Residual archives on organochlorine insecticides in the core sediment of a tropical estuary, India

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ABSTRACT: A comprehensive evaluation of the residual levels of Organochlorine insecticides (OCIs) in the sediment cores of Cochin Estuarine System (CES) is highlighted in this research article. It assessed the distribution pattern and impact of these xenobiotics in this environmental niche. Fifteen persistent organochlorine compounds (OCs) were quantitatively analysed in the six sediment core samples collected from specific sites of CES, during November 2009. Among these contaminants, residual levels of HCH, Cyclodienes and DDT were the dominant entities. According to the sediment quality guidelines (SQGs), the higher concentration of these persistent toxicants found in the CES was enough to pose ecological risk to the bottom dwelling consumers. This study provides a better understanding of these trace organics in the environment and could develop more effective strategies for protecting this vulnerable ecosystem from further pollution. Further, sediment screening bioassays can also be conducted for both sediment quality evaluation and identification of existing potent toxicants.

Keywords: Cochin estuarine system, ecological risk, organochlorine insecticide, sediment core.

INTRODUCTION

In the natural environment, all chemicals are subject to physical, chemical and biological processes that can act on their chemical structure causing degradation and eventual removal or a considerable reduction in their potential for harmful effects. However, some chemicals do not break down or slowly break down in the environment (Long et al., 1995). In addition, degradation processes might lead to the production of non-degradable by-products. These substances are known as persistent chemicals and are long-lived, under prevailing environmental conditions. They enter into the environment through many pathways such as direct application for pest and vector control, urban and industrial waste water discharges, runoff from non-point sources, aerosol and particulate deposition rainfall etc.

Estuarine sediments act both as a short or long term reservoir for many types of organic/inorganic contaminants (OCIs, PAHs, PCBs, trace metals etc). Diffusion, advection, mixing and re-suspension of the sediment will affect the distribution of these trace contaminants in the aquatic niche. Ecotoxicological assessments on surface sediments, as well as deep sediment deposits are used to determine the complex relationship between contamination flux and fate of the pollutants in different compartments of the aquatic system. Estuarine core sediment geochemistry allows extrapolating pollution histories to be

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studied and judged and is an extremely useful tool used in conjunction with environmental monitoring assessments. Moreover, sediment core analysis is interesting, as the bottoms water body are records of objects and materials which have fallen into the aquatic system over a period of time. They are unique and closely linked with the geochemical history of the earth. Therefore, the sequential monitoring studies of aquatic sediment records are valuable to assess the extent and effect of human inputs in the present and the past and it can predict variances in the contaminant inventory over a broad interval of time (Vink et al., 1999; Brandengerger et al., 2008; Schwarzbauer, 2010).

Presently, India is considered the largest pesticides manufacturing country in Asia and twelfth largest in the world with 90,000 tons of annual pesticide production (Tanabe et al., 1994; Monirith et al., 2003; Khan, 2010; Pozo et al., 2011; Filiz and Tolga 2012). Both industrial and agricultural sources contribute significant amounts of these contaminants to the environment through seepage, disposal and evaporation (Tolosa et al., 2010). In a study conducted in India on the examination of the flux of HCH, it was reported that most of the HCH applied annually were lost to the atmosphere (Takeoka et al., 1991). The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of OCIs leads to their accumulation in biological tissues and subsequently magnify the residual levels in organisms progressing up the food chain (Sujatha et al., 1993; Barakat et al., 2002; Pandit et al., 2006; Akhil and Sujatha, 2012). During the last two decades, many studies have reported the residual status of OCIs in different environmental matrices in Asian coastal areas (Sarkar and Sengupta, 1987, 1988, 1991; Takeoka et al., 1991; Pandit et al., 2006; Sarkar et al., 1997, 2008), indicating the presence of major emission sources in these regions. Only a few reports were published regarding the budgetary status on conservative pesticides in CES (Sujatha and Chacko, 1991; Sujatha et al., 1993, 1994a, 1999; Akhil and Sujatha, 2014; Dsikowitzky et al., 2014) and all these reports actually focused on their spatial distribution trends. The present study determined the sources and residual archives of OCIs in the core sediments of CES and also provides added information on whether any adverse effects would occur on the benthic community in the future.

MATERIALS AND METHODS

Study area and sampling sites

The Kerala State, a narrow strip of land, lies on the South Western side of Peninsular India with a long coast (560 km) and an average width of 80 km, lying between the Arabian Sea on the west and a continuous mountain chain (Western Ghats) on the east. The topography of this area covers altitudes ranging from below mean Sea level to above ~2600 m the area in the Western Ghats. It is characterised by 44 short and swift flowing monsoon fed perennial rivers, originating from the Western Ghats and 41 of them drain into either the estuaries or the Arabian Sea. The most conspicuous feature of this coast is the wide spread distribution of estuaries and lagoons which are thought to be the remnants of the receding Sea. The area has a tropical humid climate with a temperature range of 13 to 42°C and an average rainfall of 3000 mm (Krishnan Nair, 1996; Soman, 1997; Menon et al., 2000). The study area, the Cochin Estuary (Lat. 9° 30' -10° 10' N and Lon. 76° 15' - 76° 25'E), is situated in the central part of Kerala which extends between the cities of Azhikode in the north and Alleppy in the south, running parallel to the Arabian Sea. It is generally wide (0.8-1.5 km) and deep (4-13 m) towards the south, but becomes narrow (0.05-1.5 km) and shallow (0.5-3

