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Chlorinated Pesticides and Polychlorinated Biphenyls in the Coral Reef Skeleton of the Egyptian Red Sea Coast

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Chlorinated organic compounds have a wide range of industrial and agricultural applications. They include pesticides such as dichlorodiphenyltrichloroethane (DDT) and lindane (γ-HCH or gamma-hexachloro-cyclohexane) as well as polychlorinated biphenyls (PCBs) which are used in a range of industrial applications including dielectrics in electrical transformers. Organochlorines have been implicated in reproductive and immunological abnormalities observed in birds and marine mammals (Livingston 1976). The highest concentrations of organochlorines have been associated with centers of urbanization in most studies (NRC 1989; Alvarez Pineiro et al. 1995; Agnihotri et al. 1996; Thompson et al. 1996; Abd-Allah et al. 1998; El Nemr et al. 2003).

Synthetic organochlorines have been considered a serious threat to the long-term health of the marine environment for many years. The main reasons are their strong accumulation in lipid tissues of marine biota as well as their high toxicity for marine organisms and slow degradation for several members of this group. Various effects of pollution on coral reef organisms and communities have been documented (Wood and Johannes 1975; Loyta and Rinkevich 1980; Hatcher et al. 1989; Rogers 1989; Hughes 1994; Khaled et al. 2003; El-Sikaily et al. 2003). However, these efforts were made mainly to the coral reef environment and not to the coral reef itself. To the best of our knowledge research about organochlorine contamination in the coral reef skeleton are very limited.

There are numerous reports about the prevalence of organochlorine residues in the Egyptian Coastal marine environment; however, there are no reports about the coral reef in the Egyptian coasts (DANIDA 1996; EIMP 1996). This invited us to determine the residues of organochlorine pollutants in the coral reef skeleton of the Egyptian Red Sea coast.

MATERIALS AND METHODS

The coral reef sampling stations were located along the Red Sea coast starting from Marsa Alam to Taba (about 900 km, Figure 1). Coral reef samples (*Acropora* sp.) were collected at 20 sites within a period of two weeks during April 1999. At each site, large parts of coral reef were collected within a reef area

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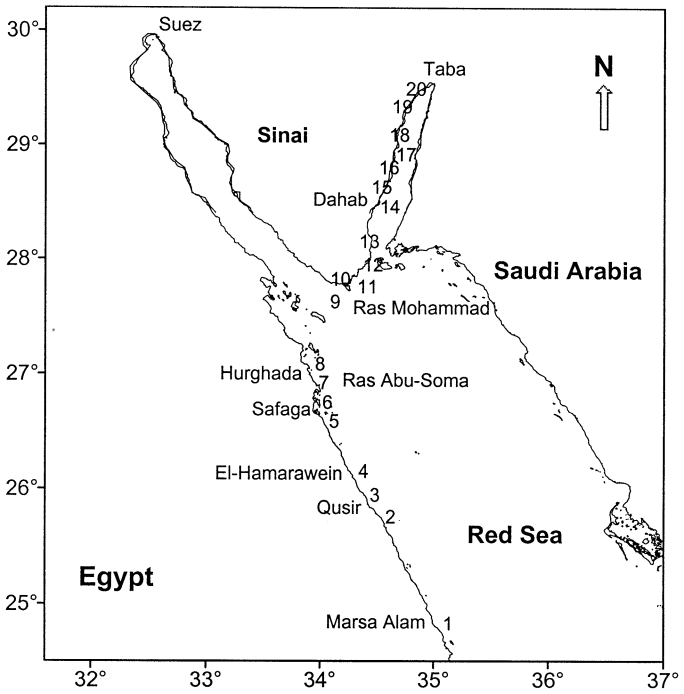

Figure 1. Sampling locations in the Egyptian Red Sea.

of 1 km^2 at each of the 20 sites, with collection depth ranging from 2-5 m. Coral samples were collected from the top of the colonies, avoiding areas of discontinuities where additional sediment had been taken into the skeleton during a partial mortality, injury, or invasion by bioeroders (Scott 1990). Coral samples were sun-dried, placed in pre-cleaned aluminum bags, and transported to the laboratory. Coral samples were washed with distilled water and dried in an oven at 50 °C for 48 hr. Sub-samples (100-150 g) of coral skeleton containing at least the last 4 years of skeletal growth (based on growth rates of 5-6 mm/year, (Guzman et al. 1991) were crushed and homogenized before extraction with organic solvents.

