Bull. Nat. Inst Oceanogr. & Fish., ARE, 17 (1) 1991: 71 - 77.

RESIDUE LEVELS OF HEXACHLOROBENZENE (HCB) AND POLYCHLORINATED BIPHENYLS (PCB'S) IN THE MEDITERRANEAN WATER AND SEDIMENTS OFF THE NILE DELTA.

M.M. ABBAS, K. EL-GENDY^{*}, A.M. ABD-AALLA, H.A. ALI^{*}, G. TANTAWY^{*}, AND A.H. EL-SEBAE^{*}.

National Institute of Oceanography and Fisheries, * Faculty of Agriculture, Alexandria university Alexandria.

ABSTRACT

Residues of HCB and PCB's were analyzed by capillary gas chromatography in water column and sediment off the Nile Delta, Mediterranean Sea. The ambient PCB's and HCB levela found were very low, and in most cases below their detection limita. Ar-1242 values were relatively higher compared to Ar-1260. The relationship between PCB's and HCB concentrations and sediment extractable organic matter (EOM) content is evident. The concentration factor between sediment and water (S/W) was calculated.

INTRODUCTION

The high lipophilicity and low biodegradability of PCB's induce special serious problems to the environment. Aquatic environment is the universal solvent that receives the major amounts of these chemicals and the media in which many food chains originate. The presence of BCP's environnmental contaminants has been confirmed by Jensen (1966) in samples collected for pesticides residue analysis. Although concentrations of PCB's in biota, sediments and water of the Mediterranean Sea have been determined (Elder, 1976; Elder and Villeneuve, 1977; Basturk et al., 1980 and Burns and Villeneuve, 1987), yet the available data on the Egyptian coast are limited except few locations along the narrow coastal zone.

The present investigation was undertaken to determine residue levels of HCB and PCB's (Ar-1242 and Ar-1260) in surface and subsurface waters from 21 locations, representing 38 samples; as well as bottom sediments at 16 locations off the Nile Delta, Mediterranean Sea (Fig. 1). This study was done for the first time along the Nile Delta coastline region along 200 km from west to east, and seawards (100 km) to the north; as shown in Fig. 1.

MATERIAL AND METHODS

Samples were collected using a Remote Controlled Battery NTP sampler for water and a Van-Veen grab for sediments. Sediment samples were immediately wrapped into heavy duty aluminium foil (2 layers), and stored at -18°C for not more than one week.





The layout of investigated stations off the Nile Delta.

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a) Water samples:

Seawater samples were immediately transferred to a separatory funnel (4.0 1) and then extracted with n-hexane (3x80 ml). The organic layer was carefully separated and rotary evaporated down to 10 ml, at Ca. 45° C. The concentrated extract was desulphurized (whenever required), desiccated through a Pasteur florisil microcolumn and eluted with n-hexare (5 ml) followed by ether/hexane (5 ml, 5 %). The eluted fractions were combined and N₂ evaporated down to 1 ml. The cleaned-up sample extract (1 ml) was then fractionated on a silica fractionating column. Samples were analyzed using a Varian 3400 GLC-ECD system equipped with SE-54 Vetreus silica capillary column, and Varian 4290 Integrator.

b) Sediment samples:

Homogenized sediment samples (each of 30 gm wet weight) were thoroughly mixed with an internal standard (1 ml contains 50 ug), 2,3,5-trichlorobiphenyl, (2,3,5-TCB) and soxhlet extracted with n-hexane (200 ml) for 8 h. The extract was rotary evaporated down to 10 ml and thoroughly mixed with vigorous shaking and an aliquot was saved for (EOM) determination. Sediment concentrated extracts were treated with Hg metal prior to GLC analysis in order to remove sulphur residues. The concentrated desulphurized extract was desiccated through a Pasteur florisil water sampĺes. A portion of the microcolumn as for for moisture homogenized sediment sample was used determination. GLC-identification and determination of PCB's Ar-1242 and Ar-1260 and HCB were achieved by matching unknown peaks against authentic standards (BDH) using RT and RRT values.

RESULTS AND DISCUSSION

HCB, AR-1242 and Ar-1260 levels were detected in all water samples; ranging from 0.4 to 72.7 ng/l (HCB), 13 to 131.8 ng/l (total PCB's). Table 1 indicates that PCB's and HCB, showed the highest occurrence at site-6 (Off-Rosetta Branch of the Nile Delta) followed by site-1 for HCB 23.80 ng/l and site 8 for PCB's (41.29 ng/l). Such high concentrations found at site-6, can be explained by the findings of Basturk et al (1980) who reported comparable high values in samples taken from the Mediterranean coast near river mouth or estuary areas of crowded population and industrial activity. The tendency of PCB's towards accumulation slowly decreased with depth, ranging from 15.4 ng/l (surface water, as mean), down to 13.2 ng/l (bottom water). In contrast, HCB mean concentration levels tend to increase with depth from 7.8 ng/l (surface) to 8.9 ng/l (bottom). The mean concentrations were 8.9 ng/l (Ar-1242) and 6.5 ng/l (Ar-1260) at surface water; while near bottom depth, the mean concentrations were 7.0 ng/l (Ar-1242) and 6.2 ng/l (Ar-1260) as shown in Table 1. Values of PCB's were reported for near shore Mediterranean waters (Elder,

