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# Marine Organic Micropollutants

## A Case Study of the Sundarban Mangrove Wetland

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## A Case Study of the Sundarban Mangrove Wetland

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Santosh Kumar Sarkar
Department of Marine Science
University of Calcutta
Calcutta, West Bengal, India

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# Preface

Micropollutants, or Persistent Organic Pollutants (POPS), are a group of xenobiotic lipophilic organic compounds characterized by their semivolatile, persistent, bioaccumulative and toxic nature. POPs are of considerable interest to scientists, environmental quality managers and policy makers, and are drawing increasing global attention due to their adverse immunological, teratogenic and neurological impacts on humans and other living beings. The book provides regional case studies on the characteristics, sources, analytical techniques, distribution and ecotoxicological aspects of three selective POPs, namely organochlorine pesticides (OCPs), polychlorinated phenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), in coastal regions of the Indian Sundarban wetland (a UNESCO World Heritage Site), an iconic mangrove wetland with rich biodiversity. Measurements of their concentrations and evaluation of ecological risk in this vast coastal environment are of significant importance to protect environmental health. Substantial work has been carried out by international organizations, such as the United Nations Environment Program (UNEP), the Intergovernmental Forum on Chemical Safety (IFCS) and the International Program on Chemical Safety (IPCS), on the characteristics, hazards and fate of POPs. The book adds to the literature by highlighting impacts of these pollutants to the environment in low-lying coastal zones (LLCZ) of this region that are already problems such as siltation, eutrophication, coastal development, aquaculture and pollution due to vibrant growth in industrial and agricultural sectors. The book is intended to serve as a reliable and up-to-date reference source for students, teachers and researchers engaged in the fields of chemical oceanography, ecotoxicology and pollution management.

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I sincerely hope this will provide greater understanding and stimulate greater interest in the topic of organic micropollutants. Constructive suggestions for improvement of the text are gratefully appreciated.

# Contents

# Acronyms

| | |
|---|---|
| BCF | Bioconcentration factor |
| DDD | Dichlorodiphenyldichloroethane |
| DDE | Dichlorodiphenyldichloroethylene |
| DDT | Dichlorodiphenyltrichloroethane |
| DDTs | Dichlorodiphenyltrichloroethane isomers |
| ERL | Effects range low |
| ERM | Effects range median |
| HCH | Hexachlorocyclohexane |
| HCHs | Hexachlorocyclohexane isomers |
| HMW | High molecular weight |
| LMW | Low molecular weight |
| OCP | Organochlorine pesticide |
| OCs | Organochlorines |
| op′-DDD | op′-Dichlorodiphenyldichloroethane |
| op′-DDE | op′-Dichlorodiphenyldichloroethylene |
| op′-DDT | op′-Dichlorodiphenyltrichloroethane |
| PAH | Polycyclic aromatic hydrocarbon |
| PAHs | Polycyclic aromatic hydrocarbon isomers |
| PCB | Polychlorinated biphenyl |
| PCBs | Polychlorinated biphenyl isomers |
| PEL | Probable effects level |
| POP | Persistent organic pollutant |
| POPs | Persistent organic pollutant isomers |
| pp′-DDD | pp′-Dichlorodiphenyldichloroethane |
| pp′-DDE | pp′-Dichlorodiphenyldichloroethylene |
| pp′-DDT | pp′-Dichlorodiphenyltrichloroethane |
| SQG | Sediment quality guideline |
| TEL | Threshold effects level |
| UNEP | United Nations Environment Program |
| USEPA | US Environment Protection Agency |

