those already published, where Baumard *et al.* [19] measured total PAHs from 0.3 to 100 ng g⁻¹ in the Western Mediterranean. Concentrations from 48.1 to 86.5 ng g⁻¹, for the sum of 14 PAHs have been reported for coastal areas in the north-west Mediterranean Sea [20]. The PAHs patterns differ according to the emission sources [21–23], and several PAH concentration diagnostic ratios have been extensively used in order to identify and quantify the contribution of each source of contamination to the specific compartments [24, 25]. The reported ratios should be treated with caution, as biogeochemical and physical process may alter the PAH profiles during transport. Differences in reactivity, volatility, water solubility, and sorption rates among the PAHs could lead to the incorrect designation of the sources. The general distribution of the PAHs in all sediments reflects the high contribution of pyrolytic sources because of the predominance of parent PAHs over their alkylated derivatives [26, 27]. The ratio of methyl phenanthrene to phenanthrene (MePh/Ph) was <1 for all stations (table 2). Yunker *et al.* [28] stated that the anthracene:phenanthrene ratio was <0.1, which is considered as an indication of fossil fuel inputs, while a ratio >0.1 indicates a dominance of combustion source. For all sediments in our study, the ANT/PHE ratio was >0.1 (table 2). The sum of

Table 1. Concentrations of aliphatic hydrocarbons (ng g^{-1} ; dry weight) in sediment samples collected from the western part of Alexandria during March 2005.

Compound	Station										
	3	4	5	6	7	8	9	10	11	12	13
C10	n.d.	6.840	3.507	3.570	6.373	3.280	n.d.	n.d.	4.080	5.583	8.360
C12	8.680	37.995	13.013	12.290	37.400	11.040	21.700	n.d.	14.320	18.983	16.667
C14	42.120	32.520	36.000	17.990	39.853	31.627	25.783	5.630	23.380	27.400	22.667
C16	39.880	39.795	31.240	14.530	29.480	28.253	21.117	9.780	20.720	20.250	16.400
C17	74.960	5.145	11.493	9.020	7.493	3.880	4.293	4.610	10.500	18.667	5.827
Pristane	91.040	2.655	11.240	5.480	8.440	1.413	17.850	0.883	6.980	12.083	8.493
Octadecene	61.480	5.835	9.880	4.990	11.760	3.760	4.958	3.230	7.480	23.717	4.653
C18	98.340	2.640	38.480	16.480	36.573	7.147	0.000	8.470	13.120	30.067	12.507
Phytane	58.700	2.085	11.840	4.710	3.440	n.d.	9.753	1.010	4.380	13.650	1.347
C20	143.700	12.135	28.760	13.970	29.560	7.627	8.260	4.460	13.100	39.367	7.467
C21	101.880	2.250	16.760	7.870	3.867	1.520	3.045	0.799	4.080	41.600	2.040
C22	132.400	8.025	18.840	13.930	14.160	4.707	0.000	3.810	9.740	32.650	6.987
C24	162.220	5.055	20.493	8.680	4.360	27.280	3.488	1.750	4.920	53.000	3.093
C26	280.720	1.590	51.427	15.890	32.813	33.067	22.050	7.810	32.680	102.783	45.333
Squalene	255.520	7.470	65.120	17.450	15.173	11.160	7.012	21.820	14.100	74.167	8.347
C28	267.500	9.165	43.800	93.640	8.773	2.653	211.050	5.460	34.540	91.000	383.733
C30	646.160	444.030	226.653	156.830	161.853	485.613	1751.400	624.500	384.260	578.967	1138.533
C32	391.140	58.875	212.120	107.790	58.907	33.040	249.783	5.760	47.060	250.150	129.867
C34	408.640	16.065	106.360	21.330	103.453	46.080	n.d.	25.090	n.d.	509.483	53.867
Total	3265.080	700.170	957.027	546.440	613.733	743.147	2361.543	734.872	649.440	1943.567	1876.187
Pr/Ph	1.551	1.273	0.949	1.163	2.453	n.r.	1.830	0.874	1.594	0.885	6.307

Note: n.d.: below the detection limit; n.r.: not recorded because one of the values equal zero; Pr: pristane, Ph: phytane.

Table 2. Concentrations of aromatic hydrocarbons (ng g⁻¹; dry weight) in sediment samples of the western part of Alexandria during March 2005.

