

Distribution and contamination status of phthalic acid esters in the sediments of a tropical monsoonal estuary, Cochin – India

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Abstract:

Phthalic acid esters (PAEs) are a group of endocrine-disrupting chemicals listed as priority pollutants by United States Environmental Protection Agency (USEPA 2009). This study provides baseline information on seasonal distribution and contamination status of six phthalic acid esters (Σ_6 PAEs) in sediments of a tropical estuary (Cochin-India). In general, the sediments accumulated more PAEs during the post monsoon (mean 2325 ngg⁻¹; between 1402-3121 ngg⁻¹) and monsoon (mean 1372 ngg⁻¹; between 331 - 4015 ngg⁻¹) periods indicating land run off as the major transport pathway. Moderate run off and comparatively high residence time lead to effective sorption and settling of PAEs in the surface sediments during post monsoon season. Despite a high discharge of PAEs in to the water column, their deposition on to the sediments occurs at a lower rate during monsoon than that post monsoon season. PAEs were (mean 810 ngg⁻¹; between 44-1722 ngg⁻¹) lowest in pre monsoon season. The pre monsoon season is characterised by a minimal runoff consequent to the trapping of these organic pollutants in the river catchment area. The mid and high molecular PAEs (DEHP-Di Ethylhexylphthalate , BBP-Benzyl butyl phthalate and DnBP-Di-n-butyl phthalate) were the dominant congeners relative to the low molecular weight congeners (DMP-Dimethyl phthalate and DEP-Diethyl phthalate). DEHP and BBP levels exceeded permissible risk levels indicating a serious ecological hazard to the estuarine ecosystem.

Key Words: Phthalic acid esters; Sediments; Ecological risk; Cochin estuary

1. Introduction

PAEs are a class of synthetic organic chemicals extensively used in plastic industry and consumer products. While low molecular weight PAEs are used as additives in industrial solvents, adhesives, waxes, perfumes, and insecticides (to enhance the fragrance, duration of scent, etc.), medium and high molecular weight PAEs are widely used in plasticisers (to improve handling characteristics)(Staples et al., 1997; Sun et al., 2013). Since PAEs are not chemically bonded to the polymeric matrix, they easily find their way to aquatic ecosystems through leaching, direct discharge, surface runoff and atmospheric deposition to causing serious ecological risk to the biota (Okamoto et al., 2011; Net et al., 2014). PAEs are potential endocrine-disrupting chemicals (EDCs) and carcinogenic materials which may lead to severe health problems including reproductive abnormalities(Agarwal et al., 1986; Huber et al., 1996). USEPA and European Union (EU) categorize six types of PAEs as major pollutants because they easily get attached to suspended matter/sediments due to their hydrophobic character and enter the food web (USEPA, 2009; Sun et al., 2013; Cheng et al., 2016).

Estuaries and coastal regions, being a transition zone between the land and ocean, receive high amount of organic contaminants which pose severe ecological threats to aquatic organisms (Li et al., 2015; Li et al., 2017). The source and distribution of PAEs have been comprehensively documented in numerous rivers, estuaries and coasts including Pearl River estuary, China (Li et al., 2016), Kaohsiung Harbour, Taiwan (Chen et al., 2013), Marseille Bay, Mediterranean Sea (Paluselli et al., 2018), Changjiang estuary, Chia (Zhang et al., 2018), Julong River, China (Li et al., 2017), Mediterranean Sea and Rhone river (Paluselli et al., 2017). However, studies on the distribution and contamination of PAEs in aquatic systems in India are scarce except for a few rivers (Srivastava et al., 2009; Selvaraj et al. 2014).

Cochin estuary, the largest estuarine system along the southwest coast of India, is exposed to serious environmental degradation due to increased anthropogenic activities - industrialization, urbanization, inter-tidal land reclamation, port and harbor development, and aquaculture activities(Menon et al., 2000; Salas et al., 2017). Periyar and Muvattupuzha rivers are the major sources of fresh water in the northern and southern side of the estuary respectively. More than 70 % of the industrial establishments in Kerala State are situated along the banks of these rivers and they manufacture fertilisers, pesticides, catalysts, paints, pigments, rayon, paper, textiles, ply-wood, petrochemicals, and organic chemicals(Ramzi et al., 2017; Salas et al., 2017). These industrial units consume 189,313 m³ of fresh water per day and release untreated effluents to the estuary (Salas et al., 2017). Rising pollutant levels marked by high concentrations of N, P, heavy metals, pesticides, and

poly-aromatic hydrocarbons (PAHs) have been reported (Deepulal et al., 2012; Akhil and Sujatha, 2014; Chakraborty and Babu, 2015; Ramzi et al., 2017).

The increased urban settlement has led to an exponential increase in the production and consumption of plastic materials in India, out of which more than 50-60% remains non-biodegradable (Srivastava et al., 2010; Selvaraj et al., 2015). The large number (800 units) of small-scale industries in the greater Cochin area lead to the production of more than 10 tonnes of such plastic wastes, which are a significant source of PAEs in the adjoining estuary (CPCB, 2015). Vital baseline data brought out through this study, on the status of PAEs in surficial sediments of Cochin estuary, is expected to help trigger appropriate legislative action to curb and prevent such pollution. Six PAEs listed as priority pollutants by USEPA and UE have been selected for this study owing to their high toxicity to biota.

