Dynamics and Ecological Risk of Endocrine Disrupting Organic Pollutants in Cochin Estuary, India

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By

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Certificate

This is to certify that the thesis entitled, **“Dynamics and Ecological Risk of Endocrine Disrupting Organic Pollutants in Cochin Estuary, India.”** is an authentic record of the research work carried out by Mrs Ramzi A (Reg. No.4540), under my scientific supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science & Technology, in partial fulfilment of the requirements for award of the degree of Doctor of Philosophy of Cochin University of Science & Technology and that no part thereof has been presented before for the award of any other degree, diploma or associateship in any University. Further certified that all relevant corrections and modifications suggested during the pre-synopsis seminar and recommended by the Doctoral Committee have been incorporated in the thesis.

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Declaration

I hereby declare that the thesis entitled, **"Dynamics and Ecological Risk of Endocrine Disrupting Organic Pollutants in Cochin Estuary, India."** is an authentic record of the research work conducted by me under the supervision and guidance of Dr. N Chandramohanakumar, Professor (Retd.), Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology and no part of this has previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title or recognition from any University/Institution.

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Ramzi A

Dedicated to ……

my beloved parents

Preface

Cochin estuary, the largest estuarine system along the southwest coast of India, is exposed to serious environmental degradation due to increased anthropogenic activities - industrialisation, urbanisation, inter-tidal land reclamation, port and harbour development, aquaculture activities, etc. More than 70 % of the industrial establishments in the State of Kerala are situated along the banks of these rivers. Cochin estuary receives huge amount of discharges from the various sector which carries so many pollutants.

Most of these pollutants are hydrophobic in nature and easily get attached to particulate matter and/or become incorporated into sediments. Surface sediments, therefore, act as a catalogue of the latest pollution events, besides being a sink for such pollutants. These pollutants are highly hazardous to estuarine habitat and to human health as they could trigger genotoxic, mutagenic, carcinogenic and endocrine disrupting effects in their hosts. Only scant data sets are available on the impact of endocrine disrupting pollutants in Indian estuarine systems.

Phthalic acid esters (PAEs) and Polynuclear aromatic hydrocarbons (PAHs) are potential endocrine-disrupting chemicals (EDCs) and carcinogenic materials, which could lead to grave health hazards, including reproductive abnormalities. USEPA and European Union (EU) categorise them as major pollutants because they easily get attached to suspended matter/sediments by their hydrophobic character and enter the food web.

This study, reports the results of comprehensive investigations on the background levels, the chemo-dynamics and the ecological risk of two major endocrine disrupting chemicals (PAEs and PAHs) in Cochin estuary.

The Thesis is divided into **7 Chapters**.

Chapter I: *Introduction.* This chapter discusses the introduction to the work and general outline about endocrine disrupting pollutants, such as PAHs and PAEs. It also addresses the importance of monitoring PAHs and PAEs in Cochin estuary. Previous studies, significance, main objectives and scope of the study are also furnished in this chapter.

Chapter II: *Materials and Methods*. Gives an overview of the study area and detailed description of the methodology adopted in this study, and results of general hydrographical and sedimentary characteristics.

Chapter III: *Dissolved and Particulate Phthalic Acid Esters (PAEs)*. This Chapter deals with the spatial and seasonal distribution of dissolved and particulate PAEs and its ecological risk assessment.

Chapter IV: *Sedimentary PAEs*. This Chapter analyses the enrichment of PAE in surface sediments and its ecological implications.

Chapter V: *Dissolved and Particulate PAHs*. This Chapter deals with the spatial and seasonal distributions of dissolved and particulate PAHs and their origin. It also evaluates the ecological risk caused by each congener of PAHs.

Chapter VI: *Sedimentary Poly-aromatic Hydrocarbons (PAHs)*. This Chapter provides the seasonal enrichment of PAHs along the salinity gradient of Cochin estuary in relation to the sources of PAHs. This chapter also assesses the ecological implication of PAHs in sediments.

Chapter VII: *Summary and Conclusions*. This concluding Chapter summarises the study and highlights the future scope of the present study.

Abbreviations

Ace	Acenaphthene
Acy	Acenaphthylene
AHH	Aryl Hydrocarbon Hydroxylase
An	Anthracene
ANOVA	One Way Analysis Of Variance
BaA	Benzo(a)Anthrecene
Bap	Benzo(a)Pyrene
Bbf	Benzo(B)Fluoranthene,
BBP	Benzyl Butyl Phthalate
Bkf	Benzo(K)Fluoranthene
Bper	Benzo(Ghi)Perylene ,
Ch	Chrysene
CTD	Conductivity Deapth Temperature
D.F	Detection Frequency
DbA	Dibenzo(ah)Anthracene
DCM	Dichloromethane
DEHP	Di- (2-Ethyl Hexyl)Phthalate
DEP	Diethyl Phthalate
DMP	Dimethyl Phthalate
DnBP	Di-n-Butyl Phthalate
Dnop	Di-n-Octyl Phthalate
DO	Dossolved Oxygen
EDC	Endocrine Disrupting Chemical
ERL	Effective Range Low
FID	Flame Ionization Detector
Fl	Fluorene

Flu	Fluoranthene
GC	Gas Chromatography
HMW	High Molecular Weight
IP	Indeno(1,2,3 Cd)Pyrene
IUPAC	International Union Of Pure And Applied Chemistry
LMW	Low Molecular Weight
LOD	Limit Of Detection
MEC	Measured Concentration
MPC	Maximum Permissible Concentration
MS	Mass Spectrometer
Naf	Naphthalene
OC	Organic Carbon
PAEs	Phthalic Acid Esters
PAHs	Polycyclic Aromatic Hydrocarbons
PC	Principal Components
PCA	Principal Component Analysis
PCBs	Polychlorinated Biphenyls
PEL	Probable Effect Level
Phe	Phenanthrene
POPs	Persistent Organic Pollutants
Py	Pyrene
RQ	Risk Quotient
SPM	Suspended Particulate Matter
SPSS	Statistical Package For Social Sciences
SQC	Sediment Quality Guidelines
SRC	Serious Risk Concentration
STDV	Standard Deveation

TCPAH	Total carcinogenic Polynuclear Aromatic Hydrocrabon
TDPAHs	Total Dissolved Polynuclear Aromatic Hydrocrabon
TEL	Threshold Effect Level
TEQ	Toxic Equivalent
TN	Total Nitrogen
TOC	Total Organic Carbon
TPAE	Total Phthalic Acid Esters
TPAHs	Total Polynuclear Aromatic Hydrocrabon
TPPAHs	Total Particulate Polynuclear Aromatic Hydrocrabon
TS	Total Sulfer

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INTRODUCTION

Coastal areas are thickly populated, about 40% of world's population lives within 60 miles of the coast (Alongi et al., 1998). Almost all the big cities in the world are situated at the bank of rivers and estuaries (Zwolsman, 1994). "An estuary is a semi-enclosed coastal body of water that extends to the effective limit of tidal influence, within which sea water entering from one or more free connections with the open sea, or any other saline coastal body of water, is significantly diluted with fresh water derived from drainage, and can sustain euryhaline biological species from either part or the whole of their life cycle" (Thomas, 2007). Estuaries are the transition zone between river and ocean. It is a connecting link from continental and oceanic environment (Pickard and Emery, 1982).

1.1 Estuaries and Their Importance

Estuaries constitute a very small part of the total marine hydrosphere (Pickard and Emery, 1982). Within the estuaries seawater and land-derived freshwaters are mixed, producing a wide range of brackish waters of intermediate salinity. In this mixing process, the most dominant natural waters on the earth's surface, fresh water and seawater were interacting both chemically and physically (Dietrich, 1963). In estuarine environments, there are interactions of the suspended matter with the soluble constituents of a succession of the fresh, brackish and marine waters. The exchange of solid-solution components in estuaries determines the nature of the chemical constituents delivered to the oceans from continental drainage (Pickard and Emery, 1982; Dietrich, 1963). Human involvement in the marine ecosystem is so deep. Estuarine and coastal waters are one of the major resources for a variety of human activities like fisheries, aquaculture, navigation, oil and mineral exploration etc. (Thomas, 2007). Most of the industries and power plants are situated at the bank of rivers and estuaries (Zwolsman, 1994). These estuaries while providing cheap transportation and enormous quantities of water required for cooling also serve as a water sink.

1.2 Estuarine Pollution

Pollution of estuaries can occur in two ways, firstly by the direct introduction of sewage and industrial wastes into them and secondly by the downstream transport of pollutants by rivers. Excessive nutrient discharge from sources such as septic tank discharge, sewage treatment plants, stormwater runoff, atmospheric deposition, industrial organic waste effluent, and contaminated runoff from fertilised farms or animal operations can adversely affect estuarine systems (Zwolsman, 1994). The high concentration of nutrients in estuaries can lead to eutrophication and algal blooms. As the algae decay and utilise the dissolved oxygen. The algae also prevent sunlight penetration to the water. Because of poor oxygen level and light, fish, shellfish and underwater seagrasses can die (Pickard and Emery, 1982; Dietrich, 1963). However, in recent years, man-made sources have substantially increased the flux of many pollutants to the marine environment via the atmosphere, surface run-off and direct discharge.

Nowadays we are using a lot of synthetic chemicals like pharmaceutical products, personal care product, household items, surfactants, pesticides, petroleum products, plastics etc. Due to urbanisation these chemicals used in our daily life eventually reaches the estuarine environment (Ramzi et al., 2017). Estuaries are susceptible to receive a lot of toxic substances (Ramzi et al., 2018). Metals, like mercury, pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) etc can concentrate in the water, sediment, and aquatic organisms (Naik, 2000; Balachandran et al., 2002; Martin et al., 2012). Consumption of these aquatic organisms such as bottom-dwelling organisms like shellfish and contaminated water harmed aquatic plants, animals and wildlife and also can pose a risk to human health.

1.3 Endocrine Disrupting Organic Contaminants

There are some ductless glands which secrete their hormones directly into the blood. These hormones reach a particular part of the body through blood circulation and induce specific action. Some compounds can have hormone-like effects and cause endocrine disruption by various activities. These compounds are called endocrine disrupting chemicals (Lamb et al., 2014). Presence of ECDs can affect the endocrine system by many ways, some chemicals can reduce the effects of natural hormones by blocking their interaction with their physiological binding sites, they can react directly or indirectly with natural hormones, they resemble the active site of hormones and can interact with receptor site, or they can alter the natural hormone synthesis pathway etc. (Bergman et al., 2012)

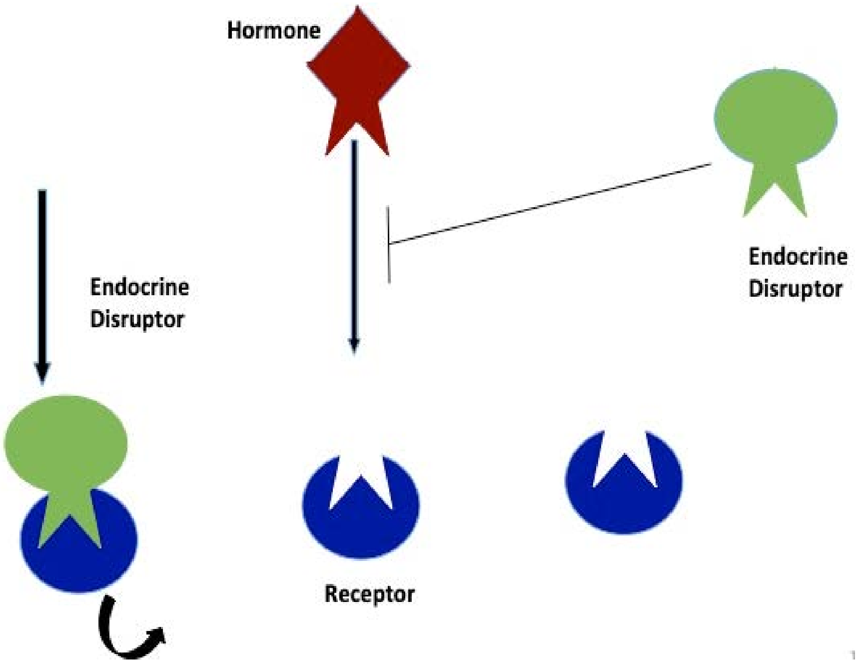


Figure 1.1: Endocrine-disrupting the activity of ECD.

Endocrine disrupting chemicals are mostly man-made, such as metals, pesticides, polychlorinated biphenyls, personal care products, phthalates, additives or contaminants in food etc. ECDs are suspected of altering the reproductive system in males and females and which can induce increase hormone-related cancer, thyroid related disorder such as abnormal growth in children, affect the immune system, metabolic disorders, bone disorders etc. (Bergman et al., 2012). Study of Background level distribution and partitioning of these ECDs are much important.

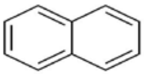
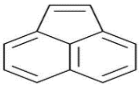
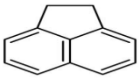
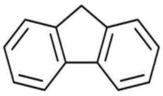
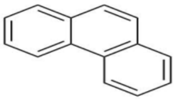
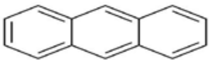
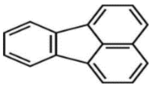
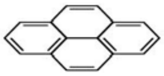
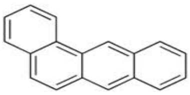
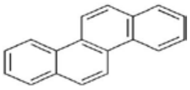
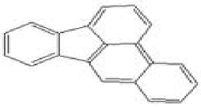
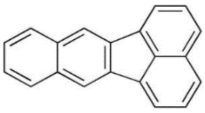
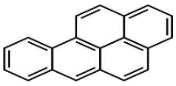
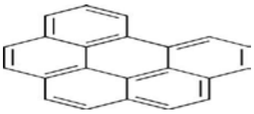
1.3.1 Polycyclic aromatic hydrocarbons (PAHs)

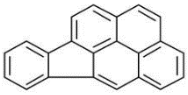
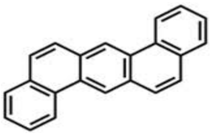
Polycyclic aromatic hydrocarbons (PAHs) are a diverse group of lipophilic organic compounds composed of multiple aromatic rings fused (Ankley et al., 1994; Law et al., 1997; Boese et al., 1999). Naphthalene

($C_{10}H_8$) being the member with the lowest molecular weight, they show variable physical-chemical and biological properties due to the difference in position and number aromatic rings (Neff, 1979). PAHs shows decreasing vapour pressure and aqueous solubility with increasing molecular weight, which influences their distribution and behaviour in the biological environment; thus, they are usually adsorbed on to the particulate matter in the atmosphere (Ravindra et al., 2008; Keshavarzifard et al., 2014). As a result, the larger molecular weight PAHs (≥ 4 rings) are mostly adsorbed onto the particulate matter in the atmosphere, while the lower molecular weight PAH can be found both free in the atmosphere and bound to particulates (Ravindra et al., 2008; Keshavarzifard et al., 2014).

Polycyclic aromatic hydrocarbons are generally classified into two groups based on their molecular weight. Low molecular weight (LMW) PAHs have three or fewer aromatic rings, while high molecular weight (HMW) PAHs have four or more rings (Law et al., 1997). LMW PAHs include 2-ring [Napthalene (Naf)] and 3-ring [(acenaphthylene (Acy), acenaphthene(Ace), fluorine (Fl), phenanthrene (Phe), anthracene (An)] while, HMW PAHs comprise four to seven rings [four ring (fluoranthene (Flu), pyrene (Py), benzo[a] anthracene (BaA), chrysene (Ch)), 5-ring, (benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP)), and 6-ring (indo [1,2,3-cd] pyrene (IP), bnzo[g, hi]perylene (Bper), dibenzo[a,h] anthracene (DbA)).

Table 1.1: Major PAHs with their molecular weights and structural identity

IUPAC Nomenclature	Molecular Weight	Structural Identity
Naphthalen (Naf)	128.29	
Acenaphthylene (Acy)	152.21	
Acenaphthene (Ace)	154.21	
Fluorene (Fl)	166.23	
Phenanthrene (Phe)	178.24	
Anthracene (An)	178.24	
Fluoranthene (Flu)	202.26	
Pyrene (Py)	202.26	
Benzo(a)anthracene (BaA)	228.30	
Chrysene (Ch)	228.30	
Benzo(b)fluoranthene (BbF)	252.32	
Benzo(k)fluoranthene (BkF)	252.32	
Benzo(a)pyrene (BaP)	252.32	
Benzo(ghi)perylene (BPer)	276.34	

Inden(1,2,3cd)pyrene (IP)	276.34	
Dibenzo(ah)anthracene (DbA)	278.36	

IUPAC- International Union of Pure and Applied Chemistry

In aquatic ecosystems, PAHs tend to sorb onto particulate matter (due to their hydrophobic nature and low solubility), and easily get settled on to the sediments (Ramzi et al., 2017). Major metabolites of PAHs, due to their greater reactivity and solubility, can cause acute toxicity to aquatic organisms, often relatively more potent than the parent compound. This phenomenon, reviewed by Arfsten et al., 1996, was aptly demonstrated by the photoinduced toxicity of PAHs (Ankley et al., 1994; Boese et al., 1999). The electrophilic metabolites are primarily recognised with causing chronic toxic effects in the form of mutagenesis, carcinogenesis and teratogenesis when they fix to cellular macromolecules (Rossi and Anderson, 1976; Chandler et al., 1997). Several studies have shown that the adverse effects of exposure of aquatic animals to sublethal levels of PAHs. For example, sublethal PAH levels have been found to cause embryo-toxicity leading to reproduction failure, abnormal growth of new offspring and negative impact on recruitment of juveniles (Neff, 1979). The juvenile stages are more sensitive to sub lethal toxicity of PAHs, with resultant effects such as interference with osmoregulation and moulting leading to mortalities of crabs, shrimps and other crustacean (Lotufo, 1997; Wirth et al., 1998)

1.3.2 Sources of PAHs.

PAHs are usually a natural product during diagenesis, though anthropogenic activities are considered to be its primary source to the environment. Based on the sources, PAHs are broadly classified as pyrogenic and petrogenic origin (Wang et al., 2012; Keshavarzifard et al., 2015; Li et al., 2015a). Pyrogenic PAHs are produced by incomplete combustion of organic matter such as grass, wood, coal, petroleum and natural gas (Zhang et al., 2015), while the petrogenic PAHs are derived from crude oil and its derivatives including gasoline, diesel, lubricating oil, asphalt etc. (Revindra et al., 2008; Keshavarzifard et al., 2014). A minor natural source of PAHs to the aquatic environment is from biosynthesis. Indirect biosynthesis of PAHs by the reduction of polycyclic quinone pigments (Aizenshtat et al.,1973; Wakeham et al., 1980). Polycyclic quinones are synthesised by bacteria, fungi, micro-algae etc. under reducing conditions these aromatic quinones are readily reduced to corresponding hydroquinones and subsequently to the parent PAHs (Aizenshtat et al.,1973).

1.3.3 Solubility and Transport of PAHs

Due to the hydrophobicity, low volatility and high persistence, PAHs are naturally associated with aeolian/suspended particles and transported through atmosphere/water (Ohkouchi et al., 1999). Solubility generally decreases as the increase of molecular weight. As a result, larger molecular weight PAHs ($\geq$ 4 rings) are almost exclusively bound to particulate matter, while lower molecular weight PAH (3 rings) can also be found dissolved in water. The most soluble PAH, naphthalene, has a solubility of about 30 ppm. Linear PAHs are less soluble than corresponding angular isomer for example anthracene less soluble than phenanthrene. Generally, PAHs are slightly less soluble in saline water than freshwater. PAHs Solubility increases with increase in temperature. In the aquatic environment, these compounds are attached to the particulate matter and get deposited to the sediment (Hu et al., 2014). Aquatic organisms may accumulate PAHs from water, sediments and food. In general, PAHs dissolved in pore water are accumulated from sediment and digestion of sediment may play an important role in the uptake of PAH by some species (Ohkouchi et al., 1999). The relative importance of the uptake routes from food and sediment is not known.

The bioconcentration factors of PAH in different species vary greatly (USEPA, 2009). Species that do not metabolise PAH at all or to only a limited extent, such as algae, oligochaetes and molluscs, and the more primitive invertebrates (protozoans, porifers and Cnidaria) accumulate high concentrations of PAHs. However, organisms that metabolise PAHs such as fish and higher invertebrates, such as arthropods, echinoderms and annelids accumulate little or no PAHs. This may cause hydrocarbon contamination in sediment and its exposure to the benthic biota may lead to acute/chronic toxicity, whereas its transfer through the food web may result in serious human health effects (Weinstein et al., 2010; Zeng et al., 2013).

1.3.4 Degradation of PAHs in the aquatic environment

In the aquatic environment, degradation of PAHs occurs through abiotic and biotic processes. The most significant among them are photooxidation, chemical oxidation and biodegradation. PAHs undergo photooxidation in the presence of sunlight, hydroxyl free radical, or other oxidising agents forms endoperoxides, which on further photolysis or pyrolysis result ring cleavage and dealkylation produce various oxidative products (Neff, 1979). In the presence of mineral carries like Al_2O_3 or SiO_2 Photooxidation of PAHs was more effective. Some bacteria and yeast species are efficient for degrading PAHs in marine and freshwater area except heavily polluted area.

1.3.5 Toxicity of PAHs

PAH exposure in humans is primarily through ingestion and inhalation. Under normal circumstances, skin contact with PAH is comparatively unimportant. Similar to other lipophilic compounds, PAHs usually are well absorbed in the body but are stored in the body very fewer, mainly in the kidney, liver and spleen. Most of the absorbed amount is then expelled into bile and eventually faeces and too much lesser extent urine. Most of the PAHs are excreted in a metabolised form, and only little amounts of the parent compound find its way into faeces and urine (Neff, 1979). PAHs are highly soluble in fats. In this form, they can quickly enter cells and become virtually unavailable for excretion. Metabolic processes tend to make PAH more water-soluble, which facilitates excretion.

Several metabolic processes participate in producing a variety of different metabolites. Phase I reactions addition of one or more hydroxyl groups to the parent compound is a phase I reactions, whereas the addition of highly water-soluble groups to the PAH molecule is phase II reactions. Phase I reactions are regulated by epoxide enzymes hydrolase and a subset of cytochrome P-450 mixed-function oxidases called aryl hydrocarbon hydroxylase (AHH) (Vandermeulen and Penrose, 1978). The structures of PAH vary greatly, but the metabolism of these compounds is similar and leads to the formation of homologous metabolites (Neff, 1979; Bogovski et al., 1999; Yuan et al., 1999).

Due to the differences in the location of the metabolic modifications and the activities of the intermediate metabolites they cause different tumours. Some of the metabolites are diol epoxide form; these diol epoxides are converted into carbonium ions. The carbonium ions can directly interact with DNA and proteins to form adducts and induce genotoxic damage (Neff, 1979). These alkylating agents are primary carcinogens, acting as initiators. Initiation is the first step in the development of cancer. The enzymes required for the conversion of parent PAH compounds into the reactive diol epoxides are found mainly in the liver, but also the lungs, skin basal cell layer, intestinal mucosa and other tissues (Neff, 1979).

PAHs may cause several toxic effects. Short-Term exposure to a high dose of several PAHs has been shown to cause death in rodents. Since environmental levels are generally much lower than some of the occupational ones, it is extremely unlikely that short-term exposure to PAH in the environment would lead to death. On the other hand, eye irritation, photophobia and skin toxicity such as dermatitis and keratosis have been demonstrated to be caused by occupational exposures to PAH (Boese et al., 1999).

Adverse respiratory effects, including acute and subacute inflammation, and fibrosis, have been proved experimentally. With B[a]Pyrine, severe and long-lasting hyperplasia and metaplasia were observed as precancerous lesions and are consistent with the general assertion that one of the main targets of PAH toxicity is the respiratory tract (Lotufo, 1997). Carcinogenic PAHs (not the noncarcinogenic ones) have been reported to suppress immunity in rodents. Furthermore, there appears to be a rough correlation between the potency of PAH as immunosuppressors and as carcinogens. Immunosuppression may, therefore, be a important toxic endpoint of PAH (Payne and Fancey, 1989). Some authors also suggest that immunosuppression may be involved in the mechanisms by which PAH induce cancer.

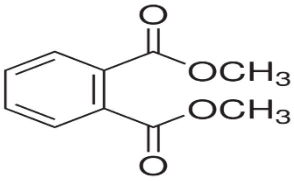
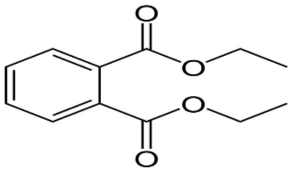
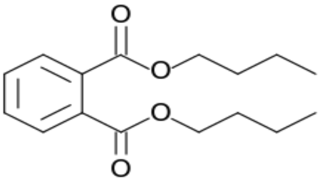
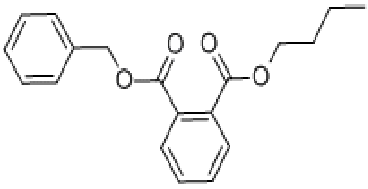
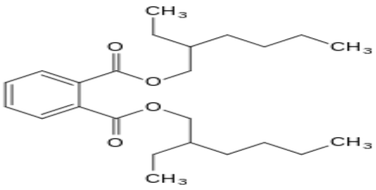
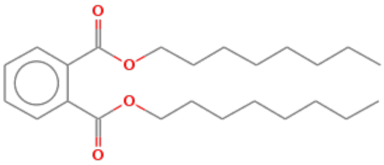
Both in vivo tests in rodents and in vitro tests using mammalian (including human) cell lines, as well as in prokaryotes were done to explain genotoxic effects for some PAHs (Yuan et al., 1999). Some PAHs appear not to be genotoxic but need to be metabolised first. Then the diol epoxides that are formed react with DNA to form DNA adducts, thus inducing genotoxic damage. Effects like skin, eye and respiratory mucosa irritation are more likely to be detected with severe exposures rather than with the characteristically lower environmental exposures (Yuan et al., 1999).

Being persistent organic pollutants (POPs), they have become the focal point of pollution research for several decades owing to their toxicity, carcinogenicity and mutagenicity which may be harmful to ecosystems and human health (Wang et al., 2012; Keshavarzifard et al., 2015; Li et al., 2015a). The US EPA has regulated at least 16 PAH fractions owing to their, persistence, prevalence and potential hazards to the environment.

1.4 Phthalic Acid Esters (PAEs)

Phthalic acid esters (PAEs) are a group of synthetic organic chemicals used widely in plastic products as softeners (plasticisers) and other 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). The most widely used phthalates are di-2-ethyl hexyl phthalate (DEHP), diisodecyl phthalate (DIDP), and the diisononyl phthalate (DINP). DEHP is the dominant plasticiser used in PVC due to its low cost. Benzylbutylphthalate (BBP) is used in the manufacture of foamed PVC, which is mostly used as a flooring material. Phthalates with small R and R' groups are used as solvents in perfumes and pesticides. 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).

Table 1.2: Different PAE congeners Studied

Name of PAE	Molecular weight (g/mol)	Structure
Dimethyl phthalate (DMP)	194.18	
Di ethyl phthalate (DEP)	224.28	
Di n butyl phthalate (DnBP)	278.35	
Butyl benzyl phthalates (BBP)	312.37	
Di-(2-ethyl hexyl)phthalate (DEHP)	390.56	
Di-n octyl phthalate (DnOP)	390.56	

1.4.1 Toxicity of PAEs

Phthalic acid esters are a main environmental pollutant and a cause for serious concern because they are found in most people's blood, tissue, urine and breast milk. PAEs are recognised as potential endocrine-disrupting chemicals (EDCs) and carcinogenic materials (Huber et al., 1996), causing severe health problems, including reproductive abnormalities (Guo et al., 2012). There are six types of PAEs listed as major pollutants by the United States Environmental Protection Agency (USEPA) and the European Union (EU) (Ventrice et al., 2013). They easily get attached to suspended matter and sediments by their hydrophobic character and enter the food web through consumption (Sun et al., 2013; Liu et al., 2014a; Liu et al., 2014c; Cheng et al., 2016).

Consumption and continues the exposure of PAEs could cause a wide variety of health issues such as

- Cancers (e.g., liver, breast, prostate, testicular, colon)
- Autoimmune diseases (e.g., lupus)
- Fertility problems (e.g., low sperm count, poor mobility of sperm, DNA damage in sperm, lower testosterone level, and ovarian dysfunction)
- Obesity, resistance to insulin, and diabetes in men
- Smaller testes and smaller genitals on average among male babies exposed to phthalates in mothers' wombs
- Asthma
- "Feminization" of male fish, frogs, and other amphibians living in a phthalates-contaminated environment

PAEs are potential endocrine-disrupting chemicals (EDCs) and carcinogenic materials, which may lead to severe health problems including reproductive abnormalities (D.K.Agarwal et al., 1986; Huber et al., 1996; Guo et al., 2012). 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; Ventrice et al., 2013; Liu et al., 2014b; Cheng et al., 2016).

1.4.2 Fate and behavior of PAEs in the marine environment

Some phthalate esters have poor solubility in water, and they can become concentrated in suspended particulate matter and sediment. Depending on the individual ester the behavior of phthalate esters in the environment varies (Staples et al., 1997; Sun et al., 2013). In general, the increase of alkyl side-chain or degree of branching, the more persistent the compound. Phthalate esters generally have low volatility, which decreases with the increasing length of the alcohol side-chain of the ester (Zhang et al., 2014; Li et al., 2016).

Phthalic acid esters show great affinities for partitioning to particulate materials in the aquatic environment. Apart from DMP and DEP, all other Phthalic acid esters exhibit substantial sorption capacity towards suspended particulates and sediments (Staples et al., 1997). DMP shows high water solubility than an affinity for partitioning to particulate materials. Partitioning tendency depends on side-chain length, it increases with the increase of side chain length. DnOP having the highest affinity for suspended particulate material in natural waters.

Biodegradation is the most important aquatic degradation process for phthalate esters (Scholz, 2003). Short side-chain phthalate esters (DMP, DEP and BBPs) are all likely to degrade easily in the aerobic aquatic environment. The longer chain PAEs, such as DnOPs, easily get adsorbed into suspended solids and more strongly to sediments, and they are likely to be more persistent, so may be less available to microbial degradation (Liu et al., 2014c) Therefore DnOPs in anaerobic sediments will tend to persist for long periods. DMP and DEP can be regarded as having poor tendency for bioaccumulation, while BBP and DnBP have an intermediate tendency. DEHP and DnOP have a greater affinity for sediments or partitioning to biota (Hassanzadeh et al., 2014)

The occurrence, distribution and ecological risks of PAEs have been comprehensively documented in numerous rivers, estuarine and coastal areas around the globe 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), Juilong River, China (Li et al., 2017), Mediterranean Sea and Rhone river (Paluselli et al., 2018). Studies on the distribution and contamination status of PAEs in aquatic systems in India are scarce except for a few rivers (Srivastava et al., 2010; Selvaraj et al., 2015).

1.5 Aim and Scope of the Study

Cochin estuary, the largest estuarine system along the southwest coast of India, is exposed to serious environmental degradation due to increased anthropogenic activities - industrialisation, urbanisation, inter-tidal land reclamation, port and harbour development, aquaculture activities, etc. (Menon et al., 2000; Salas et al., 2017). Over the last two decades, there have been numerous reports on the sporadic release of nutrients (Naik 2000; Balachandran et al. 2002; Martin et al., 2012), heavy metals (Deepulal et al., 2012a; Selvam et al., 2012; Bindu et al., 2015), other toxic metals (Kaladharan et al., 2005; Nair et al., 2006; Raveenderan and Sujatha, 2011; Mohan et al., 2012) and persistent organic pollutants (POPs) (Sujatha and Chacko, 1991; Sujatha et al., 1993, 1994; Sujatha et al., 1999; Babu et al., 2011; Akhil and Sujatha, 2014) into the Cochin estuary. These studies generally indicate the mounting pollution and its potential threat to the estuarine environment. However, no comprehensive studies where carried about endocrine disrupting pollutants in Indian estuarine system. Source fate and transport of these pollutants are still unknown. Extensive studies are, therefore, needed to understand the sources and transformation of Phthalic acid esters (PAEs) and polyaromatic hydrocarbons (PAHs) in the estuary, which are very toxic as endocrine disruptors. The objectives of the present study are to identify the sources of persistent pollutants such as PAEs and PAHs and assess their potential threats to the bioresources of the Cochin estuary.

The present study intends

- To investigate the seasonal and spatial variations of two major class of endocrine disrupting organic contaminants in the Cochin estuary; PAHs and PAEs.
- To understand the sources, behavior and fate of PAHs and PAEs in the Cochin estuary.
- To delineate the ecological risk posed by PAHs and PAEs in the estuary.

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Chapter

2

MATERIALS AND METHODS

Contents

2.1 Description of Study Area

The Cochin estuary is a part of the Vembanad-Kol system that includes a system of interconnected lagoons, bays and swamps enclosing many islands. Recognizing the ecological significance, this fragile ecosystem was designated as a Ramsar Site (No. 1214) by UNESCO Wetland Convention in 2002 (Wetlands 2002). It has two permanent opening into the Arabian sea- a southern one extending from Cochin barmouth to Thanneermukkom and a northern one extending towards north from Cochin to Azhikode. The Cochin estuary (9°40^{l}N-10°08^{l}N-76°11^{l}E-76°25^{l}E) approximately 320 km^{2} in area, wide (0.8–1.5 km) and deep (4–13 m) towards the south, but narrow (0.05–0.5 km) and shallow (0.5–2.5 m) towards the north (Balachandran et al., 2008; Gireeshkumar et al., 2013). The average rainfall in this region is ~300-320 cm yr$^{-1,}$ the hydrology of the estuary is mainly characterised by three seasons premonsoon (February -May), monsoon (June–September), postmonsoon (October–January). The estuary is heavily influenced by the Indian summer monsoon, which contributes about 71% of the annual rainfall (Qasim, 2003) The main rivers discharging into the Cochin estuary are Periyar, Pamba and

Muvattupuzha, the others being Manimala, Meenachil and Achankovil (Srinivas et al., 2003). These rivers discharge a large volume of fresh water during monsoon than compared to other seasons (Srinivas et al., 2003; Raveenderan and Sujatha, 2011). The percentage of discharge of each river is as follows Periyar (33.2), Pamba (19.7), Muvattupuzha (24.2), Manimala (8.8), Meenachil (8.3), and Achan Kovil (5.8) (Srinivas et al., 2003).

