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FULL LENGTH ARTICLE

# Organochlorines and their risk in marine shellfish collected from the Mediterranean coast, Egypt



Dalia M.S. Aly Salem, Amany El Sikaily, Ahmed El Nemr \*

*Environmental Division, National Institute of Oceanography and Fisheries, Kayet Bay, El-Anfoushy, Alexandria, Egypt*

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## KEYWORDS

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**Abstract** Shellfish is a useful tool for active environmental biomonitoring. According to levels of persistent organic pollutants (POPs) in shellfish, we can calculate the risk observed for public health. Accordingly, this study covers the determination of POP concentration in some shellfish collected from the Mediterranean coast of Egypt. The obtained results revealed that the concentrations of total OCPs range from 47.07 ng g<sup>-1</sup> to 113.9 ng g<sup>-1</sup> with an average of 85.77 ng g<sup>-1</sup>. The organochlorine pesticide (OCP) concentration in collected shellfish followed the order: Total cyclodienes < PCBs < DDTs < HCHs. Meanwhile, the total concentration of PCBs in the collected shellfish samples range from 15.13 ng g<sup>-1</sup> to 37.49 ng g<sup>-1</sup> with an average of 25.72 ng g<sup>-1</sup>. The highest PCB concentrations (37.49, and 33.42 ng g<sup>-1</sup>) were found in the samples collected from the Eastern Harbor and Abo-Qir locations, respectively. The higher chlorinated congeners are of particular environmental interest because they have a long half life and easily bioaccumulate along the trophic chain. According to the world health authorities, the concentration of POPs in shellfish of the studied area can generally be considered not to be at levels posing a health risk.

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## Introduction

Over the last decades, increasing attention has been paid to the occurrence of persistent organic pollutants (POPs) in coastal and estuarine environments. They are ranked among the top 5 priority hazardous substances along with arsenic, lead, mercury and vinyl chloride (ATSDR, 2007). PCBs were

manufactured commercially in Europe from 1929 until the mid-1980s (OSPAR, 2010), and were primarily used in industry due to their insulating and flame retardant properties. Due to their toxicity, potential to bioaccumulate on fatty tissues and biomagnification through the food chain, exposure to these pollutants is a topic of huge concern (Otchere, 2005; Tomza et al., 2006). In fact, POPs have been directly related to deleterious health problems, including endocrine disruption, reproductive disorders, cardiovascular diseases, carcinogenicity and neurotoxicity (El Nemr et al., 2011; El Nemr, 2013; Amodio et al., 2012). Their release into environment is mainly unintentional and related to human activities (Kennish, 1997; Breivik et al., 2004). The marine environment is considered as the ultimate receptor for these compounds that have been

\* Corresponding author. Tel.: +20 1007801845.

E-mail addresses: [ahmedmoustafaelnemr@yahoo.com](mailto:ahmedmoustafaelnemr@yahoo.com), [ahmed.m.elnemr@gmail.com](mailto:ahmed.m.elnemr@gmail.com) (A. El Nemr).

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detected even in remote areas, such as the Polar Regions (Stegeman et al., 2001).

Biota could potentially acquire PCBs from three sectors in the environment: atmosphere, water and food. Because of their lipophilicity, changes in PCB concentration might also be related to changes in lipid content (Nakata et al., 2002). For example, in aquatic organisms, uptake involves: adsorption/absorption/partitioning of PCBs in water through gills and epidermis and consumption of contaminated food. PCB levels in marine invertebrates are best explained by equilibrium partitioning between body lipids and ambient water. So, PCBs in the tissues of bivalves such as *Mytilus edulis* should reflect the PCB concentration in its environment.

Bivalves are widely used as bioindicators of organic pollution in coastal areas because they are known to concentrate these compounds (Coelho et al., 2006; Lobo et al., 2010; Cardoso et al., 2012, 2013), providing a time integrated indication of environmental contamination, as well as reliable information on the potential impact of seafood consumption on public health (Fang, 2004; Otchere, 2005). In comparison to fish and crustaceans, bivalves have a very low level of activity of enzymatic systems capable of metabolizing persistent organic pollutants (POPs), such as aromatic hydrocarbons and PCBs. Therefore, contaminants' concentrations, in the tissues of bivalves, more accurately reflect the magnitude of environmental contamination (Phillips, 1980, 1990). In this context, the aim of this study was to investigate and assess the level of organochlorine contaminations in shellfish tissues of the Egyptian Mediterranean coast and to establish a baseline for organochlorine residue.

## Material and methods

### Samples

Sample collection was carried out at 7 sampling points (El-Mex, Eastern Harbor, Abu Qir, Rosetta, Port Said,

El-Arish 1 and 2) from the Mediterranean Sea, Egypt (Fig. 1). Two types of biota were collected (i) Gastropoda (*Mancinella mancinella*, *Dolium galea*) from Abu Qir, El Arish 1, (ii) Bivalve (*Lutraria elliptica*, *Donax trunculus*) from El Mex, Eastern Harbor, Rosetta, El Arish 2 (Tables 1 and 2).