2. Materials and methods

Study area

Cochin estuary (9°40′-10°12′ N and 76°10′-76°30′), a micro-tidal (amplitude ~1 m) monsoonal estuary parallel to the Arabian Sea, is the largest estuarine system (256 km²) along the west coast of India (Fig. 1). Topographically, this ox-bow shaped estuary has a wider (0.8-1.5 km) and deeper (4-10 m) southern part as well as a narrow (0.05-0.5 km) and shallow (0.5-2.5 m) northern part. The estuary is connected to the Arabian Sea through a 150 m wide inlet at Munamban and a 450 m wide inlet at the Cochin barmouth. The estuarine hydrography is regulated by freshwater inputs from six rivers (Periyar, Muvattupuzha, Pamba, Manimala, Achankovil, and Meenachil) and the tidal forcing through the two inlets (Srinivas et al., 2003). During summer monsoon (June–September), the high freshwater flow (1280 m³s⁻¹) virtually converts the estuary into a freshwater ecosystem (Revichandran et al., 2012). During post monsoon period (October–December), there is a considerable reduction in the freshwater input (225 m³s⁻¹), when the increased tidal activity transforms the estuary into a partially mixed type. The river runoff is at its minimum (26 m³s⁻¹) during pre monsoon period (January- May), when the tidal activity changes the estuary into a completely mixed system (Menon et al., 2000; Gireeshkumar et al., 2013). Hydraulic barriers erected at Thanneermukkam, Pathalam and Purappallikkavu prevent seawater intrusion into the southern estuary (Kuttanad) and the northern (near Aluva) estuary during pre monsoon season (Shivaprasad et al., 2013). These barriers are found to severely reduce the flushing characteristics and increase the accumulation of pollutants in the estuary in varying degrees.

Sampling and laboratory analysis

Sediment samples were collected from 15 locations in the Cochin estuary (Fig. 1) using a Van Veen Grab (0.42 m²) during May, August and December 2013 representing pre-monsoon, monsoon and post-monsoon seasons respectively. Several deployments were carried out using the grab to obtain a well-preserved sediment sample from each station. The surface layer (4 cm) of the sediment was scooped out and transferred to amber colored glass bottles using a clean stainless steel spatula, stored in ice and transported to the laboratory and kept at -20°C until analysis. Sediment grain size was analyzed following (Folk 1980). One portion of the sediment was freeze-dried, homogenized and finely powdered using agate mortar and pestle. Total organic carbon was estimated using Vario EL III CHNS analyzer (detection limit 0.07%) after treating with 1M HCl (to remove carbonates). Acetanilide was used as the standard for the calibration of CHNS analyzer. The monthly rainfall data during the year 2013 was collected from Kerala Groundwater Department, and the seasonal averages were calculated.

Standards and reagents for PAEs

Six congeners of PAEs comprising of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butylphthalate (DnBP), Benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DnOP) at a concentration of 100 µg ml⁻¹ obtained from Supelco, USA (EPA 606-M Phthalate ester Mix) were used as a mixed standard for PAE calibration. All materials used for the analysis such as silica gel (60-120 mesh), alumina (100-200 mesh) and filter papers were subjected to Soxhlet extraction using a 1:1 mixture of methanol and dichloromethane for 72 hours. Silica gel and alumina were activated at 180°C and 250°C respectively for 16 hours followed by deactivation using distilled water. Anhydrous sodium sulfate was heated at 450°C in a muffle furnace for 6 hours, wrapped with aluminum foil and stored in sealed glass containers. Chromatography grade (Merck, Lichroslov) organic solvents were used for all extractions and analysis. All glassware was soaked in chromic acid, dried in the hot air oven and washed with methanol and dichloromethane before use.

Extraction and fractionation of phthalic acid esters

Detailed extraction procedure for the analysis of PAEs is detailed elsewhere (Zeng et al., 2008; Liu et al., 2014). 10g of freeze-dried, homogenized and finely powdered sediments were soxhlet extracted with dichloromethane for 48 hours. Elemental sulfur was removed using activated copper granules. Extracts were further concentrated using a rotary evaporator, re-dissolved in 2 ml n-hexane and passed through chromatographic glass column packed in 12 cm silica gel and 6 cm alumina. The column was eluted successively using 20 ml of n-hexane (Fraction 1), a mixture of 50 ml 7:3 n-

hexane and dichloromethane (Fraction 2) and a mixture of 50 ml 4:1 n-hexane and acetone (Fraction 3). Fraction 3 contains all PAEs, which was concentrated using a rotary evaporator and dried under a gentle stream of N₂ gas, dissolved in 100 µl n-hexane, mixed thoroughly using a vortex mixer and kept at -20°C until the analysis.

