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Polychlorinated Biphenyls and Chlorinated Pesticides in Mussels Collected from the Egyptian Mediterranean Coast

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Recently there has been increased interest in examining environmental samples for individual PCB congeners. Some PCB congeners and related compounds elicit a diverse spectrum of toxic and biochemical responses including body weight loss, dermal disorders, liver damage, thymic atrophy, reproductive toxicity, immunotoxicity, and the induction of CYP1A1 and CYP1A2 gene expression (Safe 1990). The congeners considered to be the most toxic are the non-*ortho*-substituted coplanar PCBs, including congeners 77, 126, and 169. The ability of these congeners to attain planarity makes them stereoisomers of the highly toxic 2,3,7,8-tetrachlorobenzo-*p*-dioxin (TCDD) (McFarland and Clarke 1989; Safe, 1990; Sericano et al. 1992). The mono-*ortho*-substituted PCB congeners 105, 118, 123, 114, and 167 are thought to have similar, but somewhat less potent, properties (Safe 1990; Sericano et al. 1992; Tanabe et al. 1987a,b).

The concentration of DDT's in soft tissues of mussels (*Mylitus galloprovincialis*) from the North-Western Mediterranean Coast were found to be 10608 ng g^{-1} (dry weight) in 1973-1974 by Marchand et al. (1976). The DDT concentrations in the samples were generally higher than the DDE and DDD metabolites, the latter being due to direct exposure from pesticides in the environment. PCBs were also measured in mussel soft parts at high concentrations up to 10900 ng g^{-1} (dry weight). But since the production of DDT and PCBs were reduced or controlled in the 1960s and 1970s, the environmental concentrations of these pollutants likely declined, as shown for PCBs in the open Mediterranean Sea (Villeneuve et al. 1999; Fowler 1987).

The knowledge of occurrence of organochlorine pesticides in the Egyptian Mediterranean Sea coast is limited. However, in this study, congener-specific concentrations of PCBs, DDT and its metabolites (DDT's), hexachloro-cyclohexane isomers (HCHs) and cyclodienes were measured in mussel tissues collected from the Egyptian Mediterranean coast.

MATERIALS AND METHODS

The sampling areas were located along the Egyptian Mediterranean coast, from El Mex to El Bardaweel Lake (about 500 km, Figure 1). Two types of mussels (*Modiolus auriculatus*) from 15 sites and (*Donax* sp.) from 5 sites were collected in April 2000. At each site, a large number of mussels of similar size (2-4 cm shell length) were collected, stored in cleaned aluminum containers and frozen at –20°C

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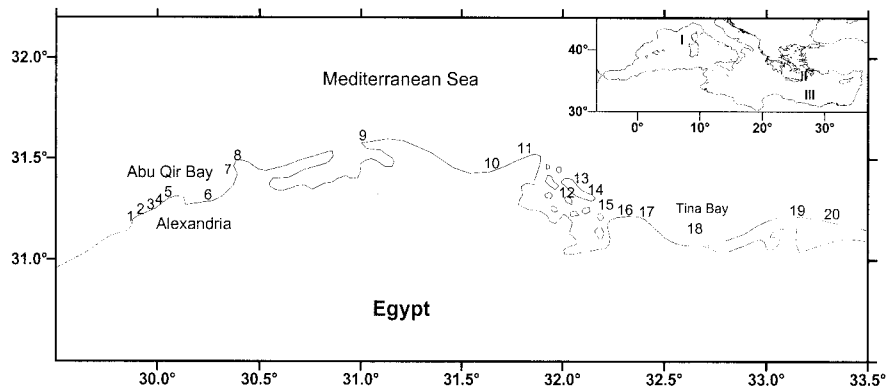

Figure 1. Position of collected samples.

until analyzed. In the laboratory mussels were pooled, opened with stainless steel knives and the soft parts were recovered. Ten gram aliquots were analyzed for PCB congeners and pesticides following well-established techniques (UNEP/IOC/IAEA 1991; IOC 1993).

Mussel (10 g of wet weight) was placed in a blender and anhydrous sodium sulfate was added. They were manually homogenized to determine whether the samples were adequately dried (normally 30 gm of anhydrous sodium sulfate was enough). Samples were blended at high speed until the mixture was well-homogenized (2-3 minutes). The mixture was transferred to a pre-cleaned extraction thimble and the dehydrated tissue was extracted with n-hexane-dichloromethane [(1:1), 200 ml] for 8 hours in a soxhlet apparatus cycling 5 to 6 times per hour. Anhydrous sodium sulfate (30 gm) 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 about 15 ml (maximum temperature: 35 °C). This was transferred to a Kuderna-Danish concentrator and concentrated with a nitrogen stream to 1 ml. This was transferred to the top of a glass column packed with 20 g Florisil, followed by elution with 70 ml of hexane for PCB congeners fraction (F1). Then the column was eluted with 50 ml mixture containing 70% hexane and 30% dichloromethane for the pesticide fraction (F2).

