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Organochlorine Insecticides and PCBs in Water, Sediment, and Fish from the Mediterranean Sea

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Organochlorine insecticides and polychlorinated biphenyls (PCBs) are world-wide distributed organic pollutants. Such compounds are characterized by their stability for long periods and may lead to marked changes in the aquatic ecosystem (Addison 1976). Uptake and accumulation of such chlorinated hydrocarbons by sediments, microorganisms and fish led to the build up of such compounds in the food chain (Macek and Korn 1970).

In Egypt and some other Mediterranean countries, wastewaters are discharged into the sea directly, or via agricultural drains. This work aims to assess the prevailing levels of organochlorine insecticides and PCBs in the sea water, sediments and some fish species collected at Port-Said. This location was selected as an example of an important recreational area, charaterized by high fish productivity, growing industrial and navigable activities.

MATERIALS AND METHODS

Water, sediments and fish samples were collected from the Mediterranean sea, at Port-Said, from an area 10 km into the sea defined by latitude 31° 20° and Longtitude 32°, 20 (Fig 1).

Sub-surface grab water samples were collected into 2-L glass stoppered bottles previously cleaned with a mixture of 15% methylene chloride in n-hexane (v:v). An adequate volume of water samples (1L) was extracted twice with 60 mL of 15% methylene chloride in n-hexane. The combined extracts were dried over anhydrous sodium sulphate and concentrated to 10 mL in a rotating evaporator.

Sediments were collected by Ekman dredge sampler (Standard Methods 1980) from three sites namely, No. 1,2 and 3, from a depth of about 20 meter. A known weight of the air dried sediments (50g) was mixed with 50g of anhydrous sodium sulphate. The mixture was transferred

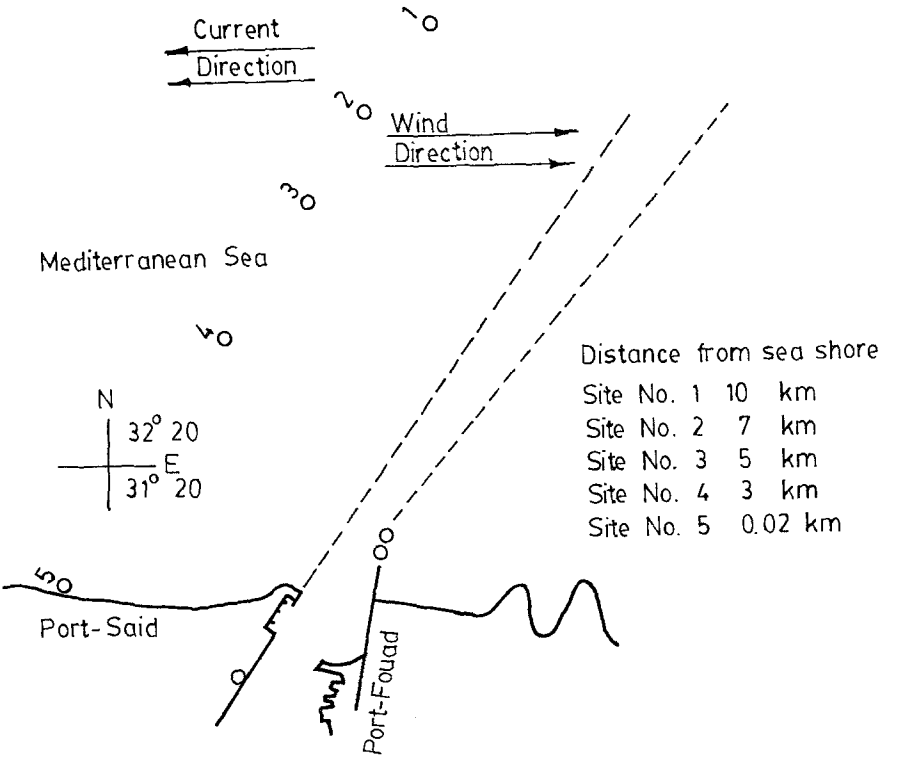

Fig 1. Schematic map showing sampling sites.

to a glass chromatographic column for further clean up and elution.