Compound	Station										
	3	5	6	7	8	9	10	11	12	13	
Naphthalene	121.030	102.200	52.500	207.717	77.875	39.870	2.530	0.934	0.697	151.860	
Triethyl benzene	0.674	0.363	n.d.	n.d.	0.168	n.d.	0.183	n.d.	0.079	0.275	
1-Methyl naphthalene	0.674	n.d.	n.d.	0.968	0.360	0.282	0.373	0.428	0.324	0.402	
1-Ethyl naphthalene	0.081	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
2,6-Dimethyl naphthalene	0.081	n.d.	n.d.	n.d.	0.109	n.d.	n.d.	n.d.	n.d.	n.d.	
Acenaphthene	1.041	n.d.	n.d.	n.d.	18.440	n.d.	0.123	n.d.	n.d.	n.d.	
2,3,6-Trimethyl naphthalene	0.539	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Fluorene	131.273	43.500	n.d.	43.700	21.875	50.505	20.585	n.d.	27.630	40.425	
Phenanthrene	288.470	162.450	n.d.	n.d.	21.295	n.d.	36.445	n.d.	n.d.	n.d.	
2-Methyl phenanthrene	1.167	0.270	n.d.	0.327	0.095	0.447	0.135	n.d.	n.d.	0.321	
1-Methyl phenanthrene	2.800	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
3,6-Dimethyl phenanthrene	0.931	n.d.	n.d.	n.d.	0.250	0.325	n.d.	n.d.	n.d.	n.d.	
Anthracene	216.860	51.750	n.d.	60.750	72.525	83.140	38.595	n.d.	35.620	59.730	
Fluoranthene	53.573	115.617	n.d.	n.d.	12.105	n.d.	n.d.	n.d.	n.d.	n.d.	
Pyrene	233.847	222.283	n.d.	n.d.	19.745	n.d.	n.d.	n.d.	n.d.	n.d.	
1-Methyl pyrene	72.543	n.d.	n.d.	n.d.	2.315	n.d.	n.d.	n.d.	n.d.	n.d.	
Benzyl butyl phthalate	0.569	1.252	n.d.	n.d.	0.111	n.d.	n.d.	n.d.	n.d.	n.d.	
Benzo[a]anthracene	201.390	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Chrysene	140.793	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Di-n-Octyl phthalate	6.463	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Benzo[b]fluoranthene	289.777	n.d.	72.900	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Benzo[k]fluoranthene	238.117	50.600	n.d.	n.d.	30.140	n.d.	n.d.	n.d.	n.d.	n.d.	
Benzo[a]pyrene	669.270	57.333	53.680	1441.067	29.240	4129.00	12 554.00	36.460	21.580	n.d.	
Dibenz[a,h]anthracene	624.493	n.d.	327.900	41.617	22.550	n.d.	n.d.	0.632	0.200	n.d.	
Benz[ghi]perylene	25375.77	n.d.	2487.360	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Indeno[1,2,3-cd]pyrene	2732.777	n.d.	1854.480	n.d.	62.435	22 628.00	n.d.	n.d.	n.d.	n.d.	
∑ PAHs	31 405.00	808.61	4848.82	1796.15	391.63	26 931.69	12 652.97	38.45	86.13	253.01	
ANT/PHE	0.752	0.319	n.r.	n.r.	3.406	n.r.	1.059	n.r.	n.r.	n.r.	
∑ PAHs _{CARC}	4517.707	58.327	2308.960	1482.683	114.225	26 757.00	12 554.00	37.092	21.780	n.r.	

Note: n.d.: below detection limit; ∑PAHs: total aromatic hydrocarbons; ANT: anthracene; PHE: phenanthrene; ∑PAHs_{CARC}: carcinogenic PAHs.