Table 1.	
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Station	Depth (m)	Positi	on	Ar 12	Ar 12	PCB's	HCB
1	0.5	31° 21,2'N	30° 00'E	7.58	5.65	12.23	23.80
1	5			5.18	9.82	15.00	13.98
1	30			1.87	15.26	17.13	19.72
2	0.5	31° 30'N	30 ⁰ 00'E	12.33	10.40	22.73	11.10
2	85			3.52	1.86	5.38	5.62
3	0.5	31° 40,2'N	30 ⁰ 00'E	4.54	2.64	7.18	8.50
3	390			3.01	4.84	7.85	9.34
4	0.5	31° 50,3'N	30 ⁰ 00'E	9.02	4.83	13.85	1.12
4	600			3.85	8.21	12.06	8.90
5	0.5	32 ⁰ 00'N	30 ⁰ 00'E	4.05	1.17	5.22	1.96
5	680			5.01	3.23	8.24	6.84
6	0.5	31° 32,6'N	30° 24,2'E	76.85	54.92	131.77	72.78
7	0.5	31° 39,9'N	30 ⁰ 25,4'E	12.33	10.40	22.73	11.09
7	14		-	2.81	3.52	6.33 [.]	11.63
8	0.5	31° 49,9'N	30° 25,2'E	25.35	14.54	39.89	4.33
9	6.5	32° 00'N	30° 25,1'E	2.69	3.66	6.35	2.40
10	0.5	31° 39,9'N	30 ⁰ 50,1'E	4.29	1.20	5.49	2.40
10	13	•	•	15.43	15.48	30.91	7.76
11	0.5	31° 49,9'N	30° 39,15'E	1.81	1.25	3.06	0.63
11	127	•	•	5.15	3.66	8.81	2.11
12	0.5	31° 39,9'N	31 ⁰ 14,19'E	2.72	3.54	6.26	3.24
12	16			20.02	20.99	41.01	12.30
13	0.5	31° 49,9'N	31° 14,19'E	1.98	1.35	3.33	7.43
14	0.5	32 00'8	31° 15'E	2.42	1.72	4.14	1.24
14	831			2.76	1.72	4.48	1.47
15	0.5	31° 39,9'N	31° 14,9'E	2.70	3.78	6.48	3.40
16	0.5	31" 40,N	31° 40'E	2.56	6.39	8.95	2.11
16	40			2.67	0.84	3.51	4.57
10	26	70		2.48	1.42	3.90	5.52
17	0.5	52° 00'N	51° 40'E	1.13	1.72	2.85	1.76
17	00 0 F	709 00.00		2.89	1.10	4.05	2.44
16	0.5	32° 20'N	51° 40'E	0.00	0.00	1.32	0.49
10	940	740 FO/N	770 05/5	2.71	1.72	4.23	1.79
19	U.)	31 3U'W	36 MJ.F	Y.30	1.24	10.92	2.94
19	00	7-9 00.00	7-9 0/ 0/-	20.73	4.20	J1.U1	7.82
20	0.5	32 UU'N	36 U4,9'E	2.05	1.07	5.(/	U.42
4 1	U.3	52" UU'N	36 30'E	1.4/	3.82	5.69	V.76

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PCB's and HCB concentrations (ng/l) in the Mediterranean Sea water.

PCB's : Ar 1242 + Ar 1260

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1976, and Elder and Villeneuve: 1977). With respect to PCB's inputs a correlation has been suggested to exist between the gross national product of an area and its rate of release of anthropogenic substances such as PCB's to the environment (Goldberg, 1976).

From Table 2, it is indicated that Ar-1242 in sediment samples was favourably detected at sites (7, 23, 8, 10 and 16). Accumulation of Ar-1260 seems to increase seawards, with 4 focal deposition at sites 1, 15 and 24, as well as site-25. The contribution of the individual PCB to the total PCB varied from site to site. Since each PCB's component has its different molecular structure as well as its physical and chemical properties, their environmental behavior and bio-accumulation are widely variable. The highest PCB's value occurred at site-7 followed by site-23 and site-8. The higher proportion of detected PCB's is manily due to Ar-1242 rather than Ar-1260, particularly at off-shore distant sites. Residues of HCB which have become virtually ubiquitous, (Zell and Ballschmiter, 1980), its abundance in the environment is the result of its wide use as a fungicide as well as being a by-product during the production of other chlorinated hydrocarbons (Villanueueva et al., 1974). HCB mean concentration was 0.8 ng/g, and the highest level found was at site-6 (6.96 ng/g, Table 2).