Fish samples were caught along the distance between sites no 3 and 4 (Fig 1). At each sampling time, two fish (200 g each) of the studies species were analyzed as a representative sample. The internal organs, head and tail of the fish were removed and analyses were carried out on the muscle tissues. A known weight of muscle (about 50 g) was chopped as fine as possible and mixed with anhydrous sodium sulphate at a ratio of 1:4. The treated sample mixtures were allowed to set for one hour and transferred to a glass chromatographic column for extraction of tested compounds. For all water, sediment and fish samples further cleanup, elution and separation of organochlorine insecticides from PCBs were carried out according to the U.S. Environmental Protection Agency (EPA) methods (1974).

Gas liquid chromatography (GLC) was utilized for the identification and measurment of the studied compounds. A Varian 3700 GLC, equipped with Ni^{63} electron capture detector and a glass column (4mm I.D. and 2 m length) was used. The column was packed with 4% SE 30+6% QF on 80/100 Chromosorb W. The column, injector, and detector temperatures were 200, 250 and 300 ^{o}C, respectively. Nitrogen was used as the carrier gas at a flow rate of

40 mL/min. All samples were analyzed for HCB, lindane, aldrin, endrin, dieldrin, chlordane, o,p̀-DDT, p,p̀-DDT p,p̀-DDE, p,p̀-DDD and PCBs. In the case of water samples, the minimum detection limit for HCB, aldrin, lindane and PCBs was 0.1 ng/L; that for chlordane, endrin, dieldrin was 0.15 ng/L; and for the DDT group and its metabolites was 0.2 ng/L. For sediments and fish, the detection limit for HCB, aldrin, lindane and PCBs was 0.1 µg/kg, that for chlordane, endrin, dieldrin was 0.15 µg/kg, and for DDT and its metabolites was 0.2 µg/kg. Chemical names of the studied compounds are to be found in Analytical Reference Standards (Watts 1981).

RESULTS AND DISCUSSION

Results presented in Table 1 show the residue levels of organochlorines and PCBs found in the Mediterranean Seawater during September 1982 to September 1983. Aldrin, endrin, dieldrin and o,p̀-DDT were not detected in any of the water samples investigated.

HCB and lindane residues were always very low compared with the other isolated organochlorine insecticides. Chlordane was identified in most water samples and its concentration ranged between 0.1 and 92.9 ng/L. p,p̀-DDT reached its highest concentration level in sea water collected in April 1983, and ranged between 0.3 and 50 ng/L. Later in June and September 1983, p,p̀-DDT residues were almost below the detection limit. Degradation products of p,p̀-DDT namely, p,p̀-DDE and p,p̀-DDD, attained their highest concentration levels in September 1982 and April 1983, (Table 1). Decline in the concentration of p,p̀-DDT, in seawater during May and September 1983, was recorded. Such a decrease in p,p̀-DDT level may be attributed to its conversion to p,p̀-DDE and p,p̀-DDD as well its uptake by sediments and living organisms. According to Patil et al (1972) 35 of 100 microbials isolated from a miscellany of sources, including open ocean water, surface films and sediments, could degrade p,p̀-DDT to p,p̀-DDD which was the main metabolite. In other studies, phytoplankton organisms converted p,p̀-DDT to p,p̀-DDE (Addison 1976).

PCBs were identified in all water samples investigated. However, PCB concentration was subject to material changes. The mean of residue levels of PCBs in water during September 1982, April, June and September 1983 were 94,41,105 and 19 ng/L, respectively. It should be noted that the concentration of total p,p̀-DDT tends to equal or exceed that of PCBs during September 1982 and April 1983. However, later in June and September 1983, the residue levels of PCBs in water exceeded the sum of DDT. In general, high PCB residue levels are associated with the discharge of wastewater (Lawrence and Mosine 1977) whereas DDT residues reflect its intensive

Table 1 Residue levels of organochlorine insecticides and PCBs in Mediterranean Sea water, ng/L