Instrumental analysis

The Concentration of different congeners of PAEs was analyzed using a Gas Chromatograph connected with a flame ionization detector (Perkin Elmer Clarus 600) and a data acquisition workstation Total Chrom. The efficacy of GC-FID method for the analysis of PAEs was detailed by Yan et al., 2010 and Gao and Chi, 2015. GC was connected with a PE-5 (5% diphenyl and 95 % dimethylsiloxane) capillary column (30 m length, 0.32 mm inner diameter, 0.25 µm thickness). The temperature of the column was maintained at 60°C for the initial 2 min, then increased at a rate of 10°C per min and between 120–300°C increased at a rate of 3°C per min and maintained at 300°C for 5 min. Injector and detector were kept at 280°C and 325°C respectively. PAE quantification was performed using a mixed standard containing 6 USEPA priority pollutants and following a five-point calibration for each congener. Each of the peaks was confirmed using a GC-MS (Perkin Elmer Clarus GC 620 - Clarus 600T MS detector) connected with a non-polar HP ultra-double-fused silica capillary column (30 m, 0.32mm internal diameter, 0.25µm film thickness). Operational conditions included an ion source of 70eV electron voltage kept at 200°C.

Quality control and quality assurance

Since PAEs are known for background contamination, it is very difficult to measure their concentrations accurately. Therefore, we have taken extreme care to minimize the contamination during the sample collection, storage, extraction, purification and GC analysis following David et al., (2003). All quality control measures were strictly followed during the analysis. A procedural blank, spiked blank and two sample duplicates were analyzed with each set of the sample (a batch of 15 samples). The method was standardized with a five-point calibration curve using the standard mixtures. The efficiency of extraction estimated by addition of standards (PAE standards mixture in triplicates containing 50, 100 and 200 ng each was mixed with 10g sediments) was 94±5% for DMP, 95±7% for DEP, 96±8% for DnBP, 83±8% for BBP, 88±9% for DEHP and 96±8% for DnOP. The PAE concentrations were corrected considering the percentage recoveries of respective PAE congeners and expressed in dry weight (Table 1).

One way analysis of variance (ANOVA) and Pearson correlation analysis was done using 'Statistical Package for Social Sciences (SPSS), version-13'. ANOVA assessed spatial and seasonal variations with season and space (stations) as a source of variation.

3. Results and discussion

Texture and TOC variations in sediments of Cochin estuary were reported previously (Ramzi et al., 2017). The central portion of the estuary was rich in fine particles (clay and silt), while coarser particles dominated the northern and southern sides (Fig. 2). TOC ranged from 0.52-5.32%, 0.55-3.76% and 0.45-3.96% in pre monsoon, monsoon and post monsoon, respectively.

Spatial and seasonal distribution of \sum_6 PAEs

Concentrations of the six PAEs identified as major pollutants by USEPA (Fig. 3) varied from 44 to 1722 (mean 810 ngg⁻¹), 331 to 4015 (mean 1372 ngg⁻¹) and 1402 to 3121 ngg⁻¹ (mean 2325 ngg⁻¹) during pre-monsoon, monsoon and post monsoon periods respectively. The distribution of PAE was characterized by an accumulation during post monsoon followed by its dilution during monsoon and pre monsoon seasons. During the premonsoon season, the central portion (stations 4-8) and southern side (stations 11 & 12) of the estuary showed PAE accumulation (1184-1722ngg⁻¹) as comparable to the inlet (Station 1) and northern side (stations 13-15). During monsoon, the PAE contents were relatively low (331-1656 ngg⁻¹) in the central portion of the estuary, while it was substantially higher in the southern (1355-4016 ngg⁻¹) and northern (1624-1747 ngg⁻¹) regions (Muvattupuzha and Periyar Rivers).

The distribution of PAEs in the sediments can be explained regarding their specific adsorption, deposition, dilution and partitioning mechanisms (Staples et al., 1997; Sun et al., 2013). During the low discharge period (pre monsoon), high molecular weight (more hydrophobic) PAEs such as DnBP, DEHP, and BBP get adsorbed on suspended particles and eventually get deposited onto sediments. The significant seasonal variation (p<0.01) reflects fluvial input influenced by the variable freshwater discharge and the tidal activity through the two inlets. During the pre-monsoon season, when freshwater flow is a minimum (Vinita et al., 2015), pollutant input is considerably reduced, as evident from the lower PAEs concentrations at the riverine side (stations 10-12 and 13-15). The significant positive correlation of organic carbon, clay and silt with all the PAE congeners (especially DEHP and BBP) during pre monsoon season indicates that the weak flow and reduced input favor a stable binding of the available PAE congeners with the organic matter in estuarine sediments (Fig.4).

An increased freshwater flow (694 mm average rainfall) during monsoon leads to increased loading of PAEs into the estuary, as is obvious from the elevated PAEs in the dissolved and particulate phases (Ramzi et al. per comm). Settling of suspended sediment is a minimum during high freshwater flow periods since flocculation occurs at increased salinity levels. While a major portion of the suspended particles containing PAEs are exported to the coastal ocean by the high freshwater flow (Vinita et al., 2015), a fraction is deposited in the estuary, as evidenced by the relatively higher proportion of PAEs in the sediments during monsoon, as compared to the pre monsoon period. Post monsoon is a transitional period when the estuary becomes highly saline, leading to increased flocculation of suspended particles (Nair and Balchand, 1993; Vinita et al., 2017). The pre monsoon season was a minimum discharge period when the input of PAEs was also low.

