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RESIDUE LEVELS OF ORGANOCHLORINE INSECTICIDES IN THE MEDITERRANEAN WATER AND SEDIMENTS OFF THE NILE DELTA.

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ABSTRACT

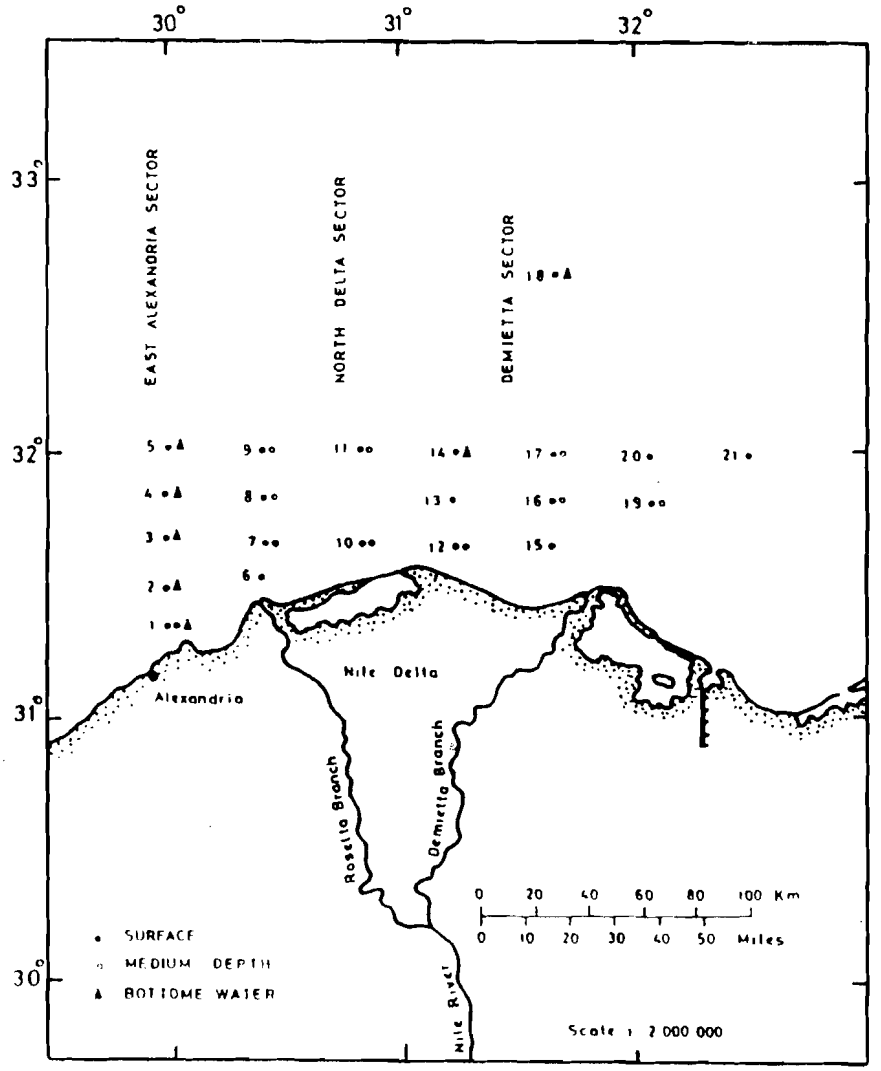
Residues of Hexachlorocyclohexane (HCHs), DDTs, cyclodienes groups were analyzed by capillary gas chromatography in wate rcolumns and sediments from off Delta Mediterranean Sea. Cyclodienes and HCH's constituted most of the OC's levels. The total OC's values in general, were found to be very low, and in most cases below the detection limit. Aldrin was the most dominant component of the cyclodiene group while -HCH and P,P' - DDE were the most dominant isomers of their groupd. A notable decreasing relationship is indicated between concentrations and water depth.

