CHLORINATED HYDROCARBONS IN THE SEDIMENTS FROM THE COASTAL WATERS OF KARACHI

ALIA BANO AND SARDAR ALAM SIDDIQUE*

PCSIR Laboratories Complex , Karachi-39, Pakistan

The concentration of chlorinated hydrocarbon (DDT, HCH, Heptachlor, DDE and Dieldrin) was determined in the samples of sediments collected from the three locations of Karachi i.e. Manora channel, Korangi Creek and Hawksbay back waters along the Karachi coast. The concentration of pesticides (Heptachlor, DDE, Dieldrin, Alpha HCH and P.P. DDT) were present in the range of 0.84-3.7, 0-0.16, 0.54-12.47, Traces-3.5, 0.15-9.53 ng/gm respectively. Two methods were used for confirmation of each pesticide i.e. internal spike method and other one was the calibration curve method.

Key words: Pesticides, Sediments, Sea pollution.

Introduction

Sediments are potential storage for chlorinated hydrocarbons and they may also be a source of pesticides for the overlying water. Total pesticide contents in fine coastal sediments are in μg/gm range and in the ng/gm range in total sediments offshore due to dilution with coarse sediments [1].

The pesticides of marine environment may accumulate in biota and sediments. Therefore, sediments and biota can be regarded as concentration indicator. When the rate of sedimentation is stable, and the effects of local disturbances (currents, bioturbation) are small, the sediment layers reflect the situation in the water mass at the time of deposition [2].

In the Indian Ocean countries, the use of pesticides particularly of DDT was quite common. Therefore, it is important to determine possible trends in the concentration of these substances in marine sediments. Although advance methodology has been adopted for the determination of pesticides pollution by pesticides but still evaluation of results become difficult due to the instable condition of Indian Ocean.

In Pakistan, pesticides are commonly used in agriculture for plant protection and in various industries and all industrial and agricultural wastes ultimately reach the coastal areas. Karachi being a coastal city, therefore, receives the pollutants through the discharges of Sindh and Lyari river. Haq [3] and Ahmed [4] pointed out the problem of pollution on the coastal area of Karachi. The important localities mentioned as polluted areas including Creeks, Hawksbay, Manora channel, Buleji and Gudyani. The main source of pollutants is the Lyari river, which brings all the industrial waste from Sindh Industrial and Trading Estate. This is the largest industrial estate of Pakistan and discharges its waste into the Manora channel. Among the south cheeks draining of Karachi, Ghizri, Korangi. Gharo and Phitti Creek are most important from pollution, point of view as they receive effluents from river Sindh.

* Institute of Marine Biology, University of Karachi, Karachi.

Materials and Methods

Sampling stations are given in Fig. 1. The collection of sediment was made from intertidal zones by hand picking during lowtide at Korangi Creek and Hawksbay (back water). However, a petersons grab was used to collect the sediments from Manora channel. The sediment samples were kept in the glass beakers to avoid the plastic because, it may contaminate the samples [5] to the laboratory.

In the laboratory the samples of sediments were squeezed and stored in a refrigerator immediately after sampling untill further analysis. Sample of sediment used as blank dried in the oven at 60° for three days and weighed in triplicates on aluminium foil and processed for further analysis. The samples were extracted with 100 ml n-pentane for 8 hrs via soxhlet extraction. Large quantities of sulpher were present in extracts of anaerobic sediments. This had to be because of its electrophilic properties, sulpher had to be removed by shaking the extract vigorously for two mins [6] with a drop of mercury. All extracts and blanks were concentrated upto 1 ml in a rotary evaporator and processed further for purification via the alumina column and silica gel column. Eluates from silica gel column were evaporated to dryness and preserved for GLC analysis. PCBSs were eluated with 10% diethylether and these were not analysed on GC due to unavailability of standard PCBS. Recovery for every pesticides was found to be above 75% during the recovery experiments and every sample was analyzed along with a blank. Indentification, quantitation was done by Gas-liquid chromatography (GLC) with electron capture detector.