m) in its northern part. Six rivers namely: Pamba, Achankovil, Manimala, Meenachil, Periyar and Muvattupuzha with their tributaries along several canals, bring freshwater into the estuary. Among these rivers, Periyar (in the north) and Muvattupuzha (in the south) have an active influence in controlling the salinity of the estuarine system. Based on the topographical, hydrological and ecological features of the estuary, the present study area was divided into three zones namely south, middle and north (Fig. 1).
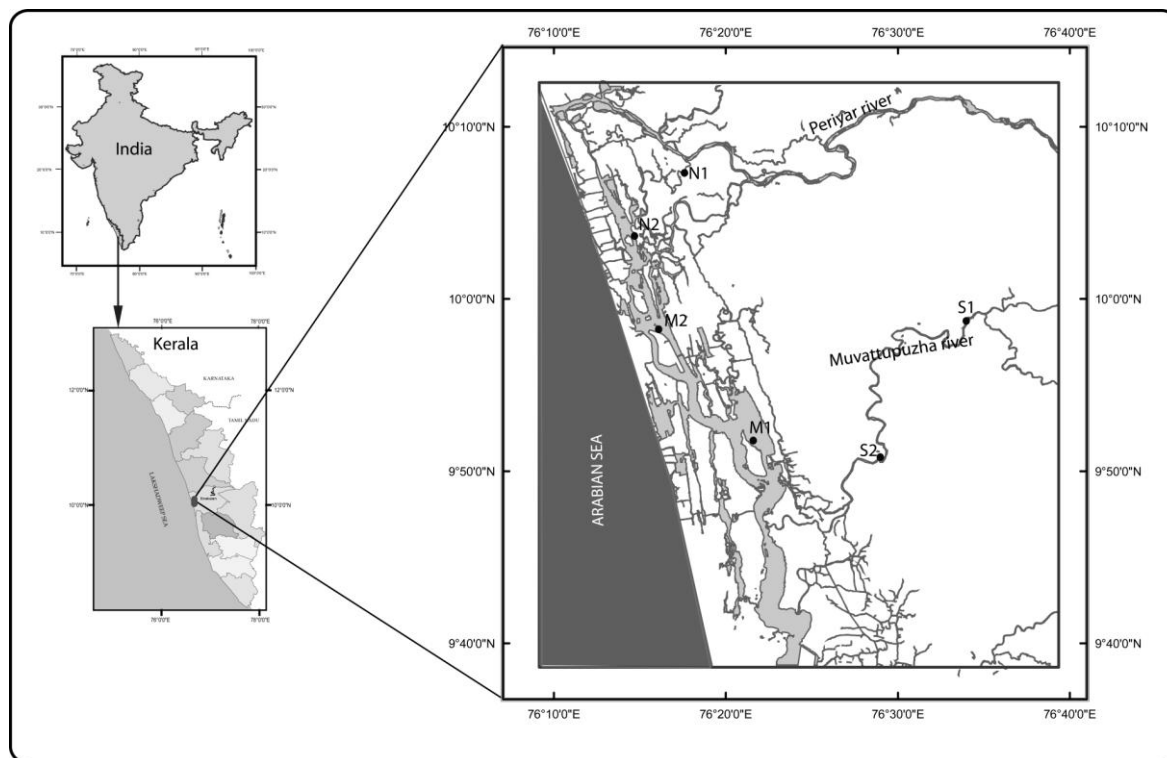

Fig. 1. Map of the study area and sampling sites

The south zone is situated in the fresh water region, and originated from the southern branch of the Muvattupuzha River. The major source of pollution in these areas is from agricultural fields (80 km^2) and the region also receives untreated effluents (104 billion liters per day) from domestic sectors (CPCB, 1996). Moreover, wastes from aquaculture fields (62 km^2), coconut husk retting yards, fish processing plants, and animal bone processing units have increased the organic pollution in this zone (Thomson, 2002). The middle zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion by making free flow of contaminants in the CES which gets settled considerably towards the head of the estuary (Madhuprathap, 1987; Balachandran et al., 2008; Akhil et al., 2013; Dsikowitzky et al., 2014). With the advent of International Container Transshipment Terminal (ICTT) project, this region has become a backbone of the economy of Kerala State. Due to enhanced containerization, resulting in improved trade and economic growth, widespread activities like dredging, piling, along with anthropogenic inputs are increasing frequently. Moreover, this zone is well regulated by a bund (namely Thannirmukham), which was constructed in order to prevent salt water intrusion into the paddy fields and the bund remains open during the monsoon season. Finally, the north zone originates from the industrial

locale of the Periyar - the life line of Kerala. The principal chemical industries of the Kerala State (~70%) are mainly located on the banks of the rivers- Periyar and Chithrapuzha (Table 1) and utilise large amounts of freshwater from the River Periyar and in turn discharges 260 million liters of effluents daily into the aquatic niche (CPCB, 1996; KPCB, 2000).