five carcinogenic PAHs [29] was the highest at stations 9 and 10 of El Max Bay showing concentrations of 26 757.0 and 12 554.0 ng g⁻¹, respectively. The major inputs of hydrocarbon pollutants in the Western coast of Alexandria are from combustion of organic matter, anthropogenic industrial activity, and/or natural fires. These sources give rise to complex mixtures of PAHs characterized by a higher abundance of parent PAHs than their alkylated derivatives. The range of total hydrocarbons (aliphatic + PAHs) in sediment was 683.8–34 670.1 ng g⁻¹ with an average of 9286.88 ng g⁻¹. The total aliphatic concentrations were higher than the corresponding aromatic fraction for all sediment samples. In addition, the recorded total *n*-alkanes were lower than those recorded in Black Sea, ranging from 1200 to 24 000 ng g⁻¹ for sediment reported by Readman *et al.* [18]. The concentration of total *n*-alkanes in various fish species (*Euthynnus alleferatus*, *Scomberomorus commerson*, *Sphyræna Sphyræna*, *Diplodus vulgaris*, and *Alepes djedaba*) varied in the range of 253–11 132 ng g⁻¹ of wet weight, and the concentration of total PAHs ranged from 3862 to 35 746 ng g⁻¹ with an average of 4472 ng g⁻¹ (table 3).

The average concentration of total PAHs was lower than that measured in mussels along the Egyptian Red Sea coast (average 5452 ng g⁻¹, wet weight) recorded by El Nemr *et al.* [30], and also lower than that recorded in bivalves from the Egyptian Mediterranean Sea (average 8180 ng g⁻¹, wet weight) recorded by El Sikaily *et al.* [31]. The concentration range of total PAHs recorded in the present study was lower than the acceptable level of total PAHs (100 µg g⁻¹ wet weight) in edible fish tissue [32].

The fish species collected from El Max Bay were generally more contaminated than that collected from the area of Kilo 21. The average concentration of PAHs in fish samples in the present study (12 112 ng g⁻¹; wet weight) was much higher than the average of PAHs (295 ng g⁻¹; wet weight) in mussels and clams reported by Law and Andrulewicz [33] for the southern Baltic Sea. Mussels are benthic organisms and therefore likely to be exposed to hydrophobic compounds. Their filter-feeding habits also would make them potentially more vulnerable to sediment-bound constituents. Nevertheless, our study recorded higher levels of hydrocarbons fractions in fish muscles than that recorded in the Baltic Sea mussels, reflecting that the Alexandria coast is more polluted than the Baltic Sea. However, the recorded value of average PAHs was lower than that recorded in different Osteichthyes fishes collected from Great Bitter lakes and El Tamsah lake (Suez Canal), with an average of 57 980 ng g⁻¹ and 87 690 ng g⁻¹, wet weight, respectively [34]. In addition, benzo[a]pyrene was the most dominant PAH fraction ranging from 1902.7 to 32 905.5, with an average of 9464.5 ng g⁻¹, wet weight in all fish species. The Joint FAO/WHO Expert Committee on Food Additives has adopted a specification, which requires that the concentration of benzo[a]pyrene should not exceed a limit of 10 µg g⁻¹. This value was exceeded in *Alepes djedaba* species (table 3).

The hydrocarbon levels in the different fish species may be associated with fish habits and ecological niches. The species that generally had the highest concentrations (*Alepes djedaba*) is a reef-associated, carnivorous fish and thus subjected to near-shore discharges. Some of the other species, e.g. *Scomberomorus commerson* and *Sphyræna Sphyræna*, are pelagic species that are more likely to be found in open water. This indicates that near-shore areas of the Alexandria coast are more polluted than offshore areas, clearly reflecting land-based sources of pollution. In addition, the ability of fish species to adapt to changes plays an important role for living in polluted areas.

3.2 PCBs and pesticides in sediment and fish

The concentrations of polychlorinated biphenyls (PCBs) ranged from 0.79 to 64.9 ng g⁻¹, with an average of 12.14 ng g⁻¹, wet weight (table 4). PCB concentrations were higher at

Table 3. Concentrations of PAHs and aliphatic hydrocarbons (ng g^{-1} ; wet weight) in fish samples collected from the western coast of Alexandria during 2005.