Appropriate dilutions of concentrating steps were performed for reliable quantition of each compound by intepotation between standard injections and most extracts were injected at various dilutions. The precautions and measures were taken thus resulted in practically ideal blank chromatograms (Chromato gram No. 1). Column material was 1.5% OV-17 on

chromosorb-W AWDMCS (80-1000 mesh) 2.1 m x 3mm inner diameter of borosilicate glass column. The injector, detector and column temperature were 200 and 180° respectively, in the iso-thermic mode.

Results and Discussion

The chlorinated hydrocarbons isolated from Manora channel, Hawksbay back waters and Korangi Creek are presented in Table 1. Data presented was obtained after substructing the blank values. It should be noted that the data from different localities cannot compared with each other because of the varied sedimentation rates and other area variations.

Heptachlor was found in the range of 1.2-1.6 ng/gm with the mean value of 0.93 ng/gm obtained through calibration curve. If judged on the basis of internal spike method the value of heptachlor ranged from 0.84-2.7 ng/gm with a mean value

1.5 ng/gm. The difference between the results of one value calculated by the two method in the order of 0.06 ng/gm may be attributed to the matrix effect. The values of DDE, dieldrin, Alpha, HCH and DDT ranged from 0.05-0.13 ng/gm, 0.53-1.98 ng/gm, 1.20 ng/gm and 0.15-6.9 ng/gm respectively using the calibration curve and the mean value of 0.09 ng/gm, 1.236 ng/gm, 206 ng/gm respectively. Whereas on the basis of internal spike method the calculated mean value of DDE and dieldrin was found to be 0.106 ng/gm and 1.125 ng/gm respectively, again the difference between the two methods may be attributed to the matrix effect. Samples from Manora channel (Fig.2) contained heptachlor, dieldrin, BHC and DDT in the mean value of 0.93 ng/gm, 1.77 ng/gm, 1.66 ng/gm respectively obtained from calibration curve. Alpha BHC was found to be present in traces. No DEE was detectable in sediment
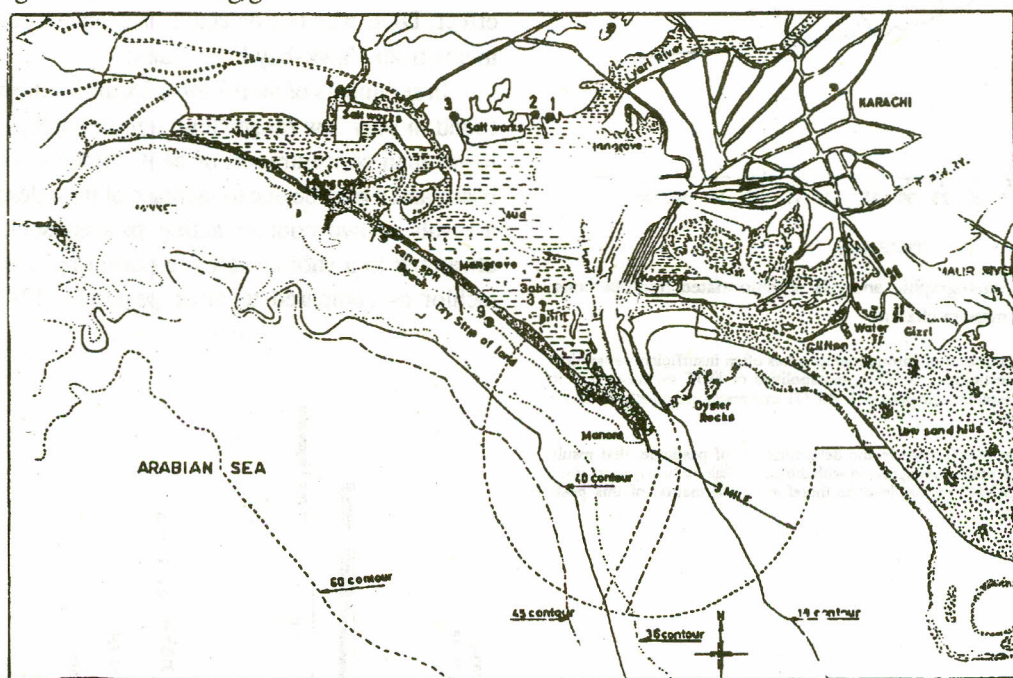

Fig. 1.