Cochin estuary is a tropical monsoonal estuary receiving a large quantity of synthetic organic wastes from various urban and industrial activities (Gireeshkumar et al., 2013). The northern, Central and southern parts of this estuary are contaminated with both organic (Polyaromatic hydrocarbons and (George et al., 2013). The environmental problems of this area are most likely the result of exhaustive and uninterrupted industrial and domestic effluent release.

2.2 Sampling and Storage

Fifteen sampling stations were fixed along the salinity gradients of the Cochin estuary covering the discharge points of both Periyar and Muvattupuzha River (Table 2.1; Figure 2.1). The Stations selected based on nature intensity and anthropogenic activities. They are classified as two Zones, Zone-I includes S1 to S6 and S9 are situated around the Cochin harbour region and this area is important for shipping, industrial and municipal activities. S7 to S15 except S9 includes in Zone II are important for agricultural activities. Water and sediments were collected during May, August and December 2013 representing premonsoon monsoon and postmonsoon periods, respectively. Sediment samples were collected using pre-cleaned Van Veen grab (0.042 m^2), and Water samples were collected using a pre-cleaned a custom made sampler (Hydrobios 5L) for analysing general chemical hydrography. Water samples for PAH and PAE analysis were carried out using a custom designed sampler made up of steel and Pyrex glass (Fig.) transferred to amber coloured glass bottles. A known volume of water sample was filtered through GF/F filter paper and the filtrate was kept at 4 °C for further extraction. Filters with the suspended particulate matter were wrapped in aluminium foil, labelled and kept frozen until the extraction.

Sediments were collected using a stainless steel Van Veen grab. Several deployments per stations were carried out to obtain undisturbed samples to avoid contamination of the sample during operation. The sediment samples were transferred to amber coloured glass bottles using a steel spatula, kept frozen until analysis.

Table 2.1: Locations of sampling stations

Station Name	Latitude	Longitude
S1 Barmouth	09°58 374^1	076°14.815^1
S2 Bolgatty	09°8.812^1	076°16.160^1
S3 Sulphur Jetty	09°57.721^1	076°16.716^1
S4 Shipyard	09°56.566^1	076°17.414^1
S5 Fishing Harbour	09°57.107^1	076°15.814^1
S6 Thevara	09°55.455^1	076°17.874^1
S7 Kumbalam	09°53.201^1	076°18.213^1
S8 Panangad	09°52.603^1	076°20.032^1
S9 Poothotta	09°50.161^1	076°20.753^1
S10 Perumbalam	09°51.427^1	076°21.949^1
S11 Murinjapuzha	09°49.779^1	076°22.637^1
S12 Moovatupuzha	09°48.707^1	076°23.947^1
S13 MurikkinPadam	09°59.392^1	076°14.509^1
S14 Cheranallur	10°03.664^1	076°16.807^1
S15 Njarakkal	10°02.961^1	076°14.264^1

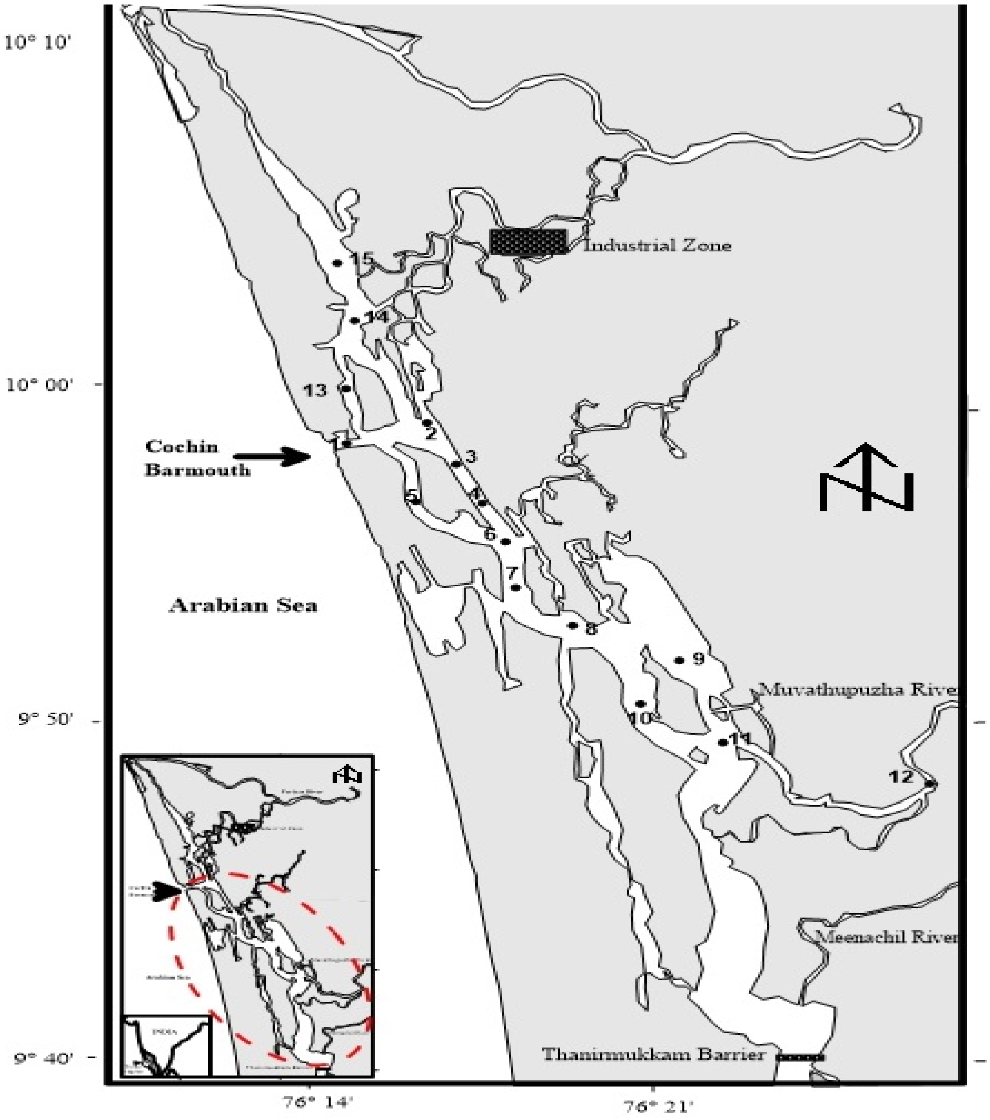


Figure 2.1: Map of the study area showing locations of sampling sites

2.2.1 Apparatus and chemicals.

All glassware that was used for the analysis of trace contaminants was thoroughly cleaned with soap and tap water. Then washed with chromic acid followed by distilled water and acetone then dried in a hot air oven. All glass wares were covered with aluminium foil and stored in a desiccator when not in use. Glasswares and plastic wares for nutrient analysis were dipped in 5 % HCl solution overnight, washed with Milli-Q water and dried in a hot air oven. All the organic solvents (n-hexane, dichloromethane, methanol and acetone) were of high purity (AR or Merck Lichrosolv). Anhydrous Na_2SO_4 was dried at 450 °C before use. Silica gel (60-120 mesh), alumina was precleaned by methanol followed by hexane, dried wrapped with aluminium foil and kept in a desiccator. Silica gel was activated at 160 °C for 16 hours and alumina at 200 ° C for 4 hours.

2.3 Analytical Methodology

2.3.1 General Water and Sedimentary Characteristics.

All the water samples were analysed by the methods suggested by Grasshoff et al. 1983 and APHA 1999. Dissolved oxygen of the water samples was measured by Winkler's method. The salinity of the water samples was estimated by Mohr-Knudsen method. Nutrient analysis was done by standard procedure (Grasshoff et al., 1983).

2.3.2 Texture Analysis

Grain sizes of sediments were determined by pipette analysis using wet sediment samples (Robert.L.Folk, 1980). The sediment samples for OC, TN, TS analyses were freeze-dried homogenised and powdered using mortar and pestle. The analyses were preceded by treatment of samples with 1M HCl to remove carbonates. The process was repeated two/three times in order to ensure the complete exclusion of carbonates and samples were washed with Milli-Q water to remove salts and finally freeze dried. Organic carbon (TOC) and total nitrogen (TN) and total sulphur (TS) were determined using CHNS analyser (Vario EL III CHNS Analyser). Acetanilide standards were used to calibrate the elemental analyser. The detection limits for OC and TN are 0.07 and

0.01, respectively. The amount of total organic matter (TOM) is obtained by multiplying the OC values with 1.80 (Muller et al., 1986).

2.3.3 Extraction of PAHs

2.3.3.1 Dissolved Phase

A direct liquid-liquid extraction procedure was applied for extracting PAHs from filtered water samples. Transfer 1 litre of the sample into a clean separating funnel. Add 40 ml 1:1 Hexane: Dichloromethane (DCM) into the sample. The funnel was vigorously shaken for 10 minutes with frequent release of pressure. The extraction mixture was allowed to settle and Hexane: DCM layer drained into 250 ml round flat bottom flask. The extraction was repeated thrice using 40 ml 1:1 Hexane: DCM and all the extracts were collected. The extract was evaporated to near dryness using rotary evaporator. The samples were quantitatively transferred to labelled 4 ml glass vials using a minimum amount of n-hexane and subsequently dried using a gentle stream of nitrogen. The residue was dissolved in 200 µL n-hexane and kept for gas chromatographic analysis.

2.3.3.2 Sediments and Suspended Particulate Matter (SPM)

Freeze dried, homogenised sediments and SPM were extracted with 2:1 mixture of dichloromethane-methanol in a Soxhlet apparatus for 48 hours and the extracts were treated with activated copper granules to remove elemental sulphur. The extract was concentrated by rotary evaporation and the residue was chromatographed using precleaned and activated 2:1 silica-alumina column. The column was eluted with 30 ml of n-hexane followed 50 ml 3:7 n-hexane in dichloromethane. The second fraction containing PAHs was evaporated to dryness, re-dissolved in 500 µL n-hexane and kept for gas chromatographic analysis.

2.3.4 Gas Chromatographic Analysis of PAHs

Sixteen PAHs (categorized by USEPA as priority PAHs) including 2-ring [Napthalene (Naf)], 3-ring (acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An)); four ring (fluoranthene (Flu), pyrene (Py), benzo[a] athracene (BaA), chrysene (Ch)), 5-ring, (benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP)), and 6-ring (indo [1,2,3-cd] pyrene (IP), bnzo[g, h, i]perylene (Bper), dibenzo[a,h] anthracene (DbA)) were analyzed using Perkin Elmer Claurus 600 GC equipped with flame ionization detector. Data acquisition was achieved using Total Chrom work station. PE-5 (5% diphenyl and 95% dimethylsiloxane) capillary column (30 m length, 0.32 mm i.d., 0.25 mm film thickness) was used. The column temperature for analyses was programmed from 60 °C (initial time, 2 min) to 120 ºC at a rate of 10 ºC per min, 120–300 ºC at a rate of 3 ºC per min, and held at 300 ºC for 5 min. The injector was kept at 280 ºC and the detector temperature set at 325 ºC. Before analysis, relevant standards were run to check column performance, peak height and resolution, and the limits of detection (LOD). With each set of samples, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, the peak of identification and quantification. The peaks were also confirmed using GC-MS (Perkin Elmer Clarus GC 620, equipped with Clarus 600T MS detector) with a non-polar HP ultra-double-fused silica capillary column (30 m, 0.32 mm internal diameter, 0.25 μm film thickness). Operating conditions were as follows: ion source of electron voltage 70 eV kept at 200 °C. Spectra were scanned from 50 to 600 m/z with a scan time of 1.50 s.

Prior to the analysis, standards (Supelco TCL Polynuclear Aromatic Hydrocarbon Mix 20-1000 µg/ml in ACN-MeOH) were run to check column performance, peak height and resolution, and the limits of detection. A solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, the peak of identification and quantification with each set of analysis. The extraction efficiency was checked by adding a known amount of PAHs standard mixture to the sediment samples, and the recovery of individual PAHs were found to be varied between 78 and 96%. All results are expressed on a dry weight basis.

2.3.5 Extraction of Phthalate Esters

2.3.5.1 Dissolved Phase

A direct liquid-liquid extraction procedure was applied for extracting phthalates from filtered estuarine water. The water samples were extracted thrice with aliquots of DCM (25 ml) in a separating funnel. The extract was evaporated to near dryness using rotary evaporator, transferred to 4ml glass vials and dried using a gentle stream of nitrogen. The residue was redissolved in 200 µL DCM and kept frozen till analysis.

2.3.5.2 Sediment and SPM

Freeze dried, homogenised and powdered sediments and frieze dried SPM samples were Soxhlet extracted with dichloromethane for 48 hours. The elemental sulphur was removed using activated copper granules. The extract was further concentrated using a rotary evaporator, re-dissolved in 2 ml n-hexane and passed through a chromatographic column (1 cm i.d. and 30 cm length) packed in 12 cm silica gel and 6 cm alumina. The column was eluted successively using 20 ml 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). The Fraction 3 containing PAEs were concentrated using a rotary evaporator, evaporated to near dryness by a gentle stream of nitrogen gas, dissolved in 100 µL n-hexane, mixed thoroughly using a vortex mixer and kept at -20 °C until the analysis.

2.3.6 Gas Chromatographic Analysis of PAEs

PAEs were analysed using a Gas Chromatograph connected with a flame ionisation detector (Perkin Elmer Clarus 600) and a data acquisition work station. The GC was Connected with a PE-5 (5% diphenyl and dimethylsiloxane) capillary column (30 m length, 0.32 mm id., 0.25 mm thickness). The temperature of the column was maintained 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 held at 300 °C for 5 min. The injector and detector were kept at 280 °C and 325 °C respectively and the peaks were detected using GC-MS (Perkin Elmer Clarus GC 620, equipped with Clarus 600T MS detector) connected with non-polar HP ultra-double-fused silica capillary column (30 m, 0.32 mm internal diameter, 0.25 µ film thickness). The operational conditions included an ion source of electron voltage 70 eV at 200 °C. PAE quantification was performed using a standard mixture of 6 USEPA priority pollutant mixture and calibrating the procedure using a five-point curve for individual PAEs. Strict quality control measures were adopted for the entire analysis. Solvent blank, standard mixture and procedural blank were run to check the error in peak identification and quantification. The extraction efficiency for individual PAE was 80-94%. All chemical analyses were carried out in triplicates and results are expressed on a dry weight basis.

2.3.7 Statistical Analysis

All the statistical analysis (One-way Analysis of variance (ANOVA), correlation and factor analysis) were done using 'Statistical Package for Social Sciences (SPSS), version-22'. Spatial and seasonal variations were assessed by ANOVA with season and stations as a source of variation. Log (x+1) transformation was used to normalize the data set and it was checked using the criteria of (Webster et al., 2001). Factor analysis was used to extract information from the most meaningful parameters which better described the overall data. In factor analysis, principal component analysis (PCA) and varimax rotation methods were used for extraction and principal deriving components (PC). Factor loading was considered significant if it was > 0.50.

2.4 Results

2.4.1 General Hydrographic Parameters

The study of hydrography parameters of the aquatic environment has great importance to understand the clear picture about general features, distribution and relative abundance of organic and inorganic pollutants. The hydrographic data of Cochin estuary is of great significance because it receives effluents from huge number of industries including major fertiliser plant, petroleum refinery, waste treatment plants, petrochemical industries etc. In addition to this, Cochin estuary has the largest port in India, harbour activities, tourism, navigational activities, saline water intrusion associated with tides, freshwater discharge from the rivers, etc. also reflect in the hydrographic data and pollutants level. There for a brief description of the general hydrographic parameters is incorporated in this section.

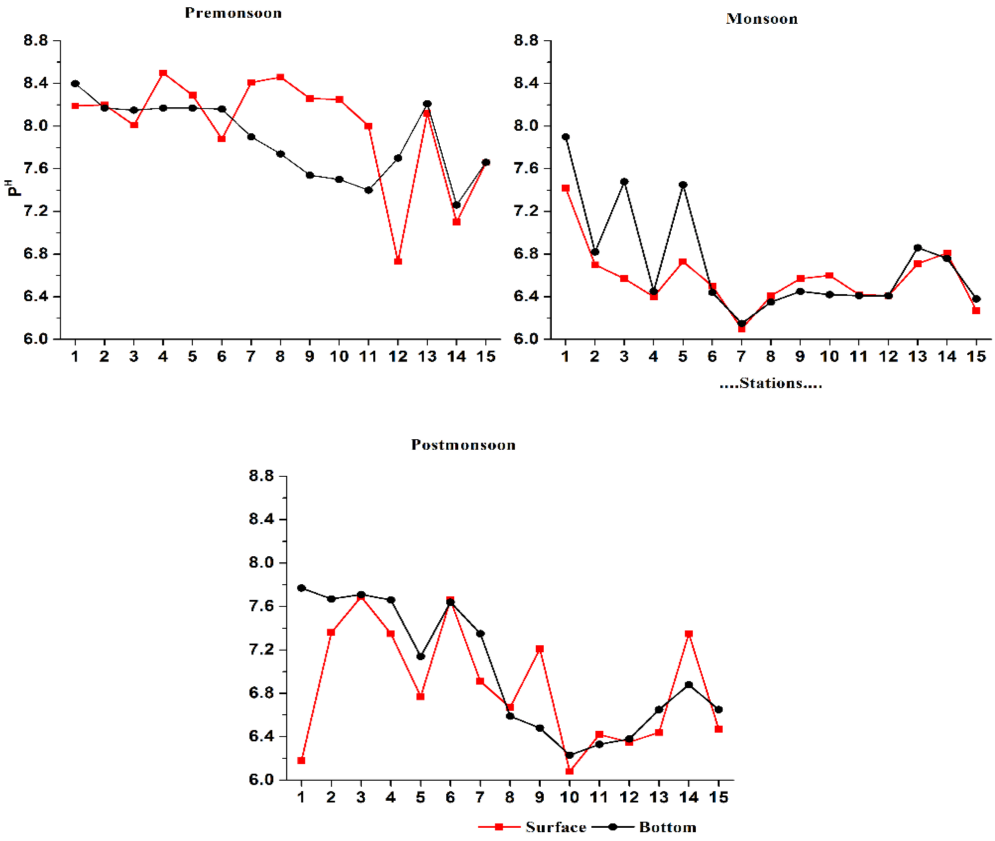


Figure 2.2: Spatial and Seasonal variation of pH in Cochin estuary

The seasonal and spatial variations of different water quality parameters of surface and bottom water were studied. Terrestrial runoff along with monsoon rainfall greatly influence the hydrography of Cochin estuary. pH in water column was slightly alkaline (except surface water of S12) during premonsoon season with an average 8 ± 0.44 and 7.8 ± 0.35 in surface and bottom water respectively, whereas the study region was slightly acidic character during monsoon season (except surface and bottom water of S1) with average 6.57 ± 0.30 in surface water and 6.72 ± 0.50 in bottom water. The pH of water column displayed a mixed character and almost neutral during postmonsoon season, showed average values with 6.86 ± 0.53 and 7.01 ± 057 surface and bottom water respectively. A number of the process like biological activities, freshwater discharge, saltwater intrusion from seas, etc. were usually attributed to the change in pH of the water column. Significant variation in pH will be a threat to aquatic life (Geetha et al., 2006).

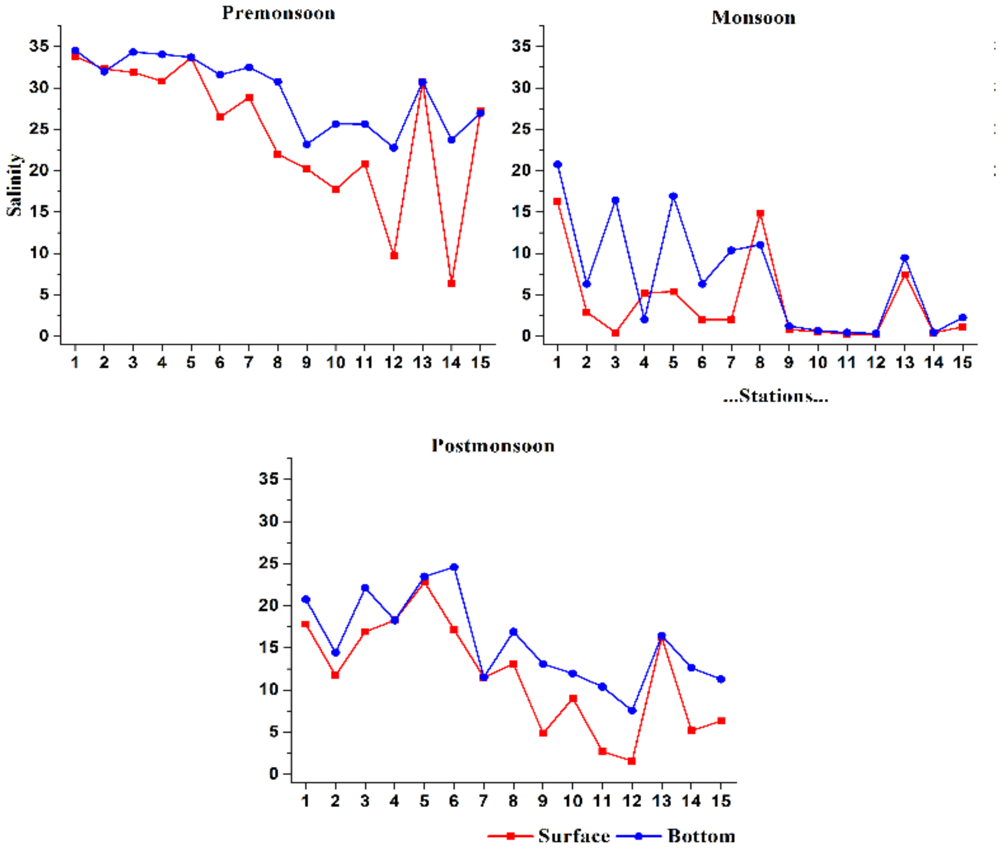


Figure 2.3: Spatial and Seasonal variation of Salinity in Cochin estuary

Salinity plays a vital role in aquatic life in an estuarine environment. In this study, large fluctuation in salinity was observed and it is mainly increased by evaporation, saltwater intrusion etc. and decreased by freshwater discharge, rainfall, and tidal activities etc. In this study, the salinity showed a wide variation from 0.22 to 34.56. The freshwater condition was prevailing during monsoon season when rainfall and river runoff is very high. During monsoon, salinity varied from 0.26 to 20.77 (average 5.82 ± 6.18). After the monsoon, the salinity started to increase. High salinity was observed during premonsoon season, which is ranged from 6.37 to 34.56 (average 27.16 ± 6.44). Postmonsoon season also displayed high salinity than monsoon, which was varied from 1.58 to 24.61 (average 13.70 ± 6.14).

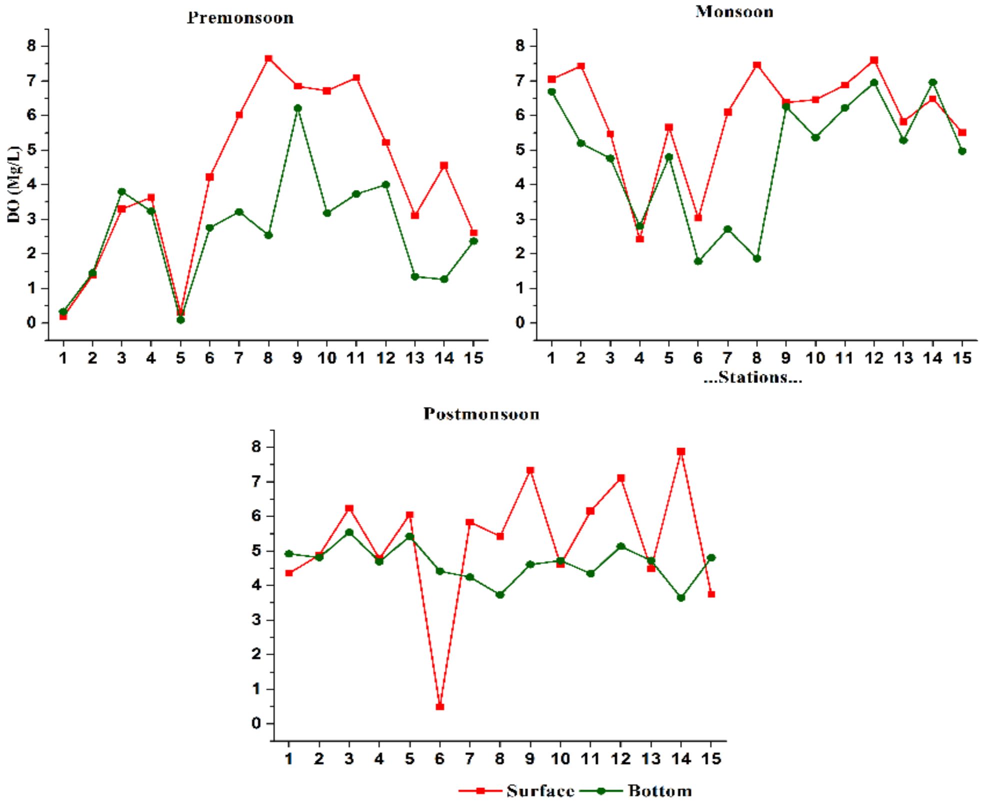


Figure 2.4: Spatial and Seasonal variation of DO in Cochin estuary

Dissolved oxygen level is an important parameter for aquatic life. It depends on temperature, salinity, biological activates, water mixing, atmospheric gas exchange etc. DO concentration in water is balanced by photosynthesis, respiration, degradation of organic matter, reaeration and physicochemical properties of water (Garnier et al., 1999; Aston, 1980). The degradation of organic matter from effluent discharge and domestic sewage may reduce the DO to extremely low or may be zero (anoxic). An adequate amount of DO is essential for the existence of aquatic life. The depletion of oxygen concentration in water leads to false odours and will harm aquatic life (Garnier et al., 1999).In this study DO varied from 0.08 to 7.88 mg/L. During premonsoon season DO concentration was very low and varied between 0.18 and 7.66 mg/L (average 4.19 ± 2.42 mg/L) and 0.08-6.21 mg/L (average 2.63 ± 1.58 mg/L) for surface and bottom water columns respectively. DO level increased during monsoon season, may be due to higher turbulence of river runoff during the rainy season. Surface DO varied from 2.42 to 7.60 mg/L (average 5.99 ± 1.5mg/L) and bottom DO from 1.78 to 6.94 mg/L (average 4.84 ± 1.77 mg/L). During postmonsoon season DO variation was noted from 0.50 to 7.88 mg/L (average 5.29 ± 1.79 mg/L) at the surface and 3.64 – 5.54 mg/L (average 4.65 ± 0.53 mg/L) bottom water respectively.

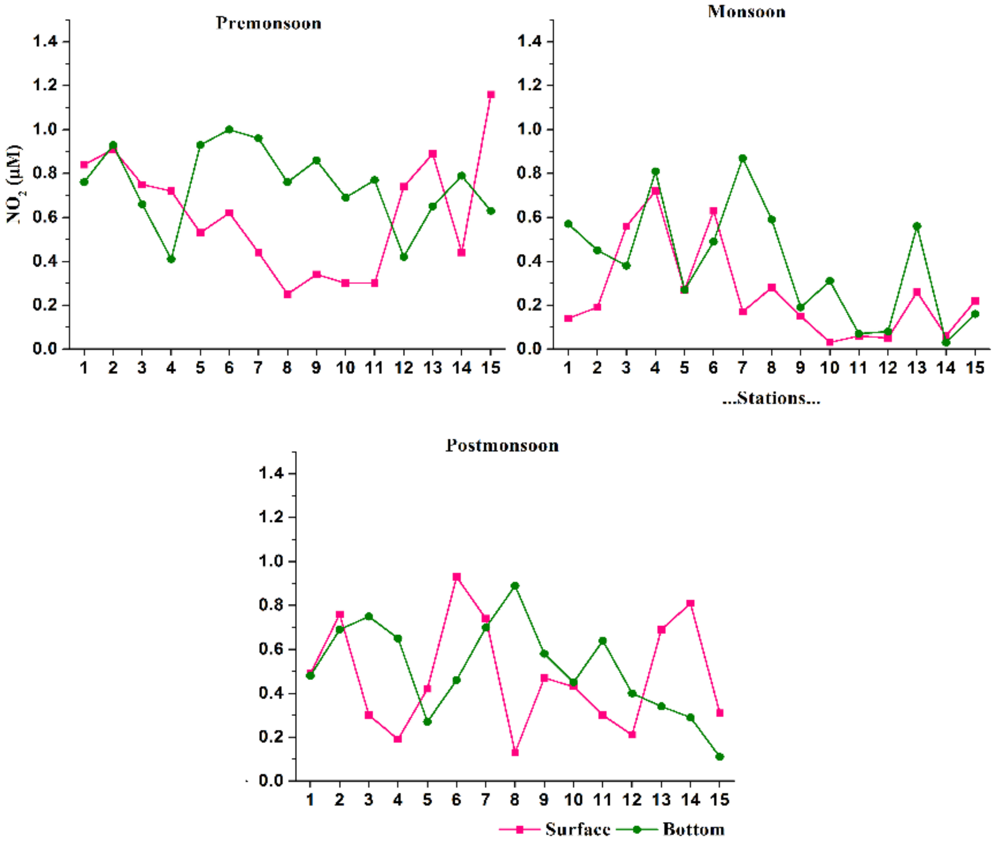


Figure 2.5: Spatial and Seasonal variation of Nitrite in Cochin estuary

Nutrient level in the water column is controlled by physical, chemical, and biological activities. Generally, bottom water shows high nutrient concentration than surface water. A higher concentration of nutrients in bottom water may be due to the nutrients available from the interstitial sediments owing prevalent dredging. Among the dissolved nutrients, different forms of nitrogen (ammonia, nitrite and nitrate) were studied.

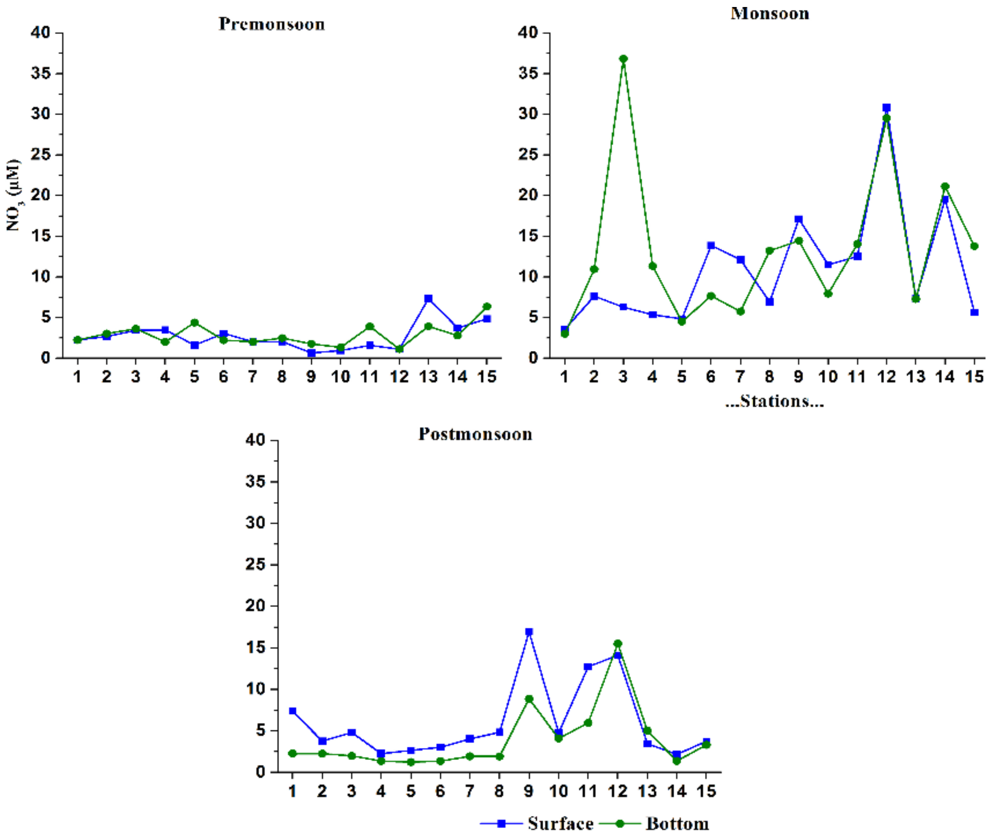
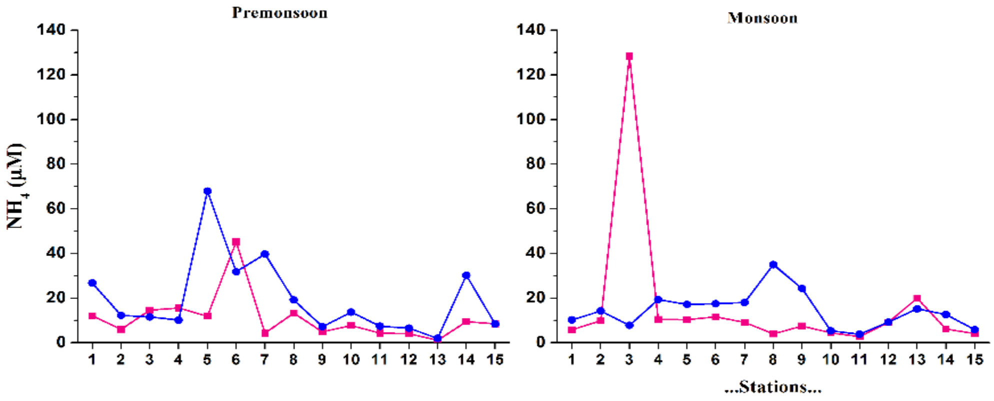


Figure 2.6: Spatial and Seasonal variation of Nitrate in Cochin estuary

Industrial zone station S2 to S10 exhibited an increase in nutrient concentration throughout the investigation period. During premonsoon season nitrite (NO_2^-) concentration in surface and bottom water varied from 0.25 – 1.16 µM (average 0.62 ± 0.27 µM) and 0.41-1.00 µM (average 0.748 ± 0.18 µM). During monsoon season its concentration reduced due to dilution. It varied n.d - 0.72 µM (average 0.25 ± 0.22 µM) and n.d – 0.87 µM (average 0.38 ± 0.28 µM). Postmonsoon season surface nitrite concentration varied from 0.13-0.93 µM (average 0.48 ± 0.25 µM) and the bottom from 0.11-0.89 µM (average 0.51 ± 0.21µM).