Table 1. Major industries and their effluent discharge to Cochin Estuary (CPCB, 1996; KPCB, 2000)

No.	Industy	Products	Production (Tones/Month)	Effluent Discharge (m^3/day)	Major Pollutants
1	Hindustan Insecticides Ltd	DDT	336		Insecticides
		HCH	500	1000	
		Endosulfan	—		
		Mancozeb	—		
		Hydrochloric Acid	140		
		Sulphuric Acid	100		
2	FACT	Ammonium Chloride	2250		Free Ammonia
		Ammonium Sulphate	18000		
		Ammonium Phosphate	16500	25400	Phosphate
		Ammonia	10200		Suspended Solids
		Phosphoric Acid	3750		
3	FACT Pertochemical	Caprolactum Nitric Acid Soda Ash	—	5040	—
4	Travancore Cochin Chemicals	Caustic Soda	2775		Free Chloride
		Liquid Chlorine	2487	6680	
		Hydrochloric Acid			Suspended solids
		Sodium Sulphate	54		
5	Binai Zinc Ltd	Zinc Slabs	1400	550	Zinc and Lead
		Cadmium	3		
6	Periyar Chemicals Ltd	Formic Acid	85	330	—
		Sodium Formate	165		
7	Travancore Chemicals Manufacturing Co.Ltd	Copper Sulphate	250		—
		Copper oxy chloride	75	720	
		Sodium Aluminate	85		
		Sulphate of Alumina	100		

Further, two core sediment samples from each of these three zones [S_1 (45cm) and S_2 (30 cm) south, M_1 (55 cm) and M_2 (60 cm) middle and [N_1 (30 cm) and N_2 (60 cm) north], were collected by pushing a hand held PVC core (150 cm long with a diameter of 6.3 cm) during November 2009 with the help of a skin diver, in varying depths (1-3.50 m) of the water body. All samples were kept in ice chest boxes on board during transportation. In the laboratory, all visible marine organisms, coarse shell fragments, and sea grass leaves and roots were removed manually with the help of stainless-steel forceps. The sediment cores were sectioned immediately at 5 cm intervals and then they were freeze-dried, sieved through a 250 μm sieve and stored at -20°C till further analysis.

Sedimentary parameters
General sedimentary characteristics such as texture and total organic carbon (TOC) were included in this study, as they are the main contributors for sorbing all types of trace contaminants in the environmental niche. The textural characteristics (sand, silt, and clay) of these sediment samples were determined using pipette analysis (Lewis, 1984). TOC was determined by treating the samples with 1M HCl to remove the carbonates and treatment was repeated two/three times in order to ensure the complete exclusion of carbonates. These samples were washed with Milli-Q water to remove salts, and finally freeze dried. Organic carbon was determined using Total Organic Carbon (TOC) analyzer (Elementar Vario Select, Germany). Samples were run with blank cups in order to correct the carbon associated with the tin cups. Standard sediments supplied by Elementar Vario Select, Germany, were used for calibration in the TOC analyzer. The detection limit for OC is 0.06%.

Analysis of organochlorine insecticides
About 5 g of the sediment samples were accurately weighed and then extracted twice with 50 mL of 1:1 hexane-acetone mixture (HPLC grade, Glaxo, Mumbai, India). Activated copper granules were added to each collection flask, in order to remove potential elemental sulphur (Sarkar et al., 1997; Lino et al., 2007). The extract was subjected to a cleanup procedure involving elution through a Florisil column (60 cm × 22 mm i.d) with 50 mL 1:1 hexane-acetone mixture and the aliquots were fractionated by elution through a silica column (250 mm × 10 mm i.d) to separate the PCBs from the polar OCIs (EPA Method 3630C and 8081A). The extract was concentrated to about 5–6 mL by means of a rotary evaporator at 50–60°C for further analysis. However, the separation and analysis of the OCIs were performed on a gas chromatograph (GC) (model 7890A, Agilent, Waldbronn, Germany) with a Ni-63 ECD and equipped with capillary column (HP-35, 30 m × 0.320 mm × 0.5 mm) using nitrogen as carrier gas (1.5 mLmin^{-1}). The GC was calibrated with a standard solution of a pesticide mixture (Supelco, USA) prepared in HPLC grade n-hexane. Solvent blanks were used to confirm the absence of any pesticide residues. Analytical reproducibility was checked by replicate measurements. Also, the quality of the analytical data of OCIs was assured using the certified reference material (CRM) 804-050 soils (Sigma-Aldrich). Identification and quantification of OCIs were accomplished using reference solutions supplied by EPA (USA) and Supelco (USA). 1 μL aliquot samples were injected onto the column. The following GC conditions were maintained: injection port temperature of 250°C, detector temperature of 350°C, oven temperature program: 110°C (5 min) at 5°C min^{-1} to 190°C (2 min) at 15°C min $^{-1}$ to 280°C (10 min).

Quality control and quality assurance
All the data were subjected to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analyzed. None of the target compounds were detected in the

procedural blanks for sediment samples. Spiked samples (10 ng of pesticide mix standard) were determined with good precision and high recoveries. The limit of detection (LOD) and relative standard deviation (RSD) of the analytical method for quantification of OCIs is as follows.

The instrumental detection limit values were calculated from the lowest standards, extrapolating to the corresponding amount of analytes that generate a signal-to-noise ratio of 3:1. The detection limit was lowest for aldrin (0.04 ng/g) and highest for endrin and 4,4'-DDT (0.19 ng/g), while the detection limit of other analytes were within the range. The average recoveries (n=3) for OCIs in the sediments revealed an efficiency of 87–103%. Moreover, the recoveries of the analysed concentrations of OCIs in CRM samples were from 75-107%, which shows that the analytical protocols used in this study can effectively determine OCI residues in sediments. Table 2 illustrates the recoveries and detection limits (DLs) of OCIs in sediments. The relative standard deviations (RSD) were below 5.0% and fall within the requirement criteria of US-EPA (Recovery: 70–130%, RSD is <30%).