### Procedure

Thirty individual shellfish of similar sizes (50–75 mm) were used for each analysis (El Nemr et al., 2003, 2012; Khaled et al., 2004). Homogenized shellfish flesh was frozen (–20 °C). Frozen samples of shellfish (soft tissues) were Soxhlet extracted for 8 h using distilled-in-glass hexane. Five gram of sample and 15 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>; 250 ml of hexane for 8 h were Soxhlet extracted. The sample extracted (hexane) was concentrated under vacuum to 5 ml and to 1 ml under a gentle stream of pure nitrogen gas. This extract was applied to a Florisil chromatography column for the separation of classes of compounds. From the Florisil column, a first fraction is obtained by the elution of 70 ml of hexane and contains mainly aroclors, HCB, DDEs, and aldrin. A second fraction is obtained by the elution of 50 ml of a mixture of hexane-dichloromethane 70:30 which contains toxaphene, DDDs, DDTs, and HCHs. A third fraction, eluted with 40 ml of dichloromethane, contains dieldrin and endrin. Activation of the Florisil was achieved by heating at 130 °C for 12 h, followed by partial deactivation of 0.5% water by weight and stored in a tightly sealed glass jar with ground glass stopper and the mixture was allowed to equilibrate for one day before use.

Each fraction was concentrated and injected into a CLASS-GC10 gas chromatograph (Shimadzu, Japan) equipped with a <sup>63</sup>Ni electron capture detector. A fused-silica capillary column (30 m × 0.32 mm × 0.52 μm) DB-1 (coated with 5% diphenyl and 95% dimethyl polysiloxane) was used for the quantification. The oven temperature was programmed from an initial temperature of 70 (2 min hold) to 280 °C at a rate of 5 °C min<sup>-1</sup> and was then maintained at 280 °C for 20 min.

**Table 1** Sampling locations, depth and pollution sources.

Location	Lon. (E)	Lat. (N)	Depth (m)	Pollution sources
El Mex	29.75°	31.18°	4.0	Industrial, agricultural, sewage, domestic discharge wastes
Eastern Harbor	29.86°	31.26°	4.5	Harbor
Abu Qir	30.08°	31.37°	4.0	Industrial, agricultural, sewage, domestic discharge wastes
Rosetta	30.33°	31.53°	5.0	Outlet of Nile River
Port Said	32.34°	31.29°	3.0	Eutrophied area
El Arish-1	33.36°	31.23°	3.0	Public beach
El Arish-2	33.39°	31.22°	3.0	Public beach

**Table 2** The identification of phylum: mollusk species collected from the studied locations along the Egyptian Mediterranean coast.

Class	Family	Genus	Scientific name	Location
<i>Gastropoda</i>	Muricidae	Mancinella	<i>Mancinella mancinella</i>	Abu Qir
	Tonnidae	Dolium	<i>Dolium galea</i>	El Arish-1
<i>Bivalvia</i>	Mactridae	Lutraria	<i>Lutraria elliptica</i>	El Mex
	Mactridae	Lutraria	<i>Lutraria elliptica</i>	Eastern Harbor
	Donacidae	Donax	<i>Donax trunculus</i>	Rosetta
	Donacidae	Donax	<i>Donax trunculus</i>	El Arish-2

Injector and detector temperatures were maintained at 270 °C and 300 °C, respectively. Helium was used as the carrier (1.5 ml min<sup>-1</sup>) and nitrogen as the make-up (60 ml min<sup>-1</sup>) gas. Concentrations of individually resolved peaks were summed to obtain the total PCB concentrations.

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 was scanned from m/z 50 to 450 at 1 s per decade. Data was also acquired in selected ion monitoring mode with a dwell time and span of 0.06 s and 0.10 a.m.u., respectively.

#### Quality control and quality assurance

To control the analytical reliability and assure the recovery efficiency and the accuracy of the results, six analyses were conducted on organochlorine compounds in the reference material IAEA – 406 provided by EIMP–IAEA. The limits of detection of OCPs were defined as three times the signal-to-noise ratio (S/N). The laboratory results showed that recovery efficiency ranged from 89.93% to 106.05% with variation coefficients of 9–14% for all organochlorine compounds. However, the recovery percentages of 97.2, 97.9, 103.0, 94.7, 99.0, 95.8, 97.9, 97.2, 92.9, 93.3, 97.0, 106.1, 97.2, 89.9 and 94.6 were evaluated for  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT,  $\gamma$ -chlordane, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin,  $\alpha$ -endosulfan,  $\beta$ -endosulfan and endosulfan sulfate, respectively. The limit of detection in the presented study was estimated to be 0.2 ng/g for PCB and 0.3 ng/g for pesticides, which was based on the minimum quantity of samples required for a discernible peak appearing on the chromatogram.