# Chapter 1
# Introduction

## 1.1 Characteristic Features of the Organic Micropollutants

Micropollutants, a group of lipophilic xenobiotic persistent organic pollutants (POPs), are semivolatile, bioaccumulative, toxic, and long-range environmental transport ability (Jones and de Voogt 1999). Organochlorines (OCs) such as Polychlorinated Biphenyls (PCBs) and chlorinated pesticides (such as HCHs and DDTs), and polycyclic aromatic hydrocarbons (PAHs) represent an important group of such hazardous substances that have caused worldwide concern as toxic environmental contaminants. In 2001, the Stockholm Convention on POPs acknowledged these as global problems. Although the occurrence of POPs at elevated levels is of great environmental concern at contaminated hot spots, the regional and global significance of the problem has received increased attention in the last decades (UNECE 1998; UNEP 2001). They have been reported to cause variety of effects including immunologic, teratogenic, carcinogenic, reproductive, and neurological problems in organisms (Kodavanti et al. 1998) and are of considerable concern to human and environmental health. In addition, some congeners have shown some effects on the endocrine system such as reducing serum concentrations of the thyroid hormones like thyroxine and triiodothyronine (Koopman-Esseboom et al. 1994). The lipophilic nature, hydrophobicity, and low chemical and biological degradation rates of these xenobiotics have led to their accumulation in biological tissues and a subsequent magnification of concentrations in organisms progressing up the food chain. Individual POPs have characteristic patterns of distribution depending on regional patterns of usage and their physicochemical properties. Considering the global distribution of POPs, it is important to understand their transport mechanism and to identify any "hot spots," where regulatory and remediation efforts are required. To evaluate the effectiveness of the regulations and remediation, monitoring of POPs is essential to protect environmental health and the importance of global monitoring of POPs was emphasized at the Stockholm Convention (Secretariat of the Stockholm Convention).

A brief account of the three studied micropollutants considered in this book is furnished below:

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### 1.1.1 *Organochlorine Pesticides*

One of the persistent organic pollutants compounds is ubiquitous in the environment. Organochlorine Pesticides (OCPs), such as DDTs, HCH, and PCBs, were produced and widely used for several purposes in the world since 1950s. Organochlorine pesticides have an extensive concern due to their environmental persistence, high toxicity, trend in bioaccumulation in fatty tissues, biomagnifications, and health risks on humans and other living beings. These xenobiotics are found distributed in different compartments in marine environments as a result of transfer by wind from long distances and from domestic and industrial discharges. They are effective pest control chemicals, used in agriculture and public health activities (malaria eradication, etc.) worldwide for the past several decades and are still in use in many developing countries. The pesticides applied on the land eventually find their way to the aquatic environment thus contaminating them. The pesticides are transported to aquatic bodies by rain runoff, rivers, and streams and associate with biotic and abiotic macroparticles (Colombo et al. 1990). They are removed from the surface to the benthic layers by settling of the particles into the water column (Allan 1986). The lipophilic nature, hydrophobicity, and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and subsequent magnification of concentrations in organisms progressing up the food chain (Swackhamer and Hites 1988; Vassilopoulou and Georgakopoulous-Gregoriades 1993). Organochlorine pesticides in aquatic environment have been reported to cause reproductive depression in aquatic biota (Helle et al. 1976).

Two types of HCH products, technical HCH and lindane, were manufactured in the past several decades. The proportion of HCH isomers (α-, β-, γ-, δ-) in the technical mixture is as follows: 55–80 % α-HCH, 5–14 % β-HCH, 8–15 % γ-HCH, and a minor proportion of δ-isomer (Li et al. 2006). Lindane is almost pure γ-isomer (γ-HCH > 90 %). The ratio of α-HCH to γ-HCH ranged between 4 and 15 in technical HCH mixtures and between 0.2 and 1 for lindane (Wurl et al. 2006). These ratios are expected to increase with distance from the source due to the biotransformation of γ-HCH to α-HCH. Among the HCH isomers, β-HCH is the most persistent and less volatile component and tends to accumulate in the environment (Haglund et al. 1997). The DDT (dichlordiphenyltrichloroethane) residues can be biodegraded to DDE (dichlorodiphenyldichloroethylene) via dehydrochlorination, an oxidative process, and DDD (dichlorodiphenyldichloroethane) involving reductive dechlorination of DDT (Mohn and Tiedje 1992). The DDT/(DDD+DDE) can be used to examine whether the DDT input is old or recent.