Site No.	Date	HCB	Lindane	Chlordane	p,p̀-DDE	p,p̀-DDD	p,p̀-DDT	Sum DDT	Total OC*	PCBs
1	17/9/1982	2.6	0.1	0.15	6.4	22.5	1.20	30.1	32.1	32.2
2		1.8	1.2	68.4	21.2	32.4	17.0	70.6	142.0	87.9
3		3.9	0.2	62.8	30.0	22.3	0.2	52.3	119.0	36.0
4		3.9	0.6	38.4	108.0	176.8	0.2	284.8	327.7	189.0
5		2.9	0.1	12.4	50.1	81.1	0.2	131.2	146.4	120.2
1	11/4/1983	0.3	0.1	10.8	21.7	1.7	0.3	23.7	34.8	37.7
2		5.0	0.2	0.1	10.5	5.6	16.6	32.7	37.9	15.7
3		0.2	7.6	7.2	11.9	7.2	33.8	52.9	67.9	36.7
4		2.0	0.1	2.2	17.9	38.0	56.9	112.8	117.0	26.7
5		12.6	0.3	5.7	36.1	13.0	50.9	100.0	118.6	89.8

* Total OC = Total organochlorine insecticides.

Table 1 Continued.

Site No.	Date	HCB	Lindane	Chlordane	p,p̀-DDE	p,p̀-DDD	p,p̀-DDT	Sum DDT	Total OC*	PCBs
1	11/6/1983	0.1	0.1	2.51	26.55	52.26	0.2	78.81	79.0	113.45
2		0.0	0.1	3.46	33.84	53.0	0.2	86.84	871.86	164.8
3		0.1	0.1	1.88	20.08	15.04	0.2	35.12	353.16	95.6
4		2.72	0.1	6.84	0.2	0.2	0.2	0.2	9.56	58.9
5		2.82	0.1	92.94	16.84	0.2	0.2	16.84	112.6	95.79
1	13/9/1983	0.1	0.1	3.11	8.62	10.61	0.2	19.23	22.34	33.74
2		0.1	3.46	3.21	0.2	6.0	0.2	6.0	12.67	15.94
3		1.35	0.61	1.53	7.24	5.31	0.2	12.55	19.22	19.45
4		0.1	0.1	0.1	0.1	0.1	0.5	0.5	0.5	12.61
5		0.34	0.2	0.1	3.02	2.28	0.2	5.3	10.94	15.84

* Total OC = Total organochlorine insecticides.

use for pest control. In addition, the concentrations of organochlorine insecticides and PCBs in sea water revealed by this study exceeded the solubility of such compounds (Train 1979). Consequently, the given values represent the sum of soluble and suspended residues of such compounds.

Residues of organochlorine insecticides and PCBs in sediments are given in Table 2. It is evident that the concentrations of studied compounds were subject to considerable variation with respect to sites and time of sampling. HCB was detected in sediments collected in April and June 1983, and its concentration ranged between 2.1 µg/L and 12 µg/kg. Later in September 1983, HCB was not detected which agrees with the extreemly low residue level of that insecticide in sea water. Residues of lindane, chlordane, endrin, p,p̂-DDT and its metabolites were detected in most sediment samples. As a general trend, the concentration of organochlorine compounds followed the order: p,p̂-DDE > p,p̂-DDD > endrin> p,p̂-DDT > lindane > chlordane HCB. The presence of p,p̂-DDT and its degradation products, at relatively high concentration in surface sediments, is an indication of its recent application and that active microbial degradation is taking place.

PCBs were alway present in sediment samples as was the case with water samples. The relatively high concentration of PCBs (200-1500 µg/kg) and DDT, in sediment, reflects its great capacity to adsorb and accumulate such pollutants. Assuming a uniform distribution of PCBs in sea water at site No 1, due to mixing and turbulence, concentration factors of 3978, 1900 and 16700 could be reached during April, June and September 1983, respectively. On the same basis, the concentration factors for DDT at site No 1, would be 34853, 3325 and 35323 as given in the previous order. Variation in the values of the concentration factor reflects the effects of the ongoing processes of adsorption-desorption and uptake by living organisms.