#### Result and discussion

Bivalves are considered suitable bioindicators for biomonitoring studies and appropriate for transplantation along coastlines (Viarengo et al., 2007) due to their wide geographical distribution, sedentary filter-feeding organisms and ability to

accumulate high levels of contaminants including metals in proportion to ambient concentrations in seawater (Goldberg, 1975; Andral et al., 2011). Tables 3 and 4 demonstrate the levels of OCPs contamination in shellfish from several stations along the Egyptian Mediterranean coast, where, OCPs detected in shellfish include,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -HCH, DDTs (*p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT), cyclodienes (aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlor, methoxy-chlor, heptachlor epoxide,  $\gamma$ -chlordane,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate) and polychlorinated biphenyls (PCBs). Concentrations of total OCPs ranged from 47.07 ng g<sup>-1</sup> to 113.9 ng g<sup>-1</sup> with an average of 85.77 ng g<sup>-1</sup>. Concentrations of OCPs in shellfish followed the order: Total cyclodienes < PCBs < DDTs < HCHs.

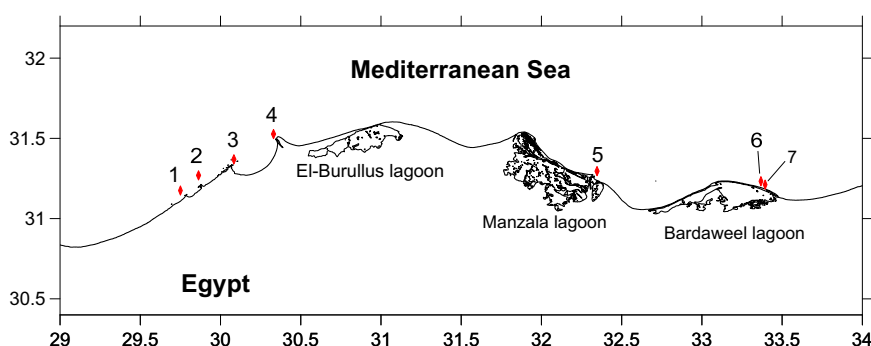
The total PCB concentrations in the studied samples ranged from 15.13 ng g<sup>-1</sup> to 37.49 ng g<sup>-1</sup> with an average of 25.72 ng g<sup>-1</sup> (Table 3). The highest concentrations (37.49 ng g<sup>-1</sup> and 33.42 ng g<sup>-1</sup>) were found in samples collected from the Eastern Harbor and Abo-Qir, respectively. The persistence of PCBs in this area may be due to the wastes dumped in these areas, intensive ship traffic and industrial activities. The lowest levels of  $\Sigma$ PCBs were found in El-Arish-2 sample (15.13 ng g<sup>-1</sup>). In general, bivalves preferentially accumulate congeners with 4, 5 and 6 chlorine substitutes (52, 101, 118, 138 and 153, respectively). Differences in the depuration rates and uptake of different congeners in the diet as well as biotransformation could explain these distributions. The most abundant PCB congeners detected in the investigated shellfish samples were PCB 52 and PCB 153 (3.74 ng g<sup>-1</sup> and 3.61 ng g<sup>-1</sup>, respectively). The PCB profile in shellfish from the Eastern Harbor and Abo-Qir bay was dominated by two hexachlorinated congeners; PCB153 being the major one followed by PCB138. The input of direct industrial and domestic discharge in the most contaminated zones, the Eastern Harbor and Abo-Qir, resulted in a larger proportion of PCB153 in relation to PCB138. PCB 153 and PCB 138 are the main constituents in Aroclor 1260 and Aroclor 1254, respectively (Carro et al., 2010). The higher chlorinated congeners are of particular environmental interest because they have a long half life and are easily bioaccumulated along the trophic chain (Pruel et al., 1993). The PCB153 predominance in shellfish was in