INTRODUCATION

The meance of organochlorine compounds pollution to the marine environment has been brought into sharp focus. Their notable stability for long periods and accumulation in sediments, microorganisms and fish led to their build up in food chain (Macek and Korn, 1970). Water is the medium that receives the major amounts of these chemicals and the media in which many food chains originate. Although the concentrations of organochlorines in biota, sediments and water of the Mediterranean Sea have been determined (Burns and Villeneuve, 1987, Basturk et al, 1980, El-Dib and Badawy 1985), at the national level most of the reported data are limited to samples collected from the narrow Mediterranean coastal zone at quite few locations (Aly and Asker, 1986 and El-Nabawi et al., 1987). From the point of view of human health and environmental hazards, the present investigation was undertaken to determine residue of levels of HCH's isomers including (γ-, β-, and α-HCH), Cyclodienes (Heptachlor, Heptachlor epoxide, Endrin, and Aldrin) and DDTs (P,P'-isomers of DDT ,DDE, DDD and o, p-isomers of DDT and DDE). This includes, surface and subsurface water samples (38) collected from 21 locations, off the Nile Dalta; representing the northern region (Fig. 1); for the first time along the coastline (200 Km) and seawards (100 Km).

Fig. 1

The layout of investigation stations
off the Nile Delta for water samples.



MATERIAL AND METHODS

Water samples were collected using a remote controlled battery (NTP) sampler while sediments samples were collected with a Van-Veen grab. Water samples were immediately transfered into a separatory funnel (4.0 l) and extracted with n-Hexane (3 x 80 ml). The organic layer was carefully separated and rotary evaporated down to 10 ml at ca. 45°C. The concentrated extract (desulphurized, whenever required) was desiccated through a Pasteur purification florisil microcolumn and eluted with n-hexane (5 ml) followed by ether/hexane (5 %, 5 ml). The eluted fractions were combined and N_2-evaporated down to 1 ml. The cleaned-up sample extract was then fractionated on silica-fractionating column. Individual compounds identification was accomplisheed against RT and RRT values of authentic standards (BDH).

RESULTS AND DISCUSSION

The levels of HCH's, DDTs, and cyclodienes were found for the studied water media. From the data (Table. 1) belonging to the surface water it is apparent that the highest pollution concentration (ng/l) occurs at site-6 in surface water 610.34 (710.8 ng/l); mostly due to cyclodienes group; followed by site-1 (218.8 ng/l) which compares to only 35.8% of that of site-6; decreasing to only 66.5 ng/l at site-7. The main OC's effluents to the Mediterranean Sea from Rosetta Nile Branch flow past site-6 (hence its highest observed levels) before being effectively diluted at site-1. Site-18 however showed the least OC's level. Hence, dilution factors seem to being effectively operating parallel to sea coast line and inwards; as expected. This generally observed eastwards where the disintigrating pollution levels is demonstrably exhibited for all other studied categories as for OC's. Likewise, occurrence of HCH's, cycodienes and DDT's seems to follow suit, mostly. These findings agree with previous data on north-west Mediterranean coast, where relatively high pollutant levels were reported for water samples taken near river mouths, or areas of high population and industrial activity (Elder, 1976).

For medium and bottom water levels (Table 1) the found OC's values correlate reasonably well with depth; tending to decrease rapidly with distance below surface likewise, dilution factors operate in similar trends advanced for surface water. However, as with the case of surface water, a substantial part of OC's is represented as cyclodienes followed by HCH's in medium and bottom waters. The tendency towards OC's accumulation (ng/l), except for few anomalies, slowly decreases with depth. It seems reasonable to point out the limited persistency of OC's in sea water, particularly at far depths. Hence it becomes evident that these components would incline to be adsorbed on sediment particulates at the bottom (as it is later treated when dealing with bottom sediments). Fowler et al., (1986) suggested a maximum residence period of Lindane in surface

Table 1.

HCHs cyclodienes, DDTs and total organochlorine compounds concentrations (ng/l) in the Mediterranean Sea waters samples.