It should be noted that a recent study has reported a high PAH accumulation in the sediments of Cochin estuary during monsoon (Ramzi et al., 2017). This is significantly different from the present study where the PAE concentrations were high in the same regions during post monsoon. This may be due to the differential degradation of PAHs and PAEs in aquatic environments. PAHs are susceptible to photolysis, chemical oxidation, and biodegradation (Abdel-Shafy and Mansour, 2016). The estuarine conditions during monsoon are characterized by reduced light, temperature and high turbidity, which may significantly reduce degradation of PAHs. During post monsoon season, the high solar irradiation and low water column turbidity favor an increased degradation of PAHs. In contrast, PAEs are resistant to photolysis and are degraded only by microbial activity (Peterson and Staples, 2003). Certain organic contaminants like surfactants can even act as a stimulant and increase the rate of biodegradation of PAHs (Rouse et al., 1994; Adrion et al., 2016). Therefore, assessment of the cumulative effects of such contaminants and their synergetic/antagonistic behavior in highly impacted aquatic environments will be a challenging task for researchers.

PAEs are extensively used in a variety of consumer, household and industrial products. For example, Polyvinyl chloride contains approximately 40% DEHP, while polyurethane, polysulfide and acrylic-based polymers contain BBP as plasticizer (Cao 2010). DnBP is used as a plasticizer in polyvinyl chloride, polyvinyl alcohol and rubber. It is also used as solvent and fixative in paints and cosmetics, whereas DnOP is extensively used in flooring, tarps, conveyer belt etc. (ECHA 2009). Besides, the lower molecular weight PAEs such as DMP and DEP are also used in cosmetics and baby care products (SCCP 2007).

Spatial and seasonal distribution of PAE congeners

The relative abundance of different PAE congeners were in the order DEHP>BBP > DnBP > DEP>DMP> DNOP in all the three seasons. DEHP concentrations were in the range n.d (not detectable) -1304ngg⁻¹, 30-3650 ngg⁻¹ and 982-2388 ngg⁻¹ in pre monsoon, monsoon and post monsoon respectively. BBP ranged from 8 to 381 ngg⁻¹ in pre monsoon, 37 to 360 ngg⁻¹ in monsoon and 207 to 502 ngg⁻¹ in post monsoon. DEHP and BBP exhibited a significant seasonal variation (p<0.01) characterized by high concentrations in post monsoon season followed by monsoon and pre monsoon seasons. However, other PAE congeners did not display any significant spatial or seasonal variability. DnBP was in the range 19 - 290 ngg⁻¹, 6 - 323 ngg⁻¹ and 3 - 349 ngg⁻¹ in pre monsoon, monsoon and post monsoon respectively. DEP and DEP were low in sediments and did not contribute significantly to the \sum_6 PAEs. DMP ranged from n.d to 159 ngg⁻¹ in pre monsoon, n.d to 153 ngg⁻¹ in monsoon and n.d to 565 ngg⁻¹ in post monsoon, whereas the DEP was in the range n.d - 565 ngg⁻¹ in pre monsoon, n.d - 240 ngg⁻¹ in monsoon and n.d - 48 ngg⁻¹ in post monsoon. DMP was high (319 ngg⁻¹) at station 5 during post-monsoon, whereas DEP was high (565 ngg⁻¹) at station 1 during pre-monsoon. The high molecular weight fraction (DnBP) was present up to 290ngg⁻¹, 323 ngg⁻¹, and 349 ngg⁻¹ during pre-monsoon, monsoon and post-monsoon, respectively. The maximum concentrations of other high molecular weight congeners were BBP (381ngg⁻¹, 360 ngg⁻¹ and 502 ngg⁻¹), DEHP (1304ngg⁻¹, 3650ngg⁻¹, and 2388 ngg⁻¹) during respective periods, while DnOP showed no significant seasonal or spatial variation (p>0.01).

High DEHP concentrations in this study indicate that its more strong sorption capacity and lower degradation (Sun et al., 2013). The major reason for its greater accumulation in sediment is its wide-spread use (IARC 2010). Accumulation of the BBP is also relevant, as it may easily enter the estuarine organisms and also human body through consumption. Enrichment of DEHP, BBP and DnBP congeners of PAEs in the estuary has serious environmental significance because they are endocrine-disrupting chemicals. The other congeners were in moderate levels as compared to other environments.

Comparison with other studies worldwide

Investigations on PAEs in estuaries around the world (including India) are scarce. A comparison of available data (Table 2) shows that Cochin estuary has the highest PAE concentrations among Indian riverine estuaries (Srivastava et al., 2010; Selvaraj et al., 2015), though it is lower than values reported elsewhere (Lake Guangzhou, Zeng et al., 2008; Lake Beijing, Zheng et al., 2014; Pearl River, Liu et al., 2014a; Pearl River estuary, Li et al., 2016; Kaohsiung Harbour,

Chen et al., 2013; Anzali Wetlands, Hassanzadeh et al., 2014; Italy, Vitali et al., 1997; and North Sea, Vethaak et al., 2005). Sedimentary PAEs are also higher than those reported for False Creek Harbour (Mackintosh et al., 2006) and Ogun River (Adeniyi et al., 2011).