Concentration levels of inorganic nitrate were plotted (Figure 2.6). Nitrate (NO_3^-) in premonsoon at surface water varied from 0.64 to 7.34 µM (average 2.71 ± 1.73 µM) and that of bottom water from 1.12 – 6.34 µM (average 2.87 ± 1.37 µM). During monsoon season it ranged between 3.56 – 30.82 µM (average 11.00 ± 7.24 µM) at the surface and 2.98 – 36.82 µM (average 13.419 ± 9.36 µM) at the bottom. During postmonsoon season, the nitrate concentration was in the range 2.16 – 16.94 µM (average 6.04 ± 4.68 µM) at surface and 1.25 – 15.49 µM (average 3.89 ± 3.86 µM) at the bottom. Nitrate concentrations peaked at S12 during monsoon season may be due to high input from land-based runoff.



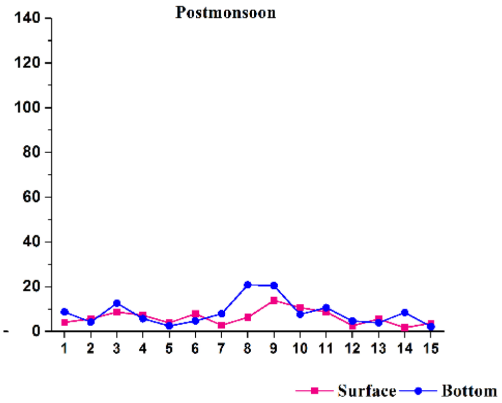
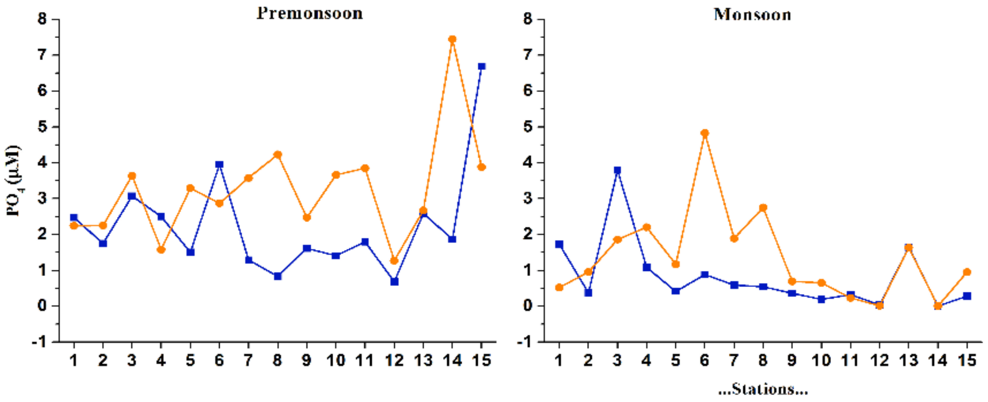


Figure 2.7: Spatial and Seasonal variation of Ammonia in Cochin estuary

Ammonia (NH_4^+) during premonsoon varied between 1.07 – 45.20 µM (average 10.82 ± 10.45 µM) at surface water and 1.93 – 67.91 µM (average 19.62 ± 17.34 µM) at bottom water. During monsoon season it varied from 2.71 to 128.38 µM (average 16.20 ± 31.32 µM) at surface water and 3.82 – 34.99 µM (average 14.35 ± 8.18 µM) at bottom water. During postmonsoon, surface concentration varied between 1.71 – 13.87 µM (average 6.22 ± 3.36 µM) and bottom concentration varied between 2.12 – 20.78 µM (average 8.33 ± 5.81 µM). Ammonia concentrations may be supplemented by Periyar river and its tributaries including Chithrapuzha, which is flowing along the industrial zone.



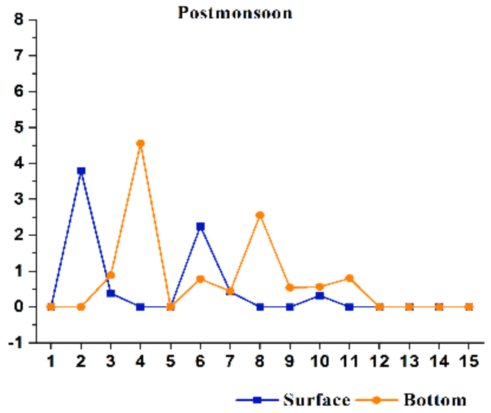
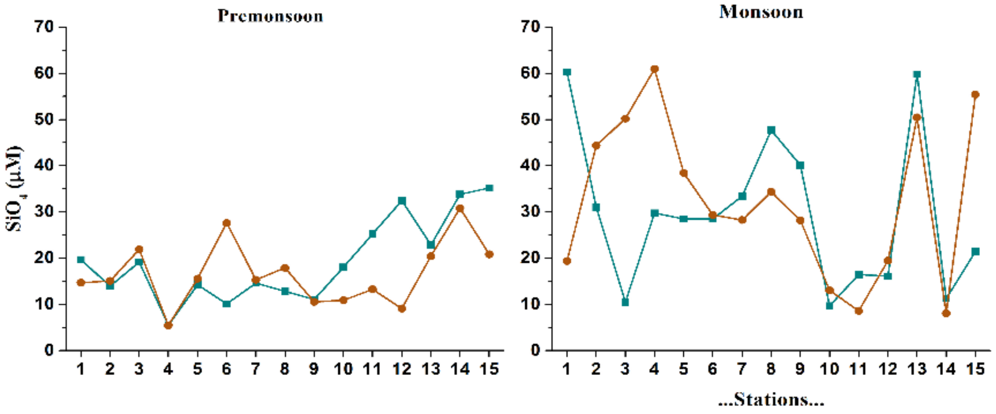


Figure 2.8: Spatial and Seasonal variation of inorganic Phosphate in Cochin estuary

Dissolved inorganic phosphate PO_4^{3-} along the study area showed 0.68 - 6.69 µM (average 2.26 ± 1.49 µM) in surface water and 1.27 – 7.45 µM (average 3.27 ± 1.45 µM) in bottom water during premonsoon season. In monsoon season it ranged from below detectable limit n.d to 3.79 µM (average 0.81 ± 0.98 µM) and n.d to 4.83 µM (average 1.36 ± 1.26 µM) surface and bottom water respectively. PO_4^{3-} displayed n.d concentration from Murinjapuzha to Muvattupuzha region during postmonsoon season. Seasonal trends show that within the estuary, higher concentrations were obtained during premonsoon than monsoon and postmonsoon.



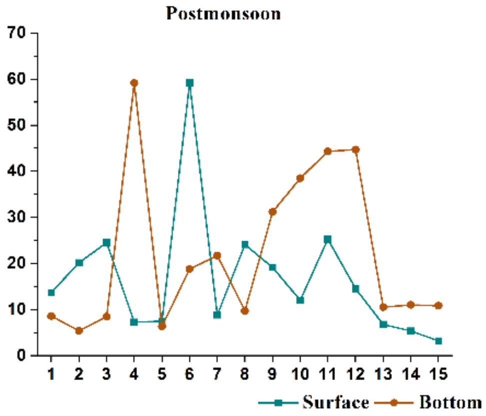


Figure 2.9: Spatial and Seasonal variation of Silicate in Cochin estuary

SiO_4^- concentration was less during premonsoon compare to other seasons. It varied from 5.51 – 35.2 µM (average 19. 25 ± 9.05 µM) and 5.47-30.82 µM (average 16.63 ± 6.85 µM) in surface and bottom water column respectively. SiO_4^- displayed higher concentration during monsoon season, which was due to increased river runoff. It varied from 9.68 to 60.26 µM (average 29.64 ± 16.55 µM) and 8.09-60.96 µM (average 55.4 ± 17.08 µM) surface and bottom water respectively. Similar to the monsoon, SiO_4^- concentration was higher during postmonsoon season surface water SiO_4^- concentration varied from 3.21-59.17 µM (average 16.78 ± 13.86 µM) and that of bottom water was 5.4 – 59.18 µM (average 21.97 ± 17.26 µM).

Seasonal fluctuations in chemical hydrography of the Cochin estuary are strongly connected to the south-west monsoon driven intense rainfall and river runoff through the six rivers connected to the system. The river discharge is maximum during monsoon (1346 m^3s^{-1}), moderate in post-monsoon (205 m^3s^{-1}) and minimum (142 m^3s^{-1}) in premonsoon period (Revichandarn et al., 2012). In pre-monsoon season, river discharge is at its minimum, and the seawater influence is maximum at the upstream, the estuary is well mixed, and homogeneity exists in water. Estuary acquires more or less a stable condition during pre-monsoon season (Gopalan et al.,1983; Menon et al., 2000). Salinity remains close to zero values over the surface layer of the estuary during the monsoon. The complete freshening of the estuary takes place during the peak monsoon period. During the monsoon season, the estuary is more dynamic, and the pH is found to be less than 7. Post-monsoon is a typical transition period. In post-monsoon, river discharge gradually decreases and tidal influence gains momentum and the estuarine condition changes to partially mixed type (Gireeshkumar et al., 2013). Similarly, the freshwater discharge keeps the peaked DO and lower pH levels, which gradually showing an increasing or decreasing trend depending upon the salinity of the system.

Generally dissolved inorganic nutrients showed inverse relation with salinity suggesting the possible terrestrial input of nutrient elements(Martin et al., 2008). A strong riverine flux influences the distribution of nitrate and silicate, whereas the correlation did not fall true for nitrite and phosphate. The high nitrate (36.82 µM) during the monsoon season attributes to influx of nitrate from river catchments. Similarly, the silicate concentration was low during premonsoon, peaked at monsoon followed by postmonsoon. Monsoon plays an important role in a significant change in the hydrographic quality of the estuary. Heavy riverine discharge during monsoon results in the rise of the nutrient level. The uplifted nutrient level may change the pelagic food web. Nutrient enrichment for the long term in the estuary may cause eutrophication, Inhibiting the survival of higher predators including fishes and also promote tolerant species.

2.4.2 General Sediment Characteristics

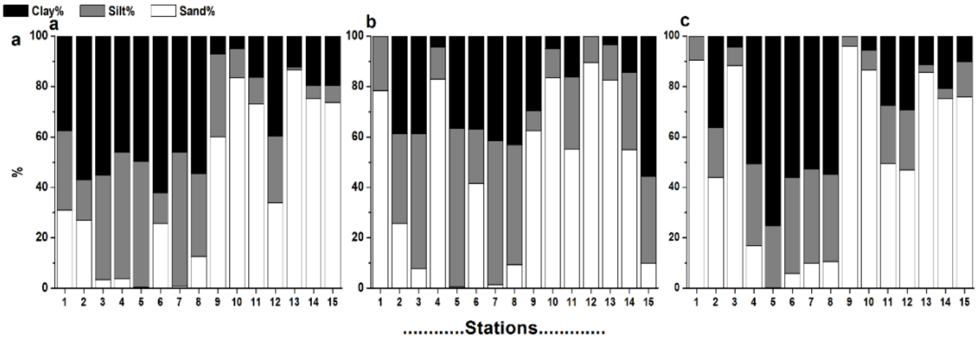
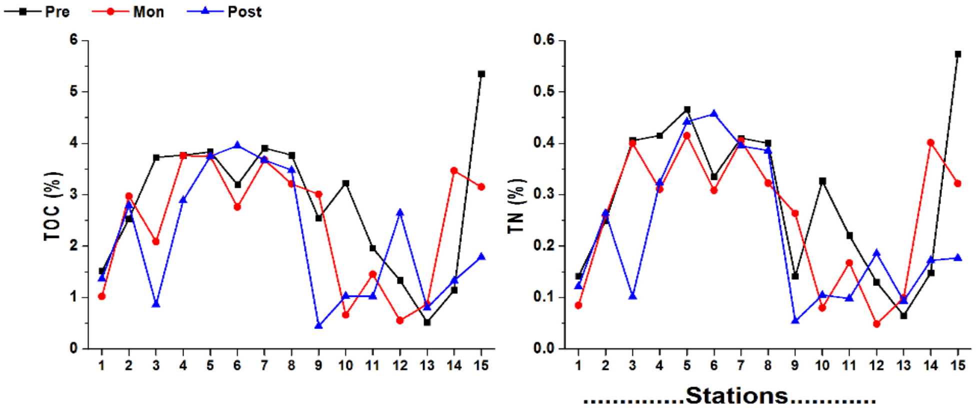


Figure 2.10: Spatial and Seasonal variation of sediment texture in Cochin estuary

The grain size distribution in surface sediments of the Cochin estuary is depicted in Fig. 2. 10 (a,b and c represent the three seasons premonsoon, monsoon and postmonsoon respectively). Mud (clay and silt) dominated in the central estuary (stations 2-8) while sand predominated in northern and southernmost parts of the estuary.



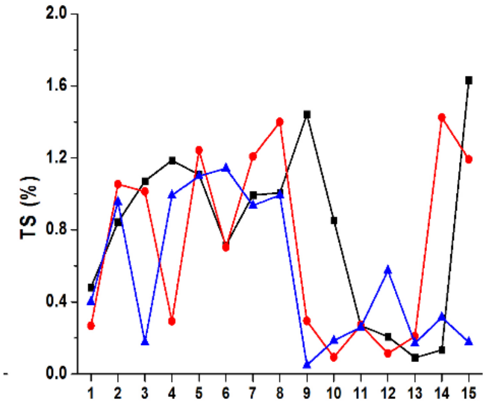


Figure 2.11: Spatial and Seasonal variation of TOC (%), TN(%), and TS(%) in Cochin estuary

TOC ranged from 0.52 to 5.32% (mean ± standard deviation; 2.82±1.32) in premonsoon, 0.55 to 3.76% (2.43±1.20) in monsoon and 0.45 to 3.96% (2.12±1.24) in postmonsoon (Fig. 3). TN ranged from 0.06 to 0.57% (0.30±0.15), 0.05 to 0.41% (0.26±0.13) and 0.05 to 0.46% (0.23±0.14) in premonsoon, monsoon and postmonsoon respectively, while TS ranged from 0.09 to 1.63% (0.80±0.48), 0.09 to 1.43% (0.72±0.51) and 0.05 to 1.14% (0.56±0.41). All these parameters (TOC, TN and TS) generally displayed similar distributional characteristics.

2.5 Conclusion

The chemical hydrography of the Cochin estuary is coupled to the sporadic introduction of nutrients and organic matter via monsoon induced rainfall and river discharge. The biogeochemical cycling of elements in this estuarine system is very dynamic and changes with various stress factors including freshwater discharge, salinity and redox conditions. Therefore, input, fate and transport of chemical contaminants (both organic and inorganic) are strongly coined with the general hydrographical condition that exists in the estuary.

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Chapter

3

DISSOLVED AND PARTICULATE PHTHALIC ACID ESTERS (PAEs)

Contents

3.1 Introduction

Phthalate esters (PAEs) are synthetic organic contaminants that are widely spread in the environment including atmosphere (Zhang et al., 2013) aquatic systems (Sun et al., 2013; Li et al., 2017) and soil (Zeng et al., 2008; Wang et al., 2013). Accumulation of PAEs in the environment is mainly due to their application in industries such as polymers, cosmetics, detergents, packing materials, printing inks, adhesives, ceramics, pharmaceuticals and repellents (Chen et al., 2013; Net et al., 2015). Lower molecular weight PAEs are used as ingredients of solvents, adhesives, waxes, pharmaceuticals, insecticides and cosmetics, whereas high molecular weight PAEs are used as plasticizers to improve the flexibility and handling of industrial products (Net et al., 2015). Therefore, their major source is terrestrial runoff, apart from the sewage discharge and atmospheric deposition (Zhang et al., 2018).

Due to their health and environmental risks, six of them are listed as priority pollutants by the United States Environmental Protection Agency (USEPA), European Union (EU) and Chinese waters list (Net et al., 2015).

They are also toxic to aquatic organisms including algae, protozoan, molluscs, crustaceans, fishes and invertebrates (Staples et al., 1997; Chen et al., 2014).

India is undergoing explosive growth in annual plastic production, as evidenced by the mounting production (> 12 x 10^9 tons) of plastic per year and its wastes (> 6 tons), projected to reach 20 x 10^9 tons by 2020 (CPCB 2015). Although the leachates from these plastic wastes are mostly composed of Phthalic acid esters (PAEs) and heavy metals like Pb and Cd (CPCB 2015). PAEs are easily released into the environment because there is no covalent bond between the phthalates and plastic in which they are mixed (Zeng et al., 2008). As plastics age and break down, the release of phthalates accelerates (Liu et al., 2014; Li et al., 2016). PAEs have low water solubility and high octanol partition coefficient; they can become concentrated in suspended matter and sediment (Wang et al., 2008; Li et al., 2017). Larger the alkyl side-chain or degree of branching, the more persistent the compound. Phthalate esters generally have low volatility, which decreases with the increasing length of the alcohol side-chain of the ester. Phthalate esters will tend to volatilize from water, either not at all or very slowly (Zeng et al., 2008).

3.2 Results

3.2.1 Total Phthalic Acid Esters ($\sum_6$PAEs) in the dissolved phase

Dissolved $\sum_6$PAEs were very high during the monsoon season followed by postmonsoon and premonsoon is plotted in figure 3.1 and the data is tabulated in appendix 1. Dissolved $\sum_6$PAEs in the surface during premonsoon season was from 0.36 to 4.00 µg/L (2.15±1.17). The highest concentration was observed at station 15 and the lowest was at station 13. During monsoon the values were from 2.38 to 27.99 µg/L (11.87±7.17). The highest concentration was observed at station 4, and the lowest was at station 1. In Postmonsoon season total PAE were 0.92 to 4.49 µg/L (2.30±1.99) with the highest concentration observed at station 11, and the lowest at station 3 and 9 are the lowest total PAE stations.

Dissolved $\sum_6$PAEs in the bottom during premonsoon season ranged from 0.48 to 6.16 µg/L (2.31±1.84), and station 14 showed the maximum PAE concentration and station 15 the minimum value. During monsoon season total PAE concentration varied from 2.39 to 13.20 µg/L (7.24±3.44). Station 14 showed the highest and station 3 showed the lowest total PAE concentration in the season. During postmonsoon season the total PAE varied from 0.56 to 7.26 µg/L (3.00±2.12). Station 4 showed the maximum and stations 2 and 12 showed the minimum PAE concentration during this season.

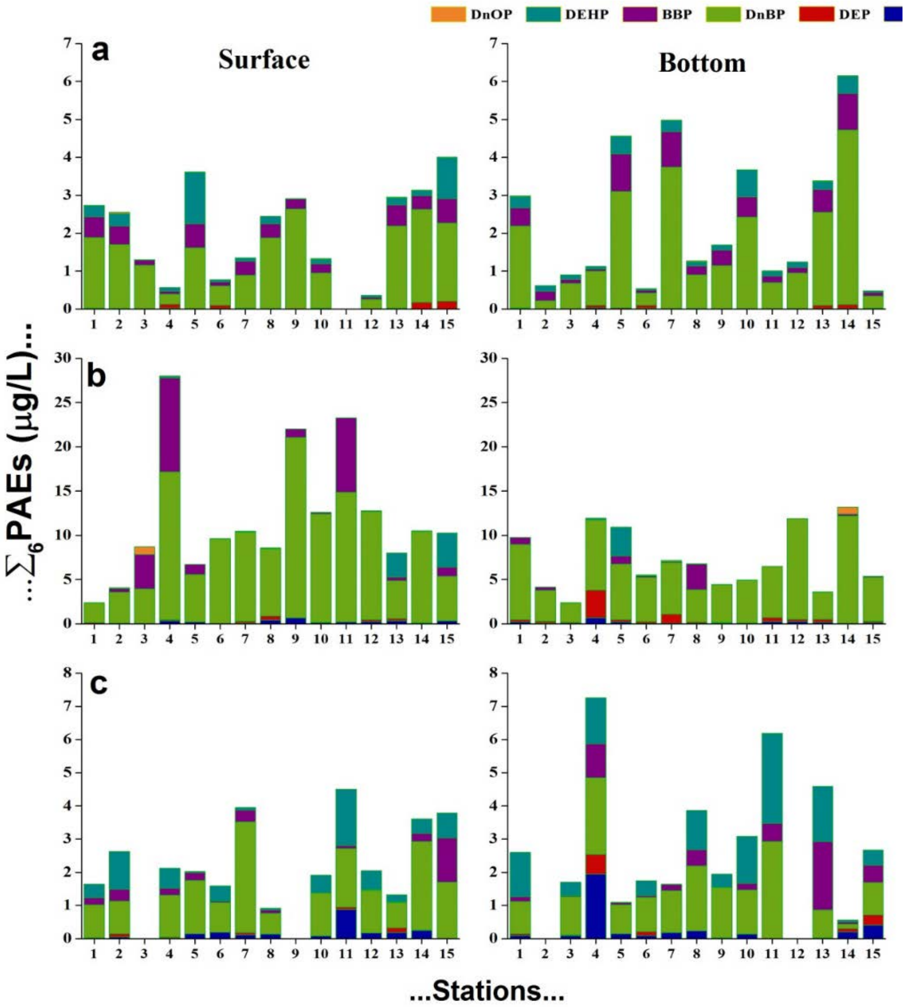

Figure 3.1: Seasonal Distribution of dissolved PAEs. Premonsoon (a), monsoon (b), postmonsoon (c).

3.2.1.1 Dimethyl Phthalate (DMP)

The seasonal distribution of dissolved DMP concentrations in bottom and surface is plotted in figure 3.2. The surface DMP during premonsoon varied between n.d-0.02 µg/L (average 0.01 µg/L). DMP during monsoon varied from n.d to 0.69 µg/L (average 0.22 µg/L). During postmonsoon concentration of DMP (surface) varied from n.d to 0.87 µg/L (average 0.15 µg/L).

Bottom water DMP concentrations during premonsoon season varied from n.d to 0.03 µg/L (average 0.009 µg/L). While During monsoon season the DMP concentration in bottom water ranged from 0.03 to 0.66 µg/L (average 0.16 µg/L) During postmonsoon season the bottom water DMP varied from n.d to 1.95 µgL^{-1} (average 0.235 µg/L).

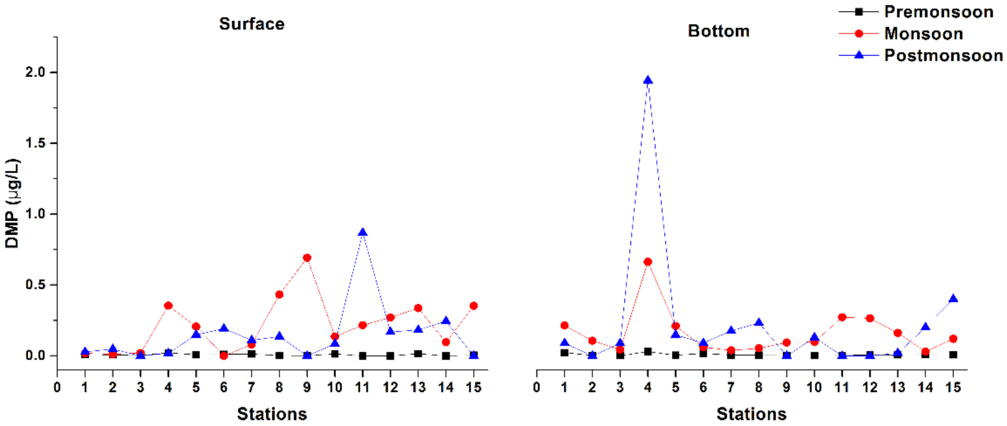

Figure 3.2: Seasonal Distribution of DMP in the dissolved phase.

3.2.1.2 Diethyl Phthalate (DEP)

The seasonal distribution of dissolved DEP concentrations in bottom and surface is plotted in figure 3.3. Dissolved DEP concentrations (surface) during premonsoon season varied between n.d and 0.20 µg/L (average 0.04 µg/L). Where as in the monsoon, it varied from n.d to 0.45 µg/L (average 0.10

μg/L). Postmonsoon surface DEP varied from n.d to 0.14 μg/L (average 0.03 μg/L) (Fig. 3.3).

Bottom water DEP during premonsoon season varied from n.d to 0.11 μg/L (average 0.03 μg/L). During monsoon season it varied from 0.01 to 3.14 μg/L (average 0.45 μg/L). During postmonsoon season the bottom water DEP varied from n.d to 0.59 μg/L (average 0.08 μg/L).

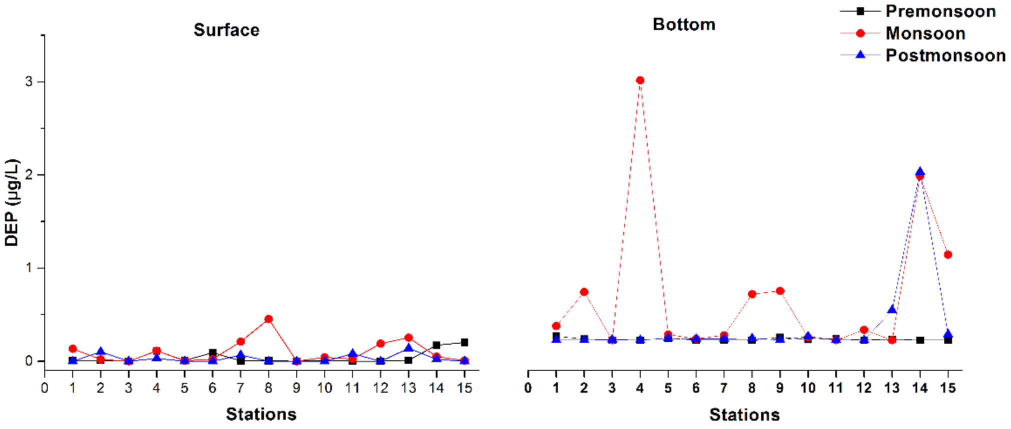

Figure 3.3: Seasonal Distribution of DEP in the dissolved phase.

3.2.1.3 Di-n-Butyl Phthalate (DnBP)

The seasonal distribution of dissolved DnBP concentrations in bottom and surface is plotted in figure 3.5. Surface water DnBP concentration during premonsoon varied from n.d to 0.65 μg/L (average 0.33 μg/L). During monsoon it varied from 2.21 to 20.37 μg/L (average 9.20 μg/L). During postmonsoon season surface water DEP varied from n.d to 3.34 µg/L (average 1.32 µg/L).

Bottom water DnBP concentrations during premonsoon season ranged from 0.07 to 1.00 µg/L (average 0.41 µg/L). DnBP concentration during monsoon season varied from 2.18 to 12.17 µgL^{-1} (average 5.94 µg/L). During postmonsoon season the bottom water DnBP varied from n.d to 2.93 µg/L (average 1.15 µg/L).

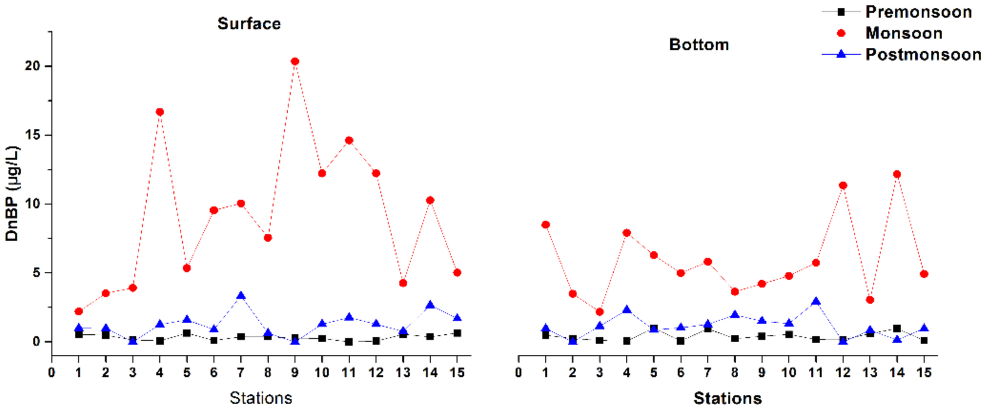

Figure 3.4: Seasonal Distribution of DnBP in the dissolved phase.

3.2.1.4 Benzyl Butyl Phthalate (BBP)

The seasonal distribution of dissolved BBP concentrations in bottom and surface is plotted in figure 3.4. Dissolved BBP concentrations (surface) during premonsoon observed from n.d to 2.64 µg/L (average 1.35 µgL^{-1}). During monsoon the surface BBP varied from 0.02 to 22.63 µg/L (average 2.62 µg/L). Where as during postmonsoon season dissolved BBP varied from n.d to 1.34 µg/L (average 0.22 µg/L).

Bottom water BBP during premonsoon season varied from 0.21 to 7.6 µg/L (average 1.84 µg/L). During monsoon season it varied from n.d to 2.83 µg/L (average 0.38 µg/L). During postmonsoon season the bottom water BBP varied from n.d to 2.06µg/L (average 0.36 µg/L).

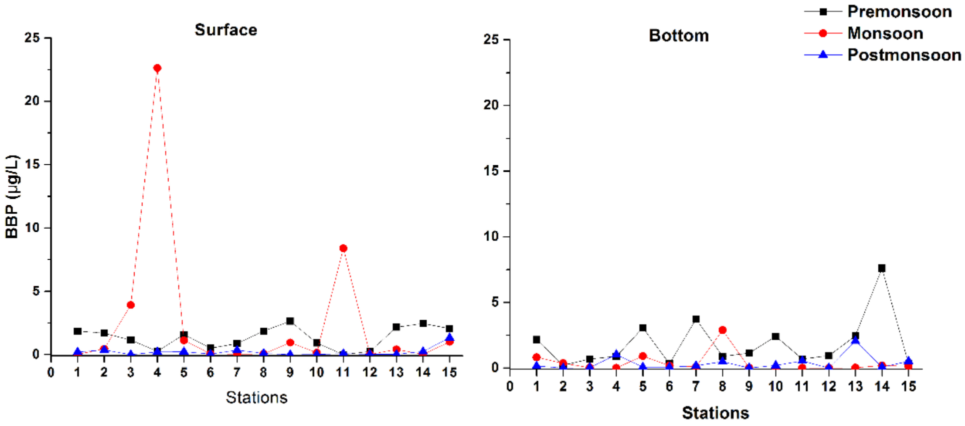

Figure 3.5 : Seasonal Distribution of BBP in the dissolved phase

3.2.1.5 Di Ethyl Hexyl Phthalate (DEHP)

The seasonal distribution of dissolved DEHP concentrations in bottom and surface is plotted in figure 3.6. Surface water DEHP concentration during premonsoon varied from n.d to 1.35 µg/L (average 0.27 µg/L). During monsoon the surface water DEHP varied from n.d to 3.86 µg/L (average 0.47 µg/L). Surface water DEHP during postmonsoon varied from n.d to 1.69 µg/L (average 0.46 µg/L).

Bottom water DEHP concentration during premonsoon season was n.d to 1.352 µg/L (average 0.27 µg/L). Whereas during monsoon season DEHP varied from n.d to 3.23 µg/L (average 0.24 µg/L). During postmonsoon season it varied from n.d to 2.72 µg/L (average 0.77 µg/L) (Fig. 3.6).

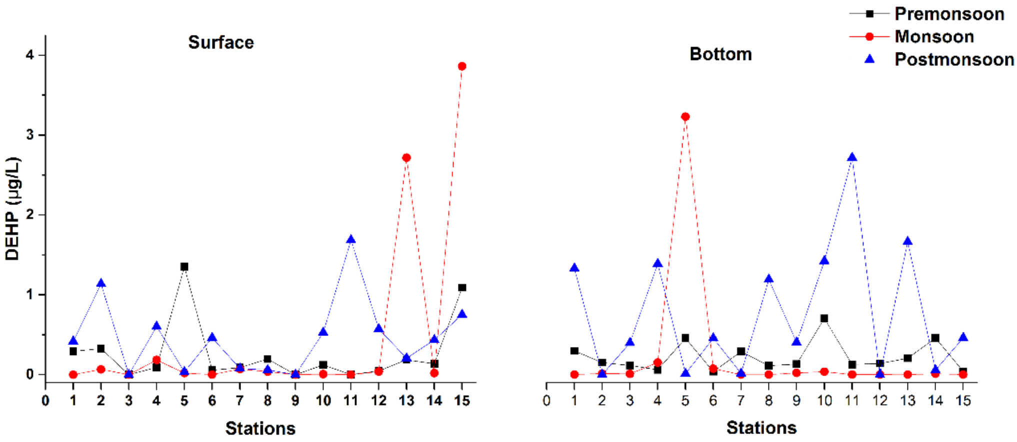

Figure 3.6: Seasonal Distribution of DEHP in the dissolved phase.

3.2.1.6 Di-n- Octyl Phthalate (DnOP)

The seasonal distribution of dissolved DnOP concentrations in bottom and surface is plotted in figure 3.7. Surface water DnOP concentration during premonsoon varied from n.d to 0.03 µg/L (average 0.01 µg/L). During monsoon the surface DEHP varied from n.d to 0.84 µg/L (average 0.07 µg/L). Bottom water DnOP during premonsoon season varied from n.d to 0.03 µg/L (average 0.01 µg/L). During monsoon season the bottom DnOP concentration varied from n.d to 0.79 µg/L (average 0.08 µg/L). During postmonsoon season the dissolved DnOP was not detectable in all stations (Fig. 3.7).