Each fraction was concentrated and injected into a Hewlett Packard 5980 series II high-resolution gas chromatograph (Hewlett Packard, USA) equipped with a ^{63}Ni electron capture detector (ECD). 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 quantification. Concentrations of individually resolved peaks were summed to obtain the total PCB concentration. An equivalent mixture provided by Dr. Ehrenstorfer-Germany with known PCB composition and content was used as the standard. Organochlorine pesticides were quantified from individually resolved peak areas with the corresponding peak areas of standards. To control the analytical reliability and assure recovery efficiency and accuracy of the results, 7 analyses were conducted on PCB compound reference materials freeze-dried mussel tissue (*Mytilus edulis*) No. 2974 (provided by EIMP-IAEA). The laboratory results showed recovery

efficiency ranged from 96-106% for PCBs with coefficient of variation of 12-18% for PCBs.

RESULTS AND DISCUSSION

A total of 20 mussel samples, covering about 500 km from the Egyptian Mediterranean coast, were analyzed for alpha-, beta- and gama- HCH, heptachor and its epoxide, aldrin, dieldrin and the DDTs, (*p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT) and polychlorinated biphenyls (PCBs) during this study. Polychlorinated biphenyl (PCBs) concentrations ranged from 8 ng g^{-1} to 437 ng g^{-1} with an average 132 ng g^{-1} of wet weight (Table 1). The PCB concentrations were higher at St. No. 1, 437 ng g^{-1}, St. No. 12, 133 ng g^{-1}, St. 7, 341 ng g^{-1}, St. 10, 294 ng g^{-1}, St. No. 2, 220 ng g^{-1} and 165 ng g^{-1}. PCBs 25 (215 ng g^{-1}, 49%) and 52 (80 ng g^{-1}, 18%) were the highest at the El-Mex location while PCB 180 had the highest concentration at the most locations (Table 1).

The concentrations of organochlorines in mussels (*Modiolus* sp. and *Donax* sp.) decreased in the order: DDTs > PCBs > HCHs > total cyclodienes (heptachlor and its epoxide derivative, aldrin and dieldrin) (Tables 1 and 2). The concentrations of total HCHs (alpha-, beta-, and gama-HCH) were in the range of 8 ng g^{-1} to 84 ng g^{-1} with an average 28 ng g^{-1}. Gamma-HCH was the major HCH component being over 50% at most stations.

The concentrations of total cyclodienes were in the range of 8 ng g^{-1} to 273 ng g^{-1} with an average 45 ng g^{-1} of wet weight. The concentration of heptachlorepoxide was 2 to 3 times more than that for heptachlor at most stations, while the concentrations of dieldrin were 1 to 1.5 times the concentrations of aldrin at most stations. The concentration of total HCHs was less than the concentration of total cyclodienes at most stations (Table 2). Although the use of HCHs in agriculture has been greater than cyclodienes and DDTs, the relatively low concentrations of HCHs in mussel tissues reflect their lower potential for bioaccumulation. Furthermore, higher vapor pressures for HCHs than for DDTs facilitate relatively rapid atmospheric dissipation in the tropics, leaving fewer residues in soil and water (Kannan et al. 1995). The average ratios of HCH to DDT concentration in mussel was ~3%, suggesting excretion of HCHs in marine mussels.

Concentrations of DDT's in the mussels were in the range of 62 ng g^{-1} to 2232 ng g^{-1} with an average 584 ng g^{-1} of wet weight. The concentration of DDT was the major one of all DDT's. The DDT percentage versus its metabolites ranged from 98% to 50%, suggesting widespread use of DDT in recent years. The metabolic transformation of DDT under oxidative conditions which lead to *p-p'*-DDE was detected in large percentage only at Gleem and Maadia locations with 54% and 43% of total DDTs, respectively. While the metabolic transformation of DDT under anaerobic conditions which lead to to *p,p'*-DDD was undetected in large percentage in all stations.

The persistence half-life ($T_{1/2}$ = 5 years) of DDT in marine systems (Carvalho et al. 1994) and recent work on the dechlorination of DDE to DDMU in anaerobic sediments $T_{1/2}$ = 6 years are similar (Quensen et al. 1998). Assuming that after 1974

Table 1. Concentration (ng/g of wet wt.) of PCB congeners in mussel samples from Egyptian Mediterranean Sea coast.