**Table 3** Average PCB in shellfish sample collected from the Mediterranean coast 2010 (ng g<sup>-1</sup> dw).

PCB Name	Est. Harbor	El-Mex	Rosetta	Abo Qir	El-Arish-1	El-Arish-2	Average	%tPCB
<i>Trichlorobiphenyl</i>								
PCB 18	2.14	1.95	3.44	1.54	5.35	3.03	2.91	11.3
PCB 28	1.64	1.23	3.53	2.24	1.40	0.69	1.79	7.0
<i>Tetrachlorobiphenyl</i>								
PCB 44	3.73	1.88	2.53	1.45	2.75	2.28	2.44	9.5
PCB 52	4.33	2.44	1.52	3.88	6.89	3.40	3.74	14.5
<i>Pentachlorobiphenyl</i>								
PCB 101	3.38	1.96	0.87	2.94	1.18	0.72	1.84	7.2
PCB 118	1.51	1.26	0.19	1.71	1.43	0.07	1.03	4.0
<i>Hexachlorobiphenyl</i>								
PCB 138	5.79	1.94	0.95	5.71	3.12	1.20	3.12	12.1
PCB 153	7.58	1.14	2.27	8.72	1.34	0.62	3.61	14.0
<i>Heptachlorobiphenyl</i>								
PCB 180	3.39	2.04	3.43	2.53	1.51	2.62	2.59	10.1
PCB 194	4.00	1.93	2.09	2.69	4.74	0.51	2.66	10.3
Total PCB	37.49	17.76	20.81	33.42	29.71	15.13	25.72	

**Table 4** Chlorinated pesticide and PCB concentrations in shellfish from the Egyptian Mediterranean coast ( $\text{ng g}^{-1}$  dw).

Pesticides name	El-Mex	Est. Harbor	Abo-Qir	Rosetta	El-Arish-1	El-Arish-2	Aver	S.D.
$\alpha$ -HCH	0.31	0.61	0.38	0.33	1.21	0.36	0.53	0.35
$\beta$ -HCH	0.50	0.54	0.41	1.52	0.73	1.55	0.88	0.52
$\gamma$ -HCH	0.78	1.76	2.37	14.41	1.74	1.23	3.72	5.27
$\delta$ -HCH	0.37	0.22	0.35	0.57	0.69	0.05	0.37	0.23
$\alpha$ -HCH/ $\gamma$ -HCH	0.40	0.34	0.16	0.02	0.69	0.29	0.32	0.23
HCHs	1.95	3.14	3.52	16.84	4.37	3.19	5.50	5.61
Aldrin	0.59	1.47	1.48	1.75	0.90	0.46	1.11	0.53
Dieldrin	0.22	0.79	0.51	0.46	2.01	0.14	0.69	0.69
Endrin	6.97	16.17	15.04	9.23	35.71	22.75	17.65	10.45
Endrin aldehyde	3.29	6.33	2.38	10.53	4.70	0.36	4.60	3.54
Endrin ketone	7.32	13.37	13.09	4.67	9.09	11.48	9.84	3.45
Heptachlor	0.08	0.17	0.21	0.62	0.24	0.12	0.24	0.19
Heptachlor epoxide	2.31	3.05	3.17	4.87	1.67	3.84	3.15	1.12
Methoxychlor	0.43	1.14	2.32	0.84	3.23	0.77	1.45	1.09
$\gamma$ -chlordane	0.68	1.70	0.39	0.42	1.93	0.90	1.00	0.66
Endosulfan ( $\alpha$ )	0.05	0.05	0.13	0.25	0.07	0.07	0.10	0.08
Endosulfan ( $\beta$ )	0.55	1.63	1.90	15.75	1.41	0.54	3.63	5.97
Endosulfan sulfate	2.54	2.69	1.74	2.41	3.19	0.33	2.15	1.01
Heptachlor/heptachlor epoxide	0.03	0.06	0.07	0.13	0.14	0.03	0.08	0.05
Total cyclodienes	25.03	48.56	42.37	51.78	64.14	41.74	45.60	12.95
<i>p,p'</i> -DDE	0.81	3.27	3.49	0.95	4.46	1.53	2.42	1.52
<i>p,p'</i> -DDD	1.18	3.64	3.78	8.59	1.88	2.97	3.68	2.61
<i>p,p'</i> -DDT	0.33	1.57	1.68	3.94	8.62	0.94	2.85	3.08
DDT/DDE	0.41	0.48	0.48	4.15	1.93	0.62	1.34	1.49
Total DDTs	2.32	8.49	8.95	13.48	14.97	5.44	8.94	4.76
PCB 18	1.95	2.14	1.54	3.44	5.35	3.03	2.91	1.39
PCB 28	1.23	1.64	2.24	3.53	1.40	0.69	1.79	0.99
PCB 44	1.88	3.73	1.45	2.53	2.75	2.28	2.44	0.78
PCB 52	2.44	4.33	3.88	1.52	6.89	3.40	3.74	1.85
PCB 101	1.96	3.38	2.94	0.87	1.18	0.72	1.84	1.12
PCB 118	1.26	1.51	1.71	0.19	1.43	0.07	1.03	0.71
PCB 138	1.94	5.79	5.71	0.95	3.12	1.20	3.12	2.18
PCB 153	1.14	7.58	8.72	2.27	1.34	0.62	3.61	3.57
PCB 180	2.04	3.39	2.53	3.43	1.51	2.62	2.59	0.75
PCB 194	1.93	4.00	2.69	2.09	4.74	0.51	2.66	1.52
Total PCBs	17.76	37.49	33.42	20.81	29.71	15.13	25.72	9.09
Total organochlorines	47.07	97.67	88.26	102.91	113.19	65.50	85.77	24.91