The residue levels of OCIs were quantitatively determined by the external standard method using peak height and standard calibration curves. For every set of 10 samples, a procedural blank and the spike samples consisting of all reagents were run in order to check the interference and cross contamination. Moreover, peak identification was conducted by the accurate retention time of each standard (±1%) and selected samples were analyzed by GC-MS (Agilent 6890N-5975) for confirmation. The mass spectrometer was operated in a positive ion electron impact energy of 70 eV and an emission current of 60 µA. Full scan data were obtained with a mass range of m/z 40-450. Scanning interval and selected ion monitoring (SIM) sampling rate were kept at 0.5 and 0.2 s, respectively. The following organochlorine pesticides were quantified: α-hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, heptachlor, aldrin, heptachlor epoxide (B), 4,4'-DDE, dieldrin, endrin, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT, α-endosulfan, and β-endosulfan.

Table 2. The recoveries, detection limits (DLs), and the analyzed results of CRM standards (804-050) of OCIs in sediments

Insecticides	Recovery (%)	DL (ng/g)	CRM standard (mg/Kg)	
			Certified value	Analyzed value
α-HCH	90 ± 3	0.10	-*	-
β-HCH	87 ± 4	0.13	-	-
γ-HCH	88 ± 3	0.09	491.6	526.1
Heptachlor	89 ± 5	0.18	-	-
Heptachlor epoxide (B)	90 ± 3	0.18	-	-
4,4'-DDE	88 ± 2	0.06	1519.6	1246
Dieldrin	88 ± 4	0.06	1862.5	1508.7
Aldrin	90 ± 5	0.04	18.04	19.1
Endrin	103 ± 4	0.19	62.2	68.3
2,4'DDD	92 ± 3	0.18	-	-
4,4'DDD	91 ± 5	0.16	1530.6	1193.9
2,4'-DDT	90 ± 2	0.15	-	-
4,4'DDT	87 ± 4	0.19	1060.1	795.1
α-Endosulfan	89 ± 5	0.18	1464.3	1142.2
β-Endosulfan	90 ± 5	0.13	1128.2	1028.8

* Not available

RESULTS AND DISCUSSION

The distribution of various organochlorine insecticides are presented in Tables 3, 4 and 5. They constitute the first judicious baseline data set in the sediment cores of CES.

Table 3. Concentration of OCIs (ng/g, dry wt.) in the sediment cores S_1 and S_2

	S1			S2					
Depth	α-HCH	β-HCH	γ-HCH	α-HCH	γ-HCH	4,4'-DDE	4,4'-DDD	Aldrin	Heptachlor
cm	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
0-5	< 0.10	< 0.13	< 0.09	< 0.10	4.34	< 0.06	33.17	< 0.04	< 0.18
5-10	4.32	< 0.13	< 0.09	< 0.10	2.12	< 0.06	16.4	< 0.04	< 0.18
10-15	1.81	< 0.13	< 0.09	< 0.10	0.81	< 0.06	32.1	1.8	0.92
15-20	< 0.10	46.4	< 0.09	< 0.10	< 0.09	2.82	6.4	3.5	2.95
20-25	12.2	184.2	0.18	1.8	< 0.09	8.12	< 0.16	0.92	< 0.18
25-30	20.82	247.1	0.29	2.168	< 0.09	14.8	< 0.16	1.2	< 0.18
30-35	< 0.10	34.1	< 0.09	NA*	NA	NA	NA	NA	NA
35-40	< 0.10	16.2	14.2	NA	NA	NA	NA	NA	NA
40-45	11.34	47.4	32.5	NA	NA	NA	NA	NA	NA

*NA: Not Available
* All other quantified OCIs were BDL

Table 4. Concentrations of OCIs (ng/g, dry wt.) in the sediment cores M_1 and M_2

	M1			M2							
Depth	Heptachlor Epoxide (B)	Endrin	Endosulfan (α)	α-HCH	β-HCH	γ-HCH	4,4'-DDE	Aldrin	Heptachlor	Endrin	Endosulfan (α)
cm	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
0-5	69.45	< 0.19	< 0.18	< 0.10	12.78	< 0.09	6.06	< 0.04	< 0.18	< 0.19	< 0.18
5-10	44.8	31.2	< 0.18	< 0.10	10.2	< 0.09	1.26	< 0.04	< 0.18	< 0.19	< 0.18
10-15	18.2	55.2	< 0.18	< 0.10	7.4	< 0.09	3.17	< 0.04	< 0.18	< 0.19	< 0.18
15-20	32.1	32.1	< 0.18	< 0.10	< 0.13	< 0.09	0.86	< 0.04	< 0.18	< 0.19	< 0.18
20-25	0.84	18.4	< 0.18	< 0.10	< 0.13	< 0.09	< 0.06	11.2	2.94	24.3	< 0.18
25-30	1.82	0.29	< 0.18	< 0.10	8.3	< 0.09	2.81	8.4	8.41	16.8	< 0.18
30-35	< 0.18	< 0.19	21.2	0.89	23.4	< 0.09	< 0.06	22.2	12.5	63.4	< 0.18
35-40	< 0.18	< 0.19	2.9	3.1	36.97	< 0.09	< 0.06	33.7	23.41	82.12	< 0.18
40-45	< 0.18	< 0.19	16.4	1.2	18.4	< 0.09	< 0.06	18.9	4.86	46.3	< 0.18
45-50	< 0.18	< 0.19	42.3	4.8	16.3	2.81	< 0.06	1.28	< 0.18	8.6	8.46
50-55	< 0.18	< 0.19	68.6	2.1	0.81	4.23	< 0.06	< 0.04	< 0.18	< 0.19	16.3
55-60	NA	NA	NA	8.82	<0.13	6.38	< 0.06	< 0.04	< 0.18	< 0.19	65.2