TABLE 1. CHLORINATED HYDROCARBONS ISOLATED FROM THE SEDIMENTS OF KORANGI CREEK, HAWKSBAY (BACK WATERS) & MONORA CHANNEL.

| Locations	Identified					Un-identified peaks (mm)							
	Haptachlor 6.25±0.75	DDE 7±0.80	Dieldrin 21.25±0.80	Alpha BHC 26±.03	DDT 44±5	I 1-2	II 2.06±	III 3.45	IV 5.6	V 10.5±5	VI 12.5±75	VII 15±.75	VIII 15±2.5
Korangi	S₁ 2.7(2.52)	0.16(0.13)	1.79(1.98)	1.1(1.2)	(6.9)	–	5	–	–	0.4	0.7	2.55	0.75
Creek	S₂ 0.96(0.80)	0.06(0.05)	1.046(1.20)	–	(0.15)	–	–	–	–	–	–	–	–
ng/gm	S₃ 0.84(1.0)	0.10(0.08)	0.54(0.53)	–	(0.2)	–	–	–	–	–	–	–	–
Manora	S₁ –	–	12.47(4.5)	–	0.93							–	–
Channel	S₂ 1.5(1.6)	–	9.23(0.66)	–	–	–	–	–	–	–	–	84	–
ng/gm	S₃ 1.1(1.2)	–	0.71(0.16)	–	–	–	–	–	–	–	–	86	–
Hawksbay	S₁ 9.2(4.8)	–	5(1.5)	3.5(5.0)	3.963(3.85)	–	–	61	61	30	25	23	2
back water	S₂ 1.9(2.0)	–	1(1.5)	–	9.53(8.0)	5.5	4.0	–	15	34	–	8	–
ng/gm	S₃ 5.6(2.8)	–	3.25(9.9)	3.5(5)	2.08(3)	–	–	88	–	48	–	8	
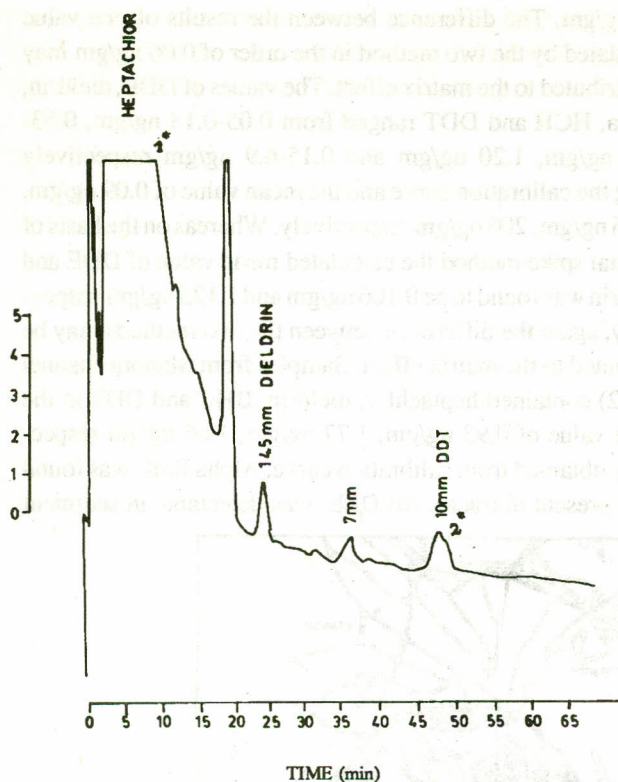
Fig. 2. Gas Chromatographic analysis of chlorinated hydrocarbons from the sediments of manora channel

Note

1. Since the packed column chromatography has often insufficient separation capacity for pesticides, therefore, matabolities of DDT mixture made it difficult of separate single peak of P-P-DDT that result irregular peak shape of the DDT peak.