**Figure 1** Map of the sampling locations along the Egyptian Mediterranean coast. 1: El-Mex, 2: Eastern Harbor, 3: Abu-Qir, 4: Rosetta, 5: Port-Said, 6: El-Arish-1, 7: El-Arish-2.

accordance with other authors and is due to the presence of chlorines at 2–4 or 5 positions in one or both rings (Leah et al., 1997; Villeneuve et al., 1999; Green and Knutzen, 2003; Piersanti et al., 2006). The most important uptake by particulate matter in sea water is for PCB 153. In the cleanest station (El-Arish-1), levels of lower chlorinated (tetrachlorobiphenyl)

and more water-soluble compounds (PCB 52) were higher than in the Eastern Harbor and Abo-Qir shellfish samples. Levels of  $\Sigma$ PCBs followed the concentration order PCB 52 > PCB 153 > PCB 138 < PCB 18 > PCB 194 > PCB 180 > PCB 44 < PCB 101 > PCB 28 > PCB 118 (Fig. 2). The same pattern of PCB distribution was found for bivalves coming from

several parts of the world; bivalves from the Baltic Sea (Pikkariainen, 2007), in the bivalve tissue from two areas of Santander Bay, Spain (González-Quijano et al., 2006) and in edible shellfish from the Adriatic Sea (Bayarri et al., 2001) (Table 5).

Once in the environment, pesticides can slowly be degraded by a combination of photochemical and biological processes. The half-lives of individual pesticides in nature have not been determined; however, the ratio of the altered or degraded compounds in relation to the parent compound can be used as an index of (a) its general environmental decline if its application is fairly constant or discontinued, (b) its transport and dispersion from an area of intensive use and (c) its resistance to degradation in the food chain (Otcere, 2005). Thus in nature, one would expect the  $\alpha$ -HCH/ $\gamma$ -HCH ratio to reflect the formulation used and the length of time since its application at the source. The  $\alpha$ -HCH isomer is known to be the most environmentally stable, whereas  $\delta$ -HCH is degraded by microorganisms and isomerizes to  $\alpha$ -HCH photochemically. The predominant presence of the  $\gamma$ -HCH isomer found in this study reflects the recent exposure to HCH. The  $\Sigma$ HCH concentrations in the shellfish samples ranged from 1.95 ng g<sup>-1</sup> to 16.84 ng g<sup>-1</sup> at El-Mex and Rosetta, respectively, with an average of 5.50 ng g<sup>-1</sup>. A high concentration of  $\gamma$ -HCH was

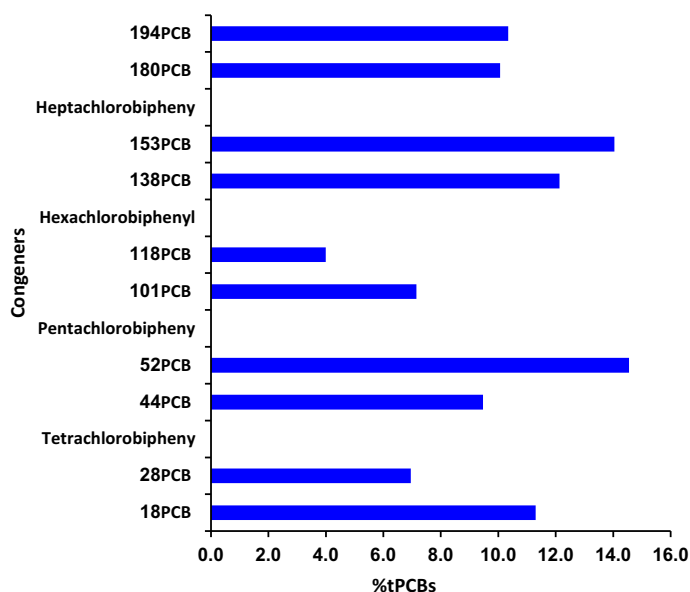
observed sharing a major portion of HCH (68% of total HCHs) followed by  $\beta$ -,  $\alpha$ - and  $\delta$ -HCH.