Station	Depth (m)	Position		HCHs	Cyclo-dienes	DDTs	OCs
1	0.5	31° 21,2'N	30° 00'E	14.51	147.80	56.464	218.774
1	5.0			2.98	90.61	1.562	95.152
1	30.0			165.93	246.66	272.804	685.394*
2	0.5	31° 30'N	30° 00'E	17.62	66.10	5.14	88.86
2	85.0			50.15	407.12	481.63	938.91*
3	0.5	31° 40,2'N	30° 00'E	6.16	42.51	1.428	50.49
3	390.0			29.47	70.52	18.647	118.46*
4	0.5	31° 50,3'N	30° 00'E	2.91	22.41	25.65	50.97
4	600.0			11.25	61.26	53.69	126.20*
5	0.5	32° 00'N	30° 00'E	0.30	2.99	2.96	6.25
5	860.0			1.86	3.84	0.02	5.72
6	0.5	31° 32,6'N	30° 24,2'E	201.54	294.98	113.82	610.34*
7	0.5	31° 39,9'N	30° 25,4'E	35.72	16.10	14.72	66.54
7	14.0			25.12	33.47	16.91	75.50
8	0.5	31° 49,9'N	30° 25,2'E	3.09	3.78	9.96	16.83
9	0.5	32° 00'N	30° 25,1'E	0.57	3.25	10.07	13.89
9	215.0			0.52	2.08	3.91	6.51
10	0.5	31° 39,9'N	30° 50,1'E	4.74	3.31	4.78	12.83
10	13.0			9.40	9.78	7.77	26.95
11	0.5	31° 49,9'N	30° 39,15'E	0.56	3.84	3.33	7.73
11	127.0			0.42	3.83	0.47	4.72
12	0.5	31° 39,9'N	31° 14,9'E	4.78	3.07	8.35	16.02
12	16.0			6.39	11.08	11.68	29.15
13	0.5	31° 49,9'N	31° 14,19'E	2.57	5.24	4.62	12.43
14	0.5	32° 00'N	31° 15'E	0.56	2.37	2.41	5.34
14	831.0			2.44	3.28	0.92	6.64
15	0.5	31° 39,9'N	31° 14,9'E	1.02	15.36	1.07	17.45
16	0.5	31° 40'N	31° 40'E	N.D	1.58	6.37	18.39
16	40.0			0.45	3.99	9.33	13.77
16	58.0			2.53	7.52	N.D	10.05
17	0.5	32° 00'N	31° 40'E	2.51	2.20	0.32	5.03
17	86.0			3.12	3.58	1.522	8.222
18	0.5	32° 20'N	31° 40'E	0.26	1.20	1.103	2.563
18	940.0			N.D	0.02	2.70	2.72
19	0.5	31° 50'N	32° 05'E	0.70	5.39	2.70	8.79
19	66.0			3.12	11.98	6.65	21.75
20	0.5	32° 00'N	32° 04,9'E	3.23	2.31	2.38	7.92
21	0.5	32° 00'N	32° 30'E	N.D	2.05	1.31	5.36

OCs : HCHs + Cyclodienes + DDTs

N.D. : not detected

* Hot points excluded from mean concentration calculation.

waters to be 13 years. However, process of degradation and volatilization would probably reduce the actual residence time in surface waters to at least one order of magnitude less than an earlier estimate that was based solely on the rate of vertical transporting.

Table 2 shows most of the monitored cyclodiene values as largely due to aldrin reach 100 % of total cyclodienes at site-18) followed by heptachlor, with other minor components including endrin and heptachlor epoxide being of negligible presence.

