

Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India

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Abstract

Analyses of environmentally persistent pollutants like polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH) isomers, and dichlorodiphenyltrichloroethane (DDT) and its metabolites in seawater and sediment samples collected from six locations along the east coast of India were carried out using High-Resolution Gas Chromatograph with High-Resolution Mass Spectrometer (HRGC-HRMS). Sediment and water from Chennai harbour and Cuddalore fishing harbour contained higher concentration of all the compounds. The highest concentration (6570 pg/g dry weight) of total PCB was found in sediment from Chennai harbour followed by sediments sampled in Chennai (opposite to Cooum River mouth) (505 pg/g), Cuddalore fishing harbour (335 pg/g) and Mandapam (251 pg/g). Concentrations in other locations were two orders of magnitude lower than Chennai harbour. A distinct PCB distribution pattern in sediment was observed between harbours and other locations. Greater concentrations of tetra-, penta- and hexachlorobiphenyls were observed in sediments of harbours and opposite to Cooum river mouth, but in other locations lower chlorinated biphenyls (di, tri and tetra-) were more. In seawater, HCH concentration was greater than DDT, but it was quite opposite in sediments. Elevated levels of DDT in sediment were observed only at highly populated urban locations, reflecting the local usage and input of this pesticide. Based on sediment/water quality criteria/guidelines, some coastal locations of the Bay of Bengal could be designated as being polluted by DDTs and γ -HCH (lindane), but not by PCBs. This investigation reveals the declining trend on the environmental burden of persistent pesticides in Indian marine environment. Data on the organochlorine concentrations found in this survey can be used as reference levels for future POPs monitoring programme.

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1. Introduction

Environmental occurrence of Persistent Organic Pollutants (POPs) are a global rather than a regional problem, because chlorinated pesticides used in tropical regions will be carried by long-range atmospheric transport and ultimately end up in polar and environmentally pristine regions, and certainly have some impact on ecosystem. In 2001, the

Stockholm Convention on POPs has acknowledged POPs as a global problem. Polychlorinated biphenyls belong to POP group of chemicals primarily used in transformers, capacitors, paints and printing inks, and also in many other industrial applications. They are amongst the industrial chemicals banned and included in the list of priority contaminants to be monitored regularly in the western countries (Hedgecott, 1994). They have been reported to cause variety of effects including immunologic, teratogenic, carcinogenic, reproductive and neurological problems in organisms (Kodavanti et al., 1998). In addition, some congeners have shown some effects on the endocrine system such as reducing serum concentrations of the thyroid hormones like thyroxine and triiodothyronine (Koopman-

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Esseboom et al., 1994). Chlorinated pesticides such as HCH and DDT are effective pest control chemicals, used in agriculture and public health activities (malaria eradication, etc.) worldwide for the past several decades and are still in use in many developing countries. Similar to PCBs, these pesticides also cause endocrine disruption and food chain biomagnification, because of their lipophilicity and environmental persistence. Though complete ban on DDTs was imposed in many developed nations, in India it was banned only for agricultural use, but still used for malaria control, and HCH also is not completely banned (still used for agriculture). About 31 banned or restricted pesticides in other countries are still in use in India and about 350,000 tonnes since 1985 and 7000 tonnes in 2001–2002 of DDT were used (<http://www.cseindia.org/>, 2002).

PCBs and chlorinated pesticides were reported in harbours, near shore sediments and Bays all over the globe (Iwata et al., 1994; Hong et al., 1995; Strandberg et al., 1998; de Mora et al., 2001; Zhou et al., 2001; Barakat et al., 2002; Fillmann et al., 2002; Hong et al., 2003). Earlier studies in Indian marine environment showed that PCBs and organochlorine pesticide residues are comparable with other developing countries, but suggested an increase in future due to continuing usage of organochlorine pesticides in agriculture and vector control measures. Distribution of organochlorine pesticides in Indian marine environment was shown by several authors (Babu Rajendran et al., 1999; Sarkar et al., 1997; Tanabe, 2000), but PCBs in Indian marine environment was scarcely reported (Tanabe, 2000). Besides, Tanabe (2000) and his research team made an extensive study on organochlorines from both east and west coasts of India mainly in organisms (mussel, fish, birds and mammals), but not on marine sediments. Findings on

chlorinated pesticides were only limited to seashore sediments (Pandit et al., 2001), except a couple of reports from offshore sediments (Sarkar and Sen Gupta, 1988; Sarkar et al., 1997). Generally, estuarine and marine sediments are the ultimate global sinks for most of the pollutants. Contamination of soil and sediments of coastal areas with persistent organochlorine compounds may be related to point sources, e.g., industrial discharges and domestic sewage, but more frequently, as in the case of pesticide pollution, it can also be attributed to precipitation, agricultural runoff, etc. The present study aims to assess the occurrence and spatial distribution of PCBs and organochlorine pesticides like HCH isomers (α , β , γ and δ), and DDT and its metabolites (DDE and DDD) in sediment and seawater from several locations in the Bay of Bengal in order to evaluate their possible potential effects on aquatic organisms. The data on concentration of organochlorines in surface sediment may also help in assessing the time trend of contamination in the near by terrestrial region.