All solvents were pesticide-grade purchased from Merck (Germany). Sodium sulfate was extracted with hexane in a soxhlet apparatus for 8 hours and then with methanol or dichloromethane for another 8 hours, then pre-combustion in a muffle furnace at approximately 400 °C overnight and cooled in greaseless desiccators. Florisil used for column chromatography was solvent extracted with n-hexane in a glass cartridge inserted into an extraction apparatus, as described by Ehrhardt (1987). After extraction, florisil was first dried in the same cartridge by passing a nitrogen stream through it and was then activated by heating the cartridge in an electric tube oven to 200 °C for 6 hours. This was followed by partial deactivation with 0.5% water by weight and stored in a tightly sealed glass jar with a ground glass stopper and the mixture was allowed to equilibrate for one day before use. The activation/deactivation procedure was made one day before use.

30 g of coral reef was soxhlet extracted with 200 ml n-hexane for 8 hours with a siphon cycle of around 10 minutes. After the extraction was completed the extract solvent was concentrated to 15 ml using a rotary evaporator at 40 °C and transferred into a Kuderna-Danish concentrator and the volume of the extract further reduced to 1 ml under a gentle stream of pure nitrogen gas.

A chromatography column was prepared using a 50 ml burette in which a piece of glass wool was added near the stopper to maintain the packing material. Then 20 g of florisil were transferred into the column followed by 1 g of sodium sulfate. The extract (1 ml) was sequentially eluted from the column with 70 ml of hexane for PCBs congeners fraction (F1). Then the column was eluted with 50 ml of mixture containing 70% hexane and 30% dichloromethane for pesticide fraction (F2). F1 and F2 were evaporated by a gentle stream of nitrogen for instrumental analysis.

A Hewlett Packard 5980 series II high-resolution gas chromatograph (Hewlett Packard, USA) equipped with a ^{63}Ni electron capture detector (ECD) was used for analysis. A fused silica capillary column (50 m × 0.32 mm × 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.

An equivalent mixture provided by Dr. Ehrenstorfer Laboratories (Augsburg, Germany) with known PCBs composition and content was used as the standard. Organochlorine pesticides were quantified from individually resolved peak areas with the corresponding peak areas of the external standards (POC mixture provided by IAEA). Confirmation of peak identity was obtained for selected extracts using GC with mass spectrometry (GC-MS) (Hewlett-Packard 5889B MS "Engine"). To control the analytical reliability and assure recovery efficiency and accuracy of the results, 5 analyses were conducted on PCB reference material 2974 provided by EIMP-IAEA. The laboratory results showed recovery efficiency ranged from 96-106% with coefficients of variation between 10-14%.

RESULTS AND DISCUSSION

GC analysis for hexane extracts of coral reef skeleton exhibited the presence of organochlorines including α-, β- and γ-HCH, dieldrin, aldrin, heptachlor, *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD as well as PCBs (Tables 1 and 2). Concentrations of all these organochlorine pesticides in samples collected from the Egyptian Red Sea coast were somewhat low in most studied area. The concentrations of organochlorines in coral reef (*Acropora* sp.) skeleton decreased in the order of PCBs > DDTs > HCHs > cyclodienes for most of the studied locations. The PCBs were present in higher concentrations relative to other organochlorines in this study. The PCB concentrations were in the range of 6.2 ng g^{-1} at stations 12, 17 and 19 to 48 ng g^{-1} at atation 15, with an average concentration of 18.9 ng g^{-1}.

Table 1. Concentration (ng g^{-1}) of PCBs congeners in coral reef samples.

Site	Location Name	28	52	101	118	138	153	180	Total
1	Marsa Alam	3.1	4.0	1.7	0.4	0.7	0.8	0.1	**10.8**
2	Qusir	5.8	7.1	4.6	1.2	2.4	3.1	0.1	**24.3**
3	Qusir Ref	9.2	9.0	8.0	1.2	2.3	3.0	4.1	**36.8**
4	El-Hamarawien	8.3	1.4	1.9	2.1	0.5	4.9	2.0	**21.1**
5	Safaga	2.1	2.1	1.3	0.4	0.6	1.3	0.7	**8.5**
6	Safaga (Pub. Beach)	3.0	3.0	1.4	0.6	0.2	0.1	1.0	**9.3**
7	Ras Abu-Soma	6.3	8.1	1.1	1.1	1.2	0.9	0.1	**18.8**
8	Hurghada NIOF	4.3	11.6	0.7	0.9	1.4	1.1	1.2	**21.2**
9	Ras Mohammad	2.2	2.9	15.2	1.0	2.4	2.3	4.8	**30.8**
10	Sharm El-Mina	1.2	3.4	4.5	4.2	2.1	2.3	1.9	**19.6**
11	Sharm El-Maya	2.0	2.1	0.7	0.1	0.1	0.1	7.9	**13.0**
12	Na'ama Bay	1.1	1.9	0.7	0.3	0.2	0.1	1.9	**6.2**
13	Nakhlat El-Tel	1.8	7.4	1.1	0.6	0.4	0.2	2.6	**14.1**
14	Dahab	1.3	1.5	1.7	0.2	0.4	0.2	5.2	**10.5**
15	Ras Mamlah	6.9	14.3	4.9	2.7	5.5	3.9	10.1	**48.3**
16	Hibeiq Ras Nabar	1.2	2.9	2.5	1.9	1.2	3.3	2.4	**15.4**
17	Nuweiba, El-Siadin	2.2	1.9	1.2	0.2	0.1	0.1	0.5	**6.2**
18	Nuweiba	5.3	6.9	1.8	4.5	1.9	1.9	3.3	**25.6**
19	Marsa Muqibila	1.4	1.5	1.7	0.3	0.2	0.1	1.2	**6.4**
20	Taba	3.6	7.7	13.7	1.9	1.8	1.5	0.9	**31.1**
Mean		**3.6**	**5.0**	**3.5**	**1.3**	**1.3**	**1.6**	**2.6**	**18.9**
Median		**2.6**	**3.2**	**1.7**	**0.95**	**0.95**	**1.2**	**1.9**	**17.1**