The distribution and concentration levels of organochlorine insecticides and PCBs in fish species investigated are shown in Tables 3 to 5. HCB was identified in Sparus auratus, Argyrops spinifer and Saurida species in May 1983. Two more species, Solea and Trichurus contained high residues of HCB in June 1983. Further changes in the concentration and distribution of HCB were observed in fish collected in September 1983 (Table 5). Lindane and chlordane were isolated from Solea vulgaris and Argyrops spinifer collected in April 1983. In June 1983, the latter two insecticides were identified in all fish species studied. Lindane reached its lowest concentration level in Sardinella aurita, and its highest residue level in Sparus auratus. Chlordane showed a wide range of concentration between 1.7 ug/kg (Sardinella aruita) and 108 µg/kg (Argyrops sp. and Trichurus

Table 2 Residue levels of organochlorine insecticides and PCBs in sediments from Mediterranean Sea at Port-Said, µg/kg.

Site No.	Date	HCB	Lindane	Chlordane	Endrin	p,p̀-DDE	p,p̃-DDD	p,p̀-DDT	Sum DDT	Total OC*	PCBs
1	1/4/1983	10.0	12.0	12.0	55.0	600.0	173.0	53.0	826.0	915.0	1500.0
2		5.0	20.0	10.0	36.0	320.0	110.0	40.0	470.0	4.4	1420.0
3		3.0	5.0	13.0	100.0	350.0	172.0	27.0	549.0	670.0	53.0
1	1/6/1983	12.0	4.5	17.0	28.0	140.0	110.0	12.1	262.2	323.7	217.0
3		2.4	14.0	31.0	46.0	95.5	152.0	13.2	260.7	354.1	200.0
1	13/9/1983	0.1	126.6	22.6	52.6	321.0	330.0	27.2	678.2	880.0	558.0
2		0.1	0.1	15.0	12.5	131.2	400.0	0.2	531.2	531.7	330.0
3		0.1	35.2	50.0	0.1	136.6	336.0	28.4	501.1	586.2	792.8

* Total OC = Total organochlorine insecticides.

Table 3 Residue levels of organochlorine insecticids and PCBs in some Mediterranean fish species, April 1983, µg/kg.

Fish	HCB	Lindane	Chlordane	Aldrin	Endrin	p,p̀-DDE	p,p̀-DDD	p,p̀-DDT	Sum DDT	Total OC*	PCBs
Solea vulgaris	0.1	20.4	5.6	0.1	0.1	8.17	48.13	0.2	56.3	82.3	124.6
Sparus auratus	12.34	0.1	0.1	0.1	0.1	39.54	14.34	12.23	66.11	78.45	240.35
Argyrops spinifer	3.84	1.52	5.57	0.1	0.1	18.53	11.13	0.2	29.66	40.59	100.43
Saurida sp.	2.49	0.1	0.1	0.1	0.1	22.46	11.24	0.2	33.7	36.19	60.11
Trichurus sp.	0.1	0.1	0.1	0.1	0.1	18.53	11.13	0.2	29.66	29.66	40.43
Sardinella aurita	0.1	0.1	0.1	0.1	0.1	10.58	12.56	4.7	27.84	27.84	30.38

* Total OC = Total organochlorine insecticides.

Table 4 Residue levels of organochlorine insecticide and PCBs in some Mediterranean fish species, June 1983.

Fish Species	HCB	Lindane	Chlordane	Aldrin	Endrin	p,p̀-DDE	p,p̀-DDD	p,p̀-DDT	Sum DDT	Total OC*	PCBs
Solea vulgaris	63.52	14.7	39.19	0.1	0.1	34.16	31.41	20.23	85.9	203.2	900.53
Sparus auratus	78.3	45.3	28.17	0.1	0.1	99.44	31.36	24.7	155.5	307.27	520.35
Argyrops spinifer	96.16	40.42	108.14	0.1	0.1	53.65	54.37	20.33	128.35	373.0	340.45
Saurida sp.	74.3	41.14	31.14	0.1	0.1	72.8	48.46	1.4	122.66	269.2	80.74
Trichurus sp.	23.85	40.4	108.73	0.1	0.1	53.4	53.7	2.2	110.3	283.28	64.45
sardinella aurita	0.1	1.22	1.69	0.1	0.1	24.3	144.0	0.2	168.3	171.2	74.7

* Total OC = Total organochlorine insecticides

sp). The distribution of lindane and chlordane in fish species collected during September 1983 exihibited a different pattern (Table 5). Aldrin and endrin were not identified in any of fish samples collected in April and May 1983. Fish samples collected in September 1983 revealed the presence of aldrin in only one sample of Argyrops spinifer whereas endrin was isolated from all other fish species studied (Tables 3 to 5). The highest concentration of endrin was found in Saurida sp. and amounted to 70 µg/kg.