2. Materials and methods

2.1. Samples

Seawater samples were collected only from Chennai harbour and Cuddalore fishing harbour. Sediment samples were collected from all the six locations shown in Fig. 1, between 0.5 and 10 nautical miles (nmi) from the shore using the grab sampler in the Department of Ocean Development (DOD, India) coastal research vessel 'RV Sagar Purvi'. The sample details are given in Table 1. The samples were kept in clean polyethylene bags and brought

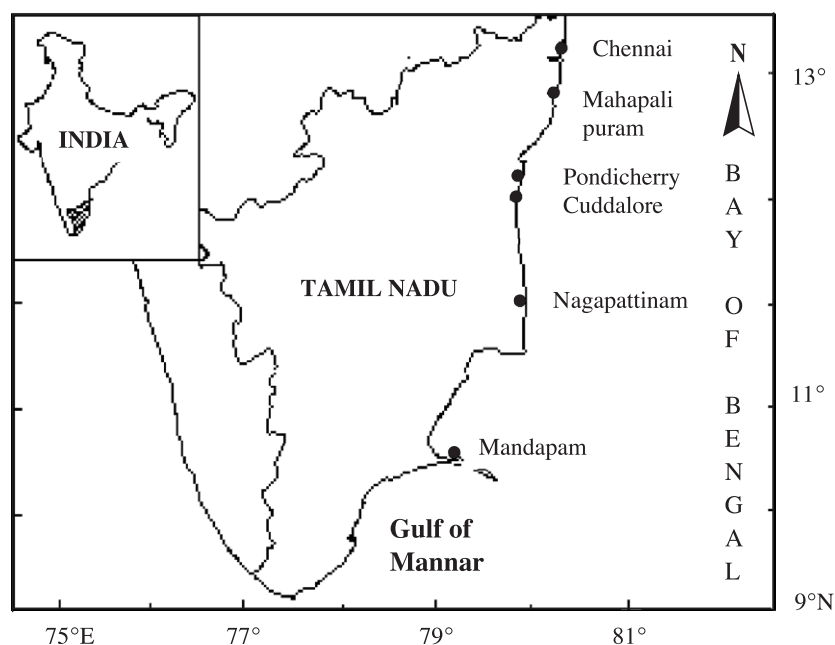


Fig. 1. Map showing the sampling sites.

Table 1
Surface sediment samples from the Bay of Bengal, India

Site No.	Site name	Date	Distance (nmi) ^a	Latitude (N)	Longitude (E)	OC %
1.	Chennai harbour	04.2.1998	0.5	13°07'	80°18'	1.52
2.	Chennai	30.1.1998	1	13°03'	80°18'	1.36
3.	Chennai	30.1.1998	3	13°03'	80°20'	0.303
4.	Chennai	30.1.1998	5	13°03'	80°22'	0.454
5.	Mahapalipuram	29.1.1998	0.4	12°28'	80°09'	0.404
6.	Mahapalipuram	29.1.1998	1.6	12°28'	80°11'	0.454
7.	Mahapalipuram	29.1.1998	3.85	12°29'	80°13'	0.454
8.	Pondicherry	25.1.1998	0.43	11°56'	79°50'	0.303
9.	Pondicherry	25.1.1998	1.35	11°55'	79°51'	0.253
10.	Pondicherry	25.1.1998	5.3	11°55'	79°55'	0.707
11.	Cuddalore harbour(F)	07.1.1998	NA	NA	NA	0.404
12.	Cuddalore	28.1.1998	0.5	11°42'	79°47'	0.454
13.	Cuddalore	28.1.1998	2.5	11°42'	79°49'	0.202
14.	Cuddalore	28.1.1998	6.5	11°42'	79°53'	0.303
15.	Nagapattinam	26.1.1998	2.5	10°46'	79°53'	0.707
16.	Nagapattinam	26.1.1998	6.5	10°46'	79°57'	0.707
17.	Mandapam	27.1.1998	0.43	09°21'	79°00'	0.454
18.	Mandapam	27.1.1998	2.5	09°22'	79°01'	0.454
19.	Mandapam	27.1.1998	6.5	09°25'	79°03'	0.909
20.	Mandapam	27.1.1998	10.5	09°28'	79°06'	2.12

^a Distance from shore; NA-not available.

to the laboratory under cold condition (4° C) and frozen at –20° C until chemical analysis. Before chemical analysis, sediment samples were air-dried in a clean laboratory condition, mixed thoroughly, and fine samples were used for chemical extraction. Sediments and XAD-2 resin columns (after passing the seawater samples) were brought to National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan for further chemical extraction and quantification.

2.2. Chemical analysis

All the chemicals and solvents used in the analyses were of analytical grade. Pesticide and PCB standards were obtained from Dr. Ehrenstorfer, Germany. Glasswares were cleaned thoroughly using soap solution and subsequently with MilliQ water (MilliQ-ICP-MS, Nihon Millipore Kogyo, Japan), acetone and dried well, wrapped in precleaned aluminum foil, baked in hot air oven at 150° C overnight and finally rinsed with hexane just before use.

Seawater extraction method was given in detail in Babu Rajendran and Subramanian (1997). Briefly, 20 L of water was passed through Amberlite XAD-2 resin column and eluted with ethanol into a separatory funnel containing hexane and hexane washed water. After complete elution, the separatory funnel was shaken, and after partitioning of organic layer, the hexane extract was collected and condensed to 5 ml using rotary vacuum evaporator (Buchi, Switzerland) and cleaned up by passing through silicagel and florisil columns.