St. No.	St. Name	**25**	**52**	**101**	**118**	**138**	**153**	**180**	Total	% of 25	% of 180
1	El Mex	215.03	79.66	32.95	41.22	22.22	14.39	31.34	436.81	49.23	7.17
2	East Harbour	30.67	38.70	11.85	2.60	2.52	1.53	132.35	220.22	13.93	60.10
3	El Shatby	7.74	16.96	3.92	1.20	0.95	0.64	64.58	95.99	8.07	67.27
4	Sidi Gaber	19.43	21.48	22.16	7.51	31.57	17.39	11.50	131.05	14.83	8.77
5	Gleem	2.10	1.88	2.76	2.68	2.98	3.29	0.77	16.45	12.78	4.67
6	Meadia	1.37	17.02	0.33	0.35	0.17	0.65	145.57	165.46	0.83	87.98
7	Rashid	18.47	9.99	4.87	5.32	4.49	5.19	292.49	340.83	5.42	85.82
8	Rashid	4.77	3.00	1.20	0.21	0.39	0.49	41.74	51.79	9.20	80.60
9	El Borg	5.96	5.41	2.15	2.49	0.99	1.56	141.05	159.61	3.73	88.37
10	New Demiatta	60.98	72.29	33.39	10.24	11.25	4.31	101.27	293.74	20.76	34.48
11	Ras El Bar	16.04	16.82	4.56	5.15	3.91	3.26	8.16	57.90	27.70	14.10
12	El Manzalla	9.95	14.02	1.86	277.33	1.31	2.42	76.15	383.04	2.60	19.88
13	El Manzalla	15.52	44.16	4.60	2.79	2.60	2.40	20.36	92.43	16.79	22.03
14	El Jamil (west)	1.77	2.49	2.31	0.56	2.22	2.60	2.92	14.88	11.92	19.60
15	El Jamil (east)	1.03	1.93	1.43	0.62	0.67	0.57	1.44	7.70	13.36	18.74
16	Port Said (west)	0.53	1.88	1.13	0.73	0.96	0.56	43.04	48.83	1.08	88.16
17	Port Said	6.55	7.87	2.83	0.65	0.70	0.62	11.16	30.38	21.57	36.74
18	Rommana	7.50	5.36	3.12	1.44	1.69	1.46	24.02	44.60	16.82	53.86
19	Bardaweel	3.85	4.68	2.45	0.90	0.87	0.83	32.86	46.44	8.29	70.75
20	Bardaweel	3.07	2.60	2.16	0.39	1.93	2.38	1.90	14.43	21.26	13.15

25 = 2,2',4-Trichlorobiphenyl; 52 = 2,2',5,5'-tetrachlorobiphenyl; 101 = 2,2',5,5'-tetrachlorobiphenyl; 118 = 2,3,4,4',5-pentachloro-biphenyl; 138 = 2,2',3,4,4',5-hexachlorobiphenyl; 153 = 2,2',4,4',5,5'-hexachlorobiphenyl; 180 = 2,2',3,4,4',5,5'-Heptachlorobiphenyl

Table 2. Concentration (ng/g of wet wt.) of pesticides in mussel from Egyptian Meditterranean Sea coast.