Table 2. Concentration (ng g^{-1}) of organochlorine pesticides in coral reef.

Site	α-HCH	β-HCH	γ-HCH	**T. HCHs**	HC	aldrin	HCE	dieldrin	**T. CYD**	*p,p'*-DDT	*p,p'*-DDD	*p,p'*-DDE	**T. DDT**	**TP**
1	5.7	1.1	4.3	**11.1**	0.1	0.2	1.2	1.6	**3.1**	3.4	1.1	3.7	**8.2**	**22.4**
2	0.1	0.2	0.5	**0.8**	0.1	0.1	0.1	0.2	**0.5**	0.1	0.6	1.7	**2.4**	**3.7**
3	0.3	0.6	0.3	**1.2**	0.1	0.2	0.1	0.2	**0.6**	0.2	1.0	1.2	**2.4**	**4.2**
4	0.1	0.2	0.6	**0.9**	0.1	0.1	0.1	0.2	**0.5**	0.1	0.4	1.5	**2.0**	**3.4**
5	3.1	7.3	2.9	**13.3**	0.1	1.0	0.9	1.4	**3.4**	1.2	6.1	3.4	**10.7**	**27.4**
6	0.8	1.1	3.6	**5.5**	0.3	0.3	0.2	0.3	**1.1**	0.8	1.0	7.9	**9.7**	**16.3**
7	3.1	8.5	3.0	**14.6**	0.1	0.5	0.4	0.3	**1.3**	0.4	1.9	2.1	**4.4**	**20.3**
8	0.2	1.1	1.2	**2.5**	0.2	0.2	0.1	0.2	**0.7**	0.1	0.9	3.0	**4.0**	**7.2**
9	1.3	1.6	1.8	**4.7**	1.6	0.9	0.9	1.0	**4.4**	1.0	2.4	2.8	**6.2**	**15.3**
10	0.2	0.4	2.3	**2.9**	0.9	0.5	0.1	0.4	**1.9**	0.1	0.9	1.8	**2.8**	**7.6**
11	0.3	0.7	1.5	**2.5**	0.2	0.2	0.1	0.1	**0.6**	0.1	0.3	11.3	**11.7**	**14.8**
12	0.3	0.6	1.4	**2.3**	0.2	0.1	0.3	0.1	**0.7**	0.1	1.0	1.4	**2.5**	**5.5**
13	0.3	0.4	1.0	**1.7**	0.2	0.1	0.1	0.1	**0.5**	0.1	0.3	6.7	**7.1**	**9.3**
14	0.2	0.4	1.1	**1.7**	0.1	0.1	0.1	0.2	**0.5**	0.1	0.9	5.2	**6.2**	**8.4**
15	0.3	0.6	1.2	**2.1**	0.2	0.2	0.1	0.5	**1.0**	0.2	1.1	4.2	**5.5**	**8.6**
16	0.2	0.5	1.7	**2.4**	0.1	0.2	0.2	0.1	**0.6**	0.1	0.3	1.6	**2.0**	**5.0**
17	0.4	0.8	1.5	**2.7**	0.4	0.3	0.1	0.2	**1.0**	0.1	0.6	9.2	**9.9**	**13.6**
18	0.3	0.5	1.6	**2.4**	0.5	0.4	0.1	0.7	**1.7**	0.2	1.7	3.5	**5.4**	**9.5**
19	0.8	1.6	1.7	**4.1**	0.1	5.1	0.1	0.2	**5.5**	0.3	0.4	9.0	**9.7**	**19.3**
20	0.2	0.3	0.3	**0.8**	0.1	0.1	0.1	0.2	**0.5**	0.1	0.3	0.6	**1.0**	**2.3**
Mean	**0.9**	**1.4**	**1.7**	**4.0**	**0.3**	**0.6**	**0.3**	**0.4**	**1.6**	**0.4**	**1.2**	**4.1**	**5.7**	**11.3**
Median	**0.3**	**0.6**	**1.5**	**2.5**	**0.2**	**0.2**	**0.1**	**0.2**	**0.9**	**0.1**	**0.9**	**3.2**	**5.5**	**9.0**

HC: heptachlor; HCE: heptachlorepoxide; T-CYD: total cyclodiene; TP: total pesticides

PCB concentrations were on average 3 fold greater than the sum of DDT concentrations and up to 15-fold at station 3 (Table 1).