Sediment samples were extracted using mechanical extraction, the detailed methodology given elsewhere (Babu Rajendran and Subramanian, 1999). About 20 g of dry sediment was taken in a 250-ml glass stoppered Erlenmeyer

flask and 20 ml of hexane washed water was added, and kept for 30 min to allow the samples to swell in water. The sample was extracted with 150 ml of acetone for 1 h on a mechanical shaker. Acetone extraction was repeated one more time. The combined supernatant was transferred into a separatory funnel containing 200 ml of hexane and 700 ml of hexane-washed water, and the funnel was thoroughly shaken for 10 min. The hexane extract was collected, water removed by passing through a layer of anhydrous sodium sulfate, and concentrated to 5 ml using rotary vacuum evaporator. Then the extract was cleaned-up with 2 ml of concentrated sulphuric acid to remove interfering substances, and subjected to florisil cleanup and silica gel fractionation. Copper granules were used for the removal of sulphur.

2.3. Instrumentation

Identification and quantification of PCBs, HCH isomers and DDT compounds were made by using high-resolution gas chromatograph (HRGC) (Hewlett-Packard 6890 series) coupled to a high-resolution mass spectrometer (HRMS) (JOEL JMS-700). The mass resolution of the spectrometer was greater than 10⁻⁴ mass units. Separation of pesticide compounds and PCBs was achieved by a HT8 capillary column (30 m×0.25 mm i.d.) coated with 8% phenyl polycarborane-siloxane at 0.25 µm film thickness (SGE Analytical science). The column oven temperature was programmed from 80° C (1.5 min) to 160° C at a rate of 40° C min⁻¹, to 170° C at 10° C min⁻¹, to 250° C at 4° C min⁻¹ and then to 320° C at 8° C min⁻¹ with a final hold time of 6.75 min. Injector and transfer line temperatures were held at 260 and 250° C, respectively. Helium was used as the carrier gas. The mass spectrometer was operated at an

electron impact (EI) energy of 70 eV, accelerating voltage of 10 kV, ionization current of 600 μA , and the target compounds were determined by selective ion monitoring (SIM) mode. Two internal standards ^{13}C CB101 and ^{13}C OCDD were used, and the recovery of all the spiked compounds through the analytical procedure was 85–95% and the detection limit was 0.02 $\mu\text{g/g}$. The final results were not corrected for recovery percentage and the sediment concentration was expressed on a dry weight basis. Procedural blanks were processed through the whole analytical procedure to check any interference and/or laboratory contamination for each set of five samples. Sediment organic carbon concentration was quantified using Total Organic Carbon Analyzer (TOC-V Series SSM-5000A, Shimadzu, Japan).

3. Results and discussion

3.1. Distribution of OCs

The concentrations of PCBs and DDTs in sediment and seawater are summarized in Tables 2 and 3, respectively. The highest concentration of 6570 $\mu\text{g/g}$ dry weight of total

PCB was found in sediment from Chennai harbour. The second highest concentration (505 $\mu\text{g/g}$) obtained at Chennai (site 2) was from a site at about 1 nmi off from the large outfalls of storm water and untreated domestic waste waters of Chennai city i.e. Cooum river. Next highest concentration of 335 $\mu\text{g/g}$ was observed at Cuddalore fishing harbour. Another sediment sampled at about 6.5 nmi from the coast of Mandapam had a higher concentration of 250 $\mu\text{g/g}$. This location falls under the Gulf of Mannar marine bioserve, one of the richest productive areas in India and totally pristine. The reason for the higher concentration of PCB here is unknown. All other sediments contain two orders of magnitude less concentration (19.9–90 $\mu\text{g/g}$) than the Chennai harbour. Similarly, Barakat et al. (2002) reported the highest concentration of PCBs (1210 ng/g^{-1}) in sediments collected from inner harbour area than the open area outside the harbour (0.9–2.8 ng/g) of Alexandria harbour, Egypt. The sediment from Alexandria harbour, Egypt had three orders of magnitude higher concentration than the Chennai harbour sediment.

Interestingly, a distinct distribution pattern of PCBs in sediment was observed between harbours and other locations. Fig. 2 shows the percentage composition of chlorobiphenyls (di- to decca-) in sediment. Greater

Table 2
PCB homologs in surface sediment ($\mu\text{g/g}$ dry wt) and water (ng/l) from the Bay of Bengal, India

Site no.	2CB	3CB	4CB	5CB	6CB	7CB	8CB	9CB	10CB	ΣPCB
<i>Sediment</i>										
1.	185	730	1576	1708	1821	479	65.4	5.19	0.59	6570
2.	40.9	82	127	93.9	115	39.1	6.7	0.46	0.10	505
3.	5.41	12.5	8.9	7.4	32.1	20.8	2.89	0.14	0.02	90.2
4.	9.74	17.2	9.9	3.0	2.0	0.66	0.05	— ^a	0.03	42.6
5.	9.3	15.9	15.1	6.8	5.9	1.5	—	0.04	—	54.5
6.	7.51	11.9	9.9	4.23	3.1	0.6	0.05	—	—	37.3
7.	6.85	9.7	8.7	3.8	3.3	0.84	0.13	—	0.02	33.3
8.	3.69	7.9	5.1	1.7	1.2	0.25	—	—	0.02	19.9
9.	4.62	9.6	5.0	1.5	1.2	0.24	—	—	0.02	22.2
10.	7.28	13.3	10.1	3.5	2.36	0.42	0.02	—	—	37.0
11.	39.9	54.7	63.5	65.2	89.7	19	2.38	0.26	0.39	335
12.	7.44	17.5	9.4	3.5	3.0	0.76	0.04	—	—	41.6
13.	10.8	21.1	10.9	2.9	2.2	0.68	0.15	—	—	48.7
14.	9.1	23.7	21.1	5.3	4.1	0.73	0.06	—	—	64.1
15.	8.89	14.8	9.1	3.0	2.3	0.47	—	0.03	—	38.6
16.	17.8	24	18.1	6.6	4.6	0.72	—	—	—	71.8
17.	19.7	9.5	6.1	2.34	1.8	0.39	—	—	—	39.8
18.	5.48	7.98	5.8	1.9	1.5	0.25	0.02	—	—	22.9
19.	221	15.8	9.6	2.7	1.5	0.40	—	—	—	251
20.	10.7	18.6	12.4	4.3	2.9	0.72	0.13	—	—	49.8
ER-L ^b										50,000
ER-M ^b										400,000
CSQG										277,000
<i>Water</i>										
1.	1.016	1.2	1.1	0.714	0.371	0.054	0.002	0.0003	0.0006	4.458
11.	0.208	0.745	0.702	0.162	0.099	0.017	0.001	0.0001	0.0001	1.934