### 1.1.2 *Polychlorinated Biphenyls*

A group of synthetic halogenated aromatic hydrocarbons has been linked to a number of environmental and public health concerns, despite their ban or restricted use (UNEP Stockholm Convention 2003; UNEP/MAP 2003). PCBs and organochlorine pesticides are among the most prevalent environmental pollutants and can be found in various abiotic (air, water, sediments, soil) and biotic (from plankton to humans) compartments (de Voogt et al. 1990; Jones and de Voogt 1999; de Boer et al. 2000, 2001). Theoretically, there are 209 PCB congeners with one to ten chlorine atoms bound to the phenyl rings and considered to be pollutants of environmental and human health concern. They are very resistant to decomposition and have an excellent insulating property as well as a high heat-absorbed capacity. Their properties have led to many industrial applications but also make PCBs one of the major environmental pollutant classes. The commonly considered key representatives of the industrial pollutants, PCBs are extensively used in electrical transformers and capacitors as heat transfer fluids and in consumer products (Eduljee 1988; Harrad et al. 1994). They enter the environment through dispersion from their identifiable and specific place of use or from incineration and landfill sites.

Although PCBs are now ubiquitous in the environment, they have resulted from industrial production without any known natural source. PCB contamination started in the 1940s, peaked in the 1970s and declined afterwards, due to prohibition of use in many countries. Nevertheless, concentrations of PCBs are still very high in many regions due to their hydrophobic nature and low solubility in water; properties which initially contributed to their widespread use (Sprovieri et al. 2007). PCBs may leach from residues within old electrical transformers and other dielectric fluids present in landfill, and once in the environment, can absorb to particulate matter and accumulate in sediments (Kang et al. 2000; Fox et al. 2001; Wiberg and Harris 2002). As such sediments commonly form the final sink for PCBs, presenting a secondary form of contamination with bioavailability being increased through resuspension after storms or dredging activities (Lee et al. 2001).

Atmospheric transport and deposition, current transport, riverine input, sea-ice transport, and biotic transport are considered to be the main sources (Macdonald et al. 2000; AMAP 2004). PCBs persist as legacy pollutants for which chronic toxicity still represents a serious environmental risk due to their stability and permanence (Wang et al. 2011; Konat and Kowalewska 2001).

### *1.1.3 Polycyclic Aromatic Hydrocarbons*

A class of ubiquitous organic compounds with two to seven condensed aromatic rings. Overall, 16 PAHs are considered by the USEPA as priority micropollutants because of their acutely toxic, carcinogenic and mutagenic properties (Law and Biscaya 1994; Connell et al. 1997; Kannan et al. 2005). PAHs are derived mainly from anthropogenic inputs, and they are products of incomplete combustion. Natural and anthropogenic sources contribute significantly to the PAH concentrations in the environments. Anthropogenic sources include combustion of fossil fuels, waste incineration, and production of coke, carbon black, coal tar pitch, asphalt, and petroleum cracking (McCready et al. 2000). Likewise, spillage of fossil fuel (e.g., huge oil spill at Mumbai-Raigad coast, western part of India occurred on 11 August, 2010) is another common anthropogenic source of PAHs, posing a threat to benthic organisms. Pyrolytic and petrogenic sources are known to generate substantially different PAH assemblages. PAHs can be introduced in the environment by various processes (Neff 1979; McElroy et al. 1989): (a) incomplete combustion at higher temperatures of recent and fossil organic matter (pyrolytic origin), (b) slow maturation of organic matter under the geochemical gradient conditions (petrogenic origin) and (c) short-term diagenetic degradation of biogenic precursors (diagenesis).

## 1.2 Micropollutants in Coastal Sediments

Sediment is a matrix of materials, which comprises detritus, inorganic and organic particles, and is relatively heterogeneous in terms of its physical, chemical, and biological characteristics (Hakanson 1992). Coastal sediments are an essential, integral, and dynamic natural resource and inadvertently constitute temporary or long-term sinks for many classes of anthropogenic contaminants including persistent organic pollutants (POPs). These are of significant concern due to their high toxicity, long environmental half-lives, and potential risk to pelagic and benthic organisms, to wildlife and human being through integrated food chain. Hence, there is an urgent need of identifying and quantifying of POPs, such as organochlorine pesticides in marine sediments around the world. Their study is an important step in mapping the possible pollution sources and exposure pathways which facilitate POPs bioavailability to sediment dwelling organisms. Moreover, they provide a chronological record of micropollutants extending over a long period of time. Sediments thus offer the prospect of serving as a chemical museum in which the history of industrial activity is preserved in a stable profile. Contamination of soil and sediments of coastal areas with persistent organochlorine compounds could be related to point sources, e.g., industrial discharges and domestic sewage. In the case of pesticide pollution, it can also be attributed to precipitation, agricultural runoff, surface run-off, and leaching. Hence, the bottom sediments represent an integrated measure of particle-bound contaminants that have deposited over a longer period of time.