*NA: Not Available
* All other quantified OCIs were BDL

Table 5. Concentrations of OCIs (ng/g, dry wt.) in the sediment cores N_1 and N_2

	N_1					N_2					
Depth	α-HCH	β-HCH	4,4'-DDE	4,4'-DDD	Aldrin	β-HCH	2,4'-DDT	4,4'-DDD	Endrin	Endosulfan (α)	Endosulfan (β)
cm	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
0-5	<0.10	<0.13	<0.06	35.9	6.08	38.26	<0.15	<0.16	103.15	<0.18	<0.13
5-10	<0.10	16.1	<0.06	18.41	1.28	18.4	<0.15	<0.16	48.2	<0.18	<0.13
10-15	1.2	4.8	8.42	8.1	<0.04	9.81	<0.15	2.1	16.4	<0.18	<0.13
15-20	4.6	1.8	62.71	<0.16	<0.04	43.1	26.4	12.1	72.6	<0.18	<0.13
20-25	6.06	<0.13	4.34	<0.16	<0.04	16.2	84.1	<0.16	7.3	42.1	8.26
25-30	<0.10	<0.13	<0.06	<0.16	<0.04	4.26	63.2	14.1	<0.19	18.6	12.3
30-35	NA	NA	NA	NA	NA	65.23	114.28	39.02	<0.19	88.17	41.2
35-40	NA	NA	NA	NA	NA	0.84	9.4	8.2	<0.19	8.9	4.21
40-45	NA	NA	NA	NA	NA	<0.13	<0.15	<0.16	<0.19	<0.18	6.34
45-50	NA	NA	NA	NA	NA	<0.13	<0.15	<0.16	<0.19	<0.18	17.2
50-55	NA	NA	NA	NA	NA	<0.13	7.6	<0.16	<0.19	14.2	64.3
55-60	NA	NA	NA	NA	NA	<0.13	63	<0.16	<0.19	62.3	154

*NA: Not Available
* All other quantified OCIs were BDL

The prevalent nature of HCH isomers were detected in most of the samples and it showed a wide range of fluctuation as delineated in this region. It was reported that *β*-HCH is more resistant to hydrolysis and environmental degradation than the other isomers. In natural environment, the isomers of *α*-HCH and *γ*-HCH were found to be transformed into *β*-HCH (Sujatha et al., 1993; Walker et al., 1999; Lee et al., 2001). Therefore, *β*-HCH should be a predominant component of HCHs in the sediment samples, if there were no fresh inputs of technical HCHs. The highest concentration (247.1 ng/g) of β-HCH was detected at 25-30 cm portion of the sediment core (S_1), which was collected from the southern part of the estuary and its residual level decreased towards the bottom of the core. In the sediment core S_2, contamination by α-HCH was detected (2.168 ng/g) at the bottom and γ-HCH residues (4.34 ng/g) were found at the top 5 cm portion of the core. The residue level of

HCH isomers were BDL in the sediment core M_1, whereas in core M_2, the concentration of β-HCH was highest at both the top and middle portions. Isomers of HCH (α and γ) were present in the bottom segment of the sediment core M_2. The β-HCH content was highest (65.23 ng/g) in the sediment core N_2 at 30-35 cm depth, collected from the northern part of the estuary. The higher concentration of the β-isomer confirms its stability and resistance to microbial degradation over other HCH isomers and earlier literatures also support this inference (Willett et al., 1998; Walker et al., 1999). A ratio of β-HCH to γ- HCH is commonly used to estimate the source of HCHs and their paths (Li et al., 2008) and the value > 1 obtained from the sediment core S_1 confirms the past use of HCH and its persistent character. This points towards the occurrence of HCH and is attributed to either the use of a technical HCH mixture (combination of α-(67%), β-(10%), γ-(15%) and (8%) in general) or the use of lindane as

the pesticide (Covaci et al., 2002). The residual levels of HCH isomers were identified in the order: β-HCH>γ-HCH>α-HCH, which supports the aforementioned inference. Moreover, previously reported results by Akhil and Sujatha (2014), also substantiate the spatial distribution pattern of these xenobiotics in the CES.

The study extends to the analysis of other xenobiotics and their metabolites/isomers in order to provide more information about the source and transport pathways in the aquatic realm. The concentration of DDT and its metabolites varied significantly in all the six sediment cores under investigation. The highest concentration (114.28 ng/g) of 2,4'-DDT was detected in sediment core N_2 at 30-35 cm section and its level diminished considerably towards the bottom. DDT can be degraded by microbes into DDE under aerobic conditions or DDD under anaerobic conditions (Zhang et al., 1999). Usually, the degradation pathway of DDT is DDT→DDE→DDD or DDT→DDD. Therefore, the ratios of DDD/DDE or/and (DDD+DDE)/DDT can be used to distinguish the degradation conditions of DDT, the 'new' or 'old' pollution sources, and the degree of degradation of DDTs (Doong et al., 2002; Yang et al., 2005). If (DDE+DDD)/DDT ratio is larger than 0.5, it would suggest that accumulated DDTs have undergone long-term degradation; if (DDE+DDD)/DDT ratio is less than 0.5, a new source of DDT may be in existence. In most cases, the ratios were larger than 0.5 suggesting that DDTs in the sediment from CES mainly came from the residues of historically used DDT. These results confirm the slow degradation pattern of DDT and heavy discharge of untreated or partially treated effluents from nearby industries into the aquatic niche. Contamination by 4,4'-DDD was highest in sediment core N_2 (39.02 ng/g) followed by cores S_2 and N_1. The presence of both 4,4'-DDE and 4,4'-DDD residues in the sediment cores S_2 and N_1 collected from the