ER-L: effects range low; ER-M: effects range median.

CSQG: Canadian Sediment Quality Guideline; ΣPCB : sum of all homologs.

^a Not detected.

^b Long et al. (1995).

Table 3
DDTs in surface sediment (ng/g dry wt) and water (ng/l) from the Bay of Bengal, India

Site no.	DDE		DDD		DDT		ΣDDT	p,p'-DDT/ p,p'-DDE
	o,p-	p,p'-	o,p-	p,p'-	o,p-	p,p'-		
<i>Sediment</i>								
1.	— ^a	0.8762	0.5367	2.785	—	0.2166	4.4145	0.25
2.	0.0167	0.6303	0.111	0.376	0.0259	0.022	1.1819	0.04
3.	—	0.0574	0.1791	0.191	—	0.0303	0.4578	0.53
4.	—	0.1315	0.1062	0.061	—	—	0.2987	—
5.	—	—	0.0474	0.0369	—	—	0.0843	—
6.	—	0.1204	0.021	0.0675	—	0.0444	0.2533	0.37
7.	—	—	—	0.0656	—	0.02	0.0856	—
8.	—	4.419	0.3317	0.0151	0.0081	0.0159	4.7898	0.004
9.	—	—	0.0162	0.0241	—	—	0.0403	—
10.	—	0.0674	0.2295	0.0336	0.0142	0.0203	0.365	0.30
11.	0.0314	2.676	0.288	0.5872	0.1313	0.3272	4.0411	0.12
12.	—	0.0387	—	0.0349	0.01	0.0143	0.0979	0.37
13.	—	0.0343	0.0172	0.0225	—	0.0171	0.0911	0.49
14.	—	0.5145	0.0803	0.1065	0.0256	0.0778	0.8047	0.15
15.	—	0.038	0.0362	0.033	—	0.011	0.1182	0.29
16.	—	0.171	0.091	0.051	0.011	0.023	0.347	0.14
17.	—	0.0351	0.0382	0.0415	—	—	0.1148	—
18.	—	0.0647	0.0679	0.091	0.0065	0.0212	0.2513	0.33
19.	—	0.0969	0.0556	0.0806	0.011	0.0265	0.2706	0.27
20.	—	0.0882	0.0277	0.0497	—	0.0299	0.1955	0.34
CSQG	—	6.75	—	8.51	—	4.77	—	—
ER-L	—	—	—	—	—	—	3.0	—
ER-M	—	—	—	—	—	—	350	—
<i>Water</i>								
1.	1.078	5.187	0.5528	2.567	0.869	2.296	12.5498	0.44
11.	0.0585	2.449	0.9068	1.9056	—	0.3118	5.6317	0.13

CSQG: Canadian sediment quality guideline; ER-L: effects range low.
ER-M: effects range median; ΣDDT: sum of DDT, DDE and DDD.
^a not detected.

concentrations of tetra-, penta- and hexachlorobiphenyls (65–78%) were observed in sediments of both harbours (Chennai and Cuddalore) and at Chennai (site 2—opposite

to Cooum river mouth). At site 3 (opposite to Cooum river mouth), hexa- and heptachlorobiphenyls were more (59%). But in other locations di-, tri- and tetrachlorobiphenyls were higher (74–98%). It seems that near the source (i.e. harbour and domestic sewage outfall) high chlorinated biphenyls were dominant and low chlorinated biphenyls were predominant in sediments away from the source. Similar distribution of PCBs in harbours and Bays were reported elsewhere. The PCB congeners in sediments of Alexandria harbour, Egypt (Barakat et al., 2002) were predominantly tetra- to heptachlorinated biphenyls. Hong et al. (2003) found high proportion of high chlorinated PCB congeners in sediment from stations inside the bays and low chlorinated congeners at stations outside the Bays (Masan and Haengam Bay) in Korea. Relative amounts of lower CBs gradually increased with distance away from Incheon harbour into the sea in Korea (Lee et al., 2001). In a recent paper, slight decrease in highly chlorinated congeners was reported in sediments offshore from south of Baku Bay, Caspian Sea (de Mora et al., 2001). However, Zhou et al. (1999) reported river sediments in Hong Kong were enriched with low chlorinated biphenyls, sum of mono-, tri- and tetrachlorobiphenyl homologs being more than half of total PCBs.