Ecological risk assessment of PAEs

Contaminants in sediments can adversely affect the benthic organisms through direct toxicity and the alteration of community structure or diversity (Chapman, 1989). Since there are no universally accepted sediment quality criteria, numerical sediment quality guidelines (SQGs) proposed by various international organizations and authors have been used to assess the ecological risk posed by a particular contaminant (MacDonald et al., 2000). PAEs that are bio-available and may cause severe eco-toxicological effects for benthic biota associated with the Cochin estuary and may have human health implications. SQGs (Zeng et al., 2008; Feng et al., 2016) help identification of PAE-related eco-toxicological effects in ecosystems. Sediment DEHP concentration of 182 ngg⁻¹ is set as its threshold effect level (TEL) and 2647 ngg⁻¹ as its probable effect level (PEL) (MacDonald et al., 1996). Concentrations below the TEL level do not pose any threat to biota, while those between TEL and PEL can cause occasional threats, and if it is > PEL, it may have lethal effects on biota. DEHP concentration, Cochin estuary sediment contained moderate levels between TEL and PEL (182-2647 ngg⁻¹) during post monsoon, indicating chances of occasional adverse impact. Similar was the condition at one location (station 12) during monsoon as well, indicating its exceedingly higher accumulation in the upstream locations (Table 3). DEHP values in the estuary were < TEL during pre monsoon and pointed to the absence of any toxicological effects due to this component.

Alternate methods such as Maximum Permissible Concentration (MPC) and Serious Risk Concentration (SRC_{eco}) are also widely employed to assess the ecological risk posed by PAEs (Verbruggen et al., 2001; Chih-Feng et al., 2016). To evaluate these indices, the PAEs concentrations are normalized to 10 % of organic matter before comparing it with MPC and SRC_{eco} values. Application of these methods on the present data shows that the DEHP, BBP and DnBP concentrations are > MPC, indicating PAE contamination of the estuary in the order DEHP > BBP > DnBP. On the other hand, concentrations of DMP and DEP are < MPC and SRC_{eco}, indicating normal levels of these congeners in the estuary (Table 3). Furthermore, (Van Wezel et al., 2000) van Wezel et al., 2000 have proposed the ERLs for DnBP and DEHP causing potential risk to the ecosystem as 0.7 and 10 µg/g in sediment containing 10 % of organic matter. A comparison shows that the present values are generally well above the ERL values. The enhanced PAE concentrations observed in Cochin estuary have serious ecological implications because, the synergistic effects due

to both PAEs and PAHs could be even severe to the entire estuarine community, which has already started showing alarming signals (Martin et al., 2011).

4. Conclusion

This study provides the first set of data on the distribution of PAEs in surface sediments of Cochin estuary. The results show that the sediments were contaminated by PAEs to varying degrees depending on the hydrodynamics of the estuary. Land drainage was found to be a major source of PAEs into the estuary. Of the six PAE congeners, DEHP and BBP congeners far exceeded their threshold limits (TEL, MPC, and SRC_{eco}) and could lead to severe detrimental biological effects on the benthic biota.

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Figure Captions

Figure 1 Map of the study area showing the locations of sampling stations.

Figure 2 Seasonal distributions of grain size and total organic carbon in surface sediments of Cochin estuary.

Figure 3 Seasonal distributions of phthalic acid esters in surface sediments of the Cochin estuary.

Figure 4 \sum_6 PAEs vs. clay, silt, and TOC in surface sediments of the Cochin estuary.