southern and northern region of the estuary, indicates significant anaerobic degradation, having occurred in addition to aerobic metabolisation of DDT. One possible anomalous point (maximum of 62.71 ng/g) in the profile for 4,4'-DDE in the sediment core N_1, is the large effluent discharge carried out by nearby industries in the CES, as reported by Dsikowitzky et al. (2014). Moreover, biodegradation of DDT into its metabolites in the riverine ecosystem may be another reason for a higher concentration of its metabolites in these sediment cores as previously reported by Zhang et al. (1999) and Peris et al. (2005) elsewhere.

A relatively high concentration of heptachlor and its isomer were detected in the sediment cores M_1 and M_2 at the top and middle portions, respectively. The residual level of aldrin ranges from BDL to 33.7 ng/g in core M_2 and the highest concentration (33.7 ng/g) was profoundly observed in the 35-40 cm section. The prevalent nature of heptachlor and aldrin in these regions indicate its direct input into the aquatic environment from nearby point sources, followed by rapid burial and preservation under anaerobic sediments (Akhil et al., 2013). Moreover, the abundance of aldrin relative to dieldrin implies that it is widely used in this region.

The highest concentration of endosulfan isomers was detected in the sampling station situated near the industrial zone (core N_2) followed by sediment cores M_1 and M_2, which were collected from the middle zone. The results of the present findings are in line with the available report on the residue levels of endosulfan-α in the surface sediments of CES, ranging from BDL to 43.2 ng/g during 2009 in the northern part of the study area (Akhil and Sujatha, 2014). These variations observed in the concentration level of OCIs and their metabolites in the estuarine sediments may be due to the high influx rate of contaminants into the estuaries through the rivers, agricultural runoff, microbial

activities and various physico-chemical characteristics of the sediments, which in turn influence the abiotic degradation of insecticides (Sarkar, 1994).

Different opinions exist regarding the relation between the concentration of POP's and the respective sediment characteristics. Several earlier researchers have observed that OCIs in sediments are mainly associated with organic matter (Knezovich et al., 1987; Doong et al., 2002; Barakat et al., 2012b) and their total content depends on the grain size distribution (Law and Andrule wicz, 1983; Doong et al., 2002). Though the present study failed to find a correlation between sediment characteristics and the residual levels of OCIs in certain sediment cores (M_1 and M_2), as shown in the Figures 2 and 3, they are in conformity with the findings of de Mora et al. (2004) and Guzzella et al. (2005) reported elsewhere.
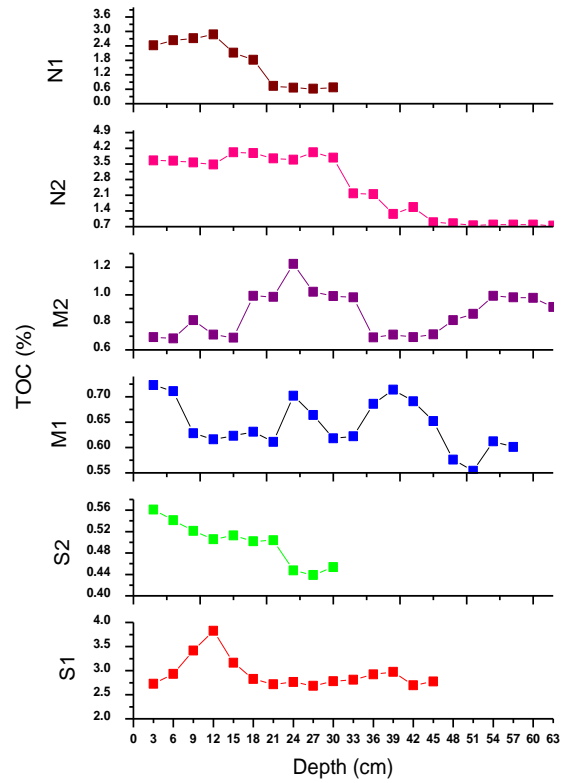