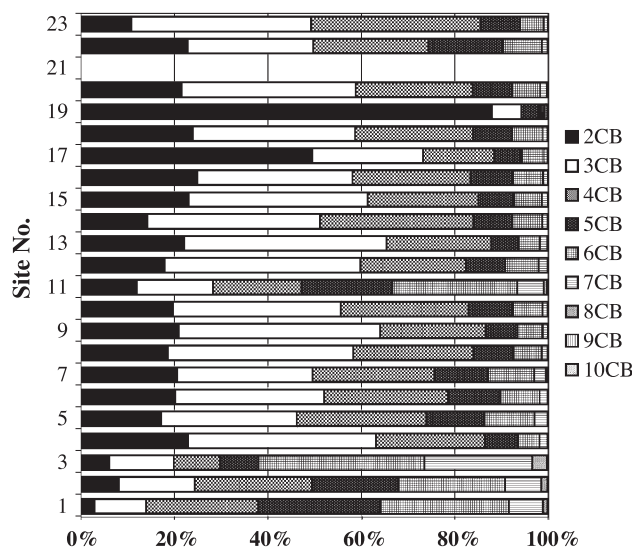


Fig. 2. Percentage composition of chlorobiphenyls in sediment (sites 1–20) and seawater (site 22—Chennai harbour; site 23—Cuddalore fishing harbour).

Behaviour of PCBs in seawater is entirely different from the sediment of the same location. In seawater, proportion of low chlorinated biphenyls (di-, tri- and tetra-) concentrations were as much as 74.4% and 85.6% in Chennai harbour and Cuddalore fishing harbour, respectively, than high chlorinated biphenyls (penta-, hexa- and hepta-) with 25.6% and 14.4%, respectively (Fig. 2). Low chlorinated biphenyls are more water-soluble than high chlorinated biphenyls which might be the reason for elevated levels of di- to tetrachloro biphenyls than penta- to heptachlorobiphenyls in seawater. As suggested by Hong et al. (2003), high-chlorinated PCBs with high Kow are likely to be adsorbed to suspended particulate material than low chlorinated PCBs. These materials then probably settle onto the bottom sediment near the source. Total PCBs in sub-surface water from Daya Bay, China (Zhou et al., 2001) varied from 91 to 1355 ng/l, which is about 50 to 300 times greater than the concentration range found in the Bay of Bengal water (1.93–4.46 ng/l). However, the authors (Zhou et al., 2001) reported predominance of high chlorinated congeners like penta-, hexa- and octachlorobiphenyls, accounting for 94% of total PCB in water in contrast to the present observation. The authors observed a similar congener pattern in sediment, too.

The levels of HCH isomers in sediment are shown in Fig. 3. The isomeric composition of HCH was not uniform. γ -HCH was always lower than other isomers although the composition is 14%, next to α -isomer (70%) in technical grade HCH used in India. Compared to α and γ -HCH, percentages of β - and δ -isomers are less in technical mixture, but both are predominant in seven samples each. As suggested by Hayes (1982), isomerization of α - to β -HCH in the environment (water) might be one of the reasons for elevated β -HCH concentration found in seven samples of this study. Moreover, β -isomer is more persistent with respect to microbial degradation and also has lowest volatility which may also accounts for its higher concentration. Further, both α and γ -HCH are more volatile,

leading to long-range transport of these compounds to far off regions. Among the earlier reports made on Indian marine sediments, Sarkar et al. (1997) found higher level of α -HCH in west coast (Arabian Sea) sediments, whereas, Pandit et al. (2001) found more of α and γ -HCH in west coast and β -HCH in east coast sediments. Total HCH concentration observed in this study is comparable with Arabian Sea sediment (0.10–6.2 ng/g) (Sarkar et al., 1997). In seawater, concentrations of α , β , γ and δ -HCH in Chennai harbour and Cuddalore fishing harbour were 5.44, 4.35, 10.1 and 2.41 ng/l, and 13.6, 4.88, 5.15 and 1.9 ng/l, respectively. The dominant isomers from both the harbours are α - and γ -HCH, indicating recent input of HCH into the harbour waters. In early 1990s, higher percentage of α -HCH followed by γ -, β - and δ -isomers in atmospheric air in a coastal location (Portonovo) near to one of the locations (Cuddalore—site 11) of the present study has been reported (Ramesh et al., 1989; Babu Rajendran et al., 1999). Though higher levels of δ -HCH observed in 7 out of 20 sediment samples occurred, in water samples it was the least recorded isomer than other isomers. In Chinese marine environment, the isomeric distribution was quite different. In Daya Bay, China, Zhou et al. (2001) found 3 out of 14 water samples contained higher levels of δ -HCH than other isomers, but in sediment the δ -isomer was less.

The total DDT concentration in this study ranged from 0.04 to 4.79 ng/g. Sarkar and Sen Gupta (1988) reported non-detectable to 790 $\mu\text{g g}^{-1}$ (wet wt.) in five sediments collected from the Bay of Bengal near Chennai, India (which is very close to one of the locations in this study, i.e. Chennai—sites 2–4). In this study, total DDT concentration in Chennai offshore sediment (sites 2–4) ranged between 0.3 and 1.18 ng/g, the maximum concentration obtained in this study is 670×10^3 times lower than the highest concentration they (Sarkar and Sen Gupta, 1988) reported in 1988. This reveals that, during the 10-year period the DDT burden in the marine environment has drastically declined, clearly indicating that DDT usage in