According to Table 3 and the foregoing discussion on DDTs components ratio in OC's-observed values, the prominent presence of P,P'-DDE as contrasted to the sporadic and diminished occurrence of other isomers, is in line with previous outlined data on the Nile Delta surveillance. However, monitored P,p'-DDT (its assumed precursor) underrated it by several order of magnitude, is greater > than 40 fold as high as p,p'-DDT. Aly and Asker (1986) reported the occurrence of o,p-DDE; p,p'-DDE, o,p-DDD; p,p'-DDD, o,p-DDT and p,p'-DDT as 33.3, 3.03, 19.02, 6.9, 3.7 and 12.8 ppt; in sequence, for Abu-Quir Bay surface water (coastal samples). El-Dib and Badawy (1985) reported p,p-isomers of DDD, DDE, and DDT mean concentrations, in the Mediterranean Sea water at Port Said to be 27.3, 21.5, and 8.98 ng/l; respectively.

On the other hand, Table 4 shows the different prevailing extents of HCH-isomers. At first glance most of the added burden is due to γ-HCH while the least being B-HCH.

However, there is an increasing need for further monitoring of these contaminants in the aquatic ecosystem to insure the protection of food sources.

Table 2.

Cyclodiene compounds concentrations (ng/l) in water column from the Mediterranean Sea.

Location	Depth (m)	Heptachlor	Aldrin	Heptachlor epoxide	Endrin
1	0.5	34.90	96.90	N.D	16.00
1	5.0	1.61	62.75	N.D	26.25
1	30.0	49.13	160.28	N.D	37.25
2	0.5	11.71	44.68	N.D	9.71
2	85.0	1.44	350.25	3.46	51.97
3	0.5	N.D	21.10	N.D	21.41
3	390.0	4.85	23.62	15.52	26.53
4	0.5	4.45	7.08	0.35	10.53
4	600.0	10.30	24.13	N.D	26.83

Table 2 (cont.)

5	0.5	N.D	1.28	N.D	1.71
5	860.0	0.56	2.06	N.D	1.22
6	0.5	102.40	122.70	N.D	69.88
7	0.5	1.71	4.68	N.D	9.71
7	14.0	8.67	9.44	0.32	15.04
8	0.5	0.64	1.96	N.D	1.18
9	0.5	0.40	1.51	N.D	1.34
9	215.0	0.52	1.56	N.D	N.D
10	0.5	1.08	1.95	N.D	0.28
10	13.0	1.96	3.04	N.D	4.78
11	0.5	0.72	1.78	N.D	1.34
11	127.0	N.D	3.20	N.D	0.63
12	0.5	0.51	1.51	N.D	1.05
12	16.0	6.94	2.21	N.D	1.93
13	0.5	0.36	1.36	N.D	3.52
14	0.5	0.23	1.51	N.D	0.63
14	831.0	0.31	2.04	0.18	0.75
15	0.5	0.51	3.51	N.D	11.34
16	0.5	1.37	0.50	0.21	N.D
16	40.0	1.23	2.76	N.D	N.D
16	58.0	1.83	3.16	N.D	2.53
17	0.5	0.45	0.85	N.D	0.90
17	86.0	1.43	1.46	N.D	0.69
18	0.5	0.40	0.41	N.D	0.39
18	940.0	N.D	0.02	N.D	N.D
19	0.5	1.03	3.23	N.D	1.13
19	66.0	8.52	3.46	N.D	N.D
20	0.5	0.1	1.43	0.09	0.69
21	0.5	N.D	1.97	N.D	0.08

N.D : Not detected

Table 3.

DDTs concentrations (ng/l) in water column samples from the Mediterranean Sea.