Sediment as a compartment is more conservative than water, as it accumulates historical data on processes within water bodies and the effect of anthropogenic factors on these processes. The water column is extremely dynamic and variations in the content of chemical substances may happen within a scale from hours to days, on the other hand, sediments act as a geological register of marine geochemistry, what makes them a suitable option to evaluate the quality of a coastal area concerning chemical contamination (Vezzulli and Fabiano 2006; Venturini et al. 2012). Pollutants can reach coastal environments in the particulate form, favoring their deposition in bottom sediments, and their bioavailability is attached to physicochemical variations. Therefore, sediments can become an import source of many such substances to the water column.

Moreover, sediments are a food source for many species and any toxic substances contained in them can be transmitted to aquatic species and can affect humans through the food chain (Rosado et al. 2015). For all these reasons, the presence of contaminants in the sediments of aquatic ecosystems has become a major environmental problem (Chapman and Wang 2001; Sainz and Ruiz 2006). When a deposit-feeder organism ingests sediment, only a fraction of the total amount of contaminant present therein is absorbed and becomes part of its body, known as the bioavailable fraction. Therefore, methods to quantify the bioavailable fraction are needed.

Due to their physical and chemical properties, estuarine sediments are highly susceptible to pollution (Hu et al. 2013). In recent years, sediments were increasingly recognized as a major sink and source of contamination; they provide an essential link between chemical and biological processes (Sheykhi and Moore 2013). Thus, the proper assessment of sediment contamination in estuaries is crucial.

## 1.3 Sundarban: An Iconic Tropical Mangrove Wetland

The Sundarban delta complex (21°31′ to 22°30′N and 88°10′N to 89°51′E), having geo-genetic link to the tectonic Bengal Basin, is created by the Ganges, Brahmaputra, and Meghna rivers in the Bay of Bengal, covering an area of ~10,000 km$^2$, shared by southern Bangladesh (62 %) and a small part (38 %) of eastern India. This has been recognized as “Delta in peril: reduction in aggradation plus accelerated compaction overwhelming rates of global sea-level rise (8–18 mm year$^{-1}$)” (Syvitski et al. 2009). This estuarine and shallow coastal system (ESCS) are characterized by prolific growth of rich and diversified continuous mangrove vegetation. The Indian part of Sundarban (area ~4110 km$^2$; 21°32′ to 22°40′N and 88°00′N to 89°00′E), is situated in the low-lying, humid, and tropical coast of the state West Bengal, eastern part of India. This is formed at the estuarine phase of the tidal Hooghly River (main offshoot of the Ganges) (as shown in Fig. 1.1), and the northern limit of this region is known as Dampier and Hodges line. This littoral tract, experiencing semidiurnal waves at regular intervals from the Bay of Bengal, has provided conducive hydrogeomorphologic conditions for the development of wild mangrove ecosystem with highly diversified floral and faunal communities. Sundarban has been acclaimed as the World Heritage Site (1987) and also as Biosphere Reserve (1989) for its capacity of sustaining an excellent biodiversity. The wetland is characterized by a complex network of rivers (Matla, Bidyadhari, Bartala, Gosaba, Saptamukhi, Jamira, Bidya) and tidal creeks, which surround hundreds of tidal islands exposed to different elevations at high- and low semidiurnal tides. Sundarban region is composed of 102 islands of which 48 are still under the cover of forest and rest of the 54 have already been deforested with subsequent conversion to arable land studded with human settlements.

The deltaic sediments are influenced by a wide variety of depositional processes and controlling factors that may reflect differential sediment supply, characteristics of the receiving basin, relative sea-level fluctuations, and human impacts. High sediment loading from the rivers and their tributaries has made considerable contributions to the deltaic depositional system. In the environment, POPs tend to adsorb