p,p̃-DDT and its metabolites were the most frequently distributed insecticide in the fish studied and presented the highest residues compared to other insecticides. The relative concentration of p,p̃-DDE and p,p̃-DDD in fish were subject to considerable variation according to fish species and sampling time. The highest residue level of total DDT was reported in April 1983, and amounted to 66.1 ug/kg in Sparus auratus which also contained the highest p,p-DDE level (48.1 ug/kg). In June 1983, highest values of total DDT as well as p,p̃-DDD were found in Sardinella aurita and amounted to 168.3 and 144 ug/kg, respectively. Meanwhile, Sparus auratus still contained the highest residue level of p,p̃-DDE (99.4 ug/kg) by that time (Table 4). Out of the several fish species studies, Trichurus sp. contained the highest level of total DDT, p,p̃-DDE and p,p̃-DDD in samples collected in September 1983. The proportions of p,p̃-DDT and its metabolites in aquatic organisms attracted the interest of several investigators. (Addison 1976, Bjerke and Brevik 1980). In general, p,p̃-DDE and p,p̃-DDT were the principal compounds in fish whereas p,p̃-DDD was present at low concentration. Results attained by this study showed that p,p̃-DDE and p,p̃-DDD are the main fractions of the total DDT in fish species collected. Previous findings by Badawy and El-Dib (1984) similarly indicated that the metabolites constitued the major fractions of DDT in fish. Differences in the p,p̃-DDT proportions may be attribated to variations in the metabolic rates, residue levels in the aquatic environment, feeding hapites and age of fish (Macek and Korn 1970, Gerlach 1981).

PCBs were found in all fish species collected which correlates with the wide distribution of PCBs in sea water and sediments. The concentration of PCBs in fish ranged between 10 ug/kg and 1167 ug/kg. Sparus auratus showed the highest residues of PCBs in April 1983, whereas Solea vulgaris contained the highest level during June and September 1983, (Tables 3 to 5). Meanwhile, Sardinella aurita contained the lowest residue levels of both DDT and PCBs. According to Edwards (1971) the DDT/PCBs ratio tends to be below 2 near industrial areas and increase with the distance away to become greater than 10 in remote regions. Results given by

Table 5 Residue levels of organochlorine insecticides and PCBs in some Mediterranean fish species, September 1983, ug/kg.

Fish Species	HCB	Lindane	Chlordane	Aldrin	Endrin	p,p̀-DDE	p,p̀-DDD	p,p̀-DDT	Sum DDT	Total OC*	PCBs
Solea vulgaris	18.42	28.15	0.1	0.1	7.63	88.68	59.71	0.2	148.39	194.96	1167.7
Sparus auratus	0.1	12.97	0.1	0.1	55.43	19.09	11.62	0.2	30.71	45.97	637.28
Argyrops spinifer	16.0	10.22	0.1	69.2	0.1	24.2	27.27	0.2	51.47	146.89	219.39
Saurida sp.	0.1	0.1	0.1	0.1	70.0	194.2	52.4	0.2	246.64	316.6	514.6
Trichurus sp.	4.46	11.57	3.9	0.1	8.4	195.9	96.48	6.54	298.89	323.35	209.59
Sardinella aurita	8.54	0.1	0.1	0.1	5.33	4.67	0.15	0.15	4.67	18.54	10.25

* Total OC = Total organochlorine insecticides.

this study, indicated that DDT/PCBs ratio was relatively low and below 2. Addison (1976) reported that the efficiency of chlorinated hydrocarbons accumulation by fish follows the order PCBs > DDT > Dieldrin > lindane. Such an order is in agreement with the observed trend of residue levels in fish collected in April 1983, taking into account that dieldrin was not detected in any of studied samples. In June 1983, three fish species namely, Saurida, Trichurus and Sardinella deviated from the previous order to exihibit higher DDT content. However, in September 1983, only Trichurus sp. showed high DDT residue compared to PCBs. The present study adds to the validity of monitoring residues of persistent pollutants which can provide basic infromation concerning the response time of the natural ecosystem.

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