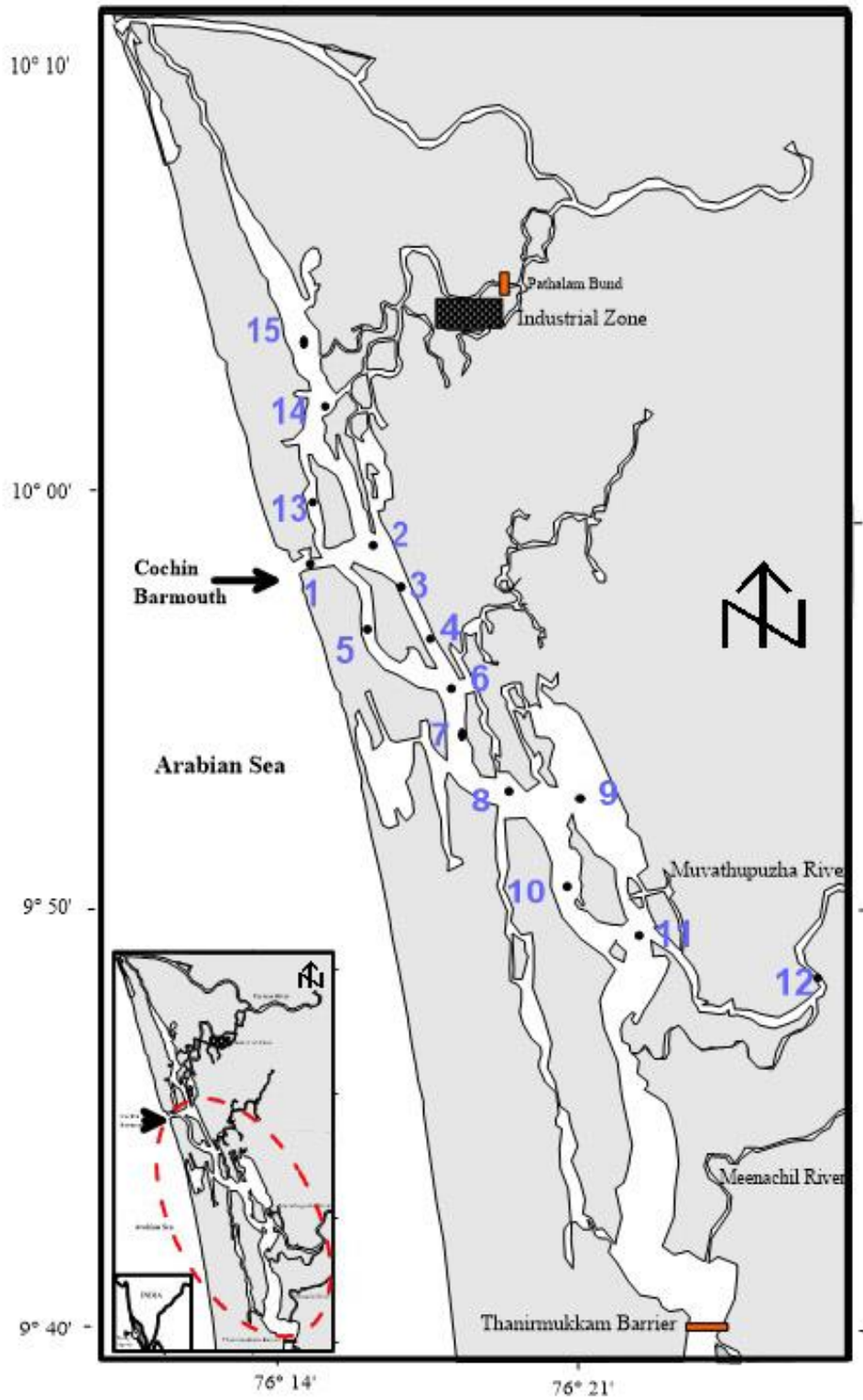


Figure 1

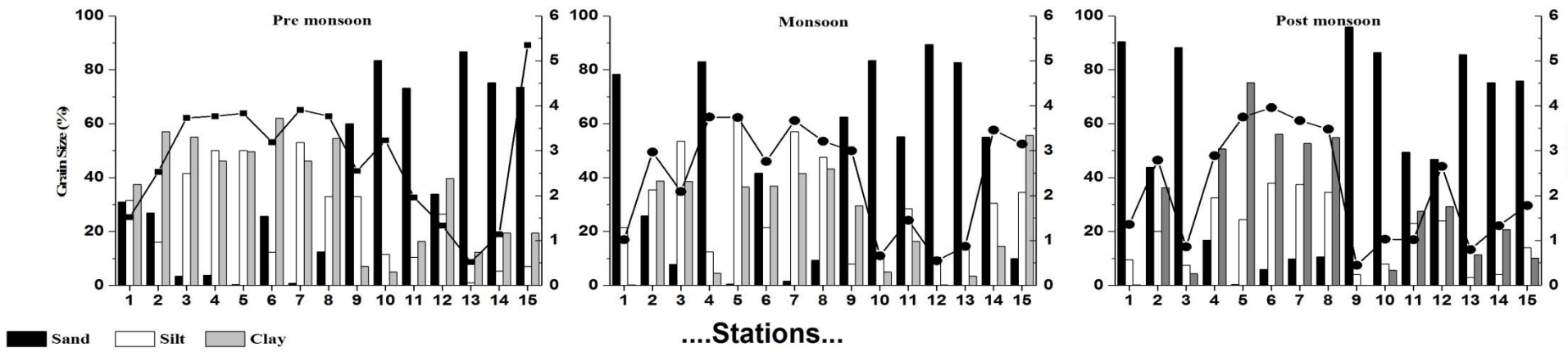
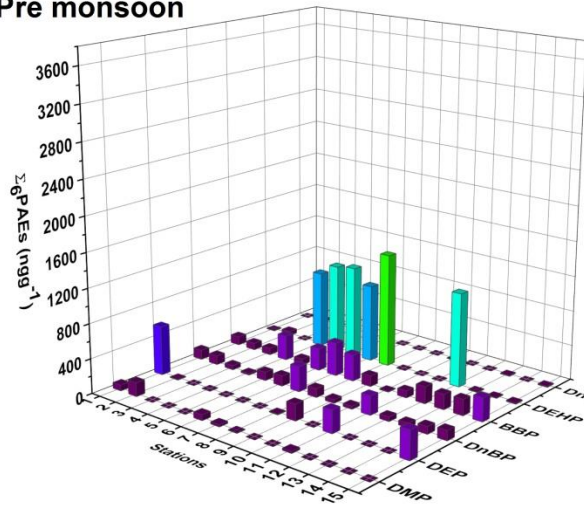
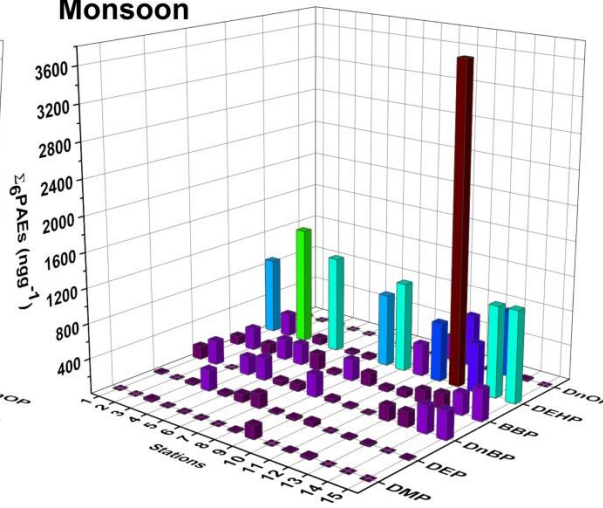