The total DDT concentrations in the shellfish samples ranged from 2.32 ng g<sup>-1</sup> to 14.97 ng g<sup>-1</sup> at El-Mex and El-Arish-1, respectively, with an average of 8.94 ng g<sup>-1</sup>. Among the DDT compounds, *p,p'*-DDD was measured at concentrations frequently higher than those of *p,p'*-DDT, suggesting the bioaccumulation of DDT from old applications. The ratio of DDT to DDE may be used as an indicator of DDT degradation since DDE makes up less than 1% of technical DDT (Larsson and Okla, 1989). A ratio of >1–5 indicates recent exposure to the parent DDT and a ratio of <5 indicates that the DDT residues arise from the food chain (Hooper et al., 1997). In this study, the ratios in all stations were less than 1 except at Rosetta which recorded >4. Anything less than 1 means that the *p,p'*-DDT had been biotransformed to DDE under aerobic conditions in all sampling sites (Table 4). DDT to DDE ratios, in this study, reflect the recent exposure to DDT (range: 0.41–4.15; Table 4). In the USA, the ratio is generally 1:10 and in the Western Mediterranean coast (Spain) between 1:7 and 1:10 (Sole et al., 1994) where the use of DDT has been banned since the mid-seventies.

The total cyclodiene concentrations in the shellfish samples ranged from 25.03 ng g<sup>-1</sup> to 64.14 ng g<sup>-1</sup> at El-Mex and

**Table 5** Median Organochlorine Concentration (ng g<sup>-1</sup> dw) in shellfish for this study compared with other regions of the world.

Location	$\Sigma$ CHLs	$\Sigma$ DDTs	$\Sigma$ HCHs	$\Sigma$ PCBs	References
Egypt	–	8.72	3.35	25.26	This study
Ghana	31	73	29	101	Otcere (2005)
Nigeria	–	81	164	122	Azokwu (1999)
Costa Rica	–	38	–	69	De la Cruz (1994)
Dominican Rep.	2.6	15	–	38	Sbriz et al. (1998)
Gulf of Mexico, USA	24	–	–	–	Sericano et al. (1996)
Brazil	–	3.5	–	7	Sericano et al. (1996)
Argentina	55	36	26	–	Sericano et al. (1996)
Hong Kong	–	–	–	325	Tanabe et al. (1987)



**Figure 2** PCB's pattern in mussel tissues of samples collected from the Mediterranean coast, Egypt.

El-Arish-1, respectively, with an average of  $45.60 \text{ ng g}^{-1}$ ; where, values for the cyclodienes (aldrin, dieldrin and endrin) showed a much higher concentration in endrin than the technical compound, which may suggest that either aldrin is no longer used in Egypt, at least not along the coast, or there is a decline in its application (Fig. 3). On the other hand, heptachlor to heptachlor epoxide ratios were similar to that of DDT and its metabolite ratios, leading to the same conclusion. These results are compared to the published data for PCBs and total DDT residues in shellfish and oysters from various regions of the world and are shown in Table 5. The variability in the regions is large, often up to three orders of magnitude. This fact alone severely limits making intra- and inter-regional comparisons. Furthermore, the uses of different species, size difference, seasonal effect, different methods of quantification, etc. all interact to confound comparisons. In general, the highest values come from areas where there are known industrial and agricultural inputs, and the lowest concentrations are found in organisms inhabiting the remote areas such as the central coast of Brazil (Otcere, 2005). According to tolerable levels of POPs in seafood for different countries, (FAO, 2005; MARA, 2008; Canadian Food Inspection Agency, 2012)

**Table 6** Factor loadings (varimax normalized with Kaiser normalized: marked loadings are  $> 0.70$ ) for three principal component factors (PCFs) for non-contaminated and for fairly contaminated areas.

Organochlorine Compounds	Component		
	PCF-1	PCF-2	PCF-3
$\alpha$ -HCH	.973	-.191	-.008
$\delta$ -HCH	.720	.466	-.156
Dieldrin	.998	-.034	.043
Endrin	.769	-.396	-.199
Methoxychlor	.827	-.093	.213
$\gamma$ -chlordane	.750	-.338	.112
Endosulfan sulfate	.704	.308	.278
<i>p,p'</i> -DDE	.759	-.202	.494
<i>p,p'</i> -DDT	.932	.203	-.264
PCB 18	.790	.066	-.590
PCB 52	.837	-.450	.190
PCB 194	.854	.095	.479
$\gamma$ -HCH	-.081	.946	-.312
Aldrin	.083	.858	.484
Endrin Aldehyde	.226	.901	-.012
Heptachlor	.119	.949	-.268
Heptachlor epoxide	-.591	.709	-.234
Endosulfan ( $\alpha$ )	-.130	.907	-.232
Endosulfan ( $\beta$ )	-.075	.950	-.303
<i>p,p'</i> -DDD	-.192	.938	-.127
PCB 28	-.011	.973	.090
PCB 180	-.501	.707	.237
$\beta$ -HCH	-.242	.322	-.787
Endrin ketone	-.045	-.514	.711
PCB 44	.379	.159	.705
PCB 101	-.077	-.078	.985
PCB 118	.405	-.259	.801
PCB 138	.205	-.108	.956
PCB 153	-.077	.186	.940
% of variance	32.45	31.63	21.72
Cumulative%	32.45	64.08	85.80