2. Due to sulpher interference in the determination of pesticide, that result unusually large peak in comparison with the other peak, unluckly there is no facilities of GC/MS in our Institite therefore, confirmation of this peak become difficult.
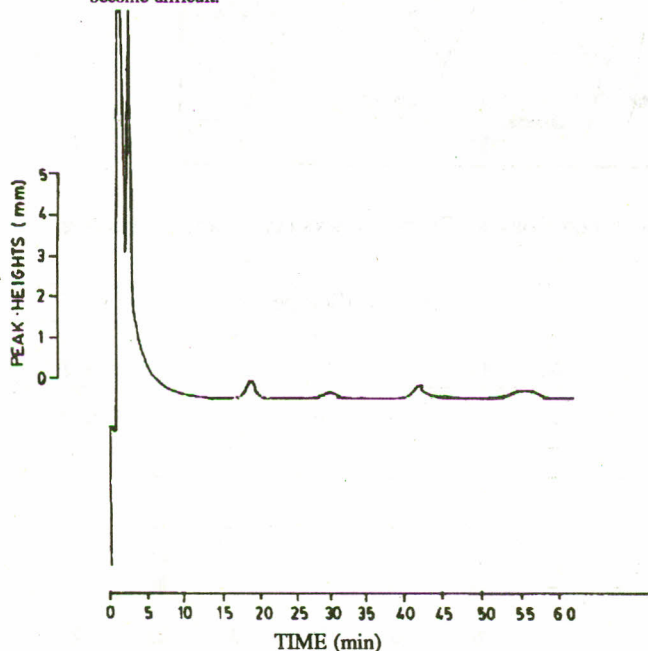

Fig. 2a. Gas chromatographic analysis of chlorinated hydrocarbons from blank of sediments of Manora Channel.

from Manora channel (Fig. 2a) on the basis of internal spike method the mean value of heptachlor dieldrin and DDT was found to be 0.86 ng/gm, 7.47 ng/gm and 1.60 ng/gm respectively. The difference in the mean values by the two methods was 0.06 ng/gm, 5.70 ng/gm and 0.06 ng/gm respectively and as already noted may be due to the matrix effect (Fig. 2a).

Samples of sediments from Hawksbay contained heptachlor dieldrin, Alpha BHC and DDT with a mean value of 3.53 ng/gm, 4.30 ng/gm, 3.33 ng/gm and 4.95 ng/gm respectively (Fig. 3) by using calibaration curve. The value of heptachlor, dieldrin, alpha BHC and DDT by internal spike method with a mean value of 5.4 ng/gm, 3.0 ng/gm and 5.19 ng/gm respectively (Fig. 3a). The difference between two methods was calculated as 2.34 ng/gm, 1.30 ng/gm, 0.79 ng/gm and 0.24 ng/gm respectively attributed due to the matrix effect. DDE was not detected in triplicate samples of sediments from Hawksbay back waters.

In sediments of all the three localities the heptachlor was found in very low range (few ng/gm range) Fig. 4 which is lower than concentration of heptachlor found in the animal tissue and it may be due to increase of their desorption rates as a result of two counter acting processes[1]. This may be attributed to a shorter half life period i.e. 2-4 years of heptachlor as compared to other pesticides [7]. Alpha HCH
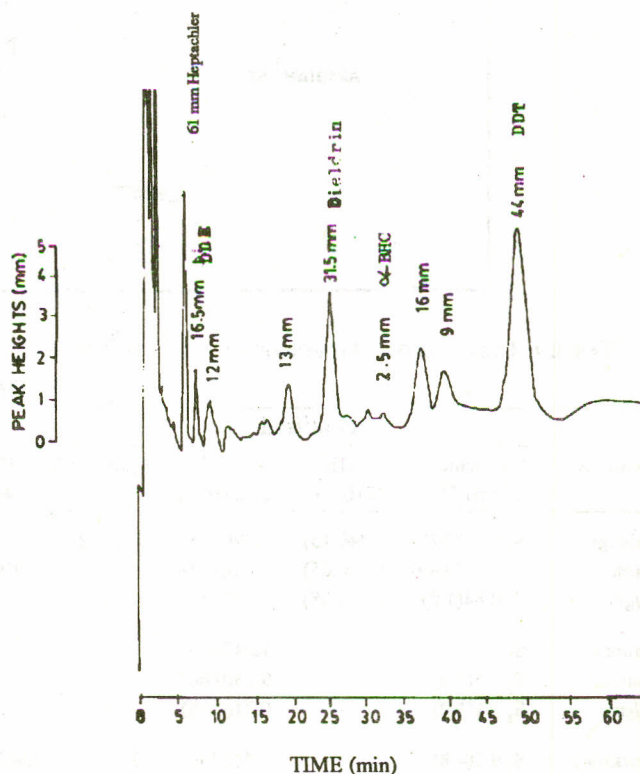