Fig. 2. Distribution pattern of TOC (%) in different cores
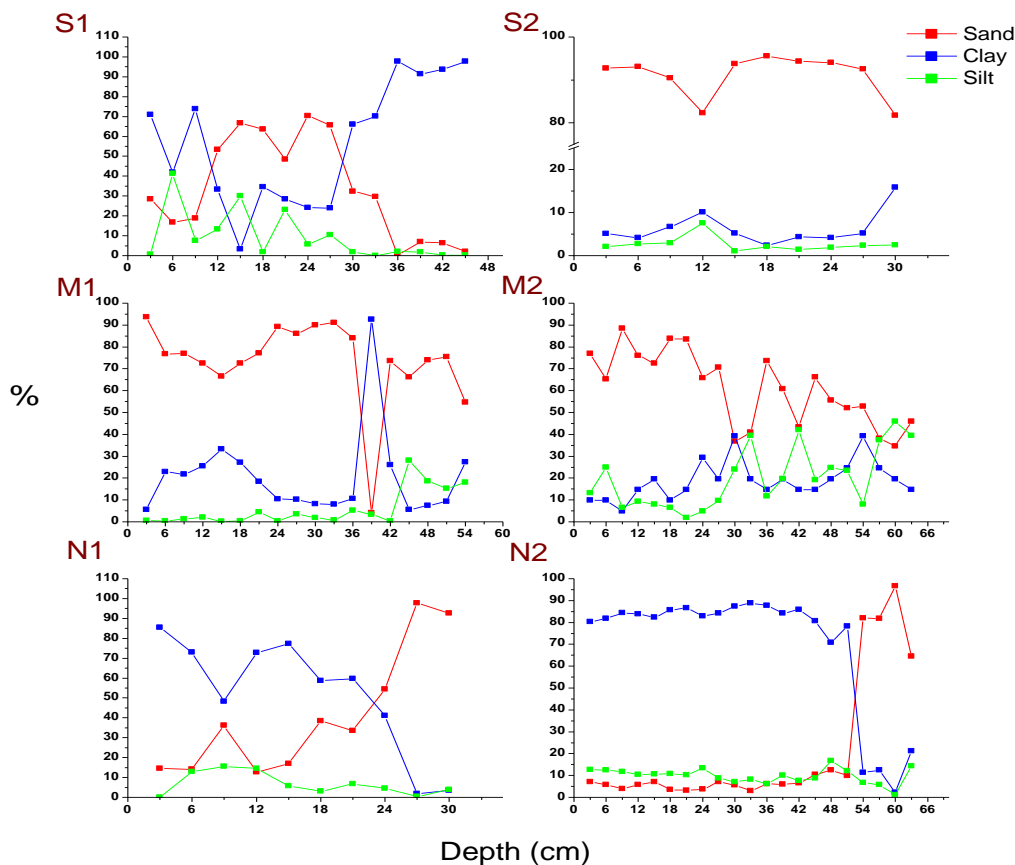

Fig. 3. Grain size distribution pattern (%) in different cores

The typical feature of OCI residues in the middle zone of CES may be controlled by direct continuous regional inputs rather than the natural sorption process on particulate organic carbon. Furthermore, the productive and varying benthic communities at the collection sites (Menon et al., 2000) contribute to the higher level of organic carbon in the sediment, masking any relationships which may exist between POPs and TOC as reported by Guinan et al. (2001).

Accurate reconstructions using sediment core profile data can often be challenging due to site specific environmental contributing factors, which may not support a stable depositional environment. Physical processes such as sediment entrainment induce mixing, winnowing and erosion, which may disturb the sediment record. Previously, Sarkar et al. (2008) reported the prevalence of DDT and its metabolites in all core sediment samples collected from Sunderban wetland ecosystem and the study revealed that there is an irregular pattern, either top to bottom or vice versa, reflecting the non-homogenous input of these compounds in the aquatic niche. A similar trend was observed in the residual levels of OCIs, in the sediment cores of CES. The erratic distribution of these contaminants might be attributed to particular hydrological characteristics of both CES and Sundarban wetland being severely influenced by the monsoon, tidal characteristics and nonhomogeneous inputs from point and nonpoint sources of these xenobiotics. The dispersion process is also influenced by estuarine mixing and resuspension processes in this typical environment. In the Mississippi river delta, Santschi et al. (2001) asserted that the presence of DDTs in the sediments can be controlled by a combination of riverine erosion processes and other sedimentary deposits during floods. In the case of CES, sediment mixing by either natural disturbances such as tidal and water currents, as well as anthropogenic activities such as land reclamation (The Hindu, 2014), influences the interpretation of chronological pollution status in this ecosystem. In addition to these, bioturbation of the sediment by benthic organisms is commonly found to be an issue (Menon et al., 2000) affecting accurate interpretation of sediment core profiles in many sites. The weak flow and the bulk industrial waste thrown out into the northern part of the estuary, leads to high organic input in this area (Akhil et al., 2013; Akhil and Sujatha, 2014) which makes the estuary a copious contaminant zone. Moreover, the elevated C/N ratio in the core sediments indicates a higher contribution of terrigenous material in the study region (Akhil et al., 2013). Recently, Dsikowitzky et al. (2014) reported that the highest contamination by HCH isomers and DDT-metabolites were detected in the water and surface sediment samples collected from the industrial area of CES. The elevated concentration of these compounds in the drainage channel samples confirms the ongoing production of these contaminants in nearby industries.

Moreover, the characteristic morphology of Cochin estuary indicates that it has a settling environment and the sediments are shown to exhibit a low to moderate energy regime in the areas away from the river mouths (Priju and Narayana, 2007). The 2D hydrodynamic model data in CES that were reported previously by Balachandran et al. (2008), reasonably conceptualised that the northern and southern zones are sensitive to environmental stress. The distinction in the residual levels among the analysed sediment cores may be attributed to the possible change in pattern of local economic development practices and waste disposal methods. Furthermore, the present research reveals that instead of restriction in usage, excessive and indiscriminate

adoptions of OCIs is still practised due to the low cost and popularity of the insecticide formulations among the local people.

Ecotoxicological concerns
To determine the potential adverse effects of organochlorine contaminants that cause adverse effects to biota, the concentration ranges of selected analytes from the sampling location were compared to the sediment quality guidelines (SQG), as shown in Table 6.