Location	Depth (m)	P,P' DDD	O,P-DDT	P,P'-DDT	O,P-DDE	P,P'-DDE
1	0.5	0.12	15.69	39.03	0.004	1.62
1	5.0	0.41	N.D	N.D	0.002	1.15
1	30.0	54.6	10.35	196.0	0.004	11.85
2	0.5	N.D	N.D	3.38	0.15	1.61
2	85.0	468.00	N.D	12.56	0.09	0.98
3	0.5	N.D	0.52	N.D	0.002	0.96
3	390.0	18.10	N.D	N.D	0.007	0.54
4	0.5	10.50	11.46	3.14	N.D	0.55
4	600.0	17.41	12.83	22.59	0.09	1.22
5	0.5	255.00	N.D	N.D	N.D	1.41
5	860.0	N.D	N.D	N.D	N.D	0.01
6	0.5	N.D	70.54	42.29	N.D	0.99
7	0.5	N.D	N.D	3.38	0.02	1.62
7	14.0	1.19	9.49	4.15	0.005	2.11
8	0.5	3.93	0.25	2.69	0.081	30.01
9	0.5	N.D	N.D	N.D	0.008	10.06
9	215.0	0.51	N.D	2.59	N.D	0.45
10	0.5	4.13	N.D	N.D	N.D	0.65
10	13.0	1.47	3.25	2.11	0.001	0.93
11	0.5	N.D	0.33	N.D	N.D	3.00
11	127.0	0.41	N.D	N.D	0.05	0.02
12	0.5	1.85	0.80	4.58	0.006	1.11
12	16.0	2.01	0.41	1.44	0.01	7.80
13	0.5	0.52	2.54	0.93	0.63	0.01
14	0.5	N.D	N.D	N.D	0.01	2.40
14	831.0	N.D	N.D	N.D	N.D	0.92
15	0.5	N.D	N.D	N.D	1.01	0.06
16	0.5	2.94	N.D	1.75	N.D	1.68
16	40.0	2.49	3.66	2.31	N.D	0.87
16	58.0	N.D	N.D	N.D	N.D	N.D
17	0.5	N.D	0.32	N.D	N.D	N.D
17	68.0	N.D	N.D	N.D	0.002	1.52
18	0.5	1.03	N.D	N.D	0.013	0.04
18	940.0	N.D	1.27	N.D	N.D	1.43
19	0.5	1.03	N.D	N.D	0.02	1.65
19	66.0	4.08	1.51	N.D	N.D	1.06
20	0.5	0.51	0.18	N.D	0.17	1.52
21	0.5	1.43	N.D	N.D	0.01	1.87

ND Not detected

Table 4.

HCHs group concentrations (ng/l) in water column samples from the Mediterranean Sea.

Location	Depth (m)	o-HCH	B-HCH	-HCH
1	0.5	0.46	0.85	13.20
1	5.0	N.D	0.18	2.80
1	30.0	44.35	72.54	49.04
2	0.5	15.94	0.44	1.24
2	85.0	17.45	16.35	16.35
3	0.5	N.D	N.D	6.16
3	390.0	2.65	13.91	12.91
4	0.5	1.71	1.20	N.D
4	600.0	2.68	2.01	6.56
5	0.5	N.D	N.D	0.3
5	860.0	0.46	0.24	1.16
6	0.5	66.10	59.84	75.60
7	0.5	15.94	16.35	3.43
7	14.0	10.49	9.99	4.64
8	0.5	0.99	0.82	1.28
9	0.5	N.D	0.17	0.40
9	215.0	N.D	N.D	0.52
10	0.5	N.D	N.D	4.74
10	13.0	1.54	3.80	4.06
11	0.5	N.D	N.D	0.56
11	127.0	0.42	N.D	N.D
12	0.5	1.66	0.47	2.65
12	16.0	2.64	0.79	2.96
13	0.5	0.75	0.18	1.64
14	0.5	N.D	N.D	0.56
14	831.0	0.36	1.10	0.98
15	0.5	N.D	0.62	0.4
16	0.5	N.D	N.D	N.D
16	40.0	0.20	0.25	N.D
16	58.0	0.83	0.37	1.33
17	0.5	1.52	0.26	0.37
17	86.0	0.03	1.53	1.56
18	0.5	N.D	0.26	N.D
18	940.0	N.D	N.D	N.D
19	0.5	0.12	0.04	0.54
19	66.0	N.D	0.26	2.86
20	0.5	0.58	1.77	0.88
21	0.5	N.D	N.D	N.D

N.D. Not detected

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