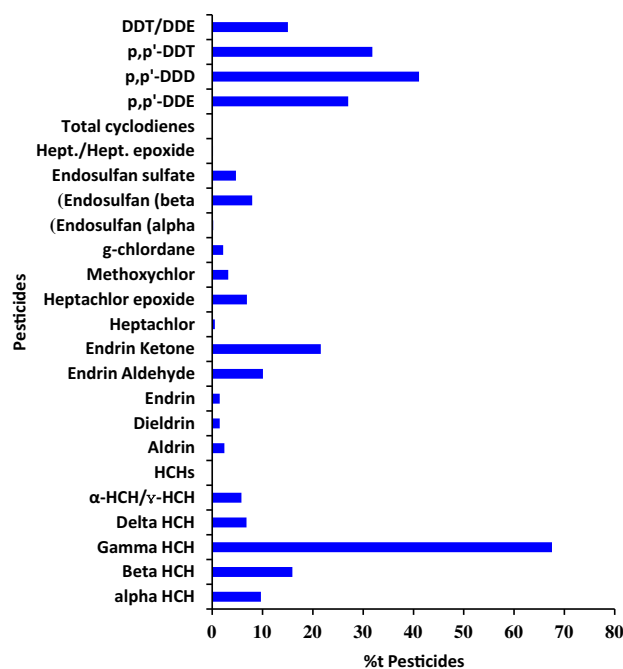
Extraction method: principal component analysis.  
Rotation method: varimax with kaiser normalization.  
Bold number: marked pollutants loadings.

DDTs and PCB concentrations in shellfish have no risk for consumers; this is shown in Table 5.