Compound	Species				
	<i>Euthynnus alleferatus</i>	<i>Scomberomorus commerson</i>	<i>Sphyræna sphyræna</i>	<i>Diplodus vulgaris</i>	<i>Alepes djedaba</i>
Naphthalene	123.480	570.440	726.467	47.940	149.153
Triethyl benzene	n.d.	0.259	0.709	0.316	n.d.
1-Methyl naphthalene	n.d.	1.920	1.547	2.560	n.d.
1-Ethyl naphthalene	n.d.	n.d.	0.207	n.d.	n.d.
2,6-Dimethyl naphthalene	n.d.	0.617	0.845	n.d.	n.d.
Acenaphthylene	n.d.	n.d.	n.d.	156.700	n.d.
Acenaphthene	n.d.	105.040	143.640	n.d.	n.d.
2,3,6-Trimethyl naphthalene	n.d.	n.d.	0.175	n.d.	n.d.
Fluorene	n.d.	60.440	50.107	175.120	59.918
Phenanthrene	n.d.	0.608	338.760	n.d.	n.d.
2-Methyl phenanthrene	n.d.	n.d.	1.309	1.514	0.545
1-Methyl phenanthrene	n.d.	n.d.	1.440	0.934	n.d.
3,6-Dimethyl phenanthrene	n.d.	0.728	0.980	0.988	n.d.
Anthracene	n.d.	201.587	243.480	281.400	101.340
Fluoranthene	n.d.	0.617	179.000	0.406	n.d.
Pyrene	n.d.	n.d.	427.573	n.d.	n.d.
1-Methyl pyrene	n.d.	n.d.	n.d.	n.d.	n.d.
BenzyI butyl phthalate	n.d.	n.d.	2.400	n.d.	n.d.
Benzo[a]anthracene	106.890	39.947	n.d.	n.d.	n.d.
Chrysene	461.557	n.d.	n.d.	n.d.	n.d.
Di- <i>n</i> -octyl phthalate	n.d.	n.d.	12.387	n.d.	46.710
Benzo[b]fluoranthene	n.d.	n.d.	n.d.	n.d.	155.183
Benzo[k]fluoranthene	449.237	266.333	331.733	691.500	1514.408
Benzo[a]pyrene	5693.380	2511.813	1902.720	4309.320	32 905.485
Dibenz[a,h]anthracene	98.560	34.853	168.760	74.600	272.633
Benz[ghi]perylene	2.193	27.987	3465.587	n.d.	n.d.
Indeno[1,2,3- <i>cd</i>]pyrene	n.d.	39.307	276.707	n.d.	540.878
Total PAHs	6935.297	3862.496	8276.532	5743.298	35 746.250
<i>n</i> -C10	20.125	37.740	28.147	43.325	42.401
<i>n</i> -C12	46.000	46.580	48.920	58.028	63.890
<i>n</i> -C14	63.000	49.130	70.467	67.522	62.650
<i>n</i> -C16	54.375	42.330	55.827	50.400	41.953
<i>n</i> -C17	49.250	n.d.	60.000	25.022	n.d.
Pristane	19.500	n.d.	31.587	10.200	n.d.
<i>n</i> -Octadecene	n.d.	n.d.	3.587	n.d.	n.d.
<i>n</i> -C18	27.375	19.210	38.947	26.311	20.979
Phytane	n.d.	n.d.	3.173	n.d.	n.d.
<i>n</i> -C20	24.750	n.d.	19.373	14.212	n.d.
<i>n</i> -C21	n.d.	n.d.	2.733	n.d.	n.d.
<i>n</i> -C22	6.150	n.d.	9.920	7.500	n.d.
<i>n</i> -C24	7.350	n.d.	4.320	2.324	14.623
<i>n</i> -C26	23.625	n.d.	19.787	19.842	201.871
Squalene	74.750	n.d.	6.440	n.d.	161.689
<i>n</i> -C28	57.625	n.d.	24.987	119.250	n.d.
<i>n</i> -C30	4263.375	58.310	448.987	4858.500	10 521.838
<i>n</i> -C32	71.250	n.d.	13.760	n.d.	n.d.
Total aliphatic	4808.500	253.300	890.960	5302.436	11 131.895

Note: n.d.: below detection limit.

St. 3 (64.94 ng g^{-1}) and St. 6 (42.44 ng g^{-1}). The concentrations of organochlorine in fish species (*Euthynnus alleferatus*, *Scomberomorus commerson*, *Sphyræna Sphyræna*, *Diplodus vulgaris*, and *Alepes djedaba*) decreased in the order: PCBs > DDTs > HCHs > total cyclodienes (aldrin, dieldrin, and endrin) (table 5).

The concentrations of total HCHs (alpha-, beta-, and gamma-HCH) ranged from 0.3 to 65.7 ng g^{-1} with an average of 16.35 ng g^{-1} , which is higher than that recorded in coral reef

Table 4. Concentration of chlorinated pesticides and PCBs (ng g^{-1} , dry weight) in sediment samples collected from western coast of Alexandria during March 2005.