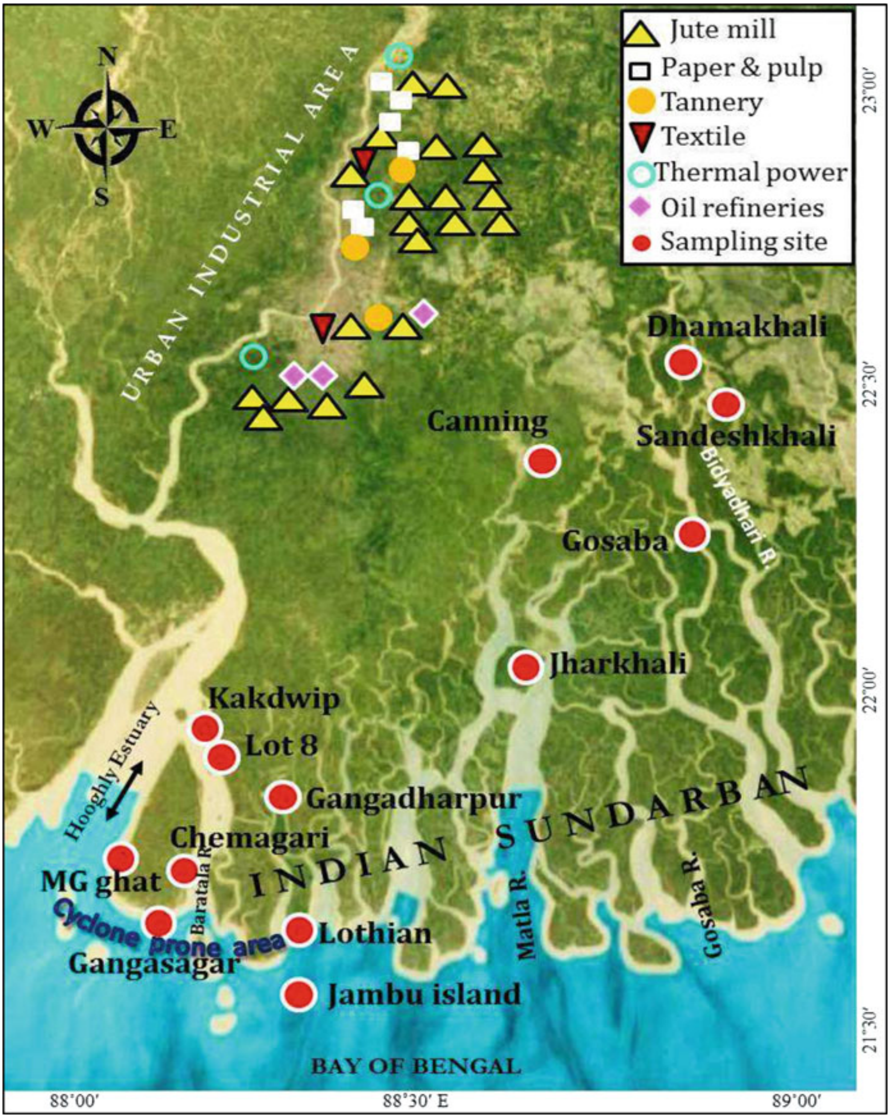

**Fig. 1.1** Map of Indian Sundarban mangrove wetland along with the adjacent Hooghly (the Ganges) River estuary showing the location of 13 sampling sites and location of the multifarious industries situated on both banks of the river

organic matter due to their chemical properties. Once they enter aquatic environments, they preferentially sorb to organic particles and are deposited in sediments.

This vulnerable and tide-dominated megadelta is one of the world's most threatened socio-natural systems, a situation projected to amplify in the twenty-first century due to both natural and anthropogenic impacts on this fragile environment. This sensitive but complex mangrove ecosystem is strongly susceptible to pollution from anthropogenic activities, such as, marine traffic and coastal construction, tourism and port activities, operation of excessive number of mechanized boats, deforestation, and increasing agricultural and aquaculture practices.