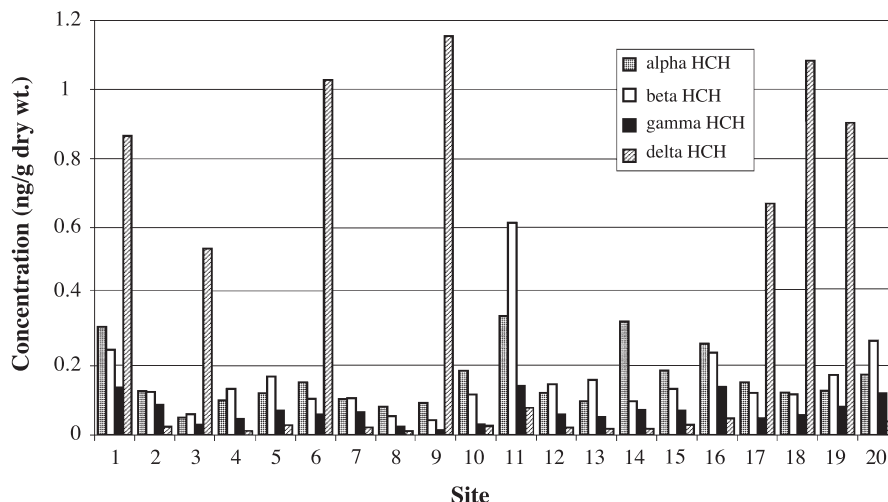


Fig. 3. HCH isomer concentrations in sediment from the Bay of Bengal, India.

India has decreased and the restrictions imposed by Indian government is effective in containing POPs. A decreasing trend of DDT in coastal atmospheric air from east coast of India has been reported earlier by Babu Rajendran et al. (1999). Similarly, Monirith et al. (2000) also reported an obvious decline of HCHs and DDTs concentrations in green mussel, *Perna viridis* from the east coast of India during 1988–1989, 1994–1995 and 1998 with 18 ± 15 , 11 ± 10 and 4.4 ± 3.4 ng/g wet wt, and 7.5 ± 3.6 , 5.8 ± 3 and 2 ± 1.8 ng/g wet wt, respectively. However, concentrations of PCBs has not decreased, but almost constant with concentrations of 4.1 ± 2 , 3.5 ± 3.5 and 4 ± 3.4 ng/g wet wt during these years, respectively. Sarkar et al. (1997) reported the concentration of total DDT in sediments from the Arabian Sea along the west coast of India was in the range of 1.14–17.59 ng/g and p,p'-DDE as the most detected metabolite. It could be inferred from the literature that China and India are the largest pesticide consumers in Asia. However, the residual burden of DDT in seawater in India (the present study) is much lower than the levels from Chinese waters. Zhou et al. (2001) reported that DDT in sub-surface water and surface sediments from Daya Bay, China varied from 26.8 to 976 ng/l, and from 0.14 to 20.27 ng/g dry wt., respectively. Ma et al. (2001) found p,p'-DDT as the predominant compound among DDTs in sediment samples of intertidal zone from the Bohai Sea and Yellow Sea in China, indicating possible recent addition of DDT to these waters.

The relative concentrations of the parent compounds and their metabolites/isomers are very useful in providing information on source and history of input to the environment and possible degradation pathways involved. In this investigation, the concentration of parent compounds (o,p- and p,p'-DDT) were always lower than the metabolites (either DDE or DDD) in all the sediment and water samples. In some sediment samples (sites 4, 5, 9 and 17), no DDT (o,p- or p,p'-) residue was measured. Pandit et al. (2001) reported DDT residues in sediments from northeast coast (coastline) of India. Among DDTs, metabolites (DDE and DDD) were at greater concentration at four locations and DDT was dominant in another location. According to Strandberg et al. (1998), the ratio of p,p'-DDT/p,p'-DDE provides a useful index to know whether the DDTs at a given site is fresh or aged. Further, a value <0.33 generally indicates an aged input. In the present study, the value of >0.33 was found in five sediments (Table 3), indicating fresh inputs of DDT to those locations. Out of five sediments, four sediments were collected from at or <2.5 nmi and the other at 10.5 nmi away from the coast. This clearly shows the possibility of long range transport of DDT to open ocean environment and/or poor degradation of DDT in offshore sediments. Considering the p,p'-DDT/p,p'-DDE ratio in seawater, it could be concluded that Chennai harbour water had recent input of DDT (p,p'-DDT/p,p'-DDE >0.44), but no fresh addition at Cuddalore fishing harbour (p,p'-DDT/p,p'-DDE <0.13).

In this investigation, water samples had higher levels of HCH than DDT, but sediment samples near major cities like Chennai (sites 1 and 2), Pondicherry (site 8) and Cuddalore (harbour—site 11) contained greater DDT levels than HCH. This reflects the local usage of the pesticides (DDT is used only in vector control in India, but HCH was used in agriculture also until recently). Usually in urban cities with high population, the frequency of spraying of DDT is always high to contain mosquito menace, which could be the reason for greater levels encountered in sediment at Chennai (4.42 ng/g) (population: 7 million), Pondicherry (4.79 ng/g) (population: 0.24 million) and Cuddalore (4.04 ng/g). Cooum and Adyar Rivers are the major receptacles of Chennai city's untreated sewage and emptying into the Bay of Bengal at Chennai. Earlier, Iwata et al. (1994) reported 20 ng/g of DDT in sediment from the Cooum River, Chennai.

The sediment levels of HCHs, DDTs and PCBs of this study are comparable with the levels quantified in lagoon sediments from the west coast of Sri Lanka (Guruge and Tanabe, 2001), which is very close to the present study area both having same tropical climate. However, they found higher proportion of α -HCH (44–48%) than β -HCH suggesting recent exposure to technical HCH.