Figure 2

Pre monsoon



Monsoon



Post monsoon

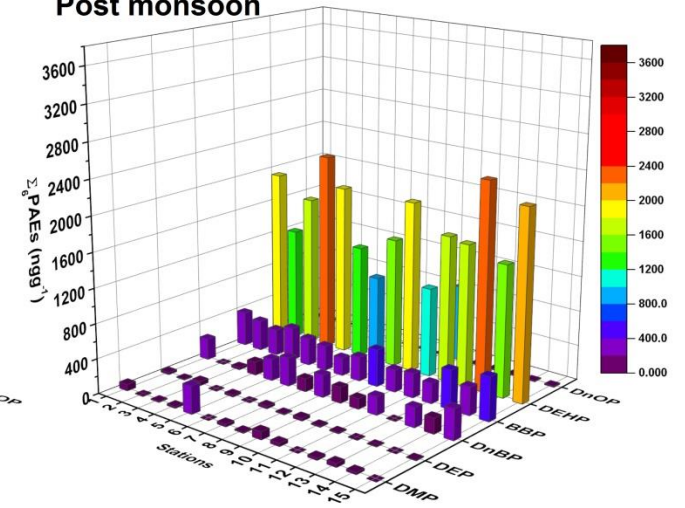


Figure 3

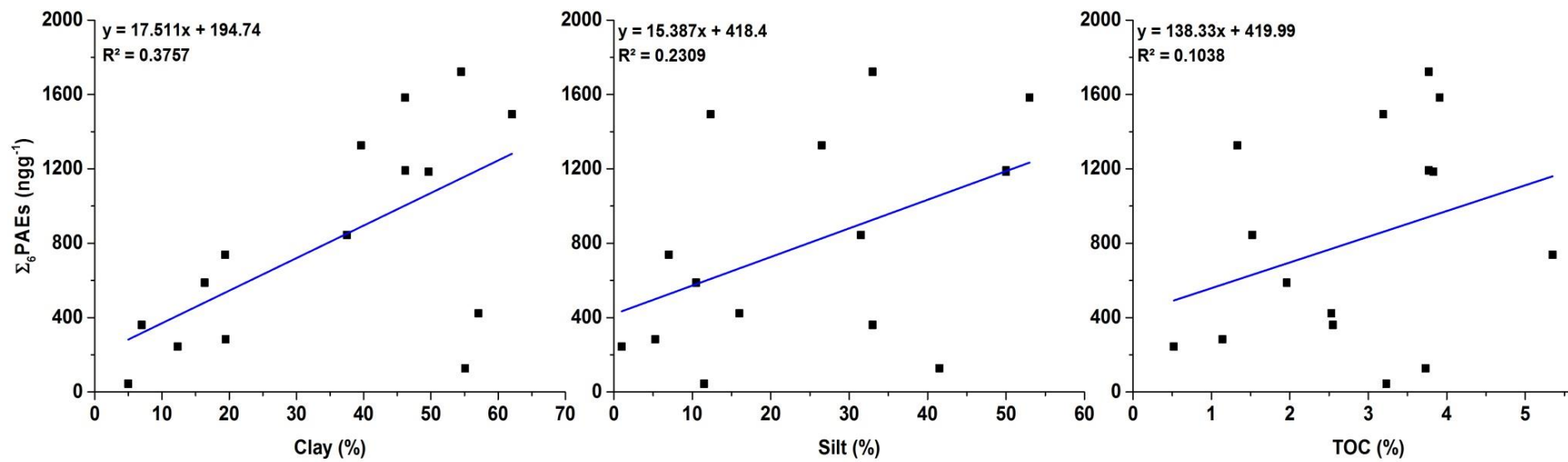


Figure 4

Table 1Summary of concentration ranges of PAEs (ngg⁻¹) in sediments of Cochin estuary.