Compound	Station									
	3	4	5	6	7	8	9	10	11	12
α -HCH	0.158	0.041	n.d.	0.058	0.030	0.068	0.048	0.049	0.025	0.102
β and γ -HCH	0.147	0.921	n.d.	2.187	0.185	0.805	0.501	0.374	0.379	0.120
Aldrin	7.998	0.074	0.057	2.872	0.673	0.164	0.060	0.169	0.042	0.051
Dieldrin	0.040	0.094	0.001	0.074	0.034	0.137	0.043	0.070	0.031	0.132
Endrin	n.d.	0.061	n.d.	0.010	0.039	n.d.	0.049	0.015	0.004	0.043
<i>o, p</i> -DDE	n.d.	0.067	n.d.	0.093	0.048	0.071	0.046	0.028	0.002	0.090
<i>p, p</i> -DDE	2.461	0.708	0.016	0.808	0.711	0.768	0.654	0.417	0.114	0.911
<i>o, p</i> -DDD	0.273	0.961	n.d.	0.051	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<i>p, p</i> -DDD and <i>o, p</i> -DDT	0.401	0.041	0.001	0.061	0.139	0.140	0.044	0.006	0.008	0.041
<i>p, p</i> -DDT	0.054	0.004	n.d.	n.d.	0.032	0.036	0.041	0.005	n.d.	n.d.
\sum PEST	11.531	2.972	0.077	6.214	1.892	2.189	1.486	1.134	0.606	1.489
PCB 28	6.975	0.221	0.152	7.582	0.277	0.336	0.237	0.164	0.085	0.349
PCB 52	57.307	9.537	0.638	34.607	0.831	3.939	1.386	1.721	1.616	1.565
PCB 101	0.251	0.178	n.d.	0.209	0.133	0.111	0.143	0.114	0.027	0.246
PCB 118	0.062	0.070	n.d.	0.018	0.042	0.056	0.055	0.040	0.011	0.107
PCB 153	0.106	0.043	n.d.	0.013	0.035	0.056	0.060	0.041	0.008	0.057
PCB 138	0.132	n.d.	n.d.	0.008	0.032	n.d.	0.035	n.d.	n.d.	n.d.
PCB 180	0.104	0.005	n.d.	n.d.	0.029	0.009	0.036	0.006	0.009	0.012
\sum PCBs	64.936	10.053	0.790	42.437	1.379	4.507	1.951	2.086	1.757	2.336
\sum Total	76.468	13.025	0.867	48.652	3.271	6.696	3.436	3.219	2.363	3.825

Note: n.d.: below the detection limit; \sum PEST: sum of total pesticides; \sum PCBs: total PCBs; \sum Total: sum of (\sum PEST + \sum PCBs).

Table 5. Concentration of chlorinated pesticides and PCBs (ng g^{-1} ; wet weight) in fish samples collected from western coast of Alexandria during February 2005.

Compound	Species				
	<i>Euthynnus alleferatus</i>	<i>Scomberomorus commerson</i>	<i>Sphyraena sphyraena</i>	<i>Diplodus vulgaris</i>	<i>Alepes djedaba</i>
α -HCH	0.104	0.182	0.150	2.674	11.327
β and γ -HCH	1.944	1.319	0.152	9.524	54.371
Aldrin	1.838	1.647	0.650	12.675	29.900
Dieldrin	0.102	0.149	0.160	1.636	15.106
Endrin	0.092	0.112	0.181	1.712	0.732
TC	2.032	1.908	0.991	16.023	45.737
<i>o, p</i> -DDE	0.153	0.227	0.275	1.319	2.465
<i>p, p</i> -DDE	5.088	3.852	5.787	25.598	18.009
<i>o, p</i> -DDD	n.d.	n.d.	n.d.	n.d.	3.861
<i>p, p</i> -DDD and <i>o, p</i> -DDT	0.328	0.597	0.689	5.125	3.633
<i>p, p</i> -DDT	0.296	0.211	0.749	4.330	3.278
DDTs	5.865	4.887	7.499	36.372	31.247
Σ PEST	9.945	8.295	8.791	64.593	142.682
PCB28	4.309	1.210	0.753	13.568	15.710
PCB 52	20.803	5.854	3.921	48.109	168.269
PCB 101	0.285	0.598	0.560	4.496	5.330
PCB 118	0.165	0.195	0.298	2.581	10.791
PCB 153	0.496	0.217	0.512	2.885	4.201
PCB 138	0.184	0.072	0.101	0.553	1.113
PCB 180	0.181	0.077	0.250	6.478	2.626
Σ PCBs	26.423	8.223	6.395	78.671	208.039
Σ Total	36.368	16.519	15.187	143.264	350.721