Fig. 4 shows the spatial variations of Σ HCH, Σ DDT and Σ PCB in sediment samples from all the locations. The total HCH concentration was lower at 0.5 nmi and highest at 2–3 nmi in all the locations, and again decreased at 6 nmi at Chennai, Mahapalipuram and Pondicherry. But, at Cuddalore, Nagapattinam and Mandapam concentrations increased at 6 nmi, suggesting transport of HCH to offshore environment through water, atmospheric transport, etc. Regarding total DDT, higher concentrations were found near the coast (0.5–1.6 nmi) at Chennai, Mahapalipuram and Pondicherry. But at Cuddalore, Nagapattinam and Mandapam, it was greater at 6 nmi than coastal (0.5–2.5 nmi) sediments. This also indicates the transport of DDT to offshore environment.

There are few reports on the relationship between organic carbon and chlorinated compounds in sediment (Lee et al., 2001). They found a correlation between total DDT and TOC in sediments of Kyeonggi Bay, Korea, but not between total HCH and TOC. However, in our study no correlation was found between sediment organic carbon and OC residue levels.

The distribution of PCBs in water between commercial harbour (Chennai) and fishing harbour was comparable, but the sediment from commercial harbour had many fold (20 times) greater concentration than fishing harbour. PCB contamination of sediment is probably attributed to intense shipping and related activities (dry-docking, repairing, overhauling and painting, etc.) in Chennai harbour and also related to human intensity/activity (discharge of sewage through Cooum and Adyar rivers) in Chennai metropolitan area than Cuddalore. Further, the order of OCs distribution in harbour sediment has been found as PCB $>$ DDT $>$ HCH

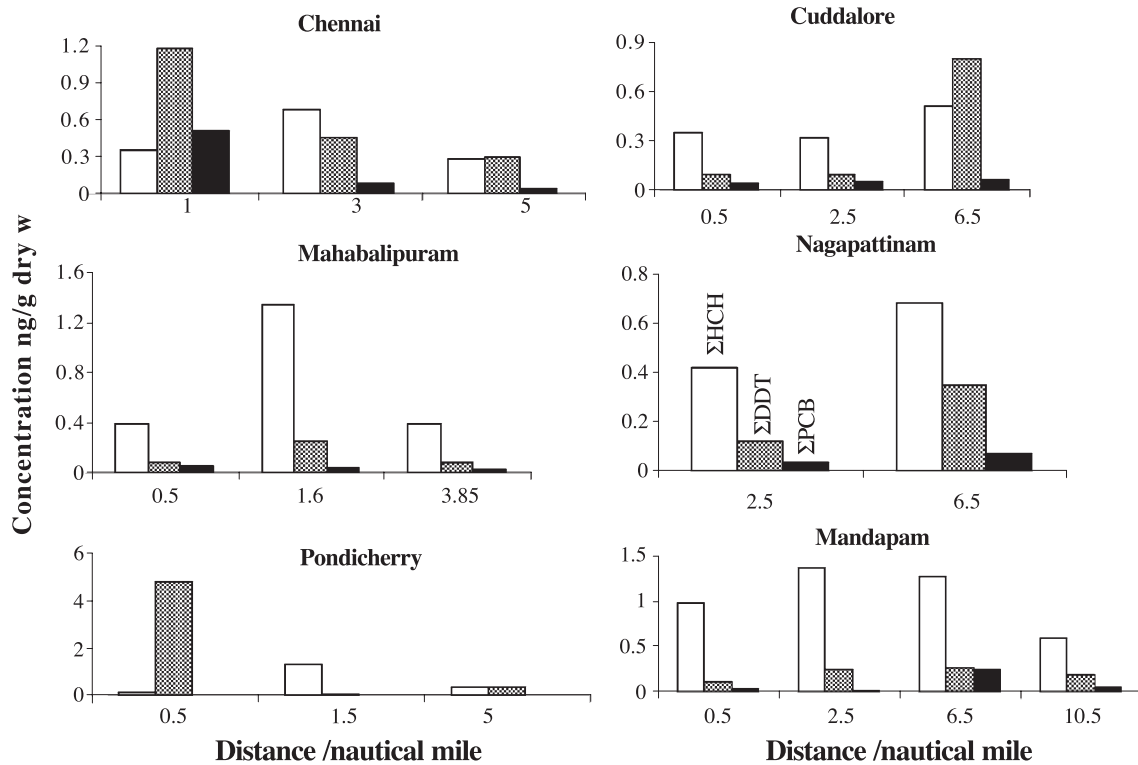


Fig. 4. Spatial variation in OC compounds concentration in sediment from the Bay of Bengal.

and DDT>HCH>PCB in Chennai and Cuddalore harbours, respectively.

A comparison of OCs in sediment from the Bay of Bengal with world waters is given in Table 4. Total PCB (0.02–6.57 ng/g dry wt.) concentrations are comparable with Caspian Sea (de Mora et al., 2001), Black Sea (Fillmann et al., 2002), Sri Lankan coast (Guruge and Tanabe, 2001) and Xiamen harbour, China (Hong et al., 1995), however, much lower than Daya Bay, China (Zhou et al., 2001), Incheon

harbour, Korea (Lee et al., 2001), Alexandria harbour, Egypt (Barakat et al., 2002) and Masan Bay, Korea (Hong et al., 2003). Regarding pesticides, total DDT concentration (0.04–4.79 ng/g) is comparable with Sri Lankan coast (Guruge and Tanabe, 2001), Black Sea—Turkey and Russian coast (Fillmann et al., 2002), Caspian Sea (de Mora et al., 2001), but lower than Xiamen harbour, China (Hong et al., 1995), Daya Bay, China (Zhou et al., 2001), Bohai and Yellow Sea, China (Ma et al., 2001), Alexandria harbour,