PAEs	LOD (µgL ⁻¹)	LOQ Sediment (ngg ⁻¹)	Pre monsoon				Monsoon				Post Monsoon		
			Range	Mean	Median	D.F	Range	Mean	Median	D.F	Range	Mean	Median
DMP	4.38	1.19	n.d- 159	23	14	87	n.d-153	17	5	73	n.d-319	46	25
DEP	4.00	1.00	n.d-565	91	5	93	n.d-241	49	23	93	1-48	15	10
DnBP	3.64	0.91	19-290	99	98	100	1-323	157	170	100	3-349	179	181
BBP	3.44	0.86	8-381	172	174	100	37-360	175	177	100	207-502	331	312
DEHP	4.00	1.00	n.d-1304	420	51	100	30-3650	863	829	100	982-2388	1685	1672
DnOP	4.38	1.19	n.d-25	4	4	80	1-753	111	2	100	7-880	69	11
∑6PAEs	-	-	44-1722	810	738	100	331-1747	1184	1363	100	1402-3121	2325	2181

LOD – Limit of Detection, LOQ-Limit of quantification, DF-Detection Frequency (%), n.d – not detected

Table 2 Comparison of PAEs in the Cochin estuary with those reported from other locations (concentrations in ngg⁻¹ dry weight).

Study Area	No. of PAEs studied	∑PAEs	DMP	DEP	DnBP	BBP	DEHP	DnOP	References
Lakes in Guangzhou City , China	16	2270-74940	1-430	28-1050	82-1260	nd-280	210-14160	nd-629	Zeng et al., 2008
Lakes of Beijing, China	15	5-8216	53-287	5-125	55-1909	9-890	338-8117	21-3479	Zheng et al., 2014
Kaohsiung Harbor, Taiwan	6	400-34800	nd	nd	nd-2780	nd	1930-86400	nd-1350	Chen et al., 2013
Pearl River Delta region, China	16	567-47300	1–19	1–91	108–12400	nd -113	415–29500	nd-181	Liu et al., 2014
Anzali Wetlands on the Coast of Caspian sea, Iran.	2	370- 62140	120 - 19020	...	250- 43120	...	Hassazadeh et al., 2014
Pearl River Estuary, China	6	880-13600	nd-1750	nd-180	56-4660	nd-160	470--8530	nd-310	Li et al., 2016
Urban soil of Beijing, China	7	1822 – 28087	nd-67	nd-252	149-936	nd- 60	170-6491	nd-172	Li et al., 2006
Taiwan China	6	900-63200	100-1100	300-30300	nd-1800	500-23900	...	Yuan et al., 2002
False Creek Harbour, Canada	13	4-2100							Mackintosh et al., 2006
Ogun River, Nigeria	4	330-2880	nd-850	80-350	190-1420	20-820	Adeleke et al., 2011
Ronnebyan/Svartan River, Sweden	4	1200-8030	nd	100-148000	Thuren, 1986
Klang River Basin, Malaysia.	6	1942000							Silva et al., 2012
Rieti District, Italy	6	94200	1200-14000	3500-76000	1500-17200	3200-487000	4000-16700	Vitali et al., 1997
North Sea, the Netherlands.	6	689-22595	1-2500	65-1200	34-1000	5.0-60	123-7600	2-55	Vethaak et al., 2005
Gomti River, India	6	0-1870	nd-490	nd-350	...	nd-340	nd-3240	nd-530	Srivastava et al., 2009
Kaveri River, India	6	2-1438	nd-2	nd-16	nd-36	nd-3	nd-278	nd-3	Selvaraj et al. 2014
Cochin Estuary, India	6	44-4015	0-318	0-565	1-349	8-2388	0-3650	0-875	This study

nd – not detected

Table 3 Comparison of the PAEs with various sediment quality guidelines

PAEs	MPC (ngg⁻¹ at 10 % TOC)	SRC_{eco} (ngg⁻¹ at 10 % TOC)	ERL (ngg⁻¹ at 10 % TOC)	Pre Mon (ngg⁻¹ at 10 % TOC)	Mon (ngg⁻¹ at 10 % TOC)	Post Mon (ngg⁻¹ at 10 % TOC)
DMP	1000	84000	-	n.d-627	n.d-508	n.d-2006
DEP	94000	580000	-	n.d-3715	n.d-828	11-719
DnBP	2100	36000	700	49-1118	4-3068	13-4066
BBP	1400	48000	-	25-3352	102-2713	564-9535
DEHP	1000	10000	1000	n.d-8098	110-65914	2675-29857
DnOP	-		-	n.d-171	2-8613	19-8566

TOC-Total organic carbon; ERL-Effective Range Low; MPC-Maximum permissible concentrations; SRC_{eco} - eco-toxicological serious risk concentration. The MPC and SRC_{eco} values are given as concentration in sediment with 10 % organic matter content (Verbruggen et al., 2001).

Highlights

- This study provides baseline information on PAEs in Cochin estuary, India.
- PAEs was in the range 44-1723ngg⁻¹ in pre monsoon, 331-1747 ngg⁻¹ in monsoon and 1402-3121 ngg⁻¹ in post monsoon.
- The predominant PAEs were DEHP, BBP, and DnBP
- DEHP and BBP in sediments exceeded permissible risk levels.
- The estuary is significantly contaminated with PAEs.