The ongoing degradation is also related to huge siltation, flooding, storm runoff, atmospheric deposition, and other stresses resulting in changes in water quality, depletion of fishery resources, choking of river mouth and inlets, and has the potential to affect sensitive species at both the individual and population level (Sarkar and Bhattacharya 2003). A significant ecological change is pronounced in this area due to reclamation of land, deforestation, huge discharges of untreated or semi-treated domestic, municipal, and agricultural wastes as well as effluents from multifarious industries carried by the rivers as well as contaminated mud disposal from harbor dredging (Sarkar et al. 2007). This coastal environment suffers from environmental degradation due to rapid human settlements, intensive boating and tourist activities, deforestation, and ongoing agricultural and aquacultural practices. A significant ecological change has been taking place in Hugli estuarine environment due to huge discharge of domestic and industrial wastes (Sarkar et al. 2007). In addition to the untreated wastes from these “point sources,” the estuary also receives a fraction of the raw sewage, discharge from highly urbanized metropolitan megacity Calcutta and Howrah. The delta is further vulnerable to chemical pollutants such as heavy metals, organochlorine pesticides, PCBs, and PAHs; all these have changed the geochemical nature of the estuary and have affected the local coastal environment including the human being (Sarkar et al. 2012; Watts et al. 2013; Zuloaga et al. 2013; Massolo et al. 2012; Gibb et al. 2016; Fattorini et al. 2012; Domínguez et al. 2010; Corsolini et al. 2012; Chatterjee et al. 2014; Antizar-Ladislao et al. 2015; Bhattacharya et al. 2014, 2015).

Thirteen sampling sites of distinctive geographical, geomorphic, and sedimentological settings with variations of energy domains were selected covering both the eastern and western flank of Sundarban, (as depicted in Fig. 1.1) namely, Dhamakhali, Sandeshkhali, Canning, Gosaba, Jharkhali, Kakdwip, Lot 8, Gangadhaupur, Chemaguri, Mayagoalinir Ghat, Gangasagar, Lothian, and Jambu Island. These sampling sites were selected considering the sediment dispersal patterns along the drainage network systems, and their position was fixed by a global positioning system (GPS). The sampling sites are representative of the variable environmental and energy regimes that cover a wide range of substrate behavior, wave–tide climate, and intensity of bioturbation (animal–sediment interaction), geomorphological, hydrodynamic regimes, and distances from the sea (the Bay of Bengal).

The areas are interspersed with a large number of islands and tidal channel systems through which semidiurnal tides of mesomacrotidal amplitude interplay with moderate to strong wave effects. The wave and tide climate of this low-lying tropical coast primarily controls the sediment dispersal patterns. Biogenic subduction and resuspension also play a significant role in the vertical and lateral transportation of sediments.

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# Chapter 2
# Organochlorine Pesticide Residues (OCPs) in Sediment Cores from Sundarban Wetland

## 2.1 Introduction

Organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT), and hexachlorobenzene (HCB) are ubiquitous, persistent, toxic, and bioaccumulative in nature. These organic compounds are of anthropogenic origin and resist photolytic, chemical, and biological degradation. Being semivolatile, they used to move long distances in the atmosphere, resulting in widespread distribution across the earth, including "remote areas" such as the Polar Regions (Allen-Gil et al. 1997). A major fraction of the OCPs released worldwide to the global environment is known to originate from Asian regions (Iwata et al. 1994a).

The relatively high hydrophobicity of OCPs leads to their accumulation in organisms and adsorption on particles. The lipophilic nature, hydrophobicity, and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and subsequent biomagnification in organisms progressing up the food chain (Borga et al. 2001). High concentrations of organochlorines have been reported in birds and marine mammals (Aguilar et al. 2002; Senthil Kumar et al. 2001). Most of these OCPs have been classified recently as endocrine disruptors that are able to interrupt physiological balance as they behave like environmental hormones (Senthil Kumar et al. 2005). These ecotoxicological concerns for OCPs in organisms have occurred (Fry and Toone 1981; Kelee et al. 1995; Podreka et al. 1998; Vallack et al. 1998), which disrupt reproductive cycles of humans and wildlife (Colborn and Smolen 1996). The concentrations of OCPs in surface sediments provide information on recent contamination, whereas concentrations of OCPs in sediment cores may provide information on contamination over decades. Several studies have reported that contamination of OCPs in the sediments from Asian coastal areas (Takeoka et al. 1991; Pandit et al. 2002; Sarkar et al. 1997; Sarkar and Sengupta 1987, 1988, 1991) indicates the presence of their major mission sources in these regions. Although most of the developed countries

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have banned or restricted the production and usage of many of these OCs during 1970s and 1980s, these chemicals are still being used in some developing countries for agricultural and aquacultural purposes (Dave 1996; Li 1999; Tanabe et al. 1994) and for the control of disease such as malaria and typhus (Wu et al. 1999; Nahn et al. 2001). In India, DDT and HCH were used extensively until recently for both agricultural and sanitary purposes. It is estimated that about 25,000 MT (metric tons) of chlorinated pesticides was used annually in India and DDT accounted for 40 % of this group (Mathur 1993). Recently, Kumar et al. (2006) and Lahiri et al. (2002) reported the presence of OCs in human milk from the northern and eastern parts of India. A broad spectrum of pesticides is used in India for agriculture as well as vector control programs and hence the impact of residues of these OCs on Indian coastal environments is of considerable interest.