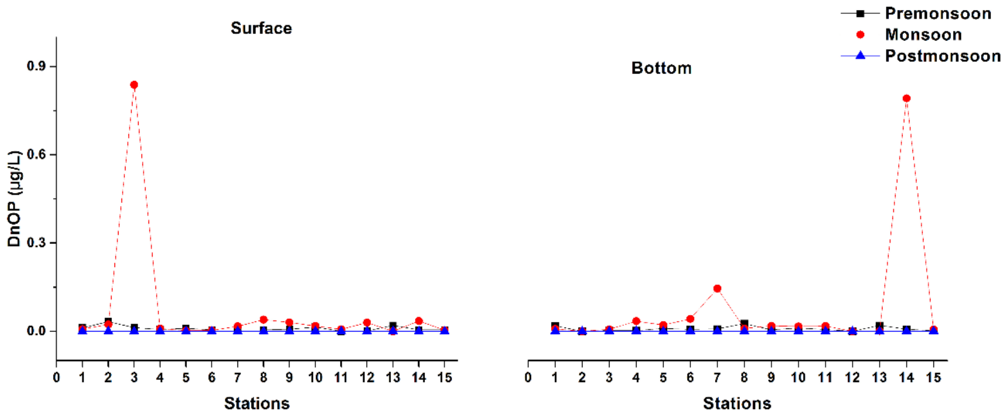

Figure 3.7: Seasonal Distribution of DnOP in the dissolved phase

3.2.1.7 Distribution of PAEs in the dissolved phase

Dissolved $\sum_6$PAEs were very high during monsoon season followed by postmonsoon and premonsoon. During monsoon period, $\sum_6$PAEs was in the range 2.38 to 27.99 µg/L (11.87±7.17) in surface and 2.39 to 13.201µg/L (7.24±3.44) in the bottom. During postmonsoon, the concentrations were lower than monsoon and ranged from 0.92 to 4.49 µg/L (2.30±1.99) in surface and 0.56 to 7.26 µg/L (3.00±2.12) in the bottom. The lowest concentrations were recorded during premonsoon season that ranged from 0.36 to 4.00 µg/L (2.15±1.17) in surface and 0.48 to 6.16 µg/L (2.31±1.84) in the bottom.

The relative abundance of PAE congeners were in the order DnBP> BBP> DEHP> DEP> DMP> DNOP during all seasons. During premonsoon, the average concentration of DnBP was 1.45 (±0.79) µg/L in surface and 1.83 (±1.93) µg/L in bottom accounting for 44 - 90 % (S) and 34 - 79 % (B) of total dissolved PAEs. During the same period, BBP contributed 9 - 28 % [average 0.35 ±0.20 µg/L] in surface and 6 - 40 % [average 0.41 (±0.34) µg/L in bottom. DEHP contributed up to 34 % [average 0.28 (±0.41)] µg/L in surface and 5 - 24 % [average 0.22 (±0.19) µg/L] in the bottom respectively. The central estuary (stations 4-6) and northern estuary (13-15) displayed high DEP levels [nd to 0.20 µg/L (0 to 19%) in surface and nd to 0.11 µg/L (0 to 14 %) in bottom]. DMP and DnOP were low and contributed 2 to 3 % of total dissolved PAEs.

During monsoon season, all the PAEs showed enrichment in the estuary. DnBP contributed 45 to 99 % (average 9.19±5.34 µg/L) in surface and 54 to 96 % (average 5.94±2.91 µg/L) in bottom, whereas BBP accounted up to 57 % (2.62±5.97 µg/L) in surface and up to 43 % (0.38±0.753 µg/L) in bottom. The concentrations of DEHP, DMP and DnOP were low during monsoon. During postmonsoon, the contribution of DnBP increased to 85 % [1.47±0.78 µg/L] in surface and 79 % [1.33±0.72 µg/L] in the bottom. The contribution of BBP was very small (6 - 9 %) with an average of 0.25±0.34 µg/L and 0.41±0.47 µg/L in surface and bottom respectively.

3.2.2 Total Phthalic Acid Esters ($\sum_6$PAEs) in the particulate phase

The total concentration of PAEs in particulate phase of surface and bottom water is plotted in figure 3.8 and the data is tabulated in appendix 2. Total Surface PAE concentration during premonsoon varied from 7.84 to 224.03

μg/g (average 85.09 μg/g). Whereas During monsoon it was varied from 30.53 to 1203.46 μgg^{-1} (average 353.2 μg/g). During Postmonsoon it was ranged from 18.86 to 308.41 μg/g (average 89.68 μg/g).

Total PAE in water (bottom) during premonsoon season varied from 14.61 to 152.32 μg/g (average 51.84 μg/g). Whereas during monsoon season it was from 32.52 to 1089.46 μg/g (average 345.65 μg/g). During postmonsoon season the bottom water PAE varied from 6.97 to 320.61 μg/g (average 77.03 μg/g).

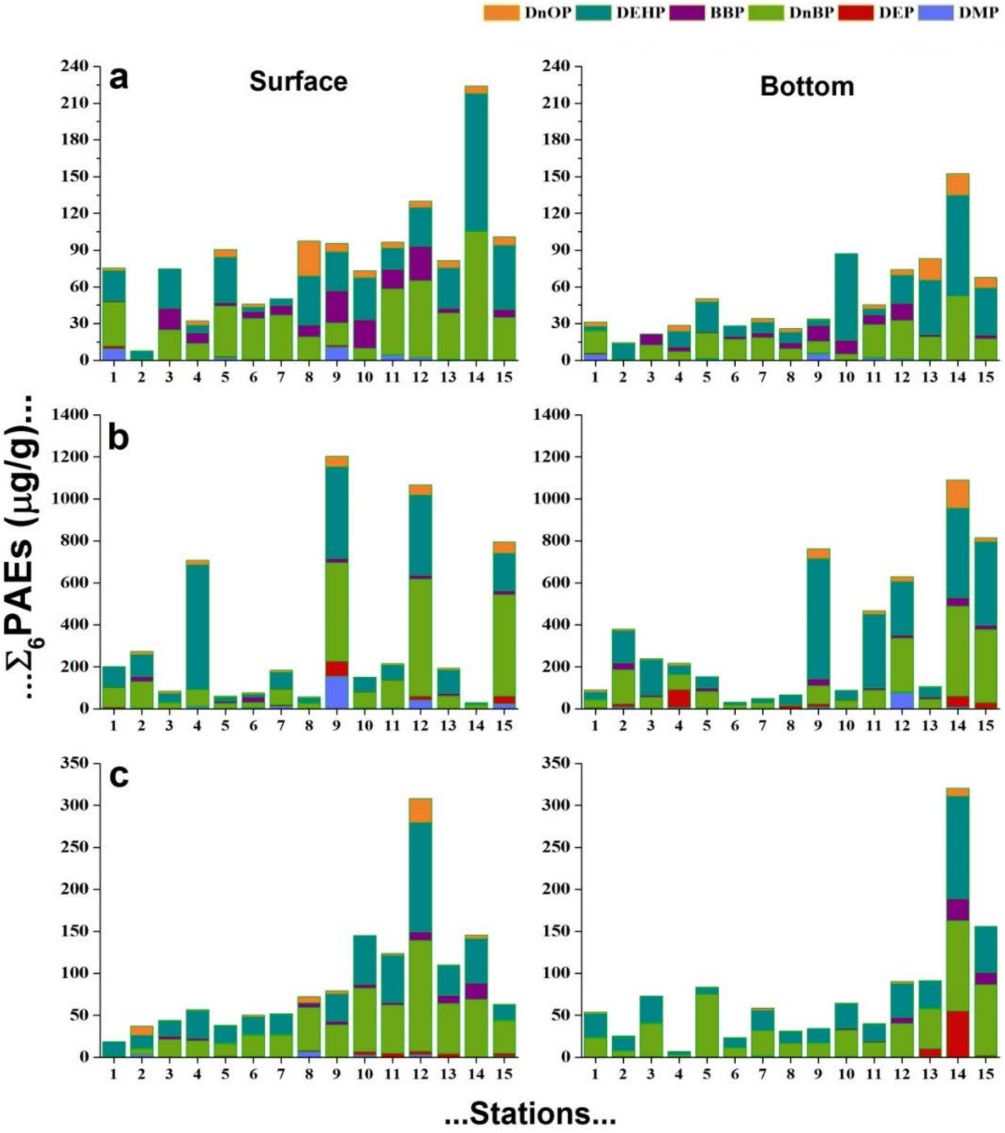

Figure 3.8: Seasonal distribution of particulate PAEs. Premonsoon (a), monsoon (b), postmonsoon (c).

3.2.2.1 Dimethyl Phthalate (DMP)

The seasonal distribution of particulate DMP concentrations in bottom and surface water is plotted in figure 3.9. Surface DMP concentration ranged between n.d-10.63 μg/g (average 2.06 μg/g), n.d-154.59 μg/g (average17.40

µg/g), and n.d-6.28 µg/g (average 1.21µg/g) during premonsoon, monsoon and postmonsoon seasons respectively. Where as bottom DMP in particulates where varied between n.d-5.32 µg/g (ave 1.03 µg/g), 0.03-76.95 µg/g (average 7.89 µg/g) and n.d-1.55 µg/g (average 0.41 µg/g) during premonsoon, monsoon and postmonsoon seasons respectively.

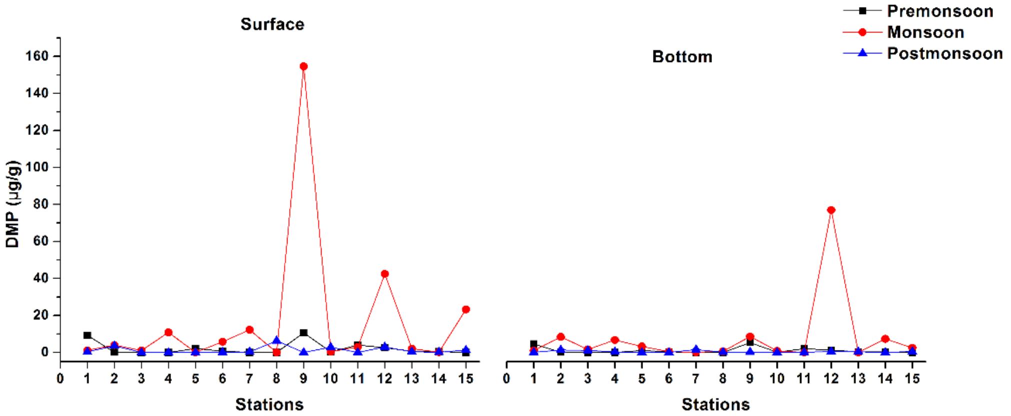

Figure 3.9: Seasonal distribution of particulate DMP

3.2.2.2 Diethyl Phthalate (DEP)

The seasonal distribution of particulate DEP concentrations in bottom and surface water is plotted in figure 3.10. DEP concentration (surface particulates) ranged between n.d-2.59 µg/g (average 0.52 µg/g), n.d-71.53 µg/g (average 10.18 µg/g) and n.d-4.96 µg/g (average 1.79 µg/g) during premonsoon, monsoon and postmonsoon seasons respectively. Where as bottom DEP concentration varied from n.d-1.29 µg/g (average 0.26 µg/g), n.d-85.23 µg/g (average 15.11 µg/g) and n.d-55.16 µg/g (average 4.68 µg/g) during premonsoon monsoon and postmonsoon seasons respectively.

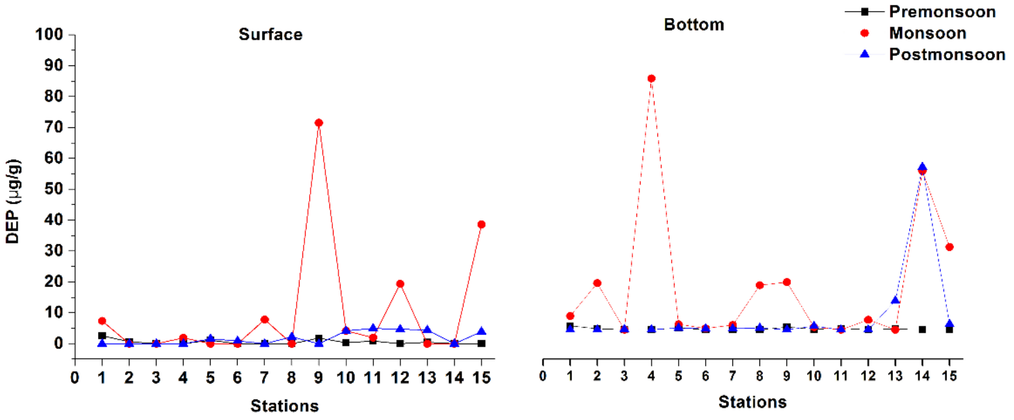

Figure 3.10: Seasonal distribution of particulate DEP

3.2.2.3 Di-n-Butyl Phthalate (DnBP)

The seasonal distribution of particulate DnBP concentrations in bottom and surface water is plotted in figure 3.11. DnBP concentration (surface) varied between 0.12-104.69 µg/g (average 35.03 µg/g), 19.05-556.12 µg/g (average 150.56 µg/g) and 0.20-131.65 µg/g (average 42.26 µg/g) during premonsoon monsoon and postmonsoon seasons respectively.

Where as in bottom it was ranged between 0.06-52.35 µg/g (average 17.51 µg/g), 0.08-427.40 µg/g (average 115.43 µg/g) and 2.39-107.33 µg/g (average 36.34 µg/g) during premonsoon monsoon and postmonsoon seasons respectively.

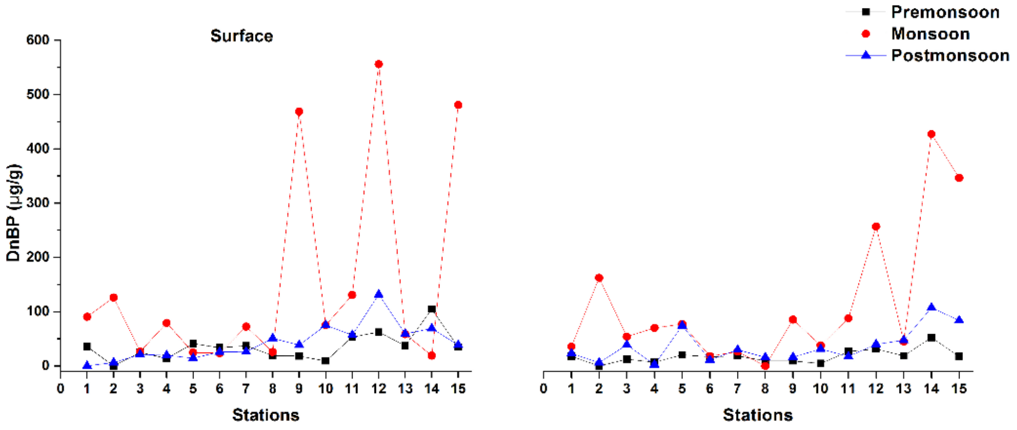

Figure 3.11: Seasonal distribution of particulate DnBP

3.2.2.4 Benzyl Butyl Phthalate (BBP)

The seasonal distribution of particulate BBP concentrations in bottom and surface water is plotted in figure 3.12. BBP concentration (surface) varied between 0.25-28.08 µg/g (average 10.66 µg/g), 0.25-28.37 µg/g (average 11.84 µg/g) and 0.62-19.50 µg/g (average 4.74 µg/g) during premonsoon monsoon and postmonsoon seasons respectively.

Where as in bottom it was ranged between 0.13-14.04 µg/g (average 5.33 µg/g), 0.07-41.23 µg/g (average 14.18 µg/g) and 0.12-26.63 µg/g (average 4.00 µg/g) during premonsoon monsoon and postmonsoon seasons respectively (Fig. 3.12).

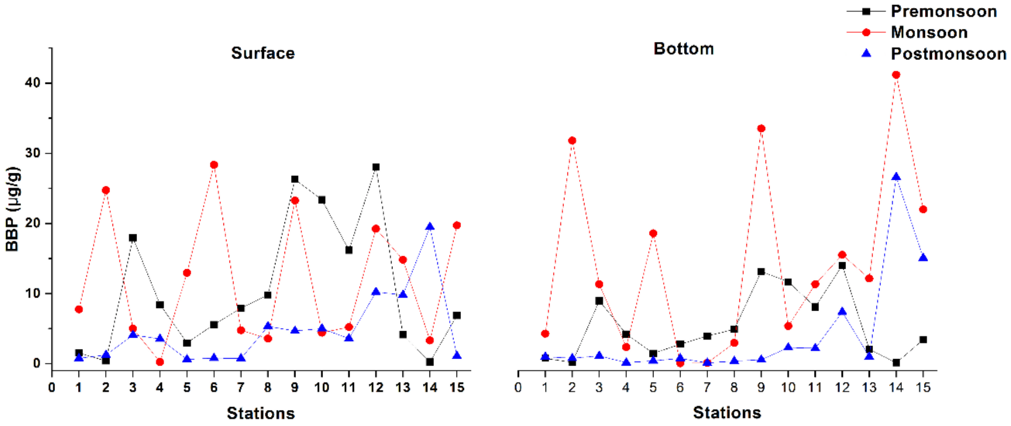

Figure 3.12: Seasonal distribution of particulate BBP

3.2.2.5 Di Ethyl Hexyl Phthalate (DEHP)

The seasonal distribution of particulate DEHP concentrations in bottom and surface water is plotted in figure 3.13. Surface DEHP concentration during premonsoon varied from 3.36 to 112.22 µg/g (average 30.98 µg/g). During monsoon it was varied from 7.20 to 594.16 µg/g (average 146.74 µg/g). Postmonsoon surface DEHP varied from 0.50 to 130.09 µg/g (average 35.32

µg/g). Bottom DEHP during premonsoon season raged from n.d to 82.04 µg/g (average 22.92 µg/g). During monsoon season it was varied between 11.57-571.63 µg/g (average 173.90µg/g) and during postmonsoon season 3.99-121.49 µg/g (average 29.97 µg/g).

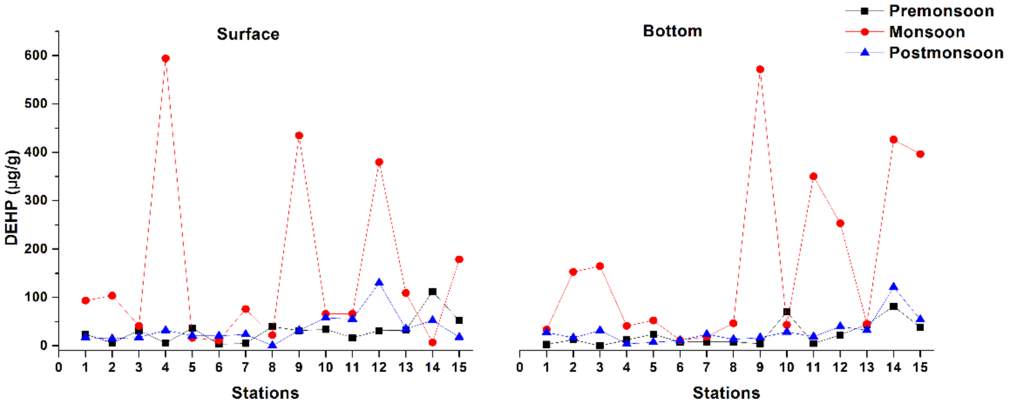

Figure 3.13: Seasonal distribution of particulate DEHP.

3.2.2.6 Di-n- Octyl Phthalate (DnOP)

The seasonal distribution of particulate DnOP concentrations in bottom and surface water is plotted in figure 3.14. Surface DnOP concentration during premonsoon varied from 0.11 to 28.74 µg/g (average 5.85 µg/g). Whereas during monsoon it was varied from 0.21 to 54.41 µg/g (average 16.47 µg/g), and during the postmonsoon season it was varied from 0.028 to 28.79 µg/g (average 4.35 µg/g).

Bottom DnOP during premonsoon season varied from n.d to 17.57 µg/g (average 4.79 µg/g). During monsoon season the bottom DnOP concentration varied from 0.04 to 133.51 µg/g (average 19.14 µg/g). Whereas during postmonsoon season the bottom DnOP concentration varied from 0.06 to 10.01 µg/g (average 1.64 µg/g).

Considering the total amount of PAEs calculated for each water and particulate matter sample it appears evident that the presence of PAEs due to the input of urban and/or industrial treated wastewaters.

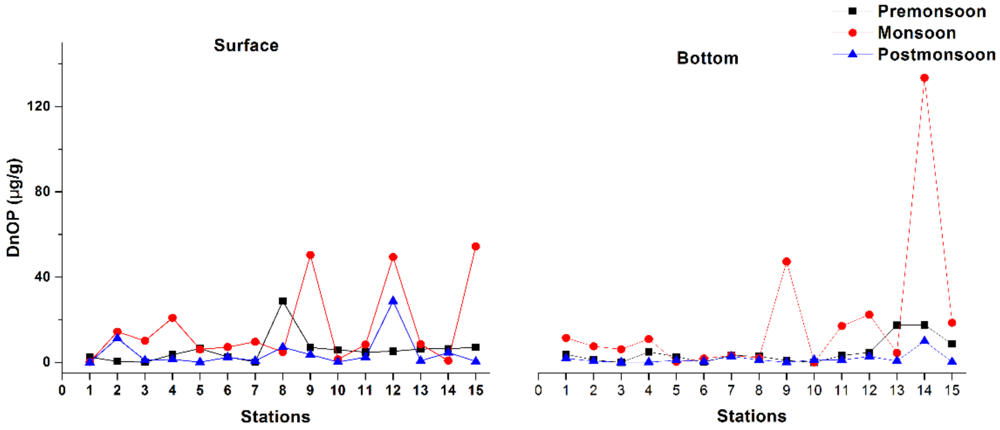

Figure 3.14: Seasonal distribution of particulate DnOP

3.2.2.7 Distribution of PAEs in the particulate phase

The *concentration* of ∑6PAEs was very high in the particulate fraction that showed significant seasonality. During premonsoon season, the average concentration of particulate PAE was 85.09±49.17 µg/g in surface and 51.84±36.09 µg/g in the bottom. It showed a substantial increase during the monsoon season with an average of 321.58±389.53 µg/g in surface and 312.20±333.65 µg/g in the bottom.

DEHP, DnBP and BBP were the predominant PAE congeners during premonsoon season with minor contributions from DnOP, DEP and DMP. The contribution of DnBP was 40 % (average 35.03±25.30 µg/g) in surface and 37 % (average 17.51±12.65 µg/g) in bottom. DEHP contributed 36 % (average 30.98±26.84 µg/g) in the surface and 38 % (average 49.12±50.57 µg/g) in the bottom respectively. The contribution of BBP was 15 % (0.25-28.08 µg/g in surface and 0.13 to 14.04 µg/g in the bottom), whereas the contribution of DnOP was low (8 %) and that of DMP and DEP were still low (<4 %).

The estuary recorded its highest particulate PAE concentrations during monsoon season with DnBP and DEHP as the dominant congeners. DnBP contributed 11 to 62 % [19.05 to 556.12 µg/g in surface and < 1 to 59 % [0.07 to 427.40 µg/g in bottom]. The contribution of DEHP accounted was 15 to 84 % (7.19 to 594.16 µg/g) in surface and 19 to 82 % (11.57 to 571.63 µg/g) in bottom. The concentration of BBP was in the range 0.25 to 28.37 µg/g (S) and 0.07 to 41.22 µg/g (B). DnOP accounted 12 % [0.21-54.41 µg/g (S) and 0.04 – 133.51 µg/g (B)].

During postmonsoon also, DEHP and DnBP were the dominant congeners followed by BBP and DnOP. DnBP ranged from 0.20 to 131.65 µg/g (S) and 2.39 to 107.33 µg/g (B), whereas the DEHP ranged from 0.50 to 130.09 µg/g (S) and 3.99 to 121.49 µg/g (B). BBP concentrations were in the range 0.62 to 19.50 µg/g (S) and 0.12 to 26.63 µg/g (B), while DnOP varied in the range 0.03 to 28.79 µg/g (S) and 0.06 to 10.01 µg/g (B). However, compared to the dominant congeners, the contribution of BBP and DnOP were only 5 % in surface and 3 % in the bottom.

3.3 Discussion

Cochin estuary is a typical tropical monsoonal estuary (Vijith et al., 2009; Shivaprasad et al., 2013) with heavy freshwater discharge during monsoon season; the river discharge is a minimum during premonsoon season and seawater influence is a maximum upstream. The estuary is well mixed and homogeneity exists in the water column. In post-monsoon, river discharge gradually decreases and tidal influence gains momentum and the estuarine condition changes to partially mixed type (Menon et al., 2000).

Table 3.1: Concentration of dissolved and Particulate PAEs around the world

L Location	No of PAEs	ΣPAEs	DMP	DEP	DnBP	BBP	DEHP	DnOP	Referance
Dissoilved PAEs (µg/L)									
The Yellow River, Taiwan China	8	n.d-18.5	n.d-3.01	n.d-3.2	17.6-57.8	-	5.40-630	n.d	Yuan et al., 2002
The Yellow River China	8	3.99-45.45	n.d-0.581	0.0115-1.09	n.d-26.0	-	0.347-31.8	n.d-0.071	Sha et al., 2007
Urban Lakes in subtropical city, South China	16	1.69-4.72	0.003-0.085	0.015-0.32	0.94-3.60	-	0.087-0.63	-	Zeng et al., 2008
The Yangtze River, China	5	0.034-91.22	n.d-0.295	n.d-0.365	n.d-0.134	-	0.011-54.7	n.d-3.20	Wang et al., 2008
Lakes Shichanai Beijing	15	0.691-1.341	0.047-0.143	0.006-0.013	0.009-0.157	n.d-0.512	0.140-0.519	0.015-0.022	Zheng et al., 2014
Lakes in Summer Palace, Beijing	15	0.576-1448	0.039-0.082	n.d-0.011	0.058-0.515	n.d-0.021	0.139-0.393	0.016-0.024	Zheng et al., 2014
Guanting Reservoir Beijing	15	0.386-3.184	0.023-0.084	n.d-0.006	n.d-0.594	n.d-1.246	0.043-0.149	0.013-0.029	Zheng et al., 2014
Pearl River Estuary, China	6	0.5-28.1	n.d-12.1	n.d-0.95	0.06-14.8	n.d	0.15-12.1	n.d-28.1	Li et al., 2016
Jiulong River estuary, Southeast China	16	3.01-26.4	0.033-0.24	0.014-091	0.30-1.77	-	0.12-12.4	-	Li et al., 2017
Cochin estuary	6	n.d-27.993	n.d-1.945	n.d-3.139	n.d-20.368	n.d-10.634	n.d-3.861	n.d-0.838	**Present study**
Particulate PAE (µg/g)									
Tha Uraban Lakes, Guangzhou	16	24.9-221	0.006-0.422	0.079-0.383	5.08-77.6	n.d-0.729	11.0-58.9	n.d-0.142	Zeng et al., 2009
Lakes Shichanai Beijing	15	178.9-8216.4	8.5-35	14.6-96.3	64.3-461.9	6.9-67.9	48.4-232.1	4.6-39.2	Zheng et al., 2014
Lakes in Summer Palace, Beijing	15	566.3-3266.2	7.1-15.7	5.2-24.2	58.0-118.6	1.5-135.4	81.9-262.8	n.d-14.5	Zheng et al., 2014
Guanting Reservoir Beijing	15	52.6-6034.2	3.2-81.7	1.8-17.3	19.3-300.2	14.1-179.6	65.4-529.0	1.3-130.0	Zheng et al., 2014
Jiulong River estuary, Southeast China	16	1.56-48.7	n.d-0.37	n.d-2.36	0.071-4.27	-	0.29-43.5	-	Li et al., 2017
Cochin estuary	6	6.97-1203.46	n.d-154.59	n.d-85.23	0.06-556.120	0.07-41.22	n.d-594.159	n.d-133.51	**Present study**

Data sets in the present study are compared with those reported from several Chinese river, lakes and estuaries as well as from other aquatic systems around the globe (Table 3.1). DnBP and DEHP dominate in the Pearl River (Liu et al., 2014; Li et al., 2016), Changjinag River (Wang et al., 2008; Li et al., 2017) and Ogun River (Adeniyi et al., 2011). PAE concentrations observed in the present study are higher than those in the Urban Lake (Zeng et al., 2008) and Lakes in Beijing (Zheng et al., 2014). With respect to particulate PAEs Cochin estuary is less contaminated than Guanting reservoir (Zheng et al., 2014) and Lakes in Beijing, but more polluted than the Uraban Lake (Zeng et al., 2008) and Jiulong River estuary (Li et al., 2017). It should be noted that many of the above studies have quantified 16 PAEs, while the present study has measured only six PAEs. High concentrations of DnBP and DEHP congeners in PAEs of the Cochin Estuary are of concern.

Pearson Correlation Analysis (Appendix 7) showed enrichment of PAEs in the freshwater region due to its proximity to the urban settlement. Mid and high molecular weight PAEs (DnBP, DEHP) varied linearly suggesting their common source in the estuary. Similarly, the low molecular weight PAEs (DMP, DEP) also showed a significant positive correlation indicating a common source. The negative correlation of PAEs with salinity and pH is supportive of their freshwater discharge into the estuary.

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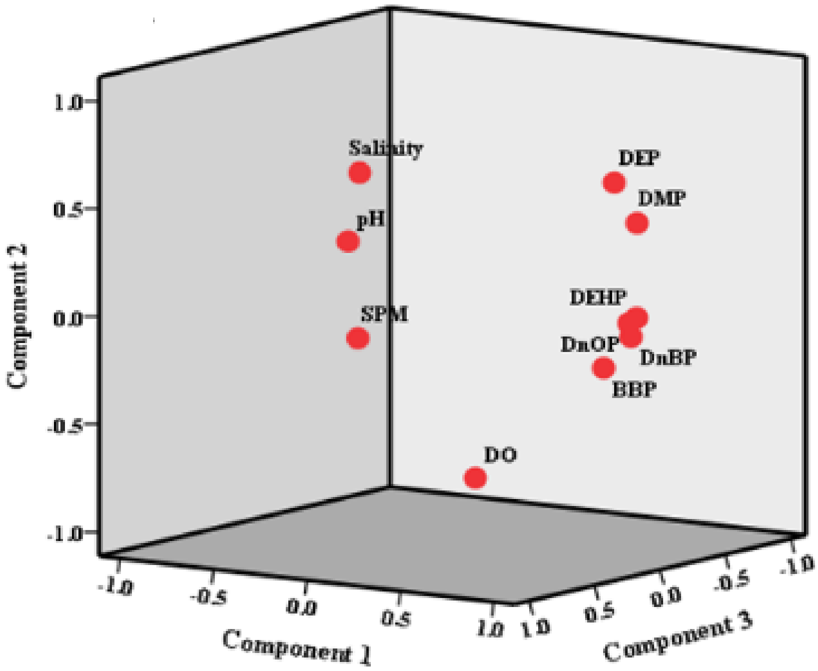
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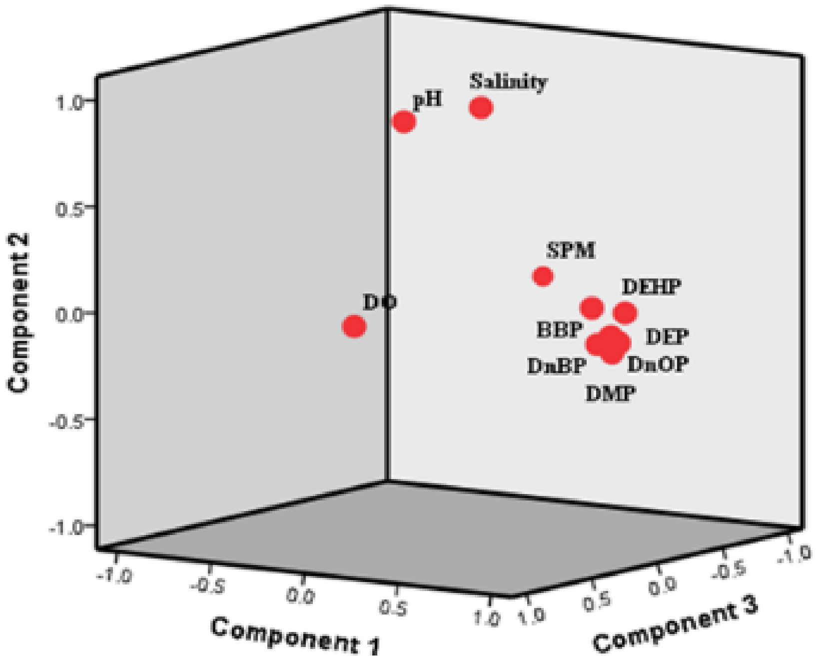
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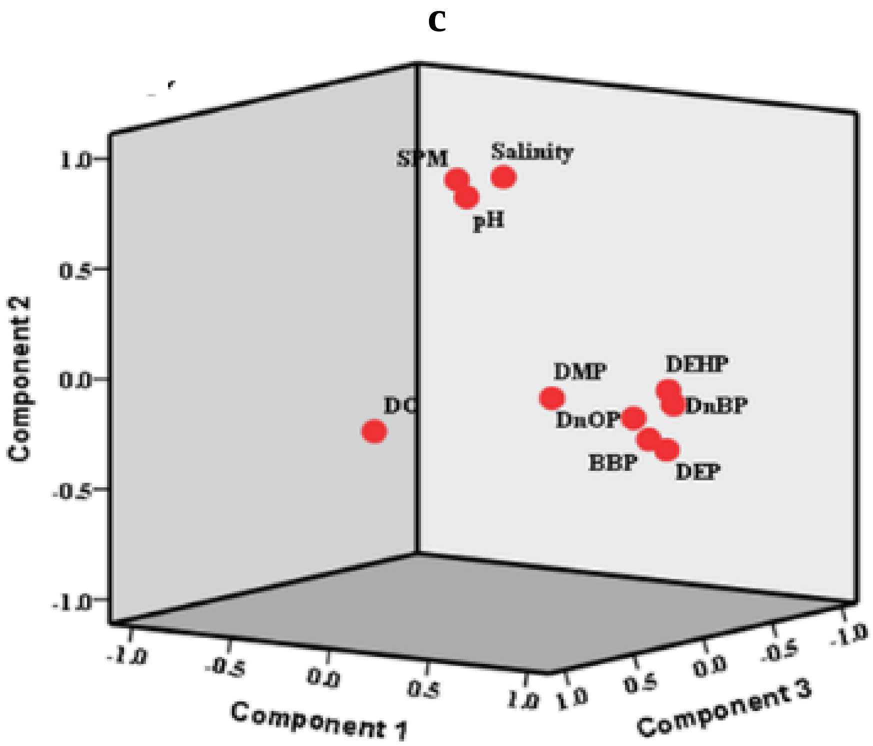

Figure 3.15: PCA results of Premonsoon (a), Monsoon (b) and Postmonsoon (c) seasons

The present data were subjected to Principal Component Analysis (Reid and Spencer, 2009; Zhang et al., 2018) to identify the factors controlling the distribution of PAEs in the estuary (Fig. 3.15) and the data are tabulated in Appendix 1. During pre-monsoon, three principal components (PCs) could explain 78 % of the variance in PAEs. PC1 explained that 44 % of the variance have significant loading from PAE (>0.5) while the pH, salinity, DO, SPM has no co-contribution at all. This indicates that the source and fate of PAE have no contribution from the hydrographic conditions. PC 2 with 21% variance have a contribution from DO and salinity. A significant contribution from DEP also is there in PC2. It may be noted that during premonsoon, the hot and arid atmosphere can lead to the evaporation of low molecular weight compounds. PCA (Fig. 3.15a) during pre-monsoon do not indicate any PAE sources, though it identifies two clusters of low molecular weight (DMP, DEP) and a mid-high molecular weight fraction. Mid and higher molecular weight PAEs are the by-products of plastic industries, while low molecular weight congeners are coming from cosmetic products. During monsoon, PC1 explained 49 % variance and all the six PAEs have significant loading in PC1 indicating terrestrial runoff as their major source in the estuary. The significant correlation with SPM (Fig. 3.15b) also confirms the above. For the postmonsoon season, 3 PCs could explain 72 % of the variance (44, 18 and 10 %) and the loading pattern is similar to monsoon. The overall analysis of PCA data suggests that mid and high molecular weight PAEs found in dissolved and particulate congeners are originating from plastic industries, while low molecular weight PAEs (DEP and DMP) are derived from cosmetic products. Also, it indicates that the terrestrial runoff is the primary source of PAEs in Cochin Estuary.