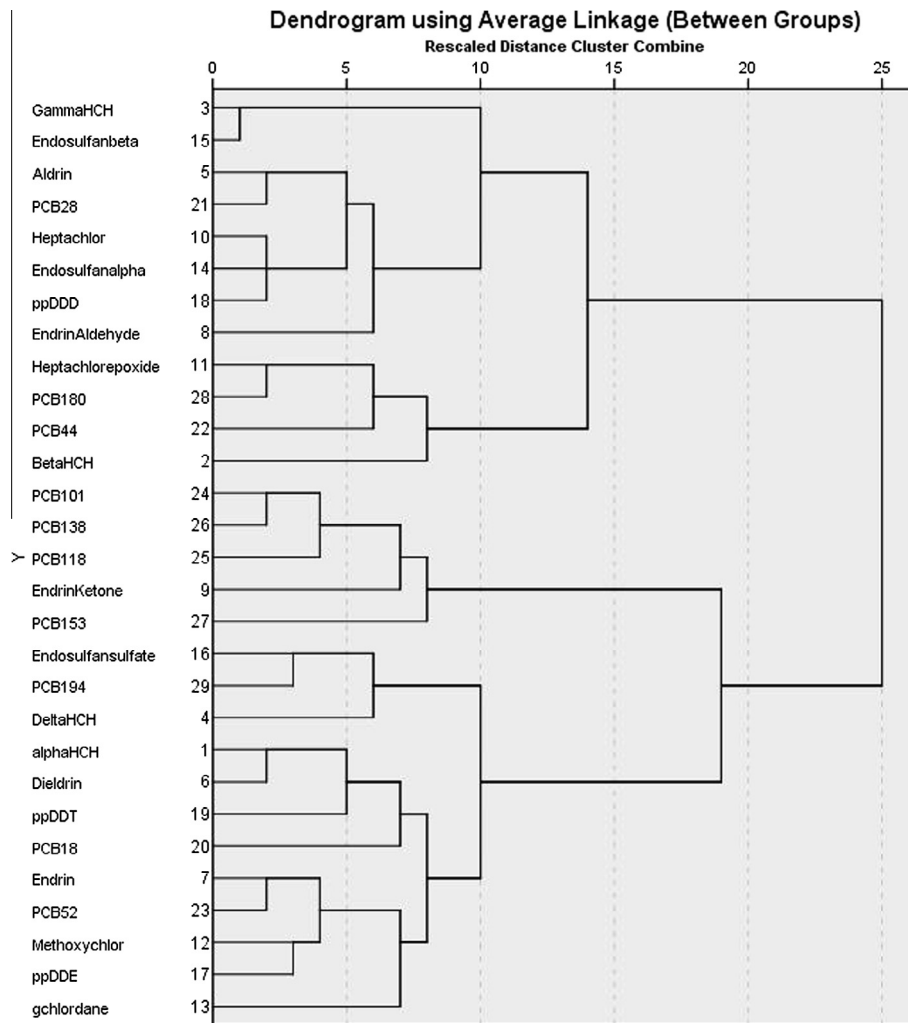
### Statistical analysis

Principal component analysis (PCA) was applied to the correlation matrix with VARIMAX normalized rotation. Cluster analysis (CA) was performed to further classify elements of different sources on the basis of similarities of their chemical properties. As the variables have large differences in scaling, standardization was performed before computing proximities, which can be done automatically by the hierarchical cluster analysis procedure. The majority of the variance (85.8%) of the scaled data was explained by three eigenvector-principal components. The first principal component factor (PCF-1) explained 32.45%. The second (PCF-2) and the third (PCF-3) principal component factors explained 31.63% and 21.72% of the total variances, respectively (Table 6). PCF-1 had a strong significant correlation with dieldrin (0.998),  $\gamma$ -HCH (0.973), *p,p'*-DDT (0.932), PCB-194 (0.854), PCB-52 (0.837), Methoxychlor (0.827), PCB-18 (0.790), endrine (0.769), *p,p'*-DDE (0.759),  $\gamma$ -chlordane (0.750),  $\delta$ -HCH (0.720) and endosulfan sulfate (0.704); PCF-2:  $\gamma$ -HCH (0.946), aldrin (0.858), endrin aldehyde (0.901), heptachlor (0.949), heptachlor epoxide (0.709),  $\alpha$ -endosulfan (0.907),  $\beta$ -endosulfan (0.950), *p,p'*-DDD (0.938), PCB-28 (0.973), PCB-180 (0.707); and PCF-3: PCB-101 (0.985), PCB-138 (0.956), PCB-153 (0.940), PCB-118 (0.801), endrine-ketone (0.711), PCB-44 (0.705) and  $\beta$ -HCH (-0.787). The property of individual organochlorine components which causes their dominance in each factor cannot be clearly indicated and their clustering was not observed (Fig. 4). Therefore, it is impossible to predict the distribution patterns of individual organochlorine components in contaminated areas.

The hierarchical cluster analysis (Ward's method applying Pearson correction) of organochlorine components using



**Figure 3** Pesticides pattern in shellfish tissues collected from the Mediterranean coast, Egypt.



**Figure 4** Hierarchical dendrogram for 30 objects represented by three variables obtained by Ward's hierarchical clustering method.

average linkage between groups and square Euclidean distance and standard deviation  $< 1$  showed a good efficiency for shellfish samples collected from the Mediterranean coast, which present different source depositions (Fig. 4). Two big clusters and two small clusters with subgroups could be distinguished. The linkage distance between classes is high (10.0–20.0) implying a significant distance between them. Statistically sufficient number of data can explain the obtained high values for linkage distance. The dendrogram of Fig. 4 shows that the first cluster contains pesticides dominantly ( $\gamma$ -HCH,  $\beta$ -endosulfan, aldrin, heptachlor,  $\alpha$ -endosulfan, *p,p'*-DDD, endrine aldehyde and only PCB 28). The second cluster is a mix of pesticides and PCBs containing  $\beta$ -HCH, heptachlor epoxyde, PCB-44 and PCB-180. The third cluster is mainly a PCB cluster (PCB 101, PCB 118, PCB 138, PCB 153 and endrin ketone). The fourth cluster could be conditionally named “pesticides” since they are various combinations of OCPs (Fig. 4).

## Conclusion

The data presented here indicates that the observed levels of POPs do not present a risk for the normal development and

survival of shellfish living in this area. In this context, the present results can serve as baseline information for further evaluating the capability of shellfish to monitor the accumulation levels of organic pollutant in this area. DDT to DDE ratios, in this study, reflect the recent exposure to DDT. On the other hand, heptachlor to heptachlor epoxyde ratios were similar to that of DDT and its metabolite ratios. The property of individual organochlorine components which causes their dominance in each factor cannot be clearly indicated and their clustering was not observed. Therefore, it is impossible to predict the distribution patterns of individual organochlorine components in contaminated areas. The linkage distance between classes is high (10.0–20.0) implying a significant distance between them. Statistically sufficient number of data can explain the obtained high values for linkage distance. The dendrogram shows that the first cluster contains pesticides dominantly ( $\gamma$ -HCH,  $\beta$ -endosulfan, aldrin, heptachlor,  $\alpha$ -endosulfan, *p,p'*-DDD, endrine aldehyde and only PCB 28). The second cluster is a mix of pesticides and PCBs containing  $\beta$ -HCH, heptachlor epoxyde, PCB-44 and PCB-180. The third cluster is mainly a PCB cluster (PCB 101, PCB 118, PCB 138, PCB 153 and endrin ketone). The fourth cluster could be conditionally named “pesticides” since they are various combinations of OCPs.

The data presented here indicates that the observed levels of POPs do not present a risk for the normal development and survival of shellfish living in this area. Also, there is probably no real health hazard for humans consuming shellfish from this area because DDT and PCB's concentrations are far below the maximum permissible tolerance levels. In this context, the present results can serve as baseline information for further evaluating the capability of shellfish to monitor the accumulation levels of organics pollutant in this area.

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