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Station	ECH mg/g	Position		Ar1242	Ar1260	PCB's	нсв
1	2.7	A		11.75	21.70	33.45	0.16
2	2.4	A		5.56	6.75	12.31	0.38
6	9.2	A		6.56	8.73	15.29	6.96
7	7.1	A		62.42	15.45	77.87	0.85
8	6.7	A		48.62	2.53	51.15	0.12
10	3.2	٨		29.81	1.63	31.44	0.32
11	0.6	٨		1.79	6.44	8.23	0.20
12	4.4	٨		5.88	6.17	12.05	0.09
13	2.8	٨		7.05	4.15	11.20	N.D
15	3.4	٨		1.56	21.70	23.26	0.65
16	1.8	٨		25.13	0.67	25.80	0.06
17	0.5	A		1.55	2.85	4.40	0.06
22	1.3	31° 49, 9N-38° 49,	15E	11.10	1.78	12.88	0.10
23	3.4	31° 37, 1N-32° 04,	8E	60.10	1.40	61.50	1.25
24	1.7	31° 40, N-32° 29,	9E	7.85	18.22	26.07	0.37
25	2.6	32° 00, N-32° 32,	ε	11.65	17.07	28.72	0.14
mean	3.4	•		18.6	8.6	27.2	0.8

PCB's and HCB concentrations (ng/g) in esdiment samples from the Mediterranean Sea.

N.D: not detected

PCB's: Ar 1242 + Ar 1260

A: See Table (1)

The maximum EOM value occurred at site-6 (9.2 mg/g) followed by sites 7, 8 and 12 (7.1, 6.7 and 4.4 mg/g, respectively) with a mean value 3.4 mg/g (Table 2). Hence there seems an apparant relationship between the high PCB's values and the corresponding high EOM. The highest sediment/water (S/W) value occurred at site, 16 (Ar-1242) and at site-15 Ar-1260 and HCB). However the pattern of distribution varies from location to another (Table 3).

Highest occurrence, profoundly demonstrates the outstanding sedimentation reservoir potencies at Nile-Mediterranean mouth within site-10 (Off Rosetta Branch), and site-15 (Off Demietta Branch) as compared to other remote sites. This may be partially due to water undercurrents that displace focal concentration points to near locations; as well as the corresponding EOM, and particularly the fine silt sediments properties.

Table 3.

Sediment/water PCB's and HCB concentration factors as calculated for surface water samples obtained from the Mediterranean Sea.

Station	Ar 1242	Ar 1260	PCB's	HCB
1	1550.0	3841.0	2528.0	7.0
2	451.0	649.0	542.0	34.0
6	85.0	15 9 .0	116.0	96.0
7	5062.5	1486.0	3426.0	77.0
8	3338.0	174.0	1282.0	28.0
10	6949.0	1358.0	5727.0	133.0
11	9 89.0	5152.0	2696.0	317.6
12	2162.0	1743.0	1925.0	28.0
13	3561.0	3074.0	3363.0	N.C
15	578.0	5741.0	3590.0	191.0
16	9816.0	105.0	2889.0	28.0
17	1372.0	1657.0	1544.0	34.0

N.C : Not calculated

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REFERENCES

- Basturk, O.; M. Dogan; I. Salihoglu and T. I. Balkas, 1980. DDT, DDE and PCB: residues in fish, crustaceans and sediments from the eastern Mediterranean coast of Turkey. Mar. Pollut. Bull., 11: 191-195.
- Burns, K.A. and J. P. Villeneuve, 1987. Chlorinated hydrocarbon in the open Mediterranean ecosystem and implications for mass balance calculations Mar. Chem., 20: 337-339.
- Elder, D.L. 1976. PCB's in N. W. Mediterranean coastal waters. Mar. Pollut. Bull., 7: 63-64.
- Elder, D.L and J. P. Villeneuve, 1977. Polychlorinated Biphenyls in the Mediterranean Sea. Mar. Pollut. Bull., 8 (1): 19-22.

Goldberg, E.D. 1976. The Health of the Oceans. Paris. UNESCO PRESS. 141-156.p.

- Jensen S. 1966. Report of a new chemical hazard. New Scientist 32, (525): 612.
- Villenueva, E.C.; R. W. Jennings; V. W. Burse and R. D. Kimbrough, 1974. Evidence of chlorobenzo-p-dioxin and chlorodibenzofurans in hexachlorobenzene. J. Agric. Food Chem., 22: 916-917.
- Zell, M, and K. Ballschmiter, 1980. Baseline studies of the global pollution. II-Global occurrence of hexachlorobenzene (HCB) and polychlorocamphenes (Toxaphene) (PCC) in biological samples. Fresenius Z. Anal. Chem. 300: 387-402.