3.3.1 Ecological Implications

Aquatic organisms are susceptible to the presence of PAEs beyond a certain level and their consumption can affect human health (Wang et al., 2013). The potential toxicity of this contaminant is normally assessed based on a risk quotient (RQ) proposed by the European technical guideline document (EC, 2003). Based on the above, the RQs for the $\sum_6$PAEs for the Cochin Estuary were calculated as RQ = MEC/PNEC, where MEC represents the measured concentration and PNEC = LC_{50}/assessment factor (LC_{50} lethal concentration, (Li et al., 2017)). Based on this, the potential toxicity due to dissolved PAE in the estuary can be classified into 3 levels (1) $RQ < 0.01$, (2) $RQ = 0.01 – 1$ and (3) $RQ > 1$ (Fig.3.16). Level 1 indicates low risk, whereas level 2 indicates medium risk and level 3 indicates high risk to the aquatic organisms. From the present study, RQ for DEP and DMP was less than 0.01 indicating minimum risk due to the congeners. While for DnBP, it ranged between 0.01 and 1 points to medium risk to aquatic life. Alarmingly, this ratio was more than 1 for DEHP, exposing high risk to organisms due to this PAE fraction. Thus the DnBP and DEHP congeners of PAEs exceeded critical limits in the Cochin Estuary, consequently becoming potentially hazardous to estuarine biota.

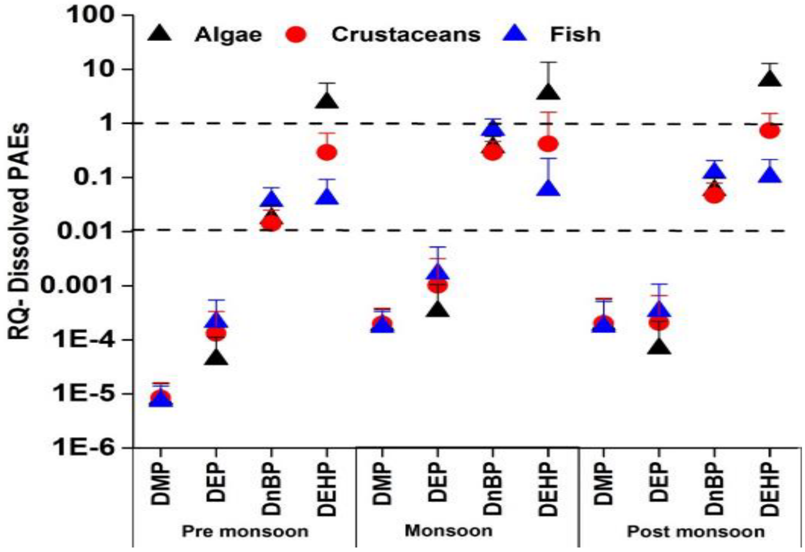

Figure 3.16: RQ values of Dissolved PAEs

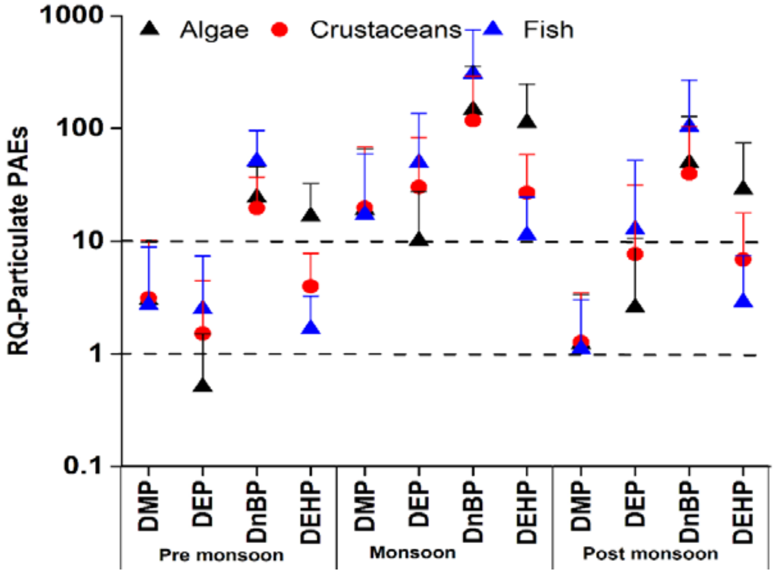

Figure 3.17: RQ values of particulate PAEs

The RQ values for particulate bound PAEs were compared with PNEC values reported for PAEs in sediment (Li et al., 2017). In this approach, RQ > 1 denotes low risk, RQ 1 to 10 medium risk and RQ > 10 reflected the high risk to the biota. Potential toxicity due to DMP and DEP congeners poses medium risk levels, while DnBP and DEHP congeners (with RQ > 10) poses a serious threat to biological organisms in the estuary (Fig. 3.17).

3.4 Conclusion

Concentrations of dissolved and particulate-bound $\sum_6$PAEs were measured in Cochin estuary to delineate contamination level due to such endocrine disrupting chemicals in this semi-urbanised ecosystem. Both dissolved and particulate-bound PAEs exhibited high concentrations during monsoon and in the subsequent postmonsoon season indicating terrestrial runoff as the major source of this contaminant into the estuary. Of the six PAEs studied, DnBP and DEHP were the dominant species in both the dissolved and particulate forms. These medium and high molecular weight PAEs are derived from a variety of plastic products in common use. Potential toxicities estimated as RQs reveal that these congeners exist in excess of critical level in both the dissolved and suspended matter thereby posing a serious hazardous ecological risk to the estuarine biota.

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Chapter

4

PAEs IN SEDIMENTS

Contents

4.1 Introduction

PAEs are a class of synthetic organic chemicals extensively used in the 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 plasticizers (to improve handling characteristics) (Staples et al., 1997; Sun et al., 2013). They reach into the estuarine environment, 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 material, which may lead to severe health problems including reproductive abnormalities (Agarwal et al., 1986; D.K.Agarwal et al., 1986; Huber et al., 1996; Guo et al., 2012). PAEs associated with dissolved and particulate phases and its ecological risks were discussed in the last chapter. Due to its hydrophobic character and high persistence they easily get settled in to sediments and enter in to food web, there for USEPA and European Union (EU) categorize six types of PAEs as major pollutants (USEPA, 2009; Sun et al., 2013; Ventrice et al., 2013; Liu et al., 2014b; Cheng et al., 2016).

4.2 Results

4.2.1 Total PAEs in sediments

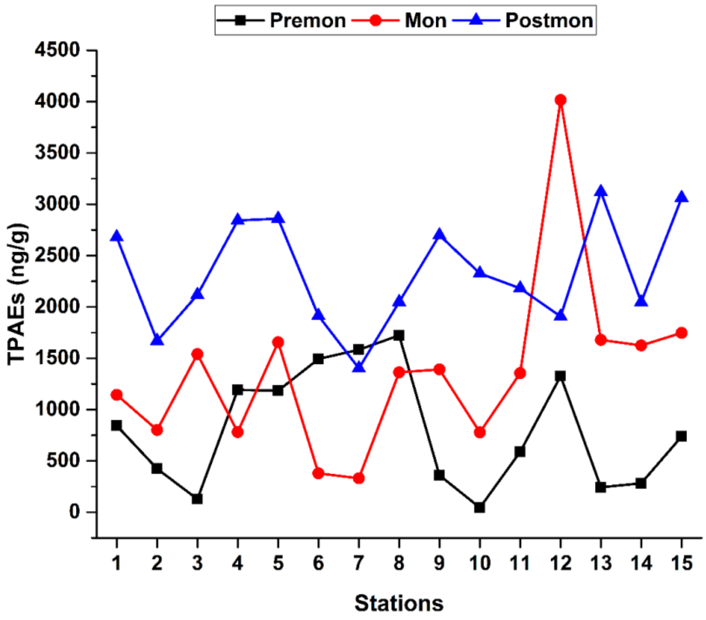

Figure 4.1: Distribution of total PAEs in surface sediments

The distribution and concentrations of USEPA listed six PAEs along the study area were studied as a major pollutant. The total concentration and distribution of PAEs in surface sediments of Cochin estuary are plotted in figure 4.1 and 4.2, respectively and the data is tabulated in appendix 3. The concentration range of PAEs in each season is tabulated in table 4.1. During the premonsoon season the total PAE (TPAE) ranged from 44.34 to 1722.55 ng/g (average810.35 ± 567.48 ng/g), maximum was recorded at station 8 and minimum was at station 10. It was ranged from 331.0 to 4015.80 ng/g (average1372.35 ± 867.95 ng/g) during monsoon; the maximum was recorded at station 12 and the minimum was at station 7. During postmonsoon, TPAE ranged from 1402.02 to 3121.10 ng/g (average 2325.40 ± 785.60 ng/g) maximum was recorded at station 13 and minimum was at station 7.

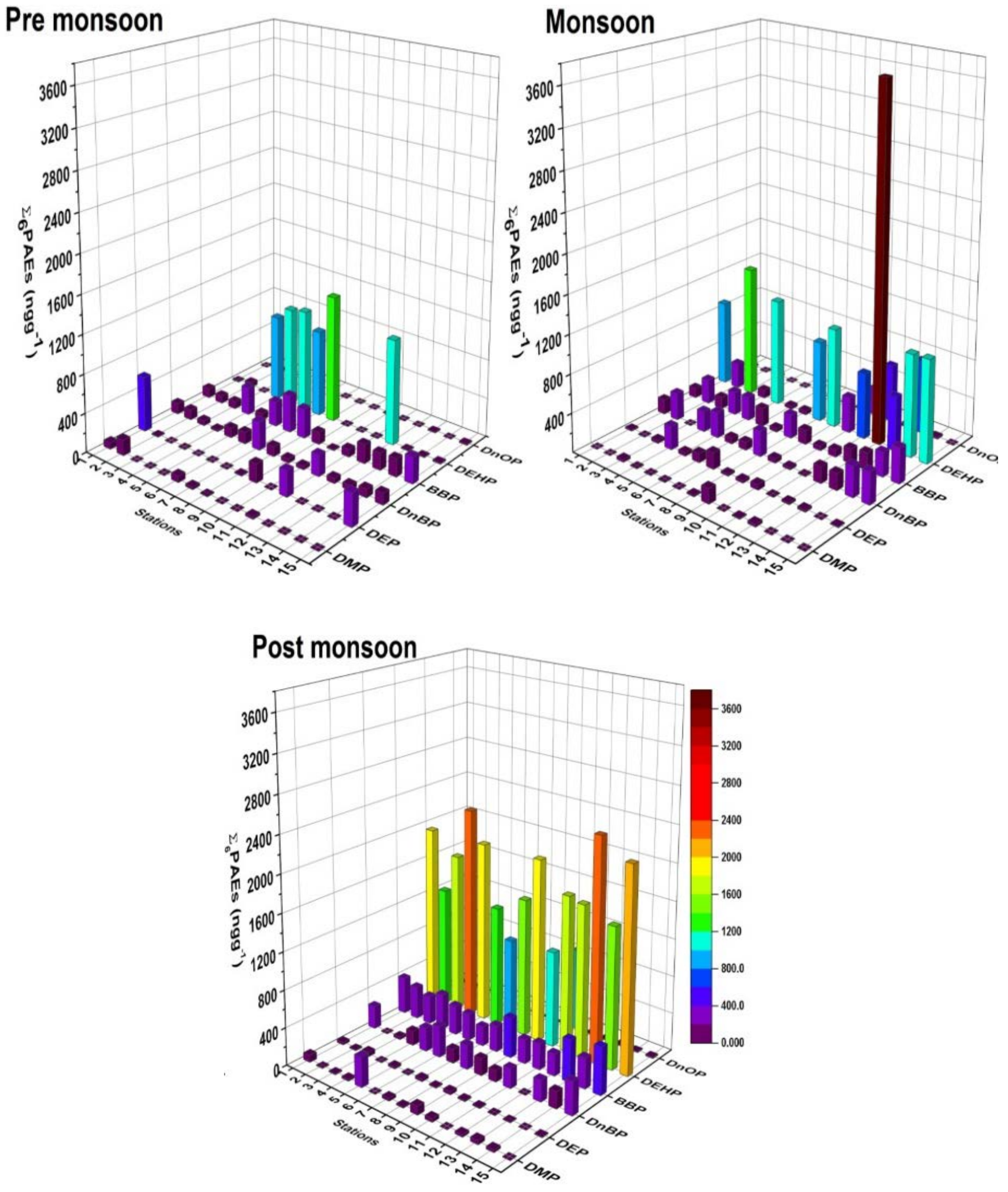

Figure 4.2: Seasonal distribution of PAEs in surface sediments

4.2.2 DMP distribution in sediments

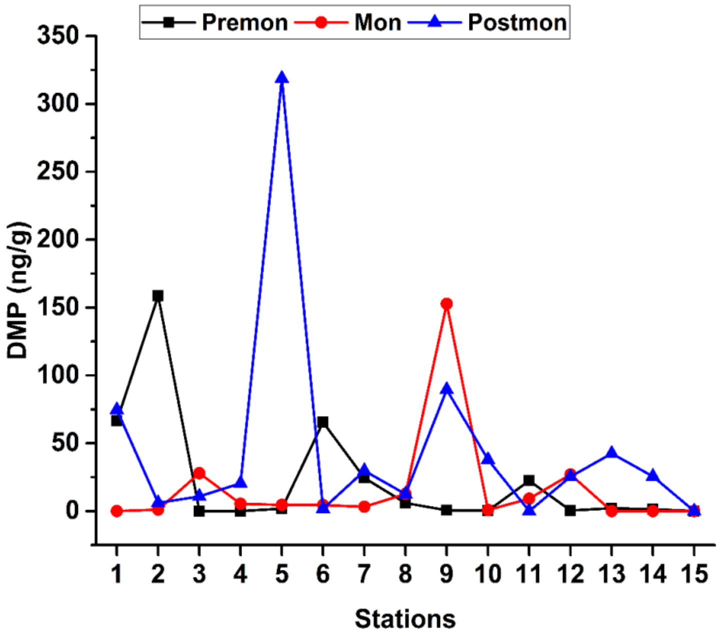

Figure 4.3: Distribution of DMP in surface sediments.

The distribution DMP along the study is plotted in 4.3. DMP concentration during premonsoon was ranged from n.d to 158.54 ng/g (average23.37 ± 43.76 ng/g) maximum concentration was at station 2 and a minimum at station 4 and 15. During monsoon, it ranged from n.d to 152.76 ng/g (average16.62 ± 38.76 ng/g) maximum was at station 9 and minimum was recorded at several stations, station 1, 13, 14, and 15. During postmonsoon season DMP concentration was varied from n.d to 318.82 ng/g (average46.39 ± 9.78 ng/g) maximum concentration was at station 5 and minimum was reported at station 11 and 15.

4.2.3 DEP distribution in sediments

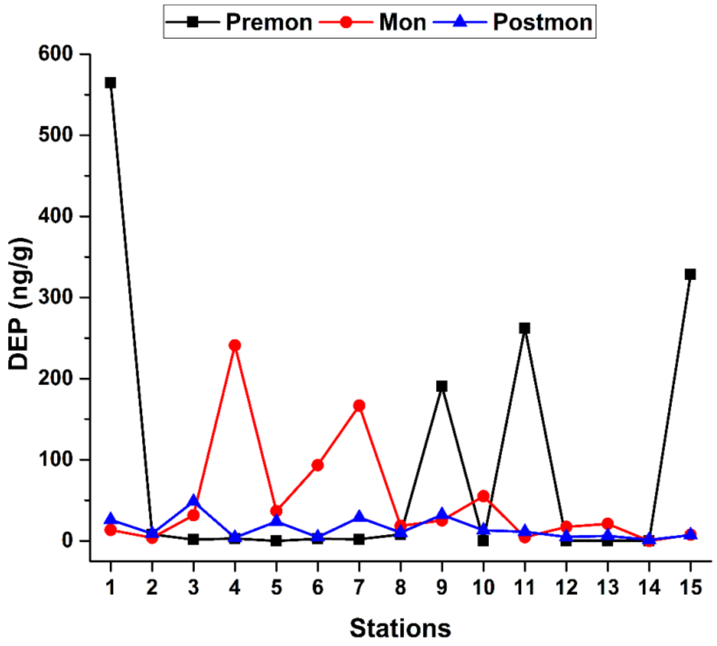

Figure 4.4: Distribution of DEP in surface sediments

The distribution DEP along the study is plotted in 4.4. DEP was ranged from n.d to 564.82 ng/g (average91.43 ± 170.45 ng/g) during premonsoon season its maximum concentration was reported at station 1 and minimum was at stations 5,13. During monsoon season it was varied from n.d to 241 ng/g (average49.07 ± 68.60 ng/g) maximum was at station 4 and the minimum was at station 14. During the postmonsoon season, DMP concentration was ranged from 1.42 to 48.45 ng/g (average15.36 ± 13.46 ng/g) maximum was observed at station 3 and the minimum was at station 14.

4.2.4 DnBP distribution in sediments

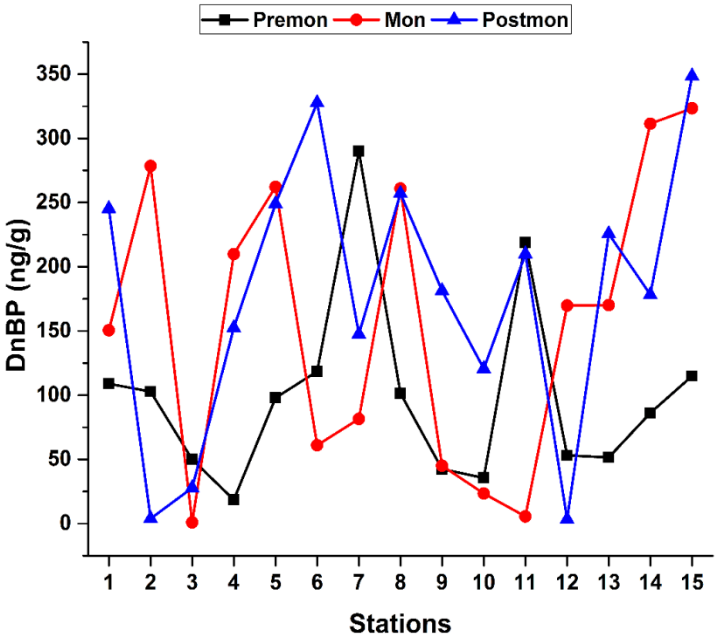

Figure 4.5: Distribution of DnBP in surface sediments.

The distribution DnBP along the study is plotted in 4.5. DnBP was ranged from 18 to 289 ng/g (average 99.37 ± 71.84 ng/g) during premonsoon season and maximum concentration observed at station 7 and the minimum was at station 4. During monsoon season it is varied from 0.89 to 323.41 ng/g (average 156.95 ± 114.60 ng/g) Maximum was at station 15 and the minimum was at station 3. DnBP ranged from 3.45 to 348.56 ng/g (average 178.57 ± 106.53 ng/g) maximum at station 15 and the minimum was at station 12.

4.2.5 BBP distribution in sediments

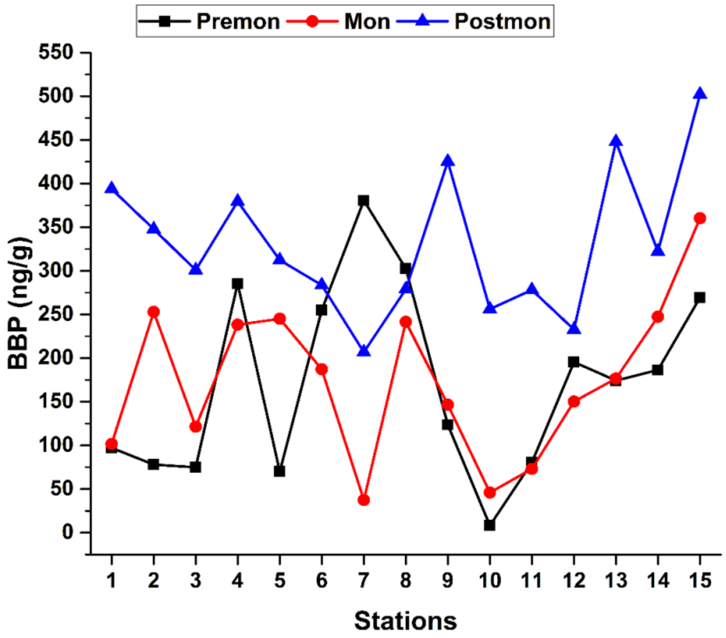

Figure 4.6: Distribution of BBP in surface sediments

The distribution BBP along the study is plotted in 4.6. During premonsoon season BBP was ranged from 8.41 to 380.64 ng/g (average 172.12 ± 107.71 ng/g). The maximum concentration was at station 7 and a minimum at station 10. It was ranged from 37.46 to 360.31 ng/g (average 175.04 ± 90.56 ng/g) during monsoon season, maximum concentration was observed at station 15 and minimum at station 7. During postmonsoon season BBP was varied from 206.93 to 502.18 ng/g (average 331.22 ± 83.73 ng/g), maximum and minimum concentration was observed similar to monsoon season.

4.2.6 DEHP distribution in sediments

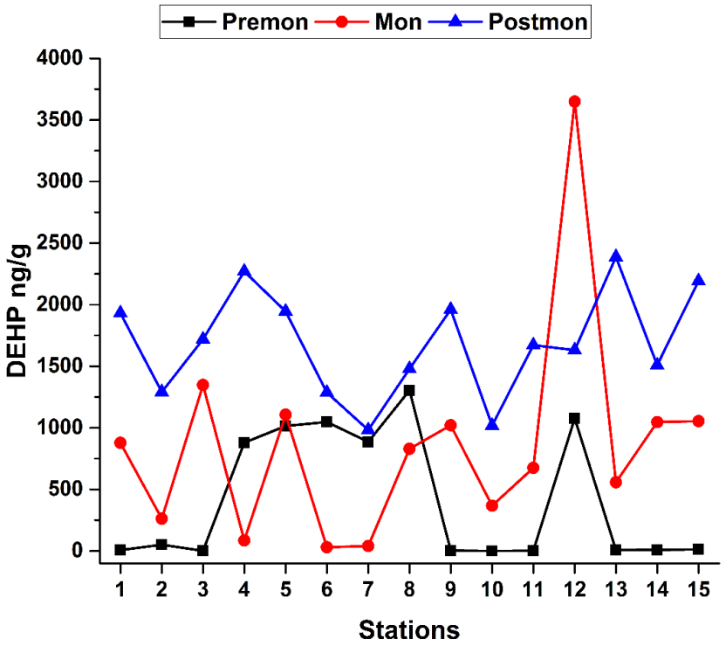

Figure 4.7: Distribution of DEHP in surface sediments.

The distribution DEHP along the study is plotted in 4.7. During premonsoon season DEHP was varied from 0.02 to 1304.28 ng/g (average420.10 ± 527.89 ng/g), maximum concentration was reported at station 8 and the minimum was at station 10. Its concentration range during monsoon was 30.34-3649.55 ng/g (average863.43 ± 880.97 ng/g) maximum was at station 12 and the minimum was at station 6. During postmonsoon season DEHP ranged from 981.91 to 2387.84 ng/g (average1685.08 ± 433.31 ng/g) maximum at station 14 and minimum at station 7.

4.2.7 DnOP distribution in sediments

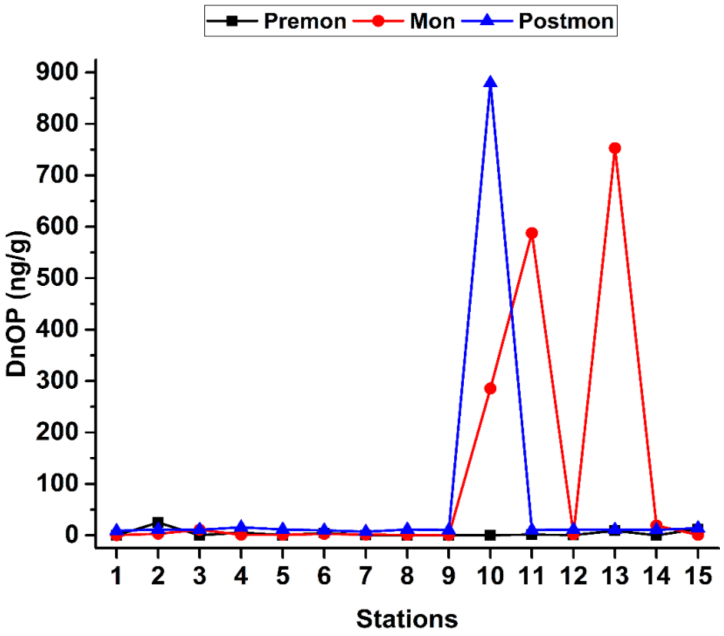

Figure 4.8: Distribution of DnOP in surface sediments

The distribution DnOP along the study is plotted in 4.8. DnOP ranged from n.d to 24.67 ng/g (average 3.96 ± 6.86 ng/g) during premonsoon, maximum was at station 2 and minimum was at stations 1,9, and 14. During monsoon, its concentration varied from 0.16 to 753.00 ng/g (average 111.24 ± 240.32 ng/g) maximum was at station 13 and minimum at station 1. During postmonsoon, DnOP varied from 7.04 to 879.70 ng/g (average 68.79 ± 224.34 ng/g) maximum was reported at station 10 and minimum at station 7.

4.3 Discussion

The distribution of PAE was characterized by an accumulation during postmonsoon followed by its dilution during monsoon and premonsoon seasons. During the premonsoon season, the central portion (stations 4-8) and southern side (stations 11 & 12) of the estuary showed PAE accumulation (1184-1722 ng/g) as compared to the inlet (Station 1) and northern side (stations 13-15). During monsoon, the PAE contents were relatively low (331-1656 ng/g) in the central portion of the estuary, while it was substantially higher in the southern (1355-4016 ng/g) and northern (1624-1747 ng/g) regions (Muvattupauzha and Periyar Rivers). In general, the post-monsoon season showed very high PAEs deposition in the central and southern regions. The distribution of PAEs in the sediments can be explained in terms of their specific adsorption, deposition, dilution and partitioning mechanisms (Staples et al., 1997; Sun et al., 2013). During the low discharge period (premonsoon), high molecular weight (more hydrophobic) PAEs 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 premonsoon season, when the 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 premonsoon season indicate that the weak flow and reduced input favour a stable binding of the available PAE congeners with the organic matter in estuarine sediments.

Table 4.1: Summary of concentration ranges of PAEs (ng/g) in sediments of Cochin estuary

PAEs	Premonsoon			Monsoon			Post Monson		
	Range	Mean	D.F	Range	Mean	D.F	Range	Mean	D.F
DMP	n.d- 159	23	87	n.d-153	17	73	n.d-319	46	93
DEP	n.d-565	91	93	n.d-241	49	93	1-48	15	100
DnBP	19-290	99	100	1-323	157	100	3-349	179	100
BBP	8-381	172	100	37-360	175	100	207-502	331	100
DEHP	0.02-1304	420	100	30-3650	863	100	982-2388	1685	100
DnOP	n.d-25	4	80	0.16-753	111	100	7-880	69	100
∑6PAEs	44-1722	810	100	331-1747	1184	100	1402-3121	2325	100

DF-Detection Frequency (%), n.d – not detected

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. 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 premonsoon period. Postmonsoon is a transitional period when the estuary becomes highly saline, leading to increased flocculation of suspended particles (Mallik and Suchindran, 1984; Nair and Balchand, 1993; Vinita et al., 2017). The premonsoon 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 region during postmonsoon. 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 the monsoon season is characterized by reduced light, temperature and high turbidity, which may significantly reduce degradation of PAHs. During postmonsoon season, the high solar irradiation and low water column turbidity favour an increased degradation of PAHs.

In contrast, PAEs are resistant to photolysis and are degraded only by microbial activity (R and A, 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 behaviour in highly impacted aquatic environments will be a challenging task for researchers. The concentration of individual PAE congeners as follows.

Table 4.2: Comparison of PAEs in the Cochin estuary with those reported from other locations (concentrations in ng/g 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	n.d-280	210-14160	n.d-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	n.d	n.d	n.d-2780	n.d	1930-86400	n.d-1350	Chen et al., 2013
Pearl River Delta region, China	16	567-47300	1–19	1–91	108–12400	n.d -113	415–29500	n.d-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	n.d-1750	n.d-180	56-4660	n.d-160	470--8530	n.d-310	Li et al., 2016
Urban soil of Beijing, China	7	1822 – 28087	n.d-67	n.d-252	149-936	n.d- 60	170-6491	n.d-172	Li et al., 2006
Taiwan China	6	900-63200	….	100-1100	300-30300	n.d-1800	500-23900	…	Yuan et al., 2002
False Creek Harbour, Canada	13	4-2100							Mackintosh et al., 2006
Ogun River, Nigeria	4	330-2880	n.d-850	80-350	190-1420	….	20-820	….	Adeleke et al., 2011
Ronnebyan/Svartan River, Sweden	4	1200-8030	….	….	…..	n.d	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	n.d-1870	n.d-490	n.d-350	…	n.d-340	n.d-3240	n.d-530	Srivastava et al., 2009
Kaveri River, India	6	2-1438	n.d-2	n.d-16	n.d-36	n.d-3	n.d-278	n.d-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

n.d – not detected

DMP was high (319 ng/g) at station 5 during post-monsoon, whereas DEP was high (565 ng/g) at station 1 during pre-monsoon. The high molecular weight fraction (DnBP) was present up to 290 ng/g, 323 ng/g and 349 ng/g during pre-monsoon, monsoon and post-monsoon, respectively. The maximum concentrations of other high molecular weight congeners were BBP (381 ng/g, 360 ng/g and 502 ng/g), DEHP (1304 ng/g, 3650 ng/g and 2388 ng/g) during respective periods, while DnOP showed no significant seasonal or spatial variation. Even though, the high DEHP concentrations in this study indicate its stronger sorption capacity and lower degradation (Sun et al., 2013), the major reason for its greater accumulation in sediment is its widespread use. Accumulation of 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.

Investigations on PAEs in estuaries around the world (including India) are scarce. A comparison of available data of various aquatic settings (Table 4.2) 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).

4.3.1 Ecological risk assessment of PAEs

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. Sediment Quality Guidelines (SQGs) (Zeng et al., 2008; Chih-Feng et al., 2016) help identification of PAE-related eco-toxicological effects in ecosystems. Sediment DEHP concentration of 182 ng/g is set as its threshold effect level (TEL) and 2647 ng/g 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 ng/g) during postmonsoon, indicates 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 premonsoon and pointed to the absence of any toxicological effects due to this component.

Table 4.3: Comparison of the PAEs with various sediment quality guidelines

PAEs	MPC (ng/g at 10 % TOC)	SRC_{eco} (ng/g at 10 % TOC)	ERL (ng/g at 10 % TOC)	Pre Mon (ng/g at 10 % TOC)	Mon (ng/g at 10 % TOC)	Post Mon (ng/g 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 (A.P, 2001).

Alternate methods such as Maximum Permissible Concentration (MPC) and Serious Risk Concentration (SRC_{eco}) are also widely used to assess the ecological risk posed by PAEs (A.P, 2001; Chih-Feng et al., 2016). In order 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 4.3). 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 700 and 1000 ng/g in sediment containing 10 % of organic matter. A comparison show 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).

4.4 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 in to 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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Chapter

5 DISSOLVED AND PARTICULATE PAHs

Contents

5.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of lipophilic organic compounds composed of more than two aromatic rings fused. They enter into the water column during organic matter diagenesis and various anthropogenic activities (Ramzi et al., 2017). PAHs are highly hydrophobic, which easily adsorbed into the particulate matter. Therefore the dissolved phase exhibit less PAHs concentration than that of particulates and sediments. PAHs are very toxic as endocrine disruptors there for extensive studies are needed to understand the sources and transformation of PAHs in the estuary.