Note: n.d.: below the detection limit; TC: total cyclodienes (aldrin + dieldrin + endrin); Σ PEST: sum of total pesticides; Σ PCBs: total PCBs; Σ Total: sum of (Σ PEST + Σ PCBs).

samples of the Red Sea (average 4 ng g^{-1}) [35]. The concentrations of total cyclodienes ranged from 0.99 to 45.74 ng g^{-1} wet weight. Although the use of HCHs in agriculture has been greater than that of cyclodienes and DDTs, the relatively low concentrations of HCHs in fish tissues reflect the lower potential for bioaccumulation. Furthermore, higher vapour pressures for HCHs than DDTs facilitate a relatively rapid atmospheric dissipation in the tropics, leaving fewer residues in sediment [36]. This was clearly found for lower HCHs concentrations than for the DDT concentrations listed in tables 4 and 5. Concentrations of DDTs in fish tissues ranged from 4.89 to 36.37 ng g^{-1} , with an average of 16.4 ng g^{-1} , wet weight.

These values were much lower than those recorded in fish samples collected from the Suez Canal (total DDTs ranging from 161 to 3100 ng g^{-1} with an average of 1087 ng g^{-1} ; wet weight [37]), and also lower than those recorded for mussels from the Egyptian Red Sea coast (ranging between 125 and 722 ng g^{-1} wet weight of total DDTs) [38]. The metabolic transformation of DDT under oxidative conditions which led to *p, p*-DDE was clearly detected for sediment samples (table 4). The same was true for *p, p*-DDE detected in fish tissues (table 5).

The persistent half-lives ($t_{0.5} = 5 \text{ yr}$) of DDT in marine systems from a study by Carvalho *et al.* [39] and recent work on the dechlorination of DDE in anaerobic sediments ($t_{0.5} = 6 \text{ yr}$) are similar [40]. Assuming that, after 1974, there have been no further releases of DDT, these half-lives would allow for an estimated reduction of DDT in the coastal environment. Nevertheless, despite the ban of DDT, there are still continuous inputs into the coastal environment, mainly by atmospheric deposition of DDT [41] and DDT leaching from agricultural soils followed by discharges into estuarine areas [42]. These inputs would help maintain DDT levels in the coastal environment, as the concentrations of total DDTs were almost the major component

of total pesticides (tables 4 and 5). Other chlorinated pesticides results either indicate a more rapid disappearance from the coastal environment than DDT [43] or a lower use there in comparison with DDT. The acceptable daily intake for PCB is 10–30 $\mu\text{g person}^{-1} \text{day}^{-1}$ [44], for DDT 1.4 $\text{pg person}^{-1} \text{day}^{-1}$ [45], and for HCH 1.8 $\text{mg person day}^{-1}$ [46].

Generally, POPs 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 [39]. 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. The maximum permissible levels of toxic DDTs, PCBs, and cyclodienes recommended by the National Academy of Sciences and National Academy of Engineering [47] for the protection of aquatic biota are 1000–5000 ng g^{-1} for PCBs and 100 ng g^{-1} for cyclodienes (all as weight concentrations in whole-body tissue). The levels recommended by the Swedish Food Regulation are 5000 ng g^{-1} for DDTs, 2000 ng g^{-1} for PCBs, and 20 ng g^{-1} for HCHs [48]. The US Food and Drug Administration (FDA) tolerance limit is 2000 ng g^{-1} wet weight for total PCBs in fish and shellfish [38]. All these values are higher than those recorded in the present study with $\sum\text{DDTs}$, $\sum\text{cyclodiene}$, and $\sum\text{PCBs}$, ranging from 0.328 to 5.125, from 0.99 to 45.74, and from 15.19 to 350.72 ng g^{-1} , wet weight, respectively (table 5).

This study provides a preliminary assessment of the level of POPs, in a restricted area of 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.

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