Chem. Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Alpha-HCH	3.4	10.1	1.6	5.5	13.1	4.4	5.9	4.4	4.3	3.2	16.2	1.1	0.6	8.9	2.2	2.9	4.2	1.2	0.9	16.9
Beta-HCH	1.5	3.8	0.7	2.4	15.3	3.5	1.6	1.0	0.9	2.3	16.4	3.7	4.5	7.9	6.5	11.2	9.1	4.7	2.8	19.9
Gamma-HCH	10.5	54.6	7.3	35.6	20.4	16.0	7.8	4.9	3.2	12.2	21.9	4.9	5.2	8.3	2.8	4.6	9.3	4.8	4.5	18.1
Total HCHs	15.4	68.5	9.5	43.5	48.9	23.9	15.4	10.3	8.4	17.7	54.4	9.7	10.2	25.1	11.5	18.7	22.7	10.6	8.2	55.0
Heptachlor	2.9	3.0	1.2	1.8	5.7	3.5	4.0	3.2	4.0	3.1	21.2	4.3	3.6	4.7	1.3	3.3	3.7	3.9	5.6	9.6
Aldrin	4.4	8.5	2.3	3.0	15.5	8.5	13.5	11.3	11.7	7.6	62.9	11.2	7.0	5.7	2.9	4.9	7.6	11.7	13.1	7.7
HCP	3.8	6.1	2.4	6.2	13.9	22.0	9.0	9.2	12.3	5.9	107.1	13.0	8.7	9.3	5.3	9.7	11.8	13.7	8.4	5.0
Dieldrin	7.4	10.2	2.5	6.3	10.8	27.8	15.6	12.0	17.8	4.4	81.5	15.9	10.9	5.1	6.9	6.2	9.9	15.1	12.5	23.1
TC	18.5	27.8	8.3	17.3	45.9	61.8	42.0	35.7	45.7	21.0	272.7	44.5	30.1	24.9	16.5	24.1	33.0	44.4	39.6	45.4
p,p'-DDD	3.2	5.0	1.7	3.8	11.6	7.5	10.1	7.7	12.4	4.5	32.2	11.0	6.7	5.3	2.6	6.5	6.0	9.9	16.7	5.1
p,p'-DDE	19.0	25.2	8.8	21.6	28.2	81.6	42.7	31.2	37.7	114.2	170.2	36.1	24.1	23.8	12.9	180.2	162.6	36.0	35.2	61.4
p,p'-DDT	545.9	1482.6	282.1	102.5	77.8	33.7	1937.1	1274.6	86.4	321.5	2029.6	199.3	484.8	249.5	46.9	237.7	289.5	347.3	95.3	239.2
Total DDTs	568.1	1512.8	292.6	127.9	117.6	122.8	1989.8	1313.5	136.5	440.2	2232.0	246.4	515.6	278.6	62.4	424.4	458.1	393.2	147.2	305.7
TP	602.0	1609.1	310.4	188.8	212.3	208.5	2047.2	1359.6	190.5	478.9	2559.1	300.6	555.9	328.6	90.4	467.1	513.7	448.2	194.9	406.2
TOC	1038.8	1829.3	406.4	319.8	228.8	374.0	2388.1	1411.3	350.1	772.6	2617.0	683.6	648.3	343.5	98.1	516.0	544.1	492.8	241.4	420.6
A	94	94	94	68	55	59	97	97	72	92	87	82	93	85	69	91	89	88	75	75
B	3	4	3	23	23	11	1	1	4	4	2	3	2	8	13	4	4	2	4	14
C	3	2	3	9	22	30	2	3	24	4	11	15	5	8	18	5	6	10	20	11
D	58	88	76	59	93	56	86	96	54	62	98	44	86	96	92	91	94	91	81	97

A = % of total DDTs to total pesticides (TP); B = % of total HCHs to total pesticides; C = % of total Cyclodienes (TC) to total pesticides; D = % of total pesticides to total organochlorines (TOC); HCP = Heptachlorepoxide

there have been no further releases 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 DDT (Villeneuve and Cattini 1986) and DDT leaching from agricultural soils followed by discharges into estuarine areas (Claisse 1989). These inputs would help maintain DDT presence in the coastal environment, as the concentrations of total DDT's were nearly the major component of total pesticides (Table 2). Other chlorinated pesticide results indicate either a more rapid disappearance from the coastal environment than DDT (ILMR 1975; Villeneuve et al. 1999) or a lower use there in comparison with DDT. The acceptable daily intake for PCB is 10-30 μg/person every day (WHO 1989), DDT is 1.4 pg/person every day (FAO/WHO 1985) and HCH is 1.8 mg/person every day (EPA 1988).

Polychlorinated organic compounds (PCOCs), such as organochlorine pesticides and PCBs, have caused extensive concerns for a long time due to their strong lipophilic properties, persistence in the environment and enrichment in food chain (Winter and Streit 1992: Marth et al. 1997). These hydropholic compounds are mainly stored in fat tissues and when fats are mobilized the toxic substances re-enter the circulatory system disturbing the organism's normal body physiology. In this study, the 20 stations investigated showed a low concentration of HCHs and cyclodienes (heptachlor, aldrin, dieldrin, heptachlorepoxide) overall. However, the organochlorine concentrations at most stations investigated were within the range of the reported data from different areas (Table 3). The higher percentage of non-degraded DDT suggests its more recent usage in the Egyptian area.

Table 3. The concentration of PCBs and pesticides in different areas.

Biota Species	Location	Type of Pollution	Range ng g^{-1} wet weight	References
Mytilus galloprovincialis	NW Med. coast	DDTs PCBs Dieldrin Lindane	20-630/5 20-630/5 1.8-36/5 0.8-3.1/5	Villeneuve et al. 1999
Mytilus galloprovincialis	France	DDTs	7.4-733/5	Claisse 1989
5 Various species	I	DDTs PCBs	1-2048 39-11356	Mladen 2000
Mullus barbatus	II	DDTs PCBs	4-400 14-1613	Mladen 2000
Mullus barbatus	III	DDTs PCBs	3-83 ND-284	Abd-Allah et al. 1998

The 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 (NAS-NAE 1972), for the protection of aquatic biota are 1000 ng g^{-1} to 500 ng g^{-1} for PCBs and 100 ng g^{-1} for cyclodienes (all as weight

concentrations in whole-body tissue). In Sweden, the recommendations are 5000 ng g^{-1} for DDTs, 2000 ng g^{-1} for PCBs and 200 ng g^{-1} for HCB (Swedish Food Regulation 1983).

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