Cochin estuary receives a large number of pollutants from various sectors like industries, urban runoff, navigation, terrestrial discharge, mining etc. (Martin et al., 2012; Ramzi et al., 2018). Over the last two decades, there have been numerous reports on the sporadic release of nutrients, heavy metals and persistent organic pollutants (POPs) into the Cochin estuary. This chapter deals with the distribution, sources, and ecological implications of dissolved and particulate-bound PAHs in the Cochin estuary.

5.2 Results

5.2.1 Total dissolved PAHs

Seasonal distribution of total dissolved PAHs is plotted in figure 5.1 and the data is tabulated in appendix 4. Total dissolved PAHs (TDPAHs) in surface water was in the range 2.24-13.13 ng/L, 1.3-11.88 ng/L, 0.73-5.38 ng/L in premonsoon, monsoon and postmonsoon seasons respectively, while in the bottom water was in the range 1.29-19.77 ng/L (premonsoon), 1.67-72.47 ng/L (monsoon), and 0.41-1.66 ng/L (postmonsoon). TDPAHs exhibited significant seasonal variation ($p<0.05$) characterised by the highest concentration in monsoon season followed by postmonsoon and premonsoon.

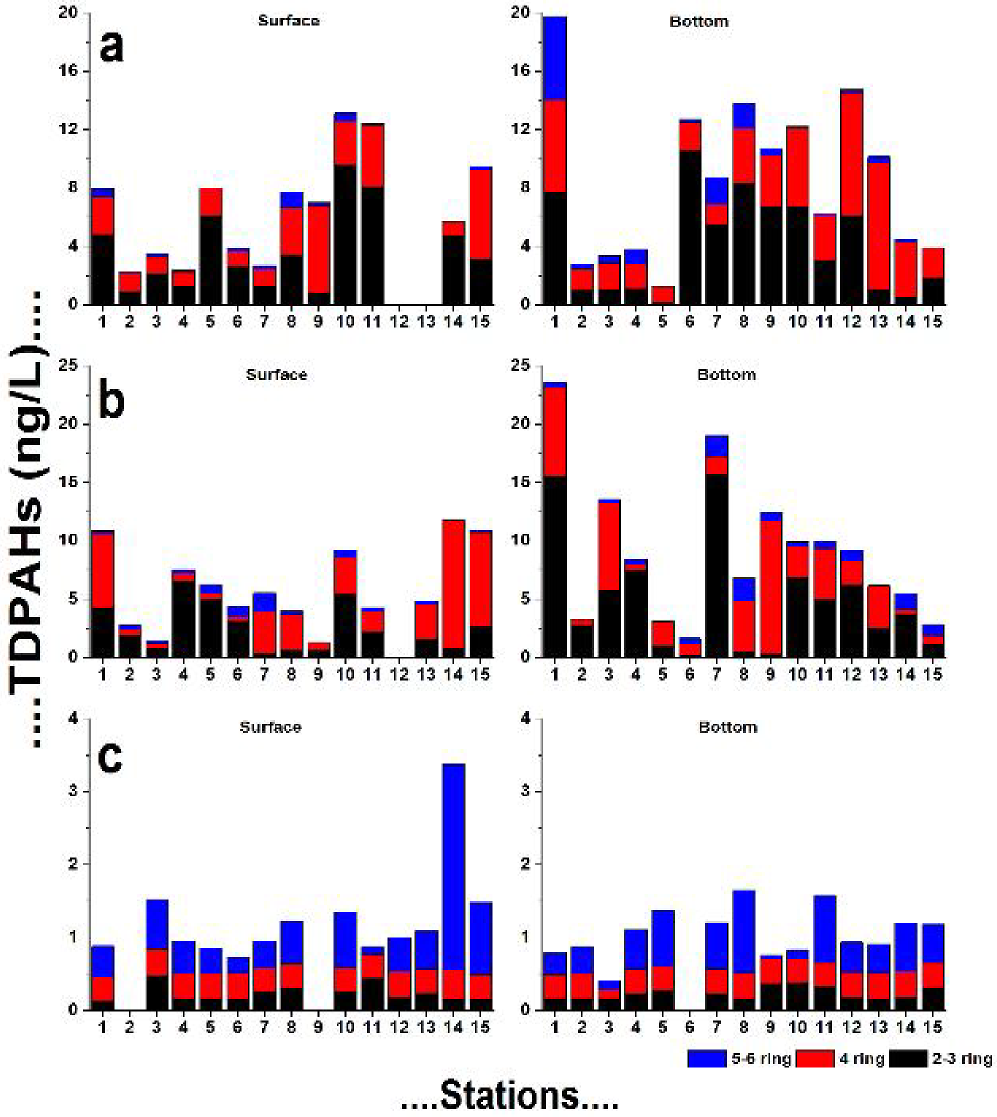

Figure 5.1: Dissolved PAHs along with the stations

5.2.1.1 2-3 ringed PAHs

The dissolved 2-3 ringed PAHs in surface and bottom water is plotted in figure 5.2. 2-3 ring PAHs such as Naphthalene, Acenaphthalene, Acenaphthene, Fluranthene, Phenanthrene and Anthracene were quantified. During premonsoon, 2-3 ringed PAHs ranged from 0.81 ng/L to 9.60 ng/L from (Surface) and 0.11 - 10.63 ng/L (Bottom). Whereas, during monsoon, it was in the range 0.68 – 6.57 ng/L (Surface) and 0.20-15.65 ng/L(Bottom). 2-3 ringed PAHs during postmonsoon ranged from 0.13 to 0.48 ng/L(Surface) and 0.16 to 0.37 ng/L (Bottom).

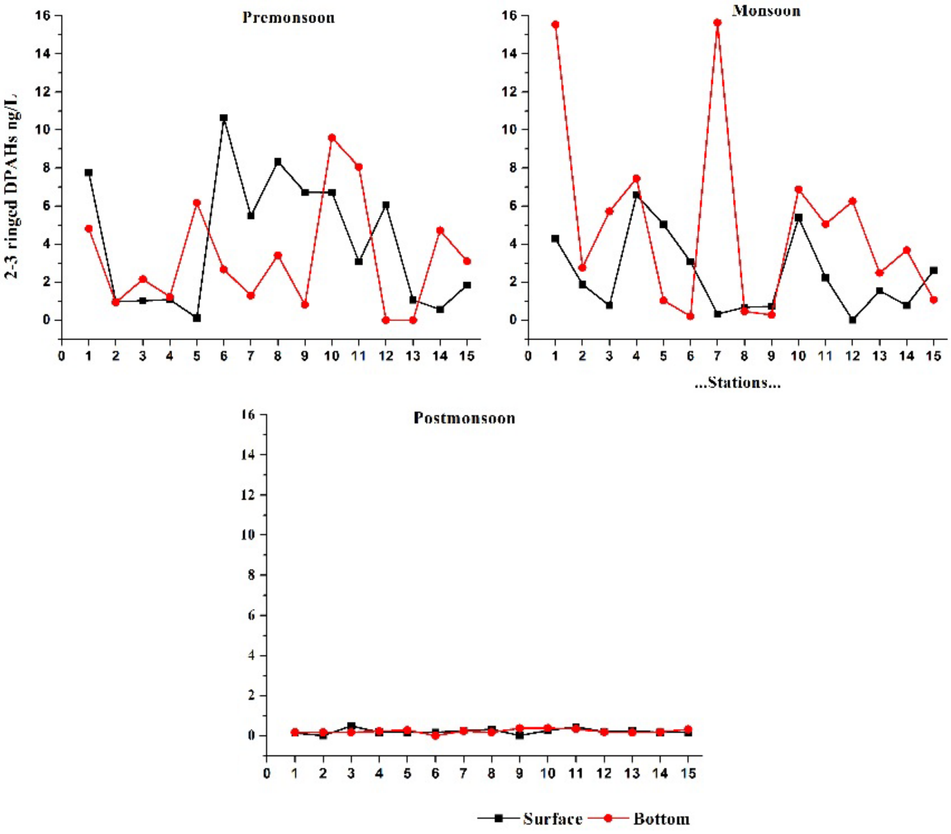

Figure 5.2: 2-3 ringed dissolved PAHs along with the stations

5.2.1.2 4 ringed PAHs

The dissolved 4 ringed PAHs in surface and bottom water is plotted in figure 5.3. 4 ringed PAHS includes Fluorine, Pyrene, Benzo(a)anthracene and chrysin. During premonsoon season 4 ringed PAHs ranged from 0.98 ng/L to 6.133 ng/L and 1.11 to 8.68 ng/Lin surface and bottom water respectively (Fig. 5.1 a), while in monsoon, it was in the range 0.54–11 ng/L(surface) and 0.46-71.43 ng/L (bottom). During postmonsoon, 4 ringed PAHs (Fig. 5.1 c) in the range 0.33 – 0.39 ng/L in surface waters and 0.12 ng/L to 0.30 ng/L in bottom waters.

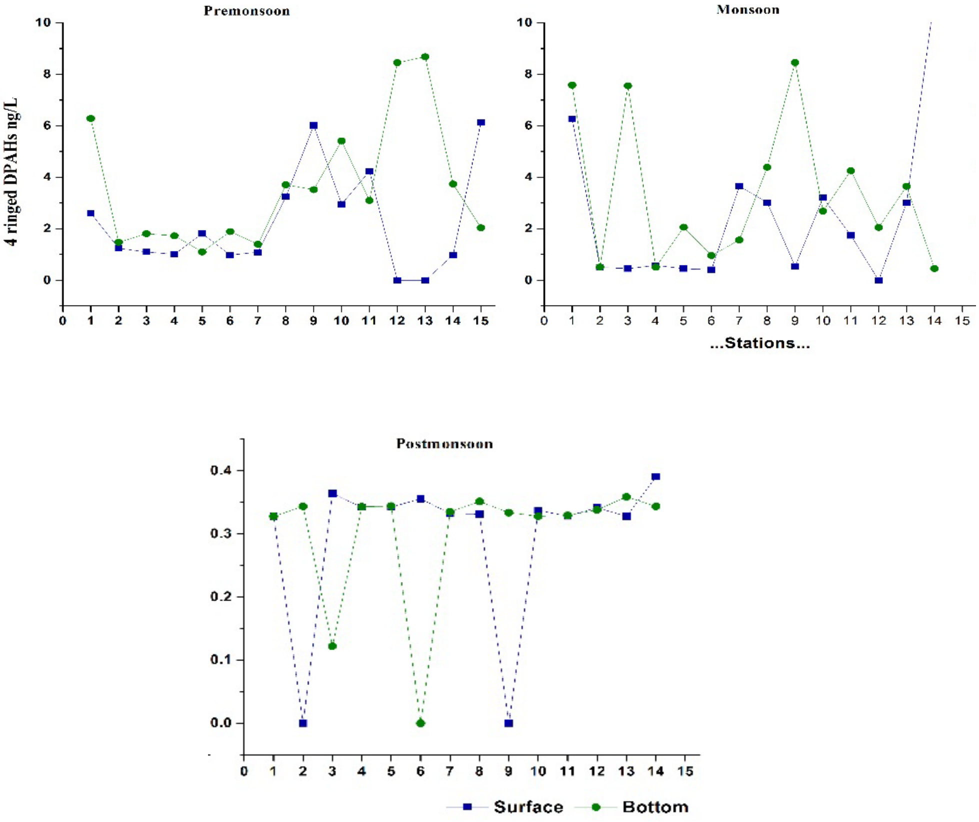

Figure 5.3: Seasonal distribution of 4 ringed dissolved PAHs along with the stations

5.2.1.3 5-6 ringed PAHs

The dissolved 5-6 ringed PAHs in surface and bottom water is plotted in figure 5.4. Benzo b fluoranthene, Benzo a pyrene, Ideno 123 cd pyrene, Benzo perylene are the 5-6 ringed PAHs. 5-6 ringed PAHs ranged from 0.01 to 1.10 ng/L in surface waters, while in the bottom waters; it was in the range 0.02 ng/L to 5.73 ng/L in premonsoon. During monsoon season, 5-6 ringed PAHs was in the range 0.03-1.55 ng/L (surface) and 0.04 -1.96 ng/L (bottom), whereas in postmonsoon, it was in the range 0.11– 4.83 ng/L (surface) and 0.06-1.14 ng/L (bottom).

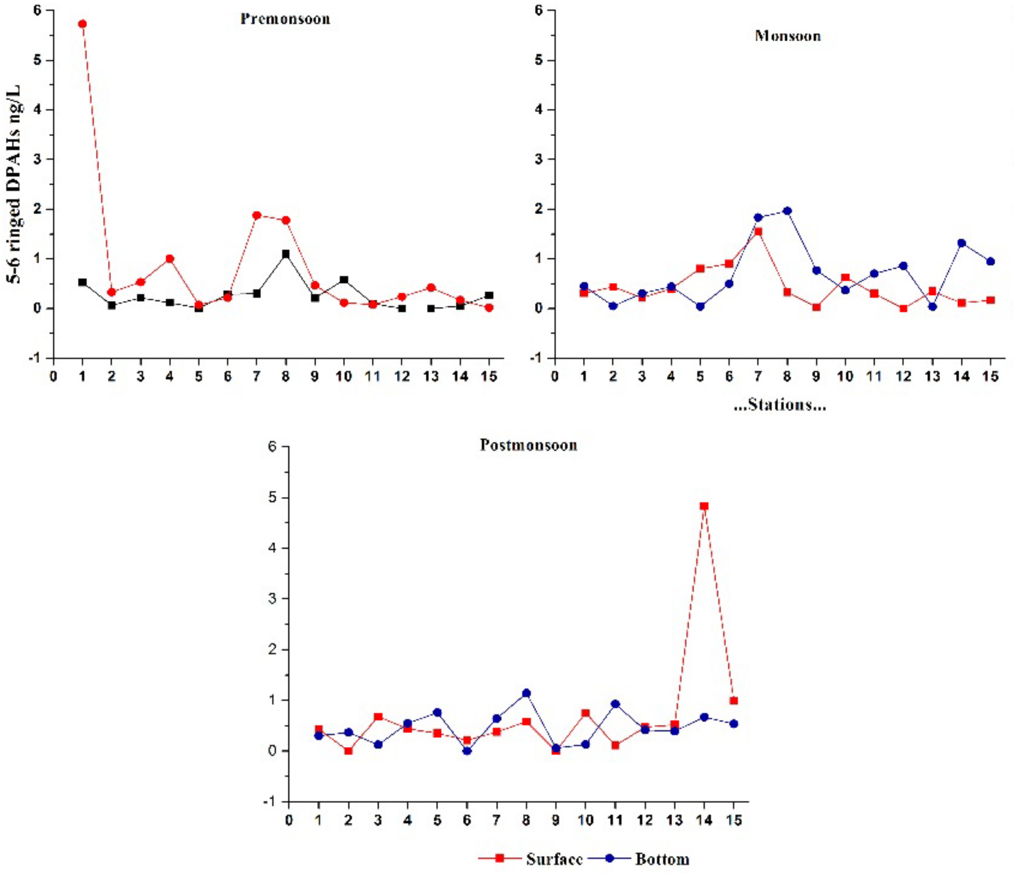

Figure 5.4: Seasonal distribution of 5-6 ringed dissolved PAHs along with the stations

5.2.2 Total Particulate PAHs

The total particulate PAHs in surface and bottom water is plotted in figure 5.5 and the data is tabulated in appendix 5.Total Particulate PAHs (TPPAHs) in surface water was in the range 1252 - 60502, 1709 - 28707 and 160-25070 ng/g in premonsoon, monsoon and postmonsoon seasons respectively, whereas, in bottom waters, the range was 198-37691, 979-41275 and 60-17763 ng/g in respective seasons. Similar to dissolved PAHs, Particulate PAHs also showed significant seasonal variation characterised by higher concentrations in monsoon followed by post and premonsoon seasons.

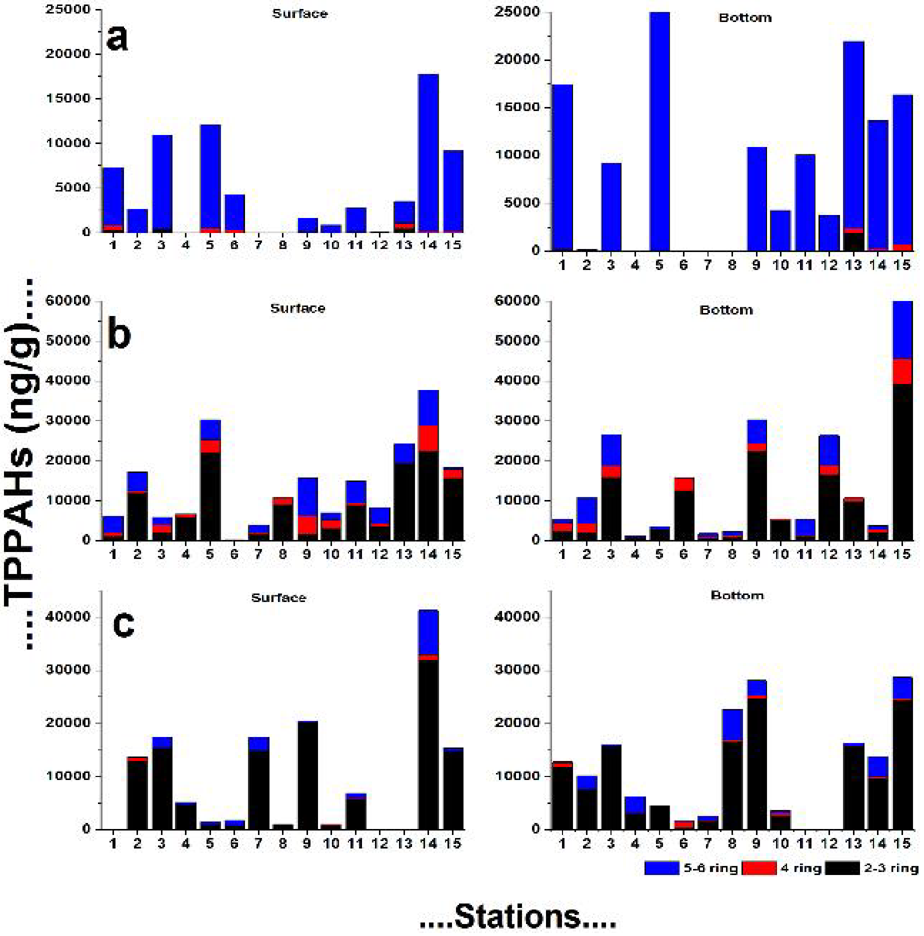

Figure 5.5: Particulate PAHs along the Stations

5.2.2.1 2-3 ringed PAHs

The particulate 2-3 ringed PAHs in surface and bottom water is plotted in figure 5.6. In premonsoon, 2-3 ringed PAHs ranged from 0.60 ng/g to 524.69 ng/g (Surface) and from 2.60 to 524.69 ng/g (Bottom) (Fig. 5.5a), whereas, in monsoon, it was in the range 153.36-22340.64 ng/g (Surface) and 582.16-39084.53 ng/g (Bottom) (Fig. 5.5b). 2-3 ringed PAHs in postmonsoon (Fig. 5.5c) ranged from 682.24 to 31956.26 ng/g (Surface) and 250.57 to 24628.87 ng/g (Bottom).

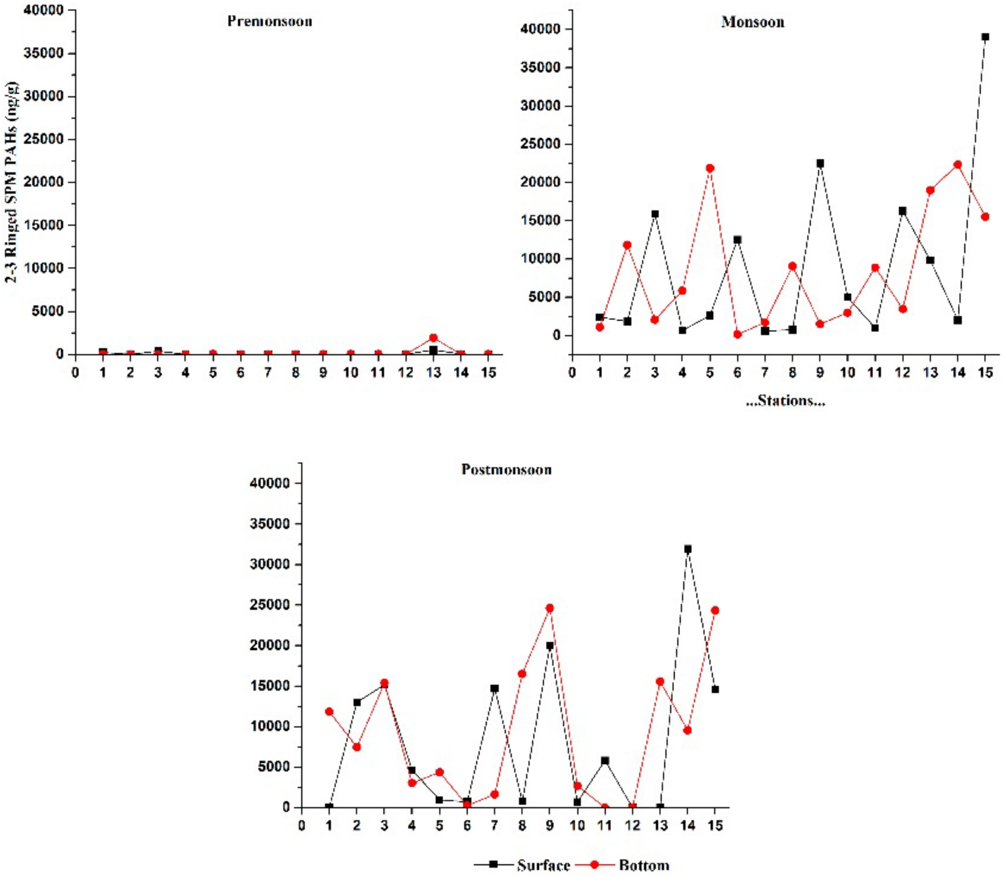

Figure 5.6: Seasonal distribution of 2-3 ringed particulate PAHs along with the stations

5.2.2.2 4 ringed PAHs

The particulate 4 ringed PAHs in surface and bottom water is plotted in figure 5.7. In premonsoon season 4 ringed PAHs ranged from 2.38 ng/g to 554.22 ng/g and 1.87 to 634.82 ng/g in surface and bottom water respectively (Fig. 5.5 a), while during monsoon, it was in the range 41.98–6435.447 ng/g (surface) and 196.48-6663.35 ng/g (bottom) (Fig. 5.5 b). During postmonsoon, 4 ringed PAHs (Fig. 5.5 c) was in the range 39.86 – 936.17 ng/g in surface waters and 82.85 ng/g to 1223.758 ng/g in bottom particulates.

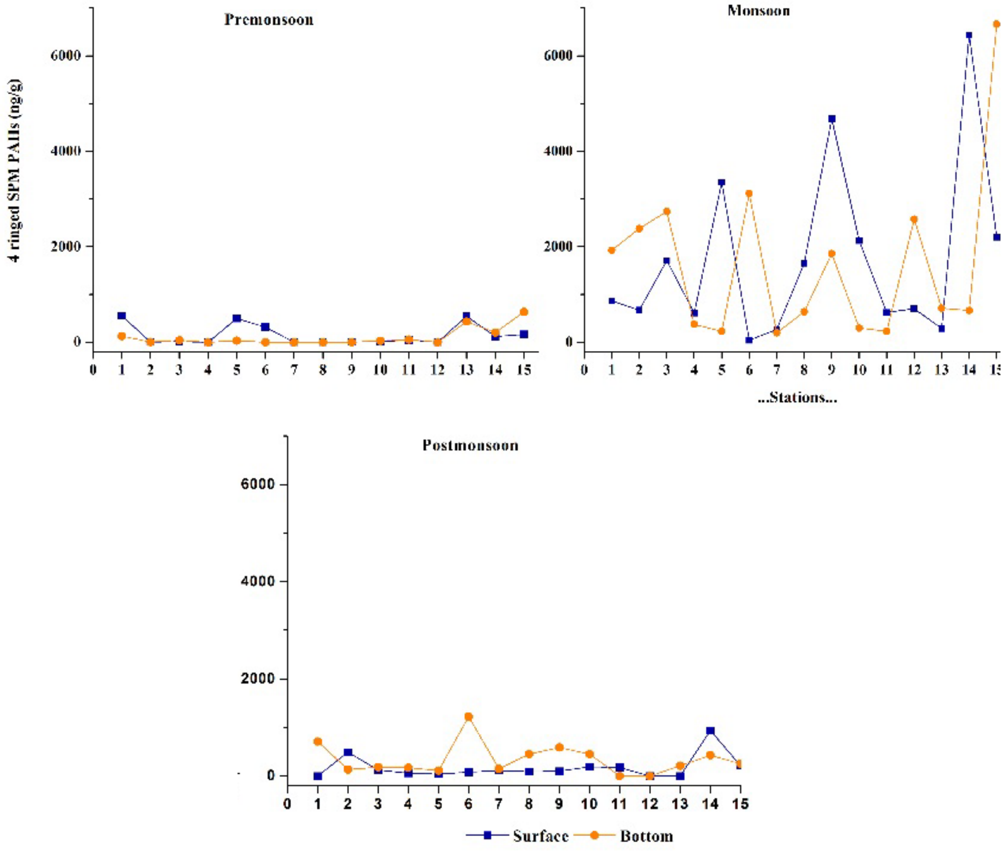

Figure 5.7: Seasonal distribution of 4 ringed particulate PAHs along with the stations

5.2.2.3 5-6 ringed PAHs

The particulate 5-6 ringed PAHs in surface and bottom water is plotted in figure 5.8. The 5-6 ringed PAHs ranged from 47.68 ng/g to 17598.84 ng/g in surface particulates, while in the bottom particulates; it was in the range 151.33 ng/g to 24993.98 ng/g in premonsoon (Fig. 5.5 a). During monsoon season, 5-6 ringed PAHs was in the range 2.63–9489.43 ng/g (surface) and 39.63-14754.46 ng/g (bottom) (Fig. 5.5 b), whereas, during postmonsoon, it was in the range 113.66– 8383.34 ng/g (surface) and 82.85- 1924.68 ng/g (bottom) (Fig. 5.5 c).

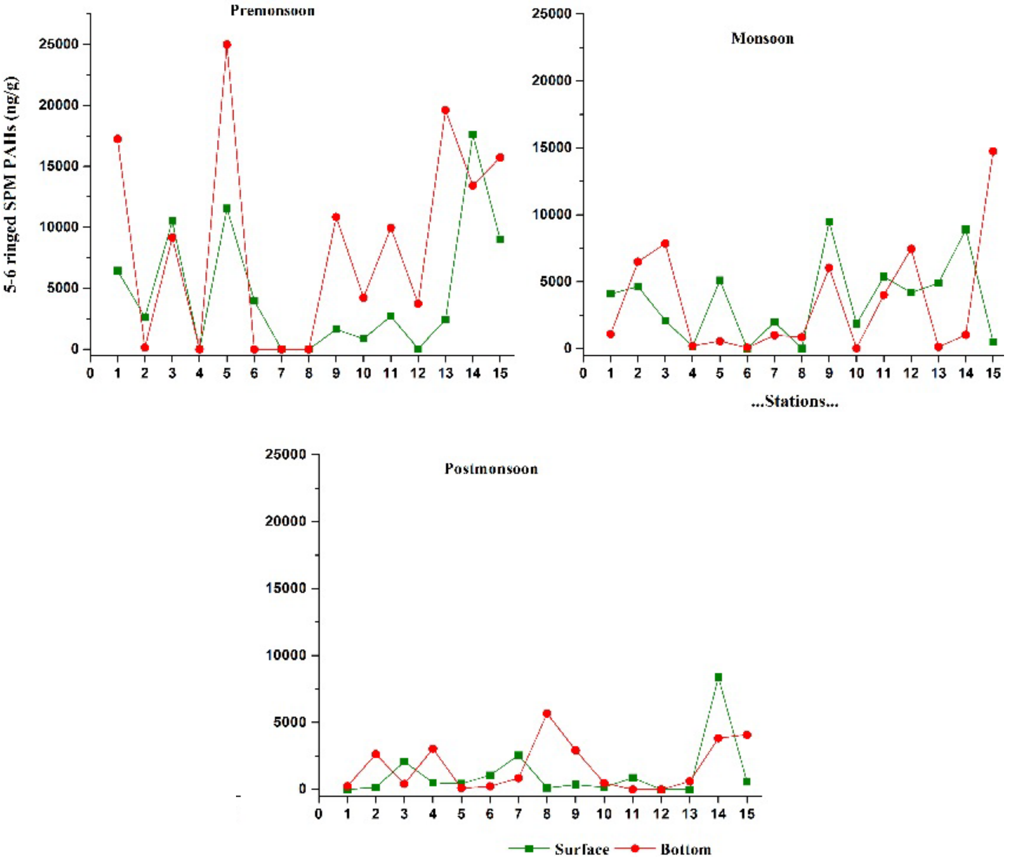

Figure 5.8: Seasonal distribution of 5-6 ringed particulate PAHs along with the stations

5.3 Discussion

5.3.1 Comparison with other aquatic systems worldwide

Cochin estuary receives huge amount of terrestrial organic matter during monsoon season (Saraladevi et al., 1986; Balachandran et al., 2003; Martin et al., 2010; Gireeshkumar et al., 2013). TDPAHs were characterized by high concentration during monsoon, followed by premonsoon and postmonsoon. The high concentration of TDPAHs recorded at central estuary during monsoon may be due to higher terrestrial discharge.

A comparison of PAH levels in water with those reported worldwide are presented in Table 5.1. TDPAH concentrations are relatively very low in Cochin estuary compared to other estuaries around the world such as Jailing River China, Gulf of Tunis Tunisia, Bahia Blanca estuary Argentina, Western Taiwan Strait South China, Dailao River watershed China, Gao-Ping River Taiwan, Tainjing estuary China, Hangzhou Coast China, Dalino River, Alexandria Coast Egypt, Daliao River estuary, Bohai Sea South China.

Similar to TDPAHs, particulate PAHs also exhibited seasonal heterogeneity characterized by higher PAHs concentration in monsoon season followed by postmonsoon and premonsoon. Similar to dissolved PAHs high concentration of PAHs during monsoon may be due to increased terrestrial runoff indicating the anthropogenic contribution of PAHs. A comparison of PAH levels in suspended particulate matter with those reported worldwide are presented in Table 5.1. Even though the TPPAHs in the present study are high at some locations, they are still lower than the values from other estuaries. It is evident from Table 5.1 that the observed TPPAH concentrations are relatively higher than Gulf of Tunis Tunisia, Mundau´–Manguaba estuary Brazil, Pearl River Estuary China, and York River VA Estuary USA, whereas the studies from Daliao River Estuary and Bohai Sea China, are comparable with Cochin estuary. However, TPPAHs are very high in Daliao River watershed, China and Tianjing, China than the Cochin estuary.

Table: 5.1: Comparison of TPAHs values with worldwide reports

Locations Dissolved PAHs in (ng/L)	Number of PAHS studied	PAHs Range	Reference
Jialing River, China	16	811.5-1585.8	Xu et al., 2012
Gulf of Tunis, Tunisia	24	139.2-1008.3	Mzoughi and Chouba, 2011
Bahia Blanca Estuary, Argentina Europe	17	n.d-4870	Arias et al., 2009
Western Taiwan Strait, South China Sea	15	12.3–58.0	Wu et al., 2011
Daliao River watershed, China	18	946.1-13448.5	Guo et al., 2007b
Gao-Ping River, Taiwan	16	10–9400	Doong and Lin, 2004
Tianjing, China	16	45.81-1272	Shi et al., 2005
Hangzhou, China	10	989–9663	Chen et al., 2004
Alexandria coast, Egypt	7	13–120	El Nemr and Abd-Allah, 2003
Daliao River Estuary, Bohai Sea South China	16	139.16–1717.87	Men et al., 2009
Cochin estuary	16	0.41-24.89	This study
Particulate PAHS in ng/g			
Gulf of Tunis, Tunisia	24	139.2-8222.4	Mzoughi and Chouba, 2011
Mundau´–Manguaba estuary, Brazil	16	454-1078	Maioli et al., 2011
Daliao River Esturay, Bohai Sea, China	16	1542.44–20094.47	Men et al., 2009
Daliao River watershed, China	18	317.5-238518.7	Guo et al., 2007b
Tianjing, China	16	938–64200	Shi et al., 2005
Pearl River Estuary, China	18	442–1850	Luo et al., 2006
York River, VA Estuary, USA	20	199–1153	Countway et al., 2003
Cochin estuary	16	60.02-60502.35	This study

5.3.2 Sources of PAHS

Low molecular weight (LMW, 2-3 rings) PAHs are generally derived from petrogenic sources or low-temperature combustion, whereas the High Molecular weight (HMW, 4-6 rings) fractions originate from pyrogenic sources (Yunker et al., 2002) (Guo et al., 2007a; Wang et al., 2015a; Wang et al., 2015b; Wang et al., 2015c). Therefore, LMW /HMW ratio can be used to identify the different PAH sources. Based on this, a LMW/HMW ratio > 1 indicates a petrogenic source, and < 1 indicates a pyrolytic source. The ratios obtained from the present study are mostly > 1 indicating a predominance of petrogenic PAHs is dominating the PAH accumulation in the Cochin estuary. This is further evidenced by the observation of Acy as a dominant fraction in this estuary by a previous study. It has been shown that low-temperature combustion of grass/wood can yield a high amount of Acy and Ace fractions of PAH (Fang et al., 2003; Cao et al., 2011; Yu et al., 2015a; Yu et al., 2015b).