The highest concentrations of PCB 28 (9.2 and 8.3 ng g^{-1}) were at station 3 and 4, PCBs 52, 138 and 180 (14.3, 5.5 and 10.1 ng g^{-1}, respectively) at station 15, PCB 101 (15.2 ng g^{-1}) at station 9, PCB 118 (4.5 ng g^{-1}) at station 18, PCB 153 (4.9 ng g^{-1}) at station 4 (Table 1).

Concentrations of total DDT in the coral skeleton (Table 2) ranged from 1 ng g^{-1} at station 20 (Taba) to 11.7 ng g^{-1} at station 11 (Sharm El-Maya) with an average 5.7 ng g^{-1}. Among DDT metabolites, *p,p'*–DDE accounted for a range from 50 to 95% of total DDT. The highest percentage of *p,p'*–DDE was found at stations 6 (81%), 11 (96%), 13 (94%), 14 (84%), 16 (84%), 17 (93%) and 19 (93%). Lowest concentrations of total DDT were recorded for stations 2, 3, 4, 10, 12, 16 and 20 (ranged from 1 to 2.5 ng g^{-1}). These results reflect few fresh-inputs of DDT to the environment along the Red Sea coast. Metabolic transformation of *p,p'*-DDT under oxidative conditions lead to *p,p'*–DDE, whereas under anaerobic conditions *p,p'*–DDD is formed. The concentration of total *p,p'*–DDT relative to total DDT showed an average of 7%, only station 1 (Marsa Alam) exhibited 41%. These high *p,p'*-DDT concentration may reflect the recently intensive use of *p,p'*–DDT in this area.

Average concentrations of total HCHs in the coral reef samples were 4 ng g^{-1} with a range of 0.8 to 14.6 ng g^{-1} (Table 2). Although the use of γ-HCH in agriculture has been much greater than *p,p'*-DDT, the average ratio of total HCHs to total DDT was 70%. The relatively low concentrations of HCHs reflect their lower potential for bioaccumulation in the coral reef skeleton. Further more, higher vapor pressures of HCHs versus *p,p'*-DDT and its metaboliets facilitate relatively rapid atmospheric dissipation (Kannan et al. 1995).

The concentration of the cyclodienes (heptachlor, aldrin, heptachlor-epoxide and dieldrin) in the skeleton were from 0.5 ng g^{-1} at stations 2, 4, 13, 14 and 20 to 5.5 ng g^{-1} at station 19, with the average 1.6 ng g^{-1} showing an average of 4-fold less than total DDT and almost half of the HCH concentration levels. The concentrations of aldrin, dieldrin and heptachlorepoxide were higher at stations 1, 5 and 9 whereas their concentration at the other stations were much lower.

The percentage of the cyclodienes, HCHs, DDTs and PCBs relative to the total organochlorine pollutants showed PCBs as dominant in most studied locations except stations 5, 17 and 19 which presented total DDT as dominant. The total cyclodienes showed ratios ranging from 1.3 to 13.7% of the total organochlorines, whereas the HCHs and total DDT exhibited ratios ranging from 2 to 37% and 2.8 to 50%, respectively.

The persistence of *p,p'*-DDT in marine systems exhibited a half-life ($T_{1/2}$) of 5 years (Carvalho et al. 1994; Quensen et al. 1998). Assuming that after 1974 there has been no further release of DDT, these half-life values 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 *p,p'*-DDT (Villeneuve and Cattini 1986) and DDT leaching from agricultural soils followed by discharges into estuarine areas (Claisse 1989). These imputes would contribute to maintain DDT in the coastal environment. Other chlorinated pesticides indicate a more rapid disappearance from the coastal environment than DDT (ILMR 1975; Villeneuve et al. 1999) or a lower use in the coastal area versus use for DDT.

The 20 sites investigated showed low concentration of organochlorine compounds in the coral reef skeleton. The highest concentrations measured for total pesticides and PCBs congener were 27.4 and 48.3 ng g^{-1}, respectively. However, the total DDT were in low concentration at most sites investigated. The concentrations of PCBs and pesticides observed in coral reef skeleton exhibited moderate differences with low accumulation for most locations.

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