Fig. 3. Gas chromatographic analysis of chlorinated hydrocarbons from the sediments of Hawksbay back waters.

consists of 60-6% of benzene hexachlorine having M.P. of 157-158°. It is a mixture of undiluted technical grade 13% of delta and 67% alpha isomers and further more it is more volatile at pH 8.1 of sea water and 'at elevated temperature, 100% dieldrin contain 85% hexachloroepoxy ethldroenols, exodimethno naphtan (HEOD) and 15% is active related com-pounds. The maximum concentration of dieldrin was observed in sediments samples of Hawksbay waters in the range of 1.00-5.00 ng/gm and minimum concentration was ob-served in the range of 0.54-1.79 ng/gm in sediments samples of Korangi Creek (Fig. 5). This variation may be due to different degree of pollution and also depends on accumulated dieldrin transport from sediments to the over lying water by molecular diffusion [8].
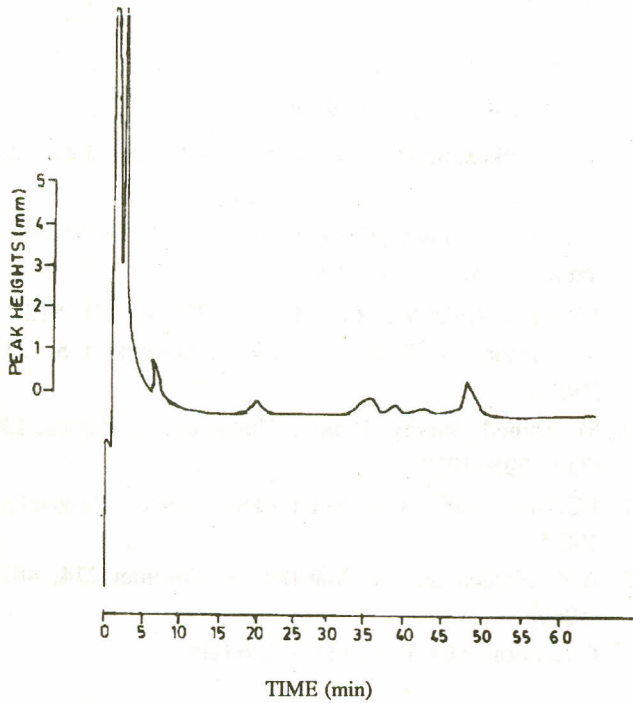

Fig. 3a. Gas chromatographic analysis of Chlorinated hydrocarbons from blank of sediments of Hawksbay back waters.
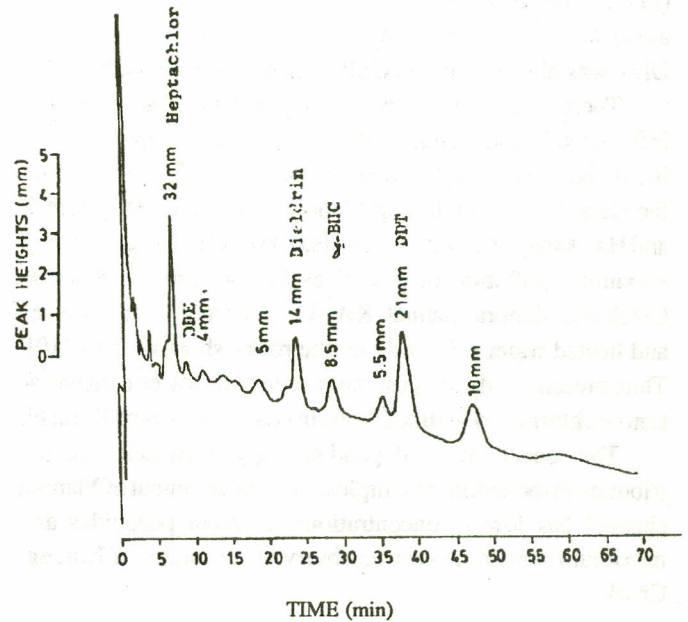