In order to understand the role of tropical developing countries as possible emission sources of POPs (persistent organic pollutants), it is necessary to elucidate the distribution, behavior, and fate of these compounds in various environmental compartments. For determination of those compounds existing in aquatic water, sediment may indicate the extent of aquatic contamination and the accumulation characteristics in aquatic ecosystems. A few reports are available regarding the residue analyses of conservative pesticides in different compartments from marine environments in India (Kannan and SenGupta 1987; Shailaja and SenGupta 1989; Ramesh et al. 1990a, b; Rajendran et al. 1992; Iwata et al. 1994b; Shailaja and Singbal 1994; Shailaja and Nair 1997; Pandit et al. 2002). A detailed account of accumulation features of organochlorine residues in fish in eastern and southern Asia and Oceania was documented by Kannan et al. (1995). Bioaccumulation profiles of organochlorine residues were also worked out in the Ganges River dolphin by Kannan et al. (1994) and Senthil Kumar et al. (1999), in paddy soil and sediments by Ramesh et al. (1991), in sediments and organisms by Senthil Kumar et al. (2001), in wildlife by Ramesh et al. (1992) and Muralidharan (1993), and in air by Ramesh et al. (1989). A preliminary account of OCPs distribution in surface sediments in this coastal environment has been recorded by Bhattacharya et al. (2003) and Guzzella et al. (2005), revealing some interesting features. Hence the work has been undertaken to evaluate the detailed account of the OCPs in sediment core samples with reference to available sediment quality and ecotoxicological standards.

## 2.2 Methodology

### *2.2.1 Study Sites*

The Indian Sundarban (21°32′ to 22°40′N and 88°85′ to 89°00′E), the largest prograding delta in the estuarine phase of the river Hooghly (the Ganges), is a unique bioclimatic zone in a typical geographical situation in the coastal region of the Bay of Bengal and has been designated a UNESCO World Heritage Site. Situated in the low-lying, humid, and tropical belt, the Sundarban wetland harbors a luxuriant mangrove chunk together with associated fauna and flora including endangered flora and fauna. The delta wetlands have many important functions contributing to the ecological, social, and economic wealth of the region, providing a valuable resource for the community, fisheries, and wildlife. Furthermore, being a natural filtering system for pollutants, the wetlands are also responsible for the physical wealth of the area. A significant ecological change is pronounced in this estuarine wetland due to discharge of municipal sewage, industrial wastes, urban runoff, outflow from agricultural areas, and atmospheric deposition together with huge siltation. Abbas and Subramanian (1984) calculated that at Calcutta the Ganges annually supplies $411 \times 10^6$ tons of the total load of the Hooghly estuary. Municipal solid waste (MSW) to the tune of 3500 Mg is generated daily in the city of Calcutta (Pal et al. 2005) and discharged into the estuarine system after partial treatment. It was revealed recently that only 20 % of the waste generated in 42 riverside municipalities is treated at sewage treatment plants (STPs), while the rest is simply dumped into the Hooghly River. Loss of biodiversity, habitat degradation, etc., are occurring in Sundarban due to the large number of activities, including navigation, intensive agriculture, fish farming, fishing, and recreational and tourist activities.

Seven sampling sites, namely, Lot 8, Kakdwip, MG Ghat, Jambu Island, Canning, Dhamakhali, and Sandeshkhali, have been chosen considering the sediment dispersal patterns along the drainage network systems (Fig. 1.1) under typical tropical mesomacrotidal conditions. The studied stations belonging to different geomorphic and tidal environments have different wave energy fluxes, erosional features, and distances from the sea (the Bay of Bengal) (Fig. 1.1). The first three stations are located on the mainstream of the River Ganges, while the rest three sites are located farther east of the wetland. These sites belong to lower deltaic plain experiencing intense semidiurