Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments Collected From Selected Estuaries of Kerala, West Coast of India

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Abstract

The investigation aims to study the source and concentration of polycyclic aromatic hydrocarbon (PAHs) fractions in the surface sediments of selected estuaries of the southwest coast of Kerala India. The concentration of PAHs ranged from 0.47 to 126.64 ng/g. The estuarine sediments were enriched by HMW-PAHs and they are occupied nearly 93.76 % of the total concentration, followed by LMW-PAHs (LMW-PAH – 6.23%). The sum of surface sediment-associated PAH distribution was higher in the inner part of the estuary, especially at Anjuthengu and Kadinamkulam estuaries. The sediment grain size and distance of the sampling point from the coast are significantly playing an important role in the distribution of the PAHs. The ratio of LMW/HMW PAHs in this study indicating that the pyrolytic process is the chief source of PAHs in the estuarine sediments. The calculated total TEQ value ranged from 0.20 to 54.80 ng/g. A comparative study suggests that the obtained TEQ value was less than the other locations of India and worldwide.

1.0 Introduction

Numerous studies have reported that polycyclic aromatic hydrocarbons (PAHs) are recognized as notable carcinogens mutagens and ubiquitous contaminants in a wide variety of mediums including air, food, sediments, and water. A wide variety of Solid-liquid extraction (SLE) methods was used to solve components of interest from solid samples such as soil or sediments using a suitable solvent. Various modes of SLE techniques such as maceration, ultrasonic-assisted extraction (UAE), microwave-assisted extraction (MAE), Soxhlet extraction (SE), and accelerated solvent extraction (ASE) were applied to extract this compound from chosen environmental samples (Ghassempour et al. 2008; Madej et al. 2018). The choice of the extraction procedure depended on several influential factors such as capital and operating cost, operation simplicity, required amount of organic solvent required, and the availability of a standardized method (Dean et al. 1997). The soxhlet extraction procedure was recommended by the US Environmental Protection Agency (US EPA) for extracting semi-volatile and non-volatile organics from solid matrices. However, they are arduous procedures, required a large amount of solvent, and not suitable for separating the thermally degradable compounds (De Castro et al. 1998).

The ultrasonic probe extraction procedure is an efficient method especially for their high extraction efficiency, lower equipment costs, ease of operation, little sample preparation, lower extraction temperatures, and suitability for trace level organic compounds in soil and sediments (Song et al. 2002; Banjoo et al. 2005). However, the efficiency of this method is depending on the solvent or solvent composition, extraction time, sample load, and water content (Berset et al. 1999). According to Sun et al. 1998, acetone was found to be the most efficient solvent for extracting the US EPA listed 16 priority pollutant PAHs in soils. The loss of hydrocarbon compounds by nearly 16% was observed during oven drying of samples at 45° C (Wong et al. 1980; Berset et al. 1999). The notable systematic study on dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments was reported at Cochin estuary by Ramzi et al. 2017. The present study aims to report the concentration of 16 USEPA listed PAHs in surface sediments of selected estuaries, west coast of Kerala, India

1.1 Study area

Kerala coastal area has been endowed with an expansive body of brackish waters including backwaters, lagoons, and estuaries including mangrove swamps. The chain of backwaters from south to north of the Kerala coast is interconnected by an extensive network of canals and they have played a significant role in the socio-economic status and cultural history of Kerala. Among the chain of backwaters, we selected four backwaters (Kayals means backwaters) namely Kadinamkulam, Anchuthengu, Kappil-Hariharapuram, Kayamkulam.

Kadinamkulam Kayal lying in between Lat 8° 35' to 8° 45' N and Long 76° 45' to 76° 56' E in the Thiruvananthapuram district. This is connected to the Veli Kayal on the southern side by the Parvathyputhanar canal and the Anchuthengu Kayal on the northern side through the lower reaches of the Vamanapuram River. Kadinamkulam backwater is connected with the sea only during the rainy season through the opening of the sand bar at Perumathura. Kappil-Hariharapuram Kayal is lying between 8°77' 75.90" to 8°78'88.13"N latitudes and 76°67'58.48" to 76°67'68.83"E longitudes. This backwater system receives freshwater input from the small river called Ayiroor Puzha. This Kayal is connected with Paravur Kayal through the Maniyamkulam canal. Kappil Kayal is widely used for fishing, retting, recreation, aquaculture, etc. Kayamkulam Kayal is a narrow stretch brackish water body, which is lying between 9° 2' and 9° 12' N latitude and 76°26' and 76°32' E longitude. During flood season, this canal system was filled with fresh water from the Pampa and Achankoil River. Kayamkulam sand bar was developed parallel to the Kayal due to the tidal influence of the Arabian Sea. Ayirumthengu mangrove ecosystem was flourished in the southern low-lying areas of Kayamkulam Lake. This mangrove ecosystem was richly vegetated by *Rhizophora* sp., *Avecenniasp.* and *Acanthus* sp.

2.0 Material And Methods

2.1 Sampling and Pre-treatment process

The surface sediments were collected from selected estuaries of the Kerala coast using a grid-based sampling method (Fig. 1). The sampling grid was created using the grid index features tool of Arc GIS 10.3. The pre-created grid plot was tracked by Locus Map Free (Version 3.50.1). The geographical coordinates of the sampling points were extracted from the KMZ extension file of the Arc GIS software package. Twenty surface sediments were collected from three selected estuaries of the Kerala coast (Kayamkulam, Anchuthengu, Kadinamkulam, and Varkala-Hariharapuram estuaries). The collected surface sediment was transferred to amber-colored glass jars using a pre-clean stainless steel spatula and kept in the icebox. The sediments were immediately transferred into the laboratory and kept under – 20°C in a deep freezer until analysis. The textural characteristics of the sediment (sand, silt, and clay) were determined by pipette analysis (Folk, 1980) in wet sediments. The surface sediments were freeze-dried, homogenized, and powdered using an agate mortar and pestle. The surface sediments were treated with 1N HCl and washed with double distilled water to remove salts and carbonates. The concentration of organic matter (OM) was estimated by exothermic heating followed by oxidation with potassium dichromate and concentrated H₂SO₄. An excess amount of dichromate was titrated against 0.5 N of ferrous ammonium sulfate (Gaudette et al., 1974).

2.2 Separation and analysis of PAHs

The sonication/ultrasonic agitation method was used to obtain higher extraction efficiencies during the extraction of the PAH fraction (Sun et al. 1998). Hence, the freeze-dried and homogenized sediment was used to extract the PAH with dichloromethane – methanol (2:1 ratio) solvent mixture in a sonication/ultrasonic agitation bath for 48 h and the obtained extract was treated with activate granular copper to remove the sulfur impurities. Finally, the extracted solution was evaporated using the rotary evaporation method and the extract was purified using the silica-alumina (2:1 ratio) column cleanup method. Later, the column was eluted with n-hexane to remove the aliphatic compounds followed by PAH compounds were eluted by n-hexane – dichloromethane mixture (3:7 ratio). The final extract was evaporated by a gentle nitrogen stream and the near-dryness extract was prepared for PAH determination using 500µl n-hexane. The USEPA listed sixteen PAHs were analyzed using a flame ionization detector on an Agilent 7890B Series Gas Chromatograph. The column temperature for analyses was initially programmed from 60°C (initial time, 2 min) at a rate of 10°C per min, 120–300°C at a rate of 3° C per min, and held at 310° C for 5 min. The injector and detector were kept at 280° C and 325° C respectively and the injection volume was 2 µL during both injection modes. The extraction efficiency was cross-checked based on the recovery output of the known amount of PAH standard mixture. The recovery of PAHs varied between 82% and 95%. All the chemical analyses were done in triplicates and output results are expressed on a dry weight basis. The sum of the PAH, high and low molecular weight rings, and potential toxic equivalent as shown in bar charts.

3.0 Results And Discussion

3.1 Concentration of LMW and HMW ring PAHs

The studied PAH fractions were classified as low molecular weight PAHs (2 and 3 rings) and high molecular weight PAHs (4 and above rings). The name of the studied PAH fractions, the number of rings, concentration range, mean, standard deviation, Toxic Effects-Range Low (ERL), Toxic Effects-Range Medium (ERM), Carcinogenic potency, and molecular weight of each PAHs were shown in Table 1. The surface sediments of the estuaries were dominated by fine-grained silt to clay grade fractions and few samples from the mouth of the estuaries were exhibiting sandy nature. The total PAH concentration ranges from 0.47 to 126.64 ng/g, with a mean value of 15.08 ng/g. In detail, the low molecular weight rings (LMW rings – 2 & 3 rings) in the sediments range from 0 to 5.42 ng/g, whereas heavy molecular weight rings (HMW rings – 4 & above rings) concentration ranges from 5.42 to 122.1 ng/g. The estuarine sediments were enriched by HMW-PAHs and they are occupied nearly 93.76 % of the total concentration, followed by LMW-PAHs (LMW-PAH – 6.23%). Among the LMW ring PAHs, Naphthalene, Acenaphthene, and Anthracene was detected as a high enriched compound, whereas HMW-PAHs was enriched by Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno[1,2,3-cd]pyrene, and Benz[ghi]perylene (Table 1). The sediment-associated 16 PAHs distribution was higher in the inner part of the estuary, especially at Anjuthengu and Kadinamkulam estuaries. Similar studies on the Cochin estuary also supported that the distance of the sampling point from the estuary mouth and inundated seawater also act as a controlling factor of the distribution of PAHs. The enrichment of PAHs in the inner part of the estuarine system was indirectly affected by sediment characteristics, fluvial and tidal flow processes. According to Safe, 1998, benzo[a]pyrene is one of the most toxic of the parent PAH, and this compound is used as a surrogate chemical marker for genotoxic organic compounds. The possible source of the PAHs was due to the proximity of anthropogenic activities such as road run-off and/or combusted particulates from vehicles or possibly the railway tracks (Vane et al. 2020). According to the previous studies, the relationship between the organic carbon/natural organic matters including humic substance coating in the mineral surface directly affected the distribution of PAHs (Stout and Emsbo-Mattingly, 2008; Ukalska Jaruga et al., 2018). Further, this investigation suggests that the relationship between TOC and PAHs showing a positive correlation in sediment cores. The negative correlation significance was shown in between grain size (sand-silt and clay ratio) from the Mersey estuary (Vane et al., 2007), whereas 16 PAHs in sediment and pore water of the Yellow river China showing a positive relationship with silt and fine grain fractions. The surface sediments of this study suggesting a similar observation especially in the inner part of the estuaries, where the sediment is enriched with fine fractions (Yu et al. 2009; Maruya et al. 1996; Maruya et al. 1997).

The PAHs reached the marine environment through both the high-temperature pyrolytic processes and the petrogenic source (Xu et al. 2007). The rapid increase of PAHs in the Cochin estuary was chiefly controlled by monsoonal changes, land/river runoff, and the combustion of pyrolytic source materials. Further, the reported total PAH concentration of the Cochin estuary was 100 times higher than in the present study. A comparative study of PAHs in sediments was compared with previously reported investigations of India and worldwide. The earlier studies on PAH distribution in aquatic ecosystems were significantly affected by sediment texture, organic content, and flow characteristics (He et al., 2014; Kumar et al., 2016; Vane et al. 2020). The concentration of PAHs in selected estuaries of the west coast was lower than in the other study region.

PAHs in sediments could cause liver neoplasm and other abnormalities in bottom-dwelling fish (Malins et al. 1988; Vethaak et al. 1992), and with delayed hatching, induction of deformities, disruption of larvae swimming activity, and DNA damage (Cousin and Cachot, 2014). The ratio between low molecular weight and high molecular weight PAH fractions can be used to identify the sources of PAH. The calculated ratio was > 1 indicates the petrogenic source of PAH, whereas ratio < 1 indicates the pyrolytic source. In this study, the ratio of LMW/HMW PAHs indicating that pyrolytic fractions dominate in these estuaries.

NOAA's sediment quality guideline was widely applied to determine the contamination level of PAHs in the aquatic system (NOAA, 1999). Long et al. 1995 suggested the two important tools such as Effect Range Low (ERL) and Effect Range Median (ERM) to determine the sediment quality level. Both indices (ERL and ERM) were helpful to enumerate the threshold value and rarely occurring adverse biological effects. The toxicological values with their effect ranges are used to assess the sediment quality, i.e. 10th percentile represented as an effect range low (ERL) and the 50th percentile ranked as effect range medium (ERM) (Long et al. 1995). The PAH distribution in the selected estuaries of Kerala indicates that the concentration of PAHs was less than the SQGs suggested ERL and ERM values. The analytical results of PAHs concluded that the surface sediments of the selected estuarine system falling under the low contamination and low-risk category.

The sediment's toxicity range was assessed from the sum of all potential carcinogenic PAH congeners (TCPAH - BaA, Chr, BbF, BkF, BaP, DbA, and InP fractions; Chen and Chen, 2011). The TCPAH values of the surface sediments of the estuaries were ranged from 16 to 44.21 ng/g. The analytical value of the TCPAH was less than the SQGs reported ERL-ERM values (1373– 8410 ng/g; Long et al., 1995). The potential toxicity is the toxic equivalent (TEQ) of individual PAH was derived using the following equation (Nasher et al., 2013; Li et al., 2015).

$$Total\ TEQ = \sum_i C_i \times TEFi$$

Where, C_i is the concentration of an individual PAH fraction and $TEFi$ is the toxicity factor of individual fractions. The TEF of BaA, Ch, BbF, BkF, BaP, IP and DbA are 0.1, 0.001, 0.1, 0.01, 1, 0.1 and 1 respectively (USEPA, 1993). The calculated total TEQ value ranged from 0.20 to 54.80 ng/g (Fig. 2). A comparative table of TEQ value with other study regions suggests that the obtained TEQ from this study was less than the other locations of India and worldwide (Table 4).

4.0 Conclusion

The outcome of the investigation suggests that the surface sediments of selected estuaries of the Kerala coast were less contaminated by other compared study areas around the world. Further, the present study area was less contaminated by polycyclic aromatic hydrocarbons (PAHs) and experiencing less ecological risk.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

Not applicable

Competing interests

No Competing interests

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Authors' contributions

Krishnamoorthy Radhakrishnan & Shaik Mohammed. Hussain : Conceptualization, Visualization

Subbiah Krishnakumar, Kaliyaperumal Sanjai Gandhi & Dhanasekaran Pradhap : Conceptualization, Investigation, Writing - original draft

Nazeerkhan Akramkhan, Palanichamy Prakasheswar & : Fieldwork & Sample collection

Subbiah Maheswaran & Anandarao Rajkumar: Investigation & Data curation

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References

1. Banjoo DR, Nelson PK (2005) Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments. J Chromatogr A 1066(1–2):9–18
2. Berset JD, Ejem M, Holzer R, Lischer P (1999) Comparison of different drying, extraction and detection techniques for the determination of priority PAHs in background contaminated soil samples. Anal Chim Acta 383(3):263–275
3. Chen CW, Chen CF (2011) Distribution, origin, and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in sediments of Kaohsiung Harbor, Taiwan. Mar Pollut Bull 63(5–12):417–423
4. Cornelissen G, Breedveld GD, Kalaitzidis S, Christanis K, Kibsgaard A, Oen AM (2006) Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. Environ sci Technol 40(4):1197–1203
5. Cousin X, Cachot J (2014) PAHs and fish—exposure monitoring and adverse effects from molecular to individual level. Environ Sci Pollut Res 2:13685–13688
6. Crane JL (2017) Ambient sediment quality conditions in Minnesota lakes, USA: Effects of watershed parameters and aquatic health implications. Sci Total Environ 607:1320–1338

7. Cornelissen G, Breedveld GD, Kalaitzidis S, Christanis K, Kibsgaard A, Oen AM (2006) Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. *Environ Sci Technol* 40(4):1197–1203
8. Dean JR, Abdullah MP, Zakaria Z (1997) Extraction of polycyclic aromatic hydrocarbons from contaminated soil using Soxhlet extraction, pressurised and atmospheric microwave-assisted extraction, supercritical fluid extraction and accelerated solvent extraction. *J Chromatogr A* 791(1–2):361–366
9. De Castro ML, Garcia-Ayuso LE (1998) Soxhlet extraction of solid materials: an outdated technique with a promising innovative future. *Anal Chim Acta* 369(1–2):1–10
10. Essien JP, Eduok SI, Olajire AA (2011) Distribution and ecotoxicological significance of polycyclic aromatic hydrocarbons in sediments from Iko River estuary mangrove ecosystem. *Environ Monit Assess* 176(1–4):99–107
11. Garcia MR, Mirlean N, Baisch PR, Caramao EB (2010) Assessment of polycyclic aromatic hydrocarbon influx and sediment contamination in an urbanized estuary. *Environ Monit Assess* 168(1–4):269–276
12. Gaudette HE, Flight WR, Toner L, Folger DW (1974) An inexpensive titration method for the determination of organic carbon in recent sediments. *J Sediment Petrol* 44:249–253
13. Guzzella L, Poma G, De Paolis A, Roscioli C, Viviano G (2011) Organic persistent toxic substances in soils, waters and sediments along an altitudinal gradient at Mt. Sagarmatha, Himalayas, Nepal. *Environ Pollut* 159(10):2552–2564
14. Ghassempour A, Heydari R, Talebpour Z, Fakhari AR, Rassouli A, Davies N, Aboul-Enein HY (2008) Study of new extraction methods for separation of anthocyanins from red grape skins: analysis by HPLC and LC-MS/MS. *J Liq Chromatogr Relat Technol* 31(17):2686–2703
15. He X, Pang Y, Song XJ, Chen BL, Feng ZH, Ma YQ (2014) Distribution, sources and ecological risk assessment of PAHs in surface sediments from Guan River Estuary, China. *Mar Pollut Bull* 80(1–2):52–58
16. Jaward FM, Alegria HA, Galindo Reyes JG, Hoare A (2012) Levels of PAHs in the Waters, Sediments, and Shrimps of Estero de Urias, an Estuary in Mexico, and Their Toxicological Effects *Scientific World Journal*
17. Kumar KSS, Nair SM, Salas PM, Peter KJP, Kumar CSR (2016) Aliphatic and polycyclic aromatic hydrocarbon contamination in surface sediment of the Chitrapuzha River, South West India. *Chem Ecol* 32(2):117–135
18. Li Q, Zhang X, Yan C (2010) Polycyclic aromatic hydrocarbon contamination of recent sediments and marine organisms from Xiamen Bay, China. *Arch Environ Contam Toxicol* 58(3):711–721
19. Li P, Xue R, Wang Y, Zhang R, Zhang G (2015) Influence of anthropogenic activities on PAHs in sediments in a significant gulf of low-latitude developing regions, the Beibu Gulf, South China Sea: distribution, sources, inventory and probability risk. *Mar Pollut Bull* 90(1–2):218–226
20. Lorgeoux C, Moilleron R, Gasperi J, Ayrault S, Bonté P, Lefèvre I, Tassin B (2016) Temporal trends of persistent organic pollutants in dated sediment cores: chemical fingerprinting of the anthropogenic impacts in the Seine River basin, Paris. *Sci Total Environ* 541:1355–1363
21. Madej K, Kalenik TK, Piekoszewski W (2018) Sample preparation and determination of pesticides in fat-containing foods. *Food chem* 269:527–541
22. Malins DC, McCain BB, Landahl JT, Myers MS, Krahn MM, Brown DW, Roubal WT (1988) Neoplastic and other diseases in fish in relation to toxic chemicals: an overview. *Aquat Toxicol* 11(1–2):43–67
23. Maruya KA, Risebrough RW, Horne AJ (1996) Partitioning of polynuclear aromatic hydrocarbons between sediments from San Francisco Bay and their pore waters. *Environ sci Technol* 30(10):2942–2947
24. Maruya KA, Risebrough RW, Horne AJ (1997) Partitioning of polynuclear aromatic hydrocarbons between sediments from San Francisco Bay and their pore waters. *Oceanogr Lit Rev* 3(44):194
25. Maskaoui K, Zhou JL, Hong HS, Zhang ZL (2002) Contamination by polycyclic aromatic hydrocarbons in the Jiulong River estuary and Western Xiamen Sea, China. *Environ Pollut* 118(1):109–122
26. Mzoughi N, Chouba L (2011) Distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter, and sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). *J Environ Monit* 13(3):689–698
27. Masood N, Zakaria MP, Halimoon N, Aris AZ, Magam SM, Kannan N, Mustafa S, Ali MM, Keshavarzifard M, Vaezzadeh V, Alkhadher SAA (2016) Anthropogenic waste indicators (AWIs), particularly PAHs and LABs, in Malaysian sediments: application of aquatic environment for identifying anthropogenic pollution. *Mar Pollut Bull* 102(1):160–175
28. NOAA (1999) Sediment Quality Guidelines Developed for the National Status and Trends Program. <http://www.ccma.nos.noaa.gov/publications/sqg.pdf>
29. Nasher E, Heng LY, Zakaria Z, Surif S (2013) Assessing the ecological risk of polycyclic aromatic hydrocarbons in sediments at Langkawi Island, Malaysia. *Sci World J.* 2013, 13
30. Oliva AL, Quintas PY, La Colla NS, Arias AH, Marcovecchio JE (2015) Distribution, sources, and potential ecotoxicological risk of polycyclic aromatic hydrocarbons in surface sediments from Bahía Blanca estuary, Argentina. *Arch Environ Contam Toxicol* 69(2):163–172
31. Perez-Fernandez B, Vinas L, Franco MA, Bargiela J (2015) PAHs in the Ria de Arousa (NW Spain): a consideration of PAHs sources and abundance. *Mar Pollut Bull* 95(1):155–165
32. Qiao M, Wang CX, Huang SB, Wang DH, Wang ZJ (2006) Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. *Environ Int* 32(1):28–33
33. Ramzi A, Rahman KH, Gireeshkumar TR, Balachandran KK, Jacob C, Chandramohanakumar N (2017) Dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of Cochin estuary, India. *Mar Pollut Bull* 114(2):1081–1087
34. Safe SH (1998) Hazard and risk assessment of chemical mixtures using the toxic equivalency factor approach. *Environ Health Perspect* 106(4):1051–1058

35. Song YF, Jing X, Fleischmann S, Wilke BM (2002) Comparative study of extraction methods for the determination of PAHs from contaminated soils and sediments. *Chemosphere* 48(9):993–1001
36. Sprovieri M, Feo ML, Prevedello L, Manta DS, Sammartino S, Tamburrino S, Marsella E (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere* 67(5):998–1009
37. Stout SA, Emsbo-Mattingly SD (2008) Concentration and character of PAHs and other hydrocarbons in coals of varying rank - implications for environmental studies of soils and sediments containing particulate coal. *Org Geochem* 39(7):801–819
38. Sun F, Littlejohn D, Gibson MD (1998) Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection. *Anal Chim Acta* 364(1–3):1–11
39. USEPA (1993) Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. EPA/600/R-93/089. Office of Research and Development, Washington
40. Ukalska-Jaruga A, Smreczak B, Klimkowicz-Pawlas A (2018) Soil organic matter composition as a factor affecting the accumulation of polycyclic aromatic hydrocarbons. *J Soils Sediment* 19:1890–1900
41. Vethaak AD, Ap Rheinallt T (1992) Fish disease as a monitor for marine pollution: the case of the North Sea. *Rev Fish Biol Fish* 2(1):1–32
42. Vane CH, Harrison I, Kim AW (2007) Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary. *UK Sci Total Environ* 374(1):112–126
43. Vane CH, Kim AW, Emmings JF, Turner GH, Moss-Hayes V, Lort JA, Williams PJ (2020) Grain size and organic carbon controls polyaromatic hydrocarbons (PAH), mercury (Hg) and toxicity of surface sediments in the River Conwy Estuary, Wales, UK. *Mar Pollut Bull* 158, 111412
44. Wong MK (1980) A study of three extraction methods for hydrocarbons in marine sediment. *Mar Chem* 9(3):183–190
45. Xu J, Yu Y, Wang P, Guo W, Dai S, Sun H (2007) Polycyclic aromatic hydrocarbons in the surface sediments from Yellow River, China. *Chemosphere* 67(7):1408–1414
46. Yu Y, Xu J, Wang P, Sun H, Dai S (2009) Sediment-porewater partition of polycyclic aromatic hydrocarbons (PAHs) from Lanzhou Reach of Yellow River, China. *J hazard Mater* 165(1–3):494–500
47. Zakaria MP, Takada H, Tsutsumi S, Ohno K, Yamada J, Kouno E, Kumata H (2002) Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs. *Environ sci Technol* 36(9):1907–1918
48. Zhou JL, Hong H, Zhang Z, Maskaoui K, Chen WJWR (2000) Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. *Water Res* 34(7):2132–2150
49. Zhang ZL, Hong HS, Zhou JL, Yu G (2004) Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China. *Sci Total Environ* 323(1–3):71–86
50. Zuloaga O, Prieto A, Ahmed K, Sarkar SK, Bhattacharya A, Chatterjee M, Bhattacharya BD, Satpathy KK (2013) Distribution of polycyclic aromatic hydrocarbons in recent sediments of Sundarban mangrove wetland of India and Bangladesh: a comparative approach. *Environ Earth Sci* 68(2):355–367

Tables

Table 1 concentration ranges, mean and standard deviation (S.D) of individual PAHs (ng/g) in the surface sediments, Kayals of West coast of Kerala, India

S.no	Name of the PAH	No of rings	Sediment (n = 20)					Carcinogenic potency ^a	Molecular weight
			Range (ng/g)	Mean (ng/g)	S.D. (ng/g)	ERL	ERM		
1	Naphthalene (Nap)	2-Ring	ND - 3.99	0.511	0.987	160	2100	D	128.18
2	Acenaphthylene (Acy)	3-Ring	ND	ND	ND	44	640	-	152.2
3	Acenaphthene (Ace)	3-Ring	ND	ND	ND	16	500	-	154.2
4	Anthracene (Ant)	3-Ring	ND - 2.12	0.106	0.474	853	1100	D	178.24
5	Phenanthrene (Phe)	3-Ring	ND - 2.15	0.250	0.579	240	1500	D	178.24
6	Fluorene (Fl)	3-Ring	ND - 0.55	0.028	0.123	19	540	D	166.23
7	Benzo(a)anthracene (BaA)	4-Ring	ND - 7.29	1.160	1.691	261	1600	B ₂	228.3
8	Chrysene (Chr)	4-Ring	ND - 6.88	0.800	1.559	384	2800	B ₂	228.3
9	Fluoranthene (Flu)	4-Ring	ND - 6.5	0.823	1.442	600	5100	D	202.26
10	Pyrene (Pyr)	4-Ring	ND - 6.71	0.763	1.492	665	2600	D	202.26
11	Benzo(b)fluoranthene (BbF)	5-Ring	ND - 12.19	1.727	2.692	320	1800	B ₂	252.32
12	Benzo(k)fluoranthene (BkF)	5-Ring	ND - 19.7	1.908	4.405	280	1620	B ₂	252.32
13	Benzo(a)pyrene (BaP)	5-Ring	ND - 21.28	2.211	4.645	430	1600	B ₂	252.32
14	Dibenzo(a,h)anthracene (DBA)	5-Ring	ND - 8.68	0.874	1.974	63.4	260	B ₂	278.35
15	Indeno [1,2,3-cd] pyrene (InP)	6-Ring	ND - 15.46	2.098	3.409	-	-	B ₂	276.34
16	Benz[ghi]perylene	6-Ring	ND - 17.41	1.074	3.951	430	1600	D	276.34

B₂ Probable carcinogen, D - not classifiable as to human carcinogenicity (USEPA carcinogenic classification^a), S.D – Standard Deviation, ND – Not detected, ERL - Toxic Effects-Range Low, ERM - Toxic Effects-Range Medium

Table 2 sample wise distribution of sand, silt and clay (in %), low molecular and high molecular weight rings (ng/g), Total PAH (ng/g) of surface sediments, Kayals of West coast of Kerala, India