Fig. 5. Gas chromatographic analysis of chlorinated hydrocarbons from the sediments of Korangi Creek.
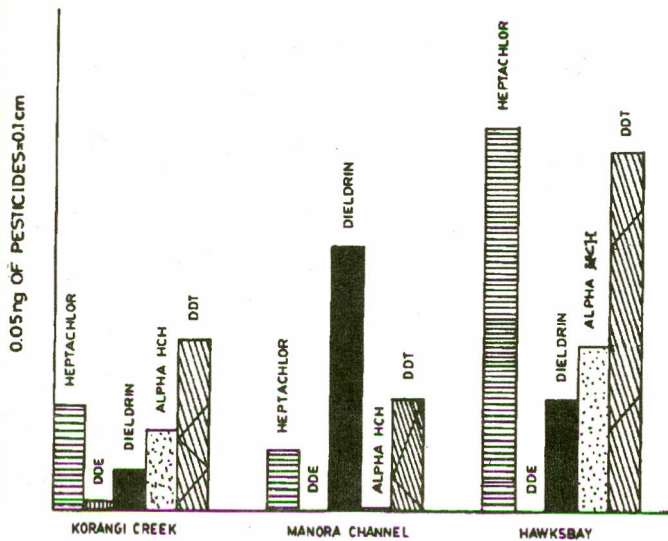

Fig. 4. Bark diagram of pesticides in samples from three locations
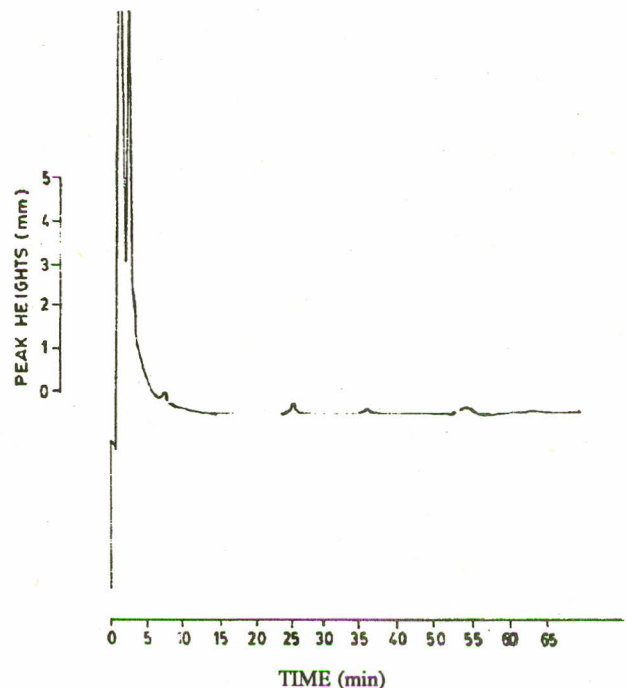

Fig. 5a. Gas chromatographic analysis of chlorinated hydrocarbons from blank of sediments of Korangi Creek.

The value of DDE sediments of Korangi Creek was (Fig. 5) found in the range of 0.06-0.16 ng/gm whereas from other two localities samples of attributed is insignificant accumulation of DDE in the sediments moreover it could be due to higher transport of pesticides from sediments to the overlying water by molecular diffusion [9].

The sediments of Hawksbay back water contained DDT in the range 2.08-9.53 ng/gm and sediments of Korangi Creek (Fig. 5a) contained in the range of 0.2-0.15 ng/gm could be attributed to the stability of sediments. Although the level of DDT was observed in the Gulf of Bothnia 20-50 ng/gm [2].

There is no doubt that coastal waters of all countries influenced by the increased outflow of sewage, domestic and industrial waste polluted areas lie like a string of pearls along the Karachi coast including Manora channel, Korangi Creek and Hawksbay back waters. The Hawksbay backwaters shown maximum pollution of pesticides as compared to Korangi Creek and Manora channel. KANUP discharges liquid wastes and heated water subtidally on the rocky shore near by [10]. Thus present study suggest the presence of lower concentration of chlorinated hydrocarbons in coastal waters of Karachi.

The concentrations depend strongly on particle size distribution in the sediment samples. The fine sediment of Manora channel has lower concentrations for most pesticides and maximum concentration was observed in samples of Korangi Creek.

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