Table 4
Organochlorine concentrations in marine sediments (ng/g dry wt.) from world waters

Location	Year	ΣPCBs	ΣDDTs	ΣHCHs	Reference
Xiamen harbour, PRC	1993	0.05–7.2	4.5–311	0.14–1.12	Hong et al. (1995)
Incheon harbour, Korea	1995	11–580	NA	NA	Lee et al. (2001)
Bohai and Yellow Sea, China	1997	nd–14.9 ^a	0.37–1417	NA	Ma et al. (2001)
Daya Bay, China	1999	0.9–27.4	0.14–20.3	0.32–4.16	Zhou et al. (2001)
West coast, Srilanka	1996–1997	0.45–4.4	0.09–1.6	0.09–0.33	Guruge and Tanabe (2001)
Alexandria harbour, Egypt	1998	0.9–1210	<0.25–885	0.25–6.0	Barakat et al. (2002)
Black Sea, Turkey	1995	0.4–4.4	0.2–7.2	0.08–1.1	Fillmann et al. (2002)
Black Sea, Russia	1995	0.3–4.7	3.3–12	0.3–0.8	Fillmann et al. (2002)
Black Sea, Ukraine	1995	5.7–6.8	35–65	1.3–2.3	Fillmann et al. (2002)
Black Sea, Romania	1995	0.1–24	0.6–72	0.2–40	Fillmann et al. (2002)
Masan Bay, Korea	1997	2.48–75	0.27–89.2	0.02–0.59	Hong et al. (2003)
Caspian Sea, Azerbaijan	2000	0.3–2.8 ^b	0.56–13.4	0.2–3.5	de Mora et al. (2001)
Caspian Sea, Russia	2000	1.3–6.4 ^b	0.01–1.9	0.01–0.8	de Mora et al. (2001)
Caspian Sea, Iran	2000	0.1–0.8 ^b	0.06–3.9	0.03–6	de Mora et al. (2001)
Caspian Sea, Kazakhstan	2000	0.03–0.6 ^b	0.01–1.9	0.01–0.3	de Mora et al. (2001)
Bay of Bengal, India	1998	0.02–6.57	0.04–4.79	0.17–1.56	This study

nd: not detected; NA: not available.

^a Sum of 10 congeners.

^b Sum of 28 congeners.

Egypt (Barakat et al., 2002), Black Sea—Ukraine and Romanian coast (Fillmann et al., 2002) and Masan Bay, Korea (Hong et al., 2003). HCH residues are comparable with almost all locations, except Black Sea—Romanian coast (0.2–40 ng/g) (Fillmann et al., 2002), where elevated HCH level was reported.

3.2. Ecotoxicological concern

Existing sediment quality guidelines (CCME, 1999; Long et al., 1995), ecotoxicological assessment criteria (OSPAR Commission, 2000) and Water Quality Criteria (Lee et al., 2001) were used for the assessment of the relative sediment/water quality and potential risk to the aquatic species in the Bay of Bengal. None of the sediment samples (Table 2 and 3) exceeded the Canadian sediment quality PEL (probable effect level, i.e. the level above which adverse effects on aquatic biota are expected to occur frequently) guideline values (total PCB 277; p,p'-DDT 4.77; p,p'-DDE 6.75 and p,p;-DDD 8.51 ng/g dry wt.) for the protection of aquatic biota for total PCBs and DDTs. Long et al. (1995) determined 10th and 50th percentile and corresponding effects range low (ER-L) and effects range median (ER-M) values based on the concentrations of contaminants in sediment and observed biological effects. The calculated ER-L and ER-M values for total DDT are 3 and 350 ng/g, and for PCBs are 50 and 400 ng/g, respectively. Total DDT concentrations in all the sediments except Chennai harbour (site 1: 4.42 ng/g), Pondicherry (site 8: 4.79 ng/g) and Cuddalore fishing harbour (site 11: 4.04 ng/g) were below the ER-L value (3 ng/g), whereas, PCB concentrations in most of the sediments were about thousand times lower than the ER-L value of 50 ng/g. The PCB concentrations at Chennai harbour, and Chennai (site 2) and Cuddalore fishing harbour were about 10 and hundred times below the ER-L level, respectively. Further more, all the sediment samples except Chennai harbour were well below the prescribed ecotoxicological assessment criteria (EAC) level of 1.0–10 ng/g for PCB (OSPAR Commission, 2000).

In the case of seawater, concentrations of γ -HCH (lindane) from both Chennai harbour (10.11 ng/l) and Cuddalore fishing harbour (5.148 ng/l) were greater than the ecotoxicological assessment criteria (EAC) range of 0.5–5.0 ng/l suggested by OSPAR Commission (2000). The total PCBs concentration from Chennai harbour and Cuddalore fishing harbour were well below the Water Quality Criteria (WQC) (Lee et al., 2001) of $0.03 \mu\text{g l}^{-1}$. From these assessments, it can be stated that the levels of the xenobiotic compounds in Indian marine environment are not alarming. Contamination by PCB in the Bay of Bengal, India is negligible/relatively very low and may not cause any toxicological effects in the marine species inhabiting the coastal Bay of Bengal. Contamination by OC pesticides (DDT and γ -HCH), do exist to some extent in Chennai, Pondicherry and Cuddalore coastal waters, that may have

some impact on resident organisms via a long-term chronic exposure.

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