Molecular indices involving various PAHs are often used to identify the sources of PAHs in sediments. This includes the derivation of ratios such as An/(An+Phe), Flu/(Flu+Py), InP/(InP+Bper), BaA/(BaA+Ch) etc. Thus, a ratio > 0.1 for An/An+Phe indicates that it is a pyrolytic source, whereas a ratio < 0.1 indicates its petroegenic origin. Similarly, a ratio > 0.5 for Flu/Flu+Py indicates its pyrolytic origin and < 0.5 indicates its petrogenic origin (Yunker et al., 2002; Maciel et al., 2015)). Based on the analysis of data of the present study, it can be attributed that, the PAH contamination of both water and particulate matter as either due to petrogenic or pyrolytic sources (Fig. 5.3 and 5.4). A ratio > 1 for An/An+Phe indicates a pyrolytic source, while that for Flu/Flu+Py indicates a petrogenic source. This may be due to the synergetic effect of various pollutants during estuarine mixing.

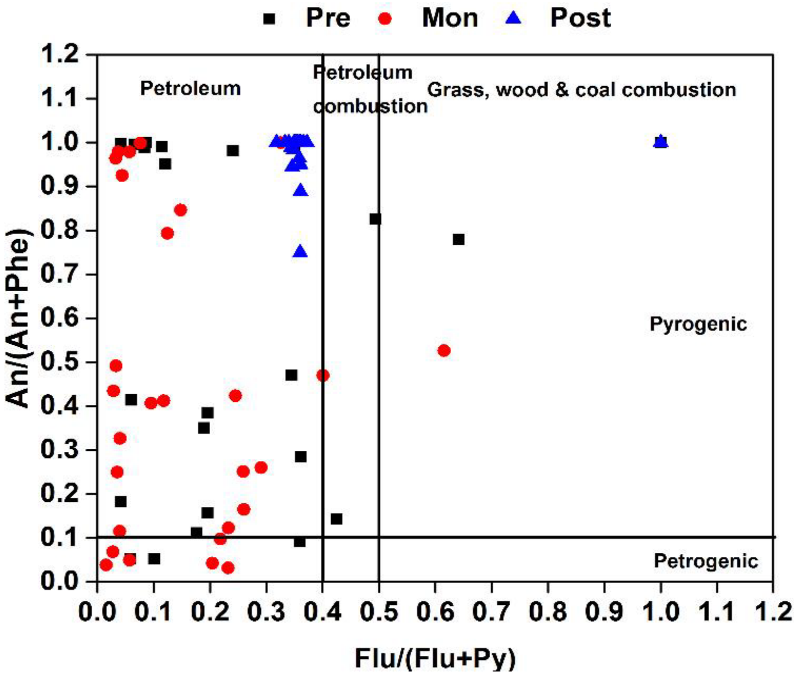

Figure 5.9: Sources of Dissolved PAHs

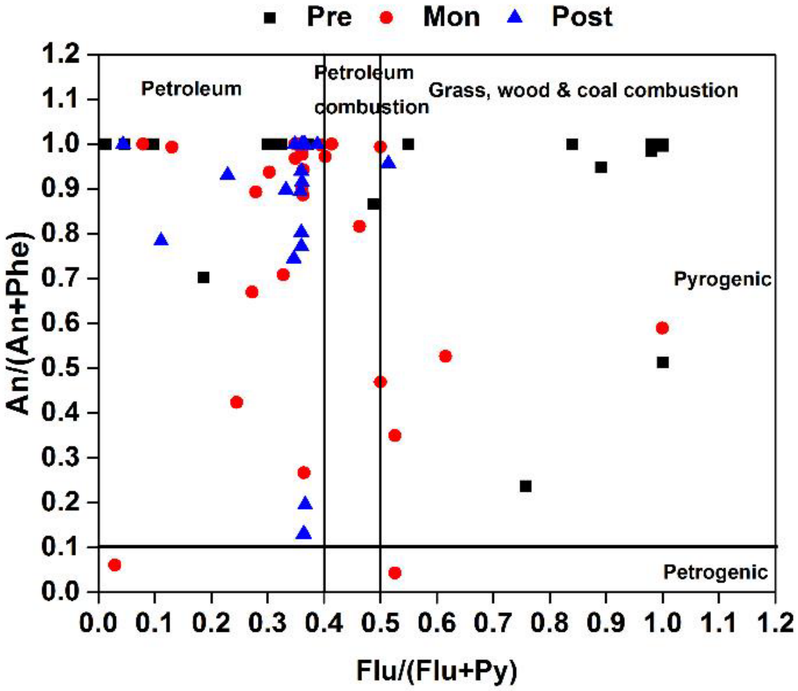

Figure 5.10: Sources of Particulate PAHs

5.3.4 Ecological risk

In order to find the potential ecological risk of PAHs in dissolved and suspended particulate phase from Cochin estuary risk quotient (RQs) were used (Kalf et al., 1997; (Kalf et al., 1997; Cao et al., 2010)

$$RQ = C_{PAH}/C_{QV}$$

Where C_{PAH} concentration of some specific PAHs in water and SPM: C_{QV} is the corresponding quality value of certain PAHs in the sample. In this study, negligible concentration (NC) and maximum permissible concentrations (MPCs) were also used

$$RQ_{NCs} = C_{PAH}/C_{QV}\ (NCs)$$

$$RQ_{MPCs} = C_{PAH}/C_{QV}\ (MPCs)$$

Where C_{QV} (NCs) and C_{QV} (MPCs) are the quality values of NCs and MPCs of PAHS in water and SPM samples. Value of RQ_{NCs} and RQ_{MPCs} in water and SPM were listed in table 5.2 and 5.3. If the value of RQNCs < 1, it indicates that the concentration of PAHs might be negligible. While RQNCs > 1 and RQMCs > 1 indicates that, the risk is high and remedial action must be undertaken at once. If RQNCs > 1 and RQMCs < 1 indicates PAHS contamination might be listed as middle level and some control measures are (Zhang et al., 2017) are essential.

In Cochin estuary, the dissolved PAHs concentration was very much lower than MPC in all the season except BaA. But in the case of particulate PAHs all low molecular weight PAHs are very much higher than MPC, which indicates a higher risk of PAHs contamination by low molecular weight PAHs.

Table 5.2: Ecological risk assessment of dissolved PAH congers

Dissolved PAHs					
PAH	**NC (ng/L)**	**MPC (ng/L)**	**Premonsoon (ng/L)**	**Monsoon (ng/L)**	**Postmonsoon (ng/L)**
Naf	12	1200	n.d-8.12	n.d-8.00	n.d-0.27
Acy	0.7	70	n.d-5.62	n.d-12.80	n.d
Ace	0.7	70	n.d-2.47	n.d-3.46	n.d-0.25
Fl	0.7	70	n.d-4.80	n.d-0.49	n.d-0.14
Phe	3	300	n.d-1.81	n.d-1.15	n.d-0.01
An	0.7	70	n.d-1.37	n.d-1.02	n.d-0.15
Flu	3	300	n.d-2.40	n.d-0.36	n.d-0.13
Py	0.7	70	n.d-8.32	n.d-7.46	n.d
BaA	0.1	10	n.d	n.d-67.75	n.d
Ch	3.4	340	n.d-3.43	n.d-1.14	n.d-0.3
BbF	0.1	10	n.d-0.5	n.d-0.28	n.d-0.44
BaP	0.5	50	n.d-1.73	n.d-1.47	n.d-0.67
IP	0.4	50	n.d-3.53	n.d-0.23	n.d-0.75
Bper	0.3	30	n.d-1.14	n.d-0.71	n.d-4.48
BkF	0.4	40	n.d-1.12	n.d-0.05	n.d-0.41
DbF	0.5	50	n.d-0.58	n.d-1.10	n.d-0.41

Table 5.3: Ecological risk assessment of particulate PAH congers

Particulate mater					
PAH	**NC (ng/g)**	**MPC (ng/g)**	**Premonsoon (ng/g)**	**Monsoon (ng/g)**	**Postmonsoon (ng/g)**
Naf	1.4	140	n.d-8.24	n.d-936.52	n.d-5684.05
Acy	1.2	120	n.d-29.59	0.00-176.73	n.d-2084.71
Ace	1.2	120	n.d-46.13	n.d-28894.55	n.d-17234.4
Fl	1.2	120	n.d-29.87	13.05-2822.16	n.d-187.8
Phe	5.1	510	n.d-32.20	n.d-3194.40	n.d-45.14
An	1.2	120	n.d- 1871	12.08-4191.94	n.d--6739.95
Flu	26	2600	n.d-178.25	12.05-4011.31	n.d-14.97
Py	1.2	120	n.d-370.38	n.d-2963.62	n.d-650.73
BaA	1.2	120	n.d-586.02	n.d-2250.93	n.d-21.10
Ch	107	10700	n.d-420.12	n.d-731.88	n.d-0.28
BbF	24	2400	n.d-983.01	n.d-608.84	n.d-3.30
BaP	27	2700	n.d-18308.66	n.d-2140.51	n.d-2.35
IP	59	59	n.d-130.37	0.087-202.3	n.d-0.08
Bper	75	7500	n.d-18308.66	0.02-6416.57	n.d-53.99
BkF	24	2400	n.d-58.81	n.d-616.36	n.d-0.484
DbF	27	2700	n.d-190.09	n.d-5064.75	n.d-208.73

5.4 Conclusion

In this chapter, the spatial and seasonal variations of dissolved as well as particulate bound PAHs, their sources and ecological implications are presented. Both dissolved and particulate-bound PAHs exhibited significant seasonal variations characterised by higher concentrations during the monsoon season, followed by post and premonsoon seasons. The ratios of high molecular to low molecular PAHs as well as various molecular indices revealed the presence of a mixture of petrogenic and pyrolytic PAHs in the water column with the dominance of petrogenic fraction. The direct petroleum input and low-temperature combustion were found to be the major contributor of PAHs in the estuary.

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Chapter

6 PAHs IN SEDIMENTS

Contents

6.1 Introduction

PAHs associated with dissolved and particulate phases, its sources and ecological risks in Cochin estuary were discussed in chapter 5. Due to hydrophobicity, low volatility and high persistence, PAHs are naturally associated with aeolian/suspended particles and transported through atmosphere/water (Ohkouchi et al., 1999). The major transport mechanisms of PAHs to estuarine and coastal systems include direct input, river/urban runoff and atmospheric fallout, including wet/dry deposition (Parinos and Gogou, 2016). In the aquatic system, these compounds are attached to particulate matter and get deposited on to the sediment (Guzzella and Depaolis, 1994; Hu et al., 2014). This may cause hydrocarbon contamination in the sediment and its consequent exposure to benthic biota may lead to acute/chronic toxicity, whereas its transfer through the food web may result in serious human health effects (Weinstein et al., 2010; Zeng et al., 2013).

6.2 Results

6.2.1 Spatial and seasonal characteristics of PAHs in surface sediments

Total PAHs ranged from 304 to 5874 ng/g in premonsoon, 493 to 14149 ng/g in monsoon and 194 to 10691 ng/g in postmonsoon (Fig. 6.1) and the data is tabulated in appendix 6. It was found that there was a profound seasonal difference ($p<0.05$) in the distribution of TPAHs with maximum concentration in the monsoon followed by postmonsoon and minimum concentrations were observed in the premonsoon season. The 2-3 ring PAHs dominated in the TPAHs recorded in sediments followed by 5-6 ring PAHs and 4 ring PAHs.

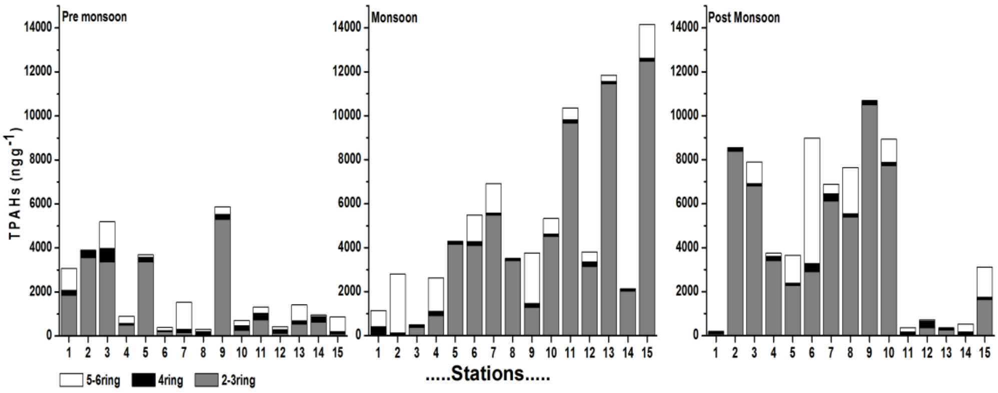

Figure 6.1: Distribution of total PAHs in surface sediments

6.2.2 2-3 Ringed PAHS

2-3 ring PAHs in the sediments such as Naphthalene, Acenaphthalene, Acenaphthene, Fluranthene, Phenanthrene and Anthracene were quantified and plotted in figure 6.2. Total concentration of these compounds ranged from 60.22 – 5304.27 ng/g (average 1382.14 ± 3361 ng/g), 27.32-12486.97 ng/g (average 4205.97 ± 4035.80 ng/g) and 65.51- 10499.84 ng/g (average 3733 ± 3508.56 ng/g) during pre monsoon, monsoon and postmonsoon seasons (Fig 6.2) respectively. Highest value was reported at station 15 (12486.97 ng/g) and lowest value was reported at S3 (27.32 ng/g) both during the monsoon season. The 2-3 ring PAHs accounted for 10 to 91%, 1 to 97% and 13 to 98% of the total PAHs in pre monsoon, monsoon and post monsoon respectively. Naphthalene exhibit higher concentration during monsoon and post monsoon season and also exhibit high concentration during pre monsoon along the saline area of the estuary. Its concentration became low and below detectable limit towards freshwater region during pre monsoon season. Among 2-3 ring PAHs Naf, Acy and Ace dominated compared to Fl, Phe and An but the later isomers were also present. The congeners Acy and Ace exhibited seasonal heterogeneity ($p<0.05$) showing maximum in monsoon followed by post monsoon and pre monsoon, whereas Phe and An ($p<0.05$) congeners peaked in pre monsoon followed monsoon and post monsoon.

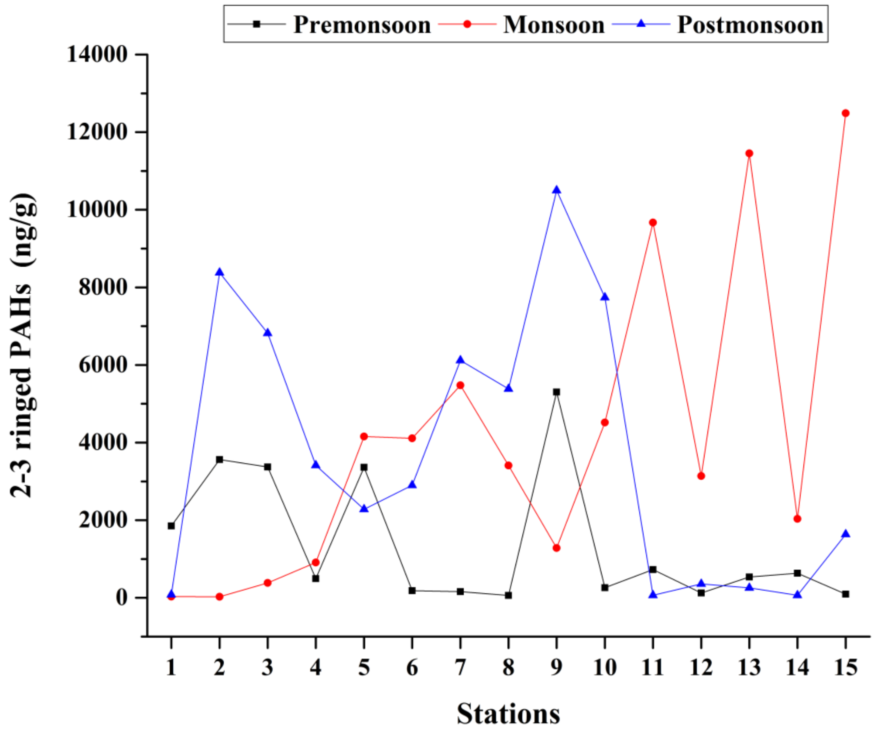

Fig. 6.2: Distribution of 2-3 ring PAHs in surface sediments

6.2.3 4 Ringed PAHs

Graph representing the seasonal and special variation of 4 ringed PAHs is given in Fig.6.3. 4 ringed PAHS includes Fluorine, Pyrene, Benzo(a)anthracene and chrysin. The total concentration of these compounds ranged as 59.62-608.79 ng/g (average 210 ± 134.49 ng/g), 98.52-373.70 ng/g (average 147.27 ± 74.57 ng/g) and 98.43-382.04 ng/g (average 172 ± 95.88 ng/g) during premonsoon, monsoon and postmonsoon (Fig. 6.3, Table 6.1) respectively. Highest and lowest values are reported at station 3 (608.79 ng/g) and station 6 (59.62 ng/g) during the premonsoon season. In 4-ring congeners, Flu and Py were present while BaA and Ch were absent.

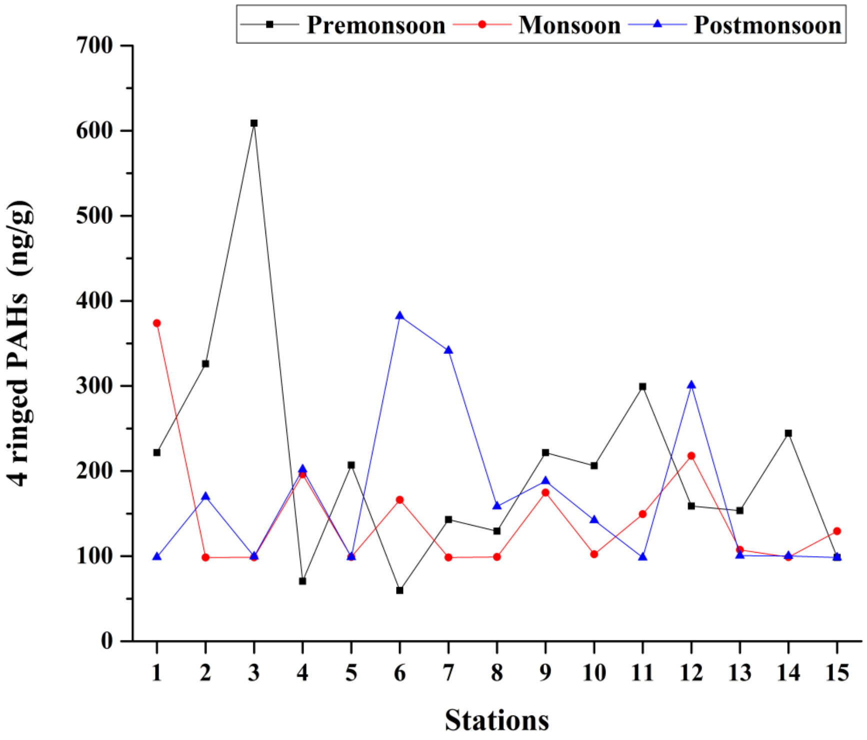

Fig. 6.3: Distribution of 4 ring PAHs in surface sediments

6.2.4 5-6 Ringed PAHs

Benzo b fluranthene , Benzo a pyrene, Ideno 123 cd pyrene, Benzo perlene are the 5-6 ringed PAHs. These are originates mainly from high temperature combustion of fossil fuels. From the results these 5-6 ringed compounds ranged from 11.00- 1231.98 ng/g (average 443 ± 417.39 ng/g), 3.88 -2680.98 ng/g (average 888.37 ± 849.00 ng/g), and 2.26-5707.33 ng/g (average 915.08 ± 1474.94 ng/g) during pre monsoon, monsoon and post monsoon (Table. 6.1) respectively. The lowest value was reported at station 13 (2.26 ng/g) and highest value was reported at station 6 (5707.34 ng/g) during post monsoon season. 5-6 ring contributed 0 to 80% in pre monsoon, 0 to 96% monsoon and 0 to 68% in post monsoon. Bper fraction was dominant among 5-6 ring compounds followed by DbA. DbA alone displayed significant spatio-temporal variations ($p<0.01$) with high concentrations in the riverside and declining towards sea. The fractions Acy and Ace exhibited seasonal heterogeneity ($p<0.05$) showing maximum in monsoon followed by post monsoon and pre monsoon, whereas Phe and An ($p<0.05$) fractions peaked in pre monsoon followed monsoon and post monsoon

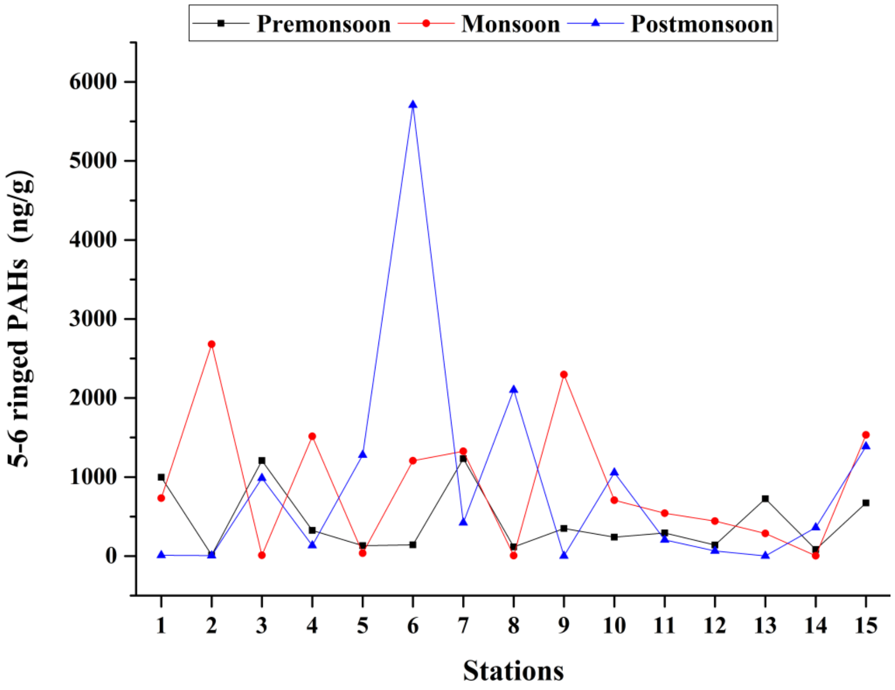

Fig. 6.4: Distribution of 5-6 ring PAHs in surface sediments

6.3 Discussion

The sediment texture, organic content and flow characteristics are found to influence the distribution of PAHs in aquatic ecosystems (Chen et al., 2013; He et al., 2014; Kumar et al., 2016). In contrast, the PAHs concentrations in the Cochin estuary did not show any correlation with sediment texture. Being a eutrophic estuary, the high pelagic and benthic productivity can result high accumulation of organic matter in sediments, which may obscure the PAH accumulation indicated by a poor correlation between PAH and TOC (r=0.05, n=45)(Table), as observed elsewhere (Guinan et al., 2001; Guzzella et al., 2005; Unlu and Alpar, 2006; Oliva et al., 2015) In the present study, the sediment texture (sand, silt and clay) also did not yield any correlation with TPAHs (r=0.05, 0.08, 0.02 respectively). This may be due to the numerous point and non-point sources of pollution apart from the high sedimentation and dredging activities in the estuary (Perillo and Piccolo, 1991; Oliva et al., 2015). The PAH levels are generally classified into low (0-100 ng/g), moderate (100-1000 ng/g), high (1000-5000 ng/g) and very high (>5000 ng/g) (Baumard et al., 1998a; Baumard et al., 1998b). The present study shows that the PAH concentrations in the Cochin estuary are at moderate to very high levels, especially in the monsoon season.

The large input of terrestrial organic matter into Cochin estuary during monsoon has been previously reported (Saraladevi et al., 1986; Bianchi et al., 2002; Balachandran et al., 2003; Martin et al., 2010; Gireeshkumar et al., 2013). The very high concentrations of TPAHs in the south estuary during monsoon may be due to its proximity to several aquacultures (62 km^2) and agriculture (80 km^2) fields (Bianchi et al., 2002; Babu et al., 2006; Martin et al., 2010). A recent study found abnormally high PAH (5046-33087 ng/g) in sediments collected from Chithrapuzha, a tributary of Periyar River (Kumar et al., 2016). The accumulated pollutants in the catchment area during the dry period are probably washed out to the estuary during monsoon.

Table 6.1: Comparison of PAHs in the present study with those reported from other estuarine and coastal systems

Study Area	No. of PAHs studied	PAHs (ng/g)	References
Yangtze River Estuary, China	16	193 - 7588	Yu et al., 2015
Pearl River estuary, China	16	126 - 3828	Zhang et al., 2015
Luan River Estuary, China,	16	5 - 545	Zhang et al., 2015
Yellow River Estuary, China	16	97.2–204.8	Hu et al., 2014
Estuaries in Haihe river basin, China	16	92 - 15886	Liu et al., 2014
Galician estuaries, NW Spain	35	44 - 7901	Perez-Fernandez et al., 2015
Bahı ´a Blanca Estuary, Argentina	17	19 - 30054	Oliva et al., 2015
Selangor River estuary, Malaysia	25	203 - 964	Masood et al., 2016
Kaohsiung Harbor, Taiwan	17	34 –16700	Chen et al., 2013
Mundaú–Manguaba estuarine-lagoon system, Brazil	16	29 - 222	Silva et al., 2013
Patos Lagoon Estuary, Brazil	16	89 - 10451	Garcia et al., 2010
Esterode Urias, estuary, Mexico	11	27 - 418	Jaward et al., 2012
Lenga Estuary, Chile	16	290 - 6118	Pozo et al., 2011
Iko River estuary mangrove system, Nigeria	16	6100 - 35270	Essein et al., 2011
Hugli river, India	16	0 - 1839	Zuloaga et al., 2013
Chitrapuzha River, India	16	5046 - 33087	Kumar et al., 2016
Cochin estuary , India	16	194 - 14149	**This study**

A comparison of PAH levels in sediments with those reported worldwide is presented in Table 6.2. Even though the TPAHs in the present study are high at some locations, they are still lower than the values from other estuaries. It is evident from Table 6.2 that observed TPAH concentrations are relatively higher than Luan River Estuary China, Selangor River estuary Malaysia, Mundaú–Manguaba estuarine-lagoon system Brazil, Esterode Urias, estuary Mexico, Yellow River Estuary China and Hugli river India, whereas the studies from Estuaries in Haihe river basin China, Kaohsiung Harbor Taiwan and Patos Lagoon Estuary Brazil are comparable with Cochin estuary. However, TPAHs are very high in Bahı´a Blanca Estuary Argentina and Iko River estuary mangrove system, Nigeria than the Cochin estuary.

6.3.1 Sources of PAHs

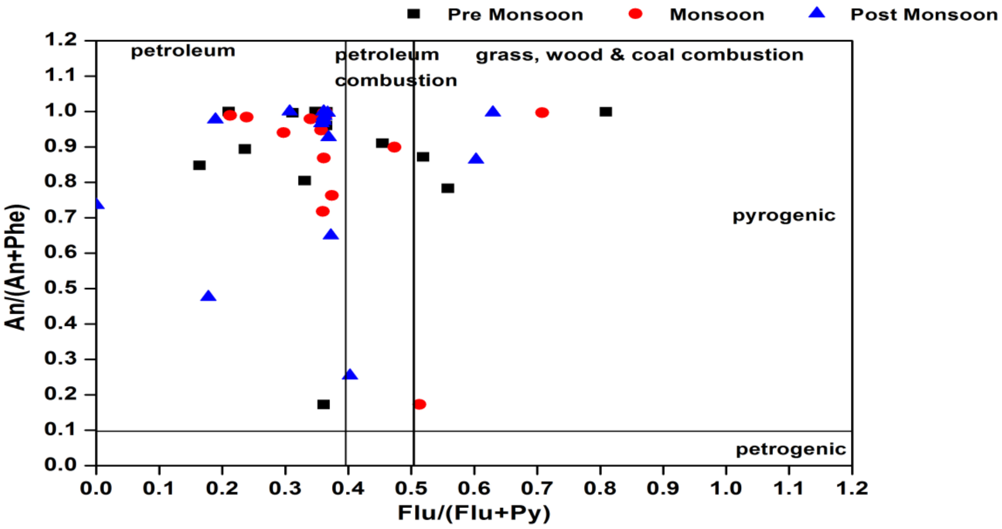

Fig. 6.5: Different sources of PAHs

Low molecular weight (LMW, 2-3 rings) PAHs are normally derived from petrogenic sources or low-temperature combustion, whereas the High Molecular weight (HMW, 4-6 rings) fractions originate from pyrogenic sources (Yunker et al., 2002; Guo et al., 2007; Wang et al., 2015a; Wang et al., 2015b; Wang et al., 2015c). Hence, LMW /HMW ratio can be used to identify the different PAH sources. Based on this, a LMW/HMW ratio > 1 indicates petrogenic source and < 1 indicates a pyrolytic source. The ratios obtained from the present study are mostly > 1 indicating that petrogenic fractions are dominating the PAH accumulation in the Cochin estuary. It has been reported that low-temperature combustion of grass/wood can yield a high amount of Acy and Ace fractions of PAH (Fang et al., 2003; Cao and Liu, 2011; Yu et al., 2015a; Yu et al., 2015b).

Molecular indices involving various PAHs are often used to identify the sources of PAHs in sediments. This includes the derivation of ratios such as An/(An+Phe), Flu/(Flu+Py), InP/(InP+Bper), BaA/(BaA+Ch) etc. A ratio > 0.1 for An/An+Phe indicates that it is a pyrolytic source, whereas the ratio < 0.1 indicates its petroegnic origin. Similarly, a ratio > 0.5 for Flu/Flu+Py indicates its pyrolytic origin and < 0.5 indicates its petrogenic origin (Yunker et al., 2002; Maciel et al., 2015). Based on this, PAH contamination of sediments can be either due to petrogenic or pyrolytic sources (Fig. 6.5). A ratio > 1 for An/An+Phe indicates a pyrolytic source, while that for Flu/Flu+Py indicates a petrogenic source. This may be due to the synergistic effect of various pollutants during estuarine mixing.

Table 6.2: Results of Principal Component Analysis-loading of principal components (PC1-PC3)

PAH	Premonsoon			Monsoon			Postmonsoon		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3
Naf	0.902	-0.116	-0.006	0.140	0.342	0.874	0.083	-0.157	-0.573
Acy	-	-	-	0.937	-0.021	-0.001	0.759	0.002	0.033
Ace	0.750	-0.197	-0.256	0.828	0.063	-0.001	0.870	-0.089	0.017
Fl	-0.243	0.839	0.083	0.382	-0.523	0.081	-0.128	-0.106	0.923
Phe	0.384	-0.225	0.052	0.413	0.172	-0.735	-0.008	0.011	-0.020
An	0.861	0.188	0.115	0.120	0.022	0.037	-0.104	-0.041	0.026
Flu	0.321	0.101	0.011	0.101	-0.183	0.055	-0.261	-0.126	0.020
Py	-0.001	0.950	-0.124	-0.525	0.147	-0.031	0.523	0.086	-0.256
BaA	0.893	-0.166	-0.140	-	-	-	-	-	-
BbF	0.046	0.090	-0.258	0.107	0.892	0.091	-0.433	0.796	-0.004
BaP	-0.126	-0.175	0.920	-0.084	0.835	0.260	0.467	0.677	0.105
IP	-0.382	-0.344	-0.051	0.197	0.457	-0.355	0.047	0.956	0.011
Bper	-0.050	-0.335	-0.431	0.012	0.344	0.051	0.449	0.269	0.724
BkF	0.214	-0.148	-0.270	-0.214	-0.041	0.227	0.336	-0.019	0.400
DbF	-0.008	0.091	0.835	0.482	0.414	0.651	-0.129	0.139	0.048
% Variance	27	19	14	24	21	12	20	19	16

The PAHs may be derived from numerous sources which eventually reaches the sediments of the estuary via various transport mechanism including river, continental and urban runoff as well as atmospheric deposition. The direct petroleum spill by the navigational and port activities also contributes substantially to the TPAH content on the surface sediments. The mixing of different PAH congers and its differential reactivity to the degradation processes may lead to complexities while assessing sources of PAHs in the sediments of the Cochin estuary. PCA was performed to further understand the sources of PAHs in the estuarine sediments. The PCA resolved five principal components (PCs) in premonsoon, 6 PCs each in monsoon and postmonsoon seasons, accounting for a cumulative variance of 80, 86 and 83 % for premonsoon, monsoon and postmonsoon seasons respectively. Among the resolved components, the first three components in each season have been taken to explain the sources of PAHs (Table 6.3). The 2-3 ring PAHs (Naf, Acy and Ace) were heavily loaded in the PC1 in all the three seasons, accounted for 27, 24 and 19 % in premonsoon, monsoon and postmonsoon respectively, which indicated the direct petroleum spill and vegetation fire (low-temperature combustion) are the major sources of PAHs into the estuary. Naf and Fl were identified as a typical tracer of petroleum source (Yunker et al., 2002; Larsen and Baker, 2003), whereas the Acy and Ace are the major PAHs produced by low-temperature combustion process (Cao and Liu, 2011; Yu et al., 2015a; Yu et al., 2015b). The biomass burning practices, which commonly used to remove the wastes from urban and rural settlements normally produces lighter PAHs (Yang et al., 2014). Furthermore, the lighter PAHs are easily transported to longer distance compared to heavier PAHs through long-range atmosphere transport (Yang et al., 2013).

The PC2 and PC3 in all the three seasons (accounted for 19 % and 14 % in premonsoon , 21% and 13% in monsoon, 19 % and 16 % in postmonsoon respectively) are characterized by high loading for PAHs such as Fl and Py, while PC3 exhibited high loading for Fl, Py, BbF, BaP, DbA BaP and DbA which indicated the input from gasoline engine exhaust and vehicular emission Boonyatumanond et al., 2007 (Larsen and Baker, 2003; Hu et al., 2014)). Hence the petrogenic, low temperature and high-temperature combustion contributed significantly to the TPAHs in surface sediments of the Cochin estuary with varying contribution from each end members in different seasons.