Location	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	1
Sand %	73	18.2	73.8	23.6	96.6	69.6	86.2	29.4	83.4	75.2	13.8	4.2	85.8	4.6	2	42	2.2	0
Silt %	26.2	80.8	25.4	76	3	25.4	13.4	70.4	16.4	24.8	85.8	95.4	14	95	97.6	57.6	97	9
Clay %	0.8	1	0.8	0.4	0.4	5	0.4	0.2	0.2	0	0.4	0.4	0.2	0.4	0.4	0.4	0.8	0
LMW rings	0	0.81	5.42	2.77	0	0	0	0	0	0.65	0	0	1.28	4.54	1.05	0	0	0
HMW rings	1.38	10.16	11.14	7.56	0.47	0.8	1.94	12.68	3.34	5.68	19.73	3.33	27.68	122.1	8.12	0.51	3.06	0
Total PAH	1.38	10.97	16.56	10.33	0.47	0.8	1.94	12.68	3.34	6.33	19.73	3.33	28.96	126.64	9.17	0.51	3.06	N
Total TEQ	0.60	4.75	7.17	4.47	0.20	0.35	0.84	5.49	1.45	2.74	8.54	1.44	12.53	54.80	3.97	0.22	1.32	0

ND – Not detected, LMW rings - Low molecular weight rings (2 & 3 rings); HMW rings - High molecular weight rings (4 & above rings), TEQ – Toxic equivalent

Table 3 comparison table of polycyclic aromatic hydrocarbon (PAHs) in the present study and other worldwide estuarine and coastal systems report

S.no	Details of the study region	Concentration Sum of PAH	References
1	Mersey Estuary, UK	626–3766	Vane et al. 2007
2	Norwegian harbors, Norway	2100–31100	Cornelissen et al. 2006
3	San Francisco Bay, USA	26.1–600	Maruya et al. 1996
4	Tokyo Bay, Japan	534–292370	Zakaria et al. 2002
5	Xiamen Harbor, China	247–480	Zhou et al. 2000
6	Minjiang River Estuary, China	112–877	Zhang et al. 2004
7	Jiulong River Estuary and Western Xiamen Sea, China	59–1177	Maskaoui et al. 2002
8	Yellow River, China	464–2621	Yu et al. 2009
9	Himalayan lakes, Nepal	67.9 ± 22.1	Guzzella et al. 2011
10	Seine River basin, France	5000 - 90,000	Lorgeoux et al. 2016
11	Minnesota lakes, USA	489.3 ± 980.5	Crane et al. 2017
12	Cochin estuary, India	194–14149	Ramzi et al. 2017
13	Chitrapuzha River, India	5046–33087	Kumar et al. 2016
14	Hugli river, India	0–1839	Zuloaga et al. 2013
15	Iko River estuary mangrove system, Nigeria	6100–35,270	Essein et al. 2011
16	Esterode Urias, estuary, Mexico	27–418	Jaward et al. 2012
17	Patos Lagoon Estuary, Brazil	89–10451	Garcia et al. 2010
18	Galician estuaries, NW Spain	44–7901	Perez-Fernandez et al. 2015
19	Selangor River estuary, Malaysia	203–964	Masood et al. 2016
20	Selected estuaries of west coast of Kerala	Present study	

Table 4 Comparison of TEQ values of surface sediments of the selected estuaries of Kerala coast, Southwest coast of India with data from other areas worldwide

Study area	TEQ (ng/g)	References
Naples Harbour, Italy	2–4723	Sprovieri et al. 2007
Kaohsiung Harbor, Taiwan	1404–1964	Chen and Chen, 2011
Bahia Blanca Estuary, Argentina	0–1969	Oliva et al. 2015
Meiliang Bay in China	94–856	Qiao et al. 2006
Xiamen Bay, China	15–282	Li et al. 2010
Ría Arousa, Spain	1.2–820	Perez-Fernandez et al. 2015
Sundarban mangrove wetland, Bangladesh	13–1014	Zuloaga et al. 2013
Sundarban mangrove wetland, India	1–2451	Zuloaga et al. 2013
West coastal of the Gulf of Tunis, Tunisia	8–666.4	Mzoughi and Chouba, 2011
Cochin Estuary, India	1–971	Ramzi et al. 2017
Selected estuaries of Kerala Southwest coast of India	0.29 – 54.80	Present study

Figures

Figure 1

sampling locations and study area map of the selected estuaries of Kerala, Southwest coast of India

Figure 2
Distribution of total TEQ, Sum of PAH, low and high molecular weight ring PAHs in the surface sediments, selected estuaries of Kerala, Southwest coast of India