Since India presently has no established SQGs, the US National Oceanic and Atmospheric Administration (NOAA) guidelines were used as interim measures to assess whether the concentrations of contaminants in sediments could relate to adverse biological impacts. These guidelines were developed based on the analysis of benthic invertebrate communities combined with chemical data from numerous modelling, laboratory and field studies, including several hazardous elements and well known organochlorine contaminants (Long et al., 1995). The

potential environmental risk of OCI residues in the CES was evaluated by two widely used SQGs, that is, the effects range low value (ERL), the effects range medium value (ERM) guidelines and probable effects level (PEL) guidelines from the Canadian Council of Ministers of the Environment (CCME, 1999; Mechdonald et al., 2000). ERLs represent chemical concentrations below which adverse effect would be rarely observed; ERMs represent the chemical concentration above which adverse effects would frequently occur. The probable effect level (PEL) defines the level above which adverse effects on aquatic biota are expected to occur frequently. The comparison of the present data with these guidelines shows that the organic contaminants have exceeded the threshold limits. Therefore, the adverse effects on benthic species can be expected at all stations. Based on earlier reported values from other regions in the world, the present study infers that sediment from CES is of higher toxicity than those from other locations (Table 7).

Table 6. Comparison of OCI concentrations in the study area (ng/g dry wt.) with toxicity guidelines

Compound	SQGs, ng/g d.w.			Stations (S)		
	ERL	ERM	PEL	S of ERL ~ ERM	S of >ERM	S of >PEL
$\sum$DDTs	1.58	46.1	51.7	M_2	N_1,N_2,S_2	N_1,N_2,S_2
o,p'- and p,p'-DDD	NA	NA	8.51			N_1,N_2,S_2
o,p'- and p,p'-DDE	NA	NA	6.75			N_1,S_2,M_2
o,p'- and p,p'-DDT	NA	NA	4.77			N_2
p,p'-DDD	2	20	7.81	None	N_1,N_2,S_2	N_1,N_2,S_2
p,p'-DDE	2.2	27	374	M_2,S_2	N_1	None
p,p'-DDT	1	7	4.77	None	None	None
Endrin	0.02	45	62.4	None	M_1,M_2,N_2	M_1,M_2,N_2
Dieldrin	NA	8	6.67		None	None
Lindane	NA	NA	1.38			M_2,S_1,S_2
Heptachlor Epoxide	NA	NA	2.74			M_1

Table 7. Distribution pattern of OCIs (ng/g dry wt.) in surface sediment samples from various ecosystems

Location	Year	∑DDT	∑HCH	Aldrin	Dieldrin	Endrin	References
Xiamen Harbour	1992	4.5-311	0.14-1.12	NA	NA	NA	Hong et al., (1995)
River Wuchuan, Southeast China	2000	0.47-2.14	0.21-3.85	0.02-0.87	0.03-0.24	0.02-0.13	Zhang et al., (2002)
Minjiang River Estuary, Southeast China	2000	1.57-13.06	2.99-16.21	0.47-2.23	0.67-1.79	0.27-2.43	Zhang et al., (2003)
Qiantan River, East China	2005	8.64-100.2	19.74-152.1	0.36-19.56	< 0.15-28.40	< 0.16-52.37	Zhou et al., (2006)
Northeastern Part of Sao Paulo State, Brazil	2004	0.05-0.92	0.12-11.01	< 0.04-0.23	0.05-0.96	< 0.05-0.25	Rissato et al., (2006)
Sunderban wetland, India	2005	0.05–11.5	0.05–12	NA	NA	NA	Sarkar et al., (2008)
Bosomtwi Lake, Ghana	2006	15.06-31.92	2.03-13.94	0.30-0.46	0.20-0.46	NA	Darko et al., (2008)
Gomti River , India	2004	1.63-368.7	BDL-155.17	< 0.11-0.89	< 0.05-1.65	< 0.05-11.96	Malik et al.,(2009)
Tamiraparani River, India	2008	< 0.01-857	< 0.01-472	< 0.02-562	< 0.03-1693	NA	Kumarasamy et al., (2011)
Maryut Lake, Egypt	2005	0.07-105.6	BDL-2.20	NA	NA	NA	Barakat et al., (2012)
Cochin Estuary	2009	BDL-229	BDL-423	BDL-33.2	BDL	BDL-103.1	Akhil and Sujatha, (2014)

NA: Not available, BDL: Below detection limits

CONCLUSION
The elevated concentration of OCIs in the northern zone of the estuary is due to the direct discharge of partially treated or untreated industrial effluents into the River Periyar. Despite the restriction in use, the prevalent nature of OCIs in the core sediment reflects the illegal use, runoff from the tributaries, the persistent nature and the lipophilic character of these contaminants. The vertical distribution of these trace contaminants in the CES, reveals an erratic pattern in all the sampling stations due to the varying environmental conditions existing in the CES. The concentrations of three isomers of HCHs showed a heterogenic distribution, where γ-HCH (lindane) and β-HCH shared the dominant part. However, the prevailing sequence of DDT metabolites indicates the slow degradation pattern of the parent compound in the sediments and heavy discharge of untreated or partially treated effluents from nearby industries into the aquatic niche. The peak concentrations of HCH isomers and DDT metabolites have the potential to induce ecotoxicological impact, as per the sediment quality guidelines.

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