6.3.2 Eco-toxicological Implications

Sediment quality guidelines (SQGs) are widely used to address the ecological effects of PAHs in aquatic ecosystems. The toxicological data with 10th percentile ranked Effect Range Low (ERL) and 50th percentile Effect Range Median (ERM), are used to assess the sediment quality (Long et al., 1995). The ERL is indicative of a threshold value, below which, adverse biological effects rarely occur, whereas, above the ERM values, adverse biological effects are expected frequently. Accordingly, the sediment quality of estuaries are broadly divided into three class's viz. *good* if they are less than ERL, *intermediate* when the values fall between ERL and ERM and *poor* if they exceed ERM (USEPA, 2012; Perez-Fernandez et al., 2015).

Table 6.3: Concentrations and risk assessment guidelines of PAHs (ng/g dry weight) in surface sediments from the Cochin estuary

	Concentration range in ng/g						
PAHs	**Premonsoon**	**Monsoon**	**Postmonsoon**	**ERL**	**ERM**	**PEL**	**TEL**
Naf	n.d.- 4557	n.d. - 1475	n.d. - 5992	160	2100	34.6	391
Acy	n.d.	n.d. - 3635	n.d. - 1711	44	640	5.87	128
Ace	n.d. - 906	n.d. - 10393	n.d. - 8084	16	500	6.71	88.9
Fl	22 - 346	n.d. - 39	n.d. - 430	19	540	21.2	144
Phe	n.d. - 167	0.1 - 83	n.d. - 29	240	1500	86.7	544
An	9 - 934	10 - 914	1- 634	853	1100	46.9	245
Flu	21 - 269	36 - 154	n.d. - 137	600	5100	113	1494
Py	37 - 236	62 - 166	62 - 264	665	2600	15.3	1398
BaA	n.d. - 275	n.d. - 162	n.d.	261	1600	74.8	693
Ch	n.d.	0 - 7	n.d.	384	2800	108	846
BbF	n.d. - 258	38 - 83	n.d. - 48	320	1800		
BaP	0.15 - 208	0.12 - 136	0.32 - 686	430	1600	88.8	763
IP	0.23 - 22	0.22 - 22	0.14 - 84				
Bper	1.20 - 1229	n.d. - 2253	n.d. - 5310	430	1600		
BkF	n.d. - 53	0.43 - 175	n.d. - 147	280	1620		
DbA	0.92 - 133	n.d. - 704	n.d. - 282	63.4	260	6.22	135

Based on the above, the PAH contamination in the Cochin estuary is classified with respect to ERL - ERM values (Table 6.3). Accordingly, during pre-monsoon, the PAHs in the estuary was generally below ERL, though one fraction (Naf) exceeded ERL at stations 1 and 2, while it was above ERM levels at three stations (3, 5, 9) indicating chances of adverse biological effects occasionally. The harbour area (stations 1, 2 and 3) displayed Ace fraction exceeding ERM, while it exceeded the ERL values at stations 4 and 5 indicating the pollution due to this fraction in the harbour area. Similarly, the Fl fraction was uniform > ERL indicating moderate contamination and chances of an occasional adverse biological effect. It should be noted that the HMW fractions were always < ERL in the estuary, except for moderate levels of Bper and DbA fractions at some stations. It can be therefore concluded that the present levels of

LMW PAHs in the Cochin estuary indicate moderate pollution, which may lead to occasional or even frequent stress/mortality to estuarine organisms. During monsoon and postmonsoon season, the situation is more critical, as the Acy and Ace concentrations exceed ERM, while other fractions (Naf, Bper, DbA) also exceeded ERL indicating frequent stress on biological organisms. Studies in the Cochin Estuary have already demonstrated a sharp decline in the diversity of macro-benthic organisms from 62 to 51 species over the last two decades (Saraladevi 1986; Martin et al., 2011).

Table 6.4: Comparison of TEQ^{carc} values of the Cochin estuary with those reported from other areas

Study Area	TEQ^{carc} (ng/g)	References
Naples harbour, Italy	2-4723	Sprovieri et al., 2007
Kaohsiung Harbor, Taiwan	1404-1964	Chen et al., 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	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	This study

The sediment toxicity can also be evaluated by taking the sum of all potential carcinogenic PAH congers (TCPAH) such as BaA, Ch, BbF, BkF, BaP, IP and DbA fractions measured in the estuary (Chen and Chen, 2011). In the present study, the TCPAH was in the range 2-411, 4-897 and 1-702 ng/g during premonsoon, monsoon and postmonsoon season respectively, which is lower than the ERL-ERM values (1373-8410 ng/g) reported for the SQGs (Long et al., 1995). The potential toxicity is the toxic equivalent (TEQ^{carc}) of BaP derived using the following equation (Peters et al., 1999; Chen and Chen, 2011; Nasher et al., 2013; Li et al., 2015a; Li et al., 2015b).

$$\text{Total TEQ}^{\text{Carc}} = \sum_{i} \text{Ci} \times \text{TEFi}$$

where, Ci is the concentration of an individual PAH fraction and TEFi is its toxicity factor relative to BaP. 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). Based on the above, the TEQ in the present study is 1-307 ng/g in premonsoon, 2-262 ng/g in monsoon and 1-971 ng/g in postmonsoon (seasonal average 70, 86, 129 ng/g) respectively. A comparison of TEQ^{carc} in the Cochin estuary with other regions are shown in Table 6.4) and it was found to be lower than areas, such as Sundarban mangrove wetland areas in India and Bangladesh, Bahia Blanca Estuary in Argentina, Naples harbour in Italy, Kaohsiung Harbor, in Taiwan, whereas TEQ^{carc} the values were comparable with Meiliang Bay in China and Ría Arousa, Spain.

6.4 Conclusion

This chapter brings out the first comprehensive report on the distribution of potential PAH pollutants in the sediments of a tropical ecosystem (Cochin estuary), India. The results show that the estuary is moderately contaminated with low molecular weight PAH fractions, which increases rapidly during monsoon season, indicating terrestrial input as a major source of this pollutant into the estuary. The dominance of 2-3 ring fractions in the PAH indicates its pathways through petrogenic and low-temperature combustion processes, while the very low levels of 5-6 ring components indicate the absence of any pyrolytic sources. The measured levels of 2-3 ring fractions in the estuary can be considered to be moderately high as they are well above the ERM levels. The TEQ^{carc} values were calculated and it ranged from 1 to 971 ng/g in the surface sediments.

Therefore, these fractions have a high eco-toxicological effect and prone to result in frequent mortality to biota. On the other hand, the high molecular weight PAHs were in low levels (above the ERL), which may cause an only occasional threat to biological organisms. Even though the 2-3 ring PAHs were high, the high molecular weight PAHs displayed comparatively lower concentrations and the TCPAHs were well below the threshold effect levels. Future studies should, therefore, concentrate more on identifying the land-based activities such as burning of wastes including the plastics and polyethylene from domestic, agricultural fields and automobile industries.

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Chapter

7

SUMMARY AND CONCLUSION

In this study, an assessment of two major classes of endocrine disrupting pollutants (PAHs and PAEs) in the Cochin estuary was carried out to delineate their sources, contamination status and ecological risk. The level of PAEs and PAHs were measured in different environmental matrices such as dissolved bound, particulate matter bound and sediments bound. Fifteen sampling stations were fixed along the salinity gradients of the Cochin estuary covering the discharge points of both Periyar and Muvattupuzha River. The Stations selected based on nature intensity and anthropogenic activities. They are classified as two Zones, Zone-I includes S1 to S6 and S9 are situated around the Cochin harbour region, and this area is important for shipping, industrial and municipal activities. S7 to S15 except S9 includes in Zone II are important for agricultural activities. Water and sediments were collected during May, August and December 2013 representing premonsoon, monsoon and postmonsoon seasons, respectively.

Chemodynamics of endocrine disrupting chemicals is closely linked with the hydrodynamics of the estuary. Cochin estuary is a typical tropical monsoonal estuary with heavy freshwater discharge during monsoon season; the river discharge is a minimum during the premonsoon season and seawater influence is a maximum upstream. The estuary is well mixed, and homogeneity exists in the water column. In post-monsoon, river discharge gradually decreases and tidal influence gains momentum and the estuarine condition changes to partially mixed type. The estuary remained well oxygenated during the entire study period characterised by comparatively higher DO levels during the monsoon season that may be due to high of river runoff. Industrial zone station S2 to S10 exhibited an increase in nutrient concentration throughout the investigation period. Nitrite (NO_2^-) concentration varied from n.d to 1.16 µM. Nitrate (NO_3^-) concentration varied from 0.64 to 36.82 µM. Nitrate concentrations peaked at S12 during monsoon season, which indicates high input from land-based runoff. Ammonia (NH_4^+) varied from 1.71 to 128.38 µM. Ammonia concentrations may be supplemented by Periyar river and its tributaries including Chithrapuzha, which is flowing along the industrial zone. Dissolved inorganic phosphate PO_4^{3-} varied from n.d to 7.45 µM. Seasonal trends show that within the estuary, higher concentrations were obtained during premonsoon than monsoon and postmonsoon. SiO_4^- concentration varied from 3.2 to 60.96 µM. SiO_4^- displayed higher concentration during monsoon season, which may be due to increased river runoff. The grain size distribution in surface sediments of the Cochin estuary in all the three seasons premonsoon, monsoon and postmonsoon mud (clay and silt) dominated in the central estuary (stations 2-8) while sand predominated in northern and southernmost parts of the estuary.

Dissolved $\sum_6$PAEs were very high during monsoon season followed by postmonsoon and premonsoon. Dissolved $\sum_6$PAEs ranged from 0.36 to 6.16 µg/L, 2.38 to 27.99 µg/L and 0.56 to 7.26 µg/L in premonsoon, monsoon and postmonsoon respectively. While in particulate bound $\sum_6$PAEs was in the range 7.84-224.03 µg/g in premonsoon, 30.53-1203.46 µg/g in monsoon and 6.97-320.61 µg/g in postmonsoon season. The results indicate that PAEs are widely distributed in the study area. Which indicates terrestrial input, as attested by a clear seasonality with substantial enrichment during monsoon (17±23 µg/l and 523±179 µg/g) and postmonsoon (8±11 µg/l and 198±167 µg/g), was identified as the primary source. DnBP (di-n-butyl phthalate) and DEHP (diethylhexyl phthalate) were found to be the dominant species. Statistical analysis identified two major clusters, in the $\sum_6$PAEs, composed of medium to high molecular weight PAEs (derived from plastic products) and low molecular weight PAEs (derived from cosmetic products).

The potential toxicity of PAEs was assessed using risk quotient (RQ). Based on this, the potential toxicity due to dissolved PAE in the estuary can be classified into 3 levels (1) $RQ < 0.01$, (2) $RQ = 0.01 – 1$ and (3) $RQ > 1$. Level 1 indicates low risk, whereas level 2 indicates medium risk and the level 3 indicates high risk to the aquatic organisms. Reasonably high potential toxicity observed for DnBP and DEHP congeners ($RQ> 1$ for dissolved, and $RQ> 10$ for particulate) is a grim pointer to their detrimental effects on human health through consumption of contaminated organisms. Although substantial enrichment of suspended matter gets flushed out of the estuary during monsoon, there is a net PAE accumulation in the estuary during postmonsoon following increased sedimentary restitution.

Pearson Correlation Analysis showed enrichment of PAEs in the freshwater region due to its proximity to the urban settlement. Mid and high molecular weight PAEs (DnBP, DEHP) varied linearly, suggesting their common source in the estuary. Similarly, the low molecular weight PAEs (DMP, DEP) also showed a significant positive correlation indicating a common source. The negative correlation of PAEs with salinity and pH is supportive of their freshwater discharge into the estuary.

$\sum_6$PAEs in sediments ranged from 44 to1722 ng/g, 331 to 4015 µg/g and 1402 to 3121 ng/g in premonsoon, monsoon and postmonsoon respectively. Sediments accumulated more PAEs during the postmonsoon and monsoon periods indicating land runoff as the major transport pathway. Moderate run off and comparatively high residence time leads to effective sorption and settling of PAEs in the surface sediments during the postmonsoon season. Despite a high discharge of PAEs into the water column, their deposition on to the sediments occurs at a lower rate during monsoon than that postmonsoon season. PAEs were lowest in premonsoon season. The premonsoon 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 ethylhexyl phthalate, 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).

Sediment Quality Guidelines (SQGs) is used to PAE-related eco-toxicological effects in ecosystems. Sediment DEHP concentration of 182 ng/g is set as its threshold effect level (TEL) and 2647 ng/g as its probable effect level (PEL). 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 in Cochin estuary sediment contained moderate levels between TEL and PEL (182-2647 ng/g) during postmonsoon, indicating chances of occasional adverse impact. DEHP and BBP levels exceeded permissible environmental limits indicating serious ecological hazard to the estuarine ecosystem. Similar was the condition at one location (station 12) during monsoon as well, indicating its exceedingly higher accumulation in the upstream locations.

Alternate methods such as Maximum Permissible Concentration (MPC) and Serious Risk Concentration (SRC_{eco}) are also widely used to assess the ecological risk posed by PAEs. In order to evaluate these indices, the PAEs concentrations are normalized to 10 % of organic matter before comparing it with MPC and SRC_{eco} values. 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.

Total dissolved PAHs showed seasonal heterogeneity. Total dissolved PAHs is varied between, 1.29-19.77 ng/L, 1.30-24 ng/L and 0.41-5.38 ng/L during premonsoon, monsoon and postmonsoon respectively. Monsoon season shows high dissolved concentration followed by premonsoon and postmonsoon. Total particulate PAHs (TPPAHs) is varied between 60.02-25070 ng/g, 198.94-60-60502 and 979-41275 ng/g during premonsoon monsoon and postmonsoon respectively. Monsoon season exhibited high particulate concentration followed by postmonsoon and premonsoon.

Information on the sources of PAHs in Cochin estuary was obtained from the selection of molecular indices. This includes the derivation of ratios such as An/(An+Phe), Flu/(Flu+Py), InP/(InP+Bper), BaA/(BaA+Ch) etc. Thus, a ratio > 0.1 for An/An+Phe indicates that it is a pyrolytic source, whereas a ratio < 0.1 indicates its petrogenic origin. Similarly, a ratio > 0.5 for Flu/Flu+Py indicates its pyrolytic origin and < 0.5 indicates its petrogenic origin. The ratios of high molecular to low molecular PAHs as well as various molecular indices revealed the presence of a mixture of petrogenic and pyrolytic PAHs in the water column with the dominance of petrogenic fraction. The direct petroleum input and low-temperature combustion were found to be the major contributor of PAHs in the estuary.

Risk quotient (RQs) were used to find the potential ecological risk of PAHs in dissolved and suspended particulate phase. There are some values negligible concentration (NC) and maximum permissible concentration (MPC) for each congener of PAHs. RQ for each congener of PAH were found out. In Cochin estuary, the dissolved PAHs concentration was very much lower than MPC in all the season except BaA. But in the case of particulate PAHs all low molecular weight PAHs are very much higher than MPC, which indicates a higher risk of PAHs contamination by low molecular weight PAHs. PAHs in surface sediments showed significant seasonal heterogeneity. TPAHs ranged between 304 - 5874 ng/g in premonsoon, 493 - 14149 ng/g in monsoon and 194 - 10691 ng/g in postmonsoon. Monsoon shows high PAHs concentration indicated that land/river runoff into the estuary as its major source. Molecular indices were used to find PAHs origin. From the results, the pyrogenic sources are predominantly derived from petroleum compounds and low-temperature combustion of wastes. Very low level of 5-6 ring PAHs indicates an absence of pyrolytic sources.

Ecological Risk Assessment-Sediment Quality Guidelines (SQG) was used to identify PAH related ecological effect. There are some values ERL (Effective Range Low) and ERM (Effective Range Median) for each congener of PAHs. If the concentration of particular PAH is below ERL that area is considered as unpolluted area, while the concentration is in between <ERL-ERM> that may cause an occasional adverse effect, if the PAH concentration is > ERM it becomes a frequent adverse impact on biota. The level of 2-3 ring PAHs fraction cross the ERM level, that is LMW PAHs are exceeded SQG. Cochin estuary is significantly contaminated with LMWPAHs. Carcinogenic PAHs ((BaA, Ch, BbF, BkF, BaP, IP and DbA) fraction levels (2-411, 4-897, 1-702 ng/g respectively during premonsoon, monsoon and postmonsoon) were low and did not pose any threat to the biota. The low potential toxicity [equivalent to benzo (a) pyrene] also indicated low carcinogenic risk.

Concentrations of dissolved, particulate, and sediment-bound PAEs and PAHs were measured in Cochin estuary to delineate contamination level due to such endocrine disrupting chemicals in this semi-urbanised ecosystem. Of the six PAEs studied, DnBP DEHP and BBP were far exceeded their threshold limit. From the PAHs results, we can conclude that the estuary is moderately contaminated with PAHs. Low molecular weight PAHs were dominant over high molecular weight PAHs. Future studies should, therefore, concentrate more on identifying the land-based activities such as burning of wastes including the plastics and polyethene from domestic, agricultural fields automobile industries and waste management.

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Appendix

1

SEASONAL RANGE OF DISSOLVED PAE (μ/L)

	Premonsoon							
	Surface				Bottom			
	Minimum	Maximum	Average	STDV	Minimum	Maximum	Average	STDV
DMP	n.d	0.02	0.01	0.01	n.d	0.03	0.01	0.01
DEP	n.d	0.20	0.05	0.07	n.d	0.11	0.03	0.04
DnBP	0.06	0.64	0.35	0.21	0.07	1.00	0.41	0.34
BBP	0.26	2.64	1.45	0.79	0.21	4.60	1.63	1.36
DEHP	n.d	1.35	0.28	0.41	0.04	0.70	0.22	0.19
DnOP	n.d	0.03	0.01	0.01	n.d	0.03	0.01	0.01
$\sum_6$PAEs	0.36	4.00	2.15	1.17	0.48	6.16	2.31	1.84
Monsoon								
DMP	n.d	0.69	0.22	0.20	0.03	0.66	0.16	0.16
DEP	n.d	0.45	0.10	0.13	0.01	3.14	0.45	0.79
DnBP	2.21	20.37	9.19	5.34	2.18	12.17	5.94	2.91
BBP	0.02	10.63	1.82	3.31	n.d	2.89	0.38	0.75
DEHP	n.d	3.86	0.47	1.17	n.d	3.23	0.24	0.83
DnOP	n.d	0.84	0.07	0.21	n.d	0.79	0.07	0.20
$\sum_6$PAEs	2.38	27.99	11.87	7.17	2.39	13.20	7.24	3.44
Postmonsoon								
DMP	n.d	0.87	0.16	0.22	n.d	1.94	0.27	0.51
DEP	n.d	0.14	0.03	0.05	n.d	0.59	0.10	0.17
DnBP	n.d	3.34	1.37	0.84	0.14	2.93	1.33	0.72
BBP	n.d	1.33	0.23	0.34	n.d	2.06	0.41	0.57
DEHP	n.d	1.69	0.50	0.47	0.01	2.72	0.89	0.81
DnOP	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
$\sum_6$PAEs	n.d	4.49	2.29	1.27	0.56	7.26	3.00	1.99

Appendix 2 SEASONAL RANGE OF PARTICULATE PAE (μ/L)

	Premonsoon							
	Surface				**Bottom**			
	Minimum	**Maximum**	**Average**	**STDV**	**Minimum**	**Maximum**	**Average**	**STDV**
DMP	n.d	10.63	2.06	3.43	n.d	5.31	1.03	1.72
DEP	n.d	2.59	0.52	0.79	n.d	1.29	0.26	0.39
DnBP	0.12	104.69	35.03	25.30	0.06	52.35	17.51	12.65
BBP	0.25	28.08	10.66	9.43	0.13	14.04	5.33	4.71
DEHP	3.36	112.22	30.98	26.84	n.d	82.04	22.92	25.18
DnOP	0.11	28.74	5.85	6.81	n.d	17.57	4.79	5.67
$\sum_6$**PAEs**	7.84	224.03	85.09	49.17	14.61	152.32	51.84	36.09
	Monsoon							
DMP	n.d	154.59	17.40	39.67	n.d	76.95	7.89	19.37
DEP	n.d	71.53	10.18	19.94	n.d	85.23	15.11	24.34
DnBP	19.05	556.12	150.56	186.15	0.07	427.40	115.43	128.17
BBP	0.25	28.37	11.84	9.20	0.07	41.22	14.18	12.98
DEHP	7.19	594.16	146.74	178.10	11.57	571.63	173.90	181.56
DnOP	0.21	54.41	16.47	18.86	0.04	133.51	19.14	33.90
$\sum_6$**PAEs**	30.53	1203.46	353.19	389.53	32.52	1089.46	345.65	333.65
	postmonsoon							
DMP	n.d	6.28	1.21	1.87	n.d	1.55	0.41	0.50
DEP	n.d	4.96	1.79	2.05	n.d	55.16	4.68	14.19
DnBP	0.20	131.65	42.26	33.51	2.39	107.33	36.34	30.48
BBP	0.62	19.50	4.74	5.12	0.12	26.63	4.00	7.40
DEHP	0.50	130.09	35.33	30.85	3.99	121.49	29.97	28.53
DnOP	0.03	28.79	4.35	7.44	0.06	10.01	1.64	2.48
$\sum_6$**PAEs**	18.86	308.41	89.68	72.36	6.97	320.61	77.03	76.85

Appendix 3 SEASONAL RANGE OF SEDIMENTARY (ng/g)

	Premonsoon			
	Minimum	**Maximum**	**Average**	**STDV**
DMP	n.d	158.54	20.07	42.11
DEP	n.d	564.82	91.43	170.45
DnBP	18.55	289.92	99.37	71.84
BBP	8.14	380.64	172.12	107.71
DEHP	0.02	1304.28	420.10	527.89
DnOP	n.d	24.67	3.96	6.86
$\sum_6$PAEs	44.34	1722.55	807.05	567.48
	Monsoon			
DMP	n.d	152.76	16.62	38.76
DEP	n.d	241.00	49.07	68.60
DnBP	0.88	323.41	156.95	114.60
BBP	37.47	360.31	175.04	90.56
DEHP	30.34	3649.55	863.43	880.97
DnOP	0.16	753.00	111.24	240.32
$\sum_6$PAEs	331.01	4015.80	1372.35	867.95
	Postmonsoon			
DMP	n.d	318.82	46.39	79.78
DEP	1.42	48.45	15.36	13.46
DnBP	3.45	348.56	178.57	106.53
BBP	206.93	502.18	331.22	83.73
DEHP	981.91	2387.84	1685.08	433.31
DnOP	7.04	879.70	68.79	224.34
$\sum_6$PAEs	1402.07	3121.10	2325.40	523.85

Appendix
4 SEASONAL VARIATION OF DISSOLVED PAHs (ng/L)

	Premonsoon							
	Surface				Bottom			
	Minimum	Maximum	Average	STDV	Minimum	Maximum	Average	STDV
2-3 ringed	0.81	9.60	3.76	2.80	0.11	10.63	4.09	3.44
4 ringed	0.98	6.13	2.57	1.87	1.11	8.68	3.63	2.50
5-6 rin	0.01	1.10	0.29	0.30	0.02	5.73	0.87	1.47
TPAHs	2.24	13.13	6.63	3.65	1.29	19.77	8.59	5.41
	Monsoon							
2-3 ringed	0.32	6.57	2.56	2.03	0.20	15.65	4.97	4.97
4 ringed	0.41	11.00	3.07	3.29	0.46	71.43	7.37	17.88
5-6 rin	0.03	1.55	0.47	0.40	0.04	1.96	0.71	0.60
TPAHs	1.30	11.88	6.10	3.49	1.67	72.47	13.04	17.53
	Postmonsoon							
2-3 ringed	0.13	0.48	0.24	0.11	0.16	0.37	0.23	0.08
4 ringed	0.33	0.39	0.34	0.02	0.12	0.36	0.32	0.06
5-6 rin	0.11	4.83	0.83	1.22	0.06	1.14	0.50	0.31
TPAHs	0.73	5.38	1.41	1.22	0.41	1.66	1.06	0.34

Appendix

5 SEASONAL VARIATION OF PARTICULATE PAHs (ng/g)

Premonsoon								
	Surface				Bottom			
	Minimum	Maximum	Average	STDV	Minimum	Maximum	Average	STDV
2-3 ringed	0.60	524.69	106.23	178.21	2.59	1928.92	195.82	574.99
4 ringed	2.38	554.22	190.99	226.00	1.87	634.82	142.28	207.66
5-6 rin	47.68	17598.84	5791.93	5346.16	151.33	24993.98	11740.90	7430.57
TPAHs	60.02	17763.11	6089.15	5409.32	160.46	25070.50	12079.00	7758.14
Monsoon								
2-3 ringed	153.36	22340.64	8484.53	7870.18	582.16	39084.53	8862.53	10937.67
4 ringed	41.98	6435.45	1749.79	1818.99	196.48	6663.35	1640.71	1741.74
5-6 rin	2.64	9489.43	3557.06	3010.30	39.63	14754.46	3444.20	4281.08
TPAHs	198.94	37691.60	13791.38	10458.37	1252.43	60502.33	13947.45	16166.69
Postmonsoon								
2-3 ringed	682.24	31956.26	10247.71	9753.45	250.57	24628.87	10556.58	8305.71
4 ringed	39.86	936.17	217.75	255.63	110.75	1223.76	389.70	314.83
5-6 rin	113.66	8383.34	1436.79	2319.24	82.85	5677.83	1932.08	1859.70
TPAHs	979.80	41275.77	11902.25	11790.69	1709.48	28707.03	12878.36	9297.95

Appendix 6

SEASONAL VARIATION OF SEDIMENTARY PAHs (ng/g)

	Premonsoon			
	Minimum	**Maximum**	**Average**	**STDV**
2-3 riged	60.22	5304.27	1535.09	1688.27
4 riged	59.63	608.79	224.52	134.49
5-6 ringed	11.00	1231.98	464.82	417.39
TPAHS	304.41	5874.06	2159.89	1833.53
	Monsoon			
2-3 riged	27.33	12486.97	4447.30	4035.80
4 riged	98.50	373.70	157.72	74.57
5-6 ringed	3.88	2680.98	941.80	849.36
TPAHS	493.47	14149.19	5486.31	3981.82
	postmonsoon			
2-3 riged	65.51	10499.84	3915.39	3508.56
4 riged	98.43	382.04	180.03	95.88
5-6 ringed	2.27	5707.34	1143.28	1474.94
TPAHS	193.86	10690.51	4893.34	3837.46

Appendix 7

Table S1 Result of correlation analysis for dissolved PAEs in premonsoon season

	DMP	**DEP**	**DnBP**	**BBP**	**DEHP**	**DnOP**	**∑6PAE**	**pH**	**Salinity**	**DO**	**SPM**
DMP	1.00										
DEP	0.18	1.00									
DnBP	-0.15	0.19	1.00								
BBP	-0.14	0.12	0.87	1.00							
DEHP	-0.10	0.23	0.38	0.58	1.00						
DnOP	0.11	-0.16	0.26	0.29	0.11	1.00					
∑6PAE	-0.14	0.24	0.97	0.94	0.59	0.26	1.00				
pH	0.46	-0.21	-0.08	0.02	0.00	0.26	-0.06	1.00			
Salinity	0.42	-0.22	-0.01	0.19	0.20	0.30	0.06	0.64	1.00		
DO	-0.21	-0.11	-0.25	-0.44	-0.44	-0.35	-0.35	-0.08	-0.63	1.00	
SPM	0.38	0.11	-0.11	-0.14	-0.12	0.09	-0.12	0.19	0.19	-0.11	1.00

Table S2 Result of correlation analysis for dissolved PAEs in monsoon season

	DMP	**DEP**	**DnBP**	**BBP**	**DEHP**	**DnOP**	**∑6PAE**	**pH**	**Salinity**	**DO**	**SPM**
DMP	1.00										
DEP	0.47	1.00									
DnBP	0.49	-0.06	1.00								
BBP	0.12	-0.15	0.41	1.00							
DEHP	0.23	-0.05	-0.16	-0.02	1.00						
DnOP	-0.25	-0.08	0.03	0.09	-0.11	1.00					
∑6PAE	0.52	-0.01	0.91	0.71	0.03	0.06	1.00				
pH	-0.14	-0.13	-0.23	-0.14	0.10	-0.03	-0.23	1.00			
Salinity	-0.10	0.04	-0.38	-0.09	0.13	-0.21	-0.31	0.70	1.00		
DO	0.06	-0.35	0.16	-0.22	-0.03	0.09	-0.01	0.22	-0.13	1.00	
SPM	-0.21	0.09	-0.28	-0.09	-0.27	-0.22	-0.30	-0.12	-0.01	-0.16	1.00

Table S3 Result of correlation analysis for dissolved PAEs in postmonsoon season

	DMP	DEP	DnBP	BBP	DEHP	DnOP	∑6PAE	pH	Salinity	DO	SPM
DMP	1.00										
DEP	0.84	1.00									
DnBP	0.26	0.13	1.00								
BBP	0.19	0.22	0.21	1.00							
DEHP	0.24	0.13	0.39	0.46	1.00						
DnOP	0.84	1.00	0.13	0.22	0.13	1.00					
∑6PAE	0.56	0.44	0.72	0.62	0.77	0.44	1.00				
pH	0.15	0.22	-0.19	-0.13	-0.24	0.22	-0.09	1.00			
Salinity	-0.05	0.10	-0.31	-0.06	-0.21	0.10	-0.24	0.52	1.00		
DO	0.05	-0.03	0.22	-0.12	-0.10	-0.03	0.11	-0.05	-0.34	1.00	
SPM	0.33	0.34	0.10	0.08	-0.01	0.34	0.16	0.37	0.68	-0.19	1.00

Table S4 Result of Pearson correlation analysis for particulate PAEs in postmonsoon season

	DMP	DEP	DnBP	BBP	DEHP	DnOP	∑6PAE	pH	Salinity	DO	SPM
DMP	1.00										
DEP	0.95	1.00									
DnBP	0.47	0.41	1.00								
BBP	0.16	-0.05	0.08	1.00							
DEHP	0.34	0.36	0.64	-0.03	1.00						
DnOP	0.29	0.31	0.23	0.01	0.42	1.00					
∑6PAE	0.56	0.51	0.88	0.18	0.88	0.47	1.00				
pH	-0.20	-0.17	-0.56	-0.18	-0.47	0.04	-0.55	1.00			
Salinity	-0.12	0.02	-0.56	-0.48	-0.54	-0.23	-0.66	0.64	1.00		
DO	-0.12	-0.30	0.07	0.60	-0.01	0.17	0.10	-0.08	-0.63	1.00	
SPM	-0.23	-0.21	-0.11	-0.14	-0.14	-0.19	-0.17	0.19	0.19	-0.11	1.00

Table S5 Result of Pearson correlation analysis for particulate PAEs in monsoon season

	DMP	DEP	DnBP	BBP	DEHP	DnOP	∑6PAE	pH	Salinity	DO	SPM
DMP	1.00										
DEP	0.49	1.00									
DnBP	0.61	0.58	1.00								
BBP	0.25	0.31	0.55	1.00							
DEHP	0.41	0.34	0.58	0.48	1.00						
DnOP	0.34	0.56	0.73	0.65	0.64	1.00					
∑6PAE	0.63	0.58	0.89	0.61	0.87	0.80	1.00				
pH	-0.15	-0.16	-0.18	0.06	-0.19	-0.12	-0.21	1.00			
Salinity	-0.28	-0.29	-0.40	-0.26	-0.34	-0.36	-0.42	0.70	1.00		
DO	0.22	-0.05	0.37	0.31	0.15	0.29	0.28	0.22	-0.13	1.00	
SPM	-0.16	-0.11	-0.31	0.20	0.06	-0.15	-0.13	-0.12	-0.01	-0.16	1.00

Table S6 Result of Pearson correlation analysis for particulate PAEs in postmonsoon season

	DMP	DEP	DnBP	BBP	DEHP	DnOP	∑6PAE	pH	Salinity	DO	SPM
DMP	1.00										
DEP	-0.07	1.00									
DnBP	0.20	0.50	1.00								
BBP	-0.01	0.68	0.72	1.00							
DEHP	0.03	0.63	0.83	0.74	1.00						
DnOP	0.47	0.27	0.59	0.39	0.68	1.00					
∑6PAE	0.14	0.68	0.94	0.81	0.96	0.68	1.00				
pH	-0.16	-0.15	-0.42	-0.19	-0.33	-0.15	-0.36	1.00			

Table : Showing different sources of PAHS.

PAH Sources	
Natural	**Anthropogenic**
Natural Petroleum	Petroleum spill
Vegetative Decay	Pesticide formulations
Rare Minerals	Sewage Sludge
Plant Synthesis (terpenes)	PAH contaminated media
Forest Fires	Road Dust
Volcanic Eruptions	Vehicles (internal combustion)
	Jet Aircraft
	Incineration
	Wood Burning
	Cigarette Smoke
	Car exhaust
	Smoked food
	Chemical Reactions

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List of Publications

[1] **Ramzi, A**., Gireeshkumar, T.R., Rahman, K.H., Manu, M., Balachandran, K.K., Chacko, J., Chandramohanakumar, N., 2018. Distribution and contamination status of phthalic acid esters in the sediments of a tropical monsoonal estuary, Cochin - India. *Chemosphere* 210, 232-238.

[2] **Ramzi, A**., Rahman, K.H., Gireeshkumar, T.R., Balachandran, K.K., Chacko, J., Chandramohanakumar, N., 2017. Dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of Cochin estuary, India. *Marine Pollution Bulletin* 114 (2), 1081-1087.

[3] **Ramzi, A.**, Gireeshkumar, T.R., Habeeb Rahman, K. , Shameem K, Balachandran, K.K. , Jacob Chacko,. Chandramohanakumar.N, (2020) Phthalic acid esters – a grave ecological hazard in tropical Cochin estuary. *Marine Pollution Bulletin* 152, 110899.

[4] **Ramzi, A.** , Gireeshkumar, T.R., Habeeb Rahman, K. Chandramohanakumar.N, The source and Distribution of Polyaromatic Hydrocarbons (PAHs) in the Cochin Estuary during monsoon Season. *OSICON 17*

[5] **Ramzi, A.** , Habeeb Rahman, K, Gireeshkumar, T.R., Endocrine-disrupting chemicals along the salinity gradient of Cochin estuary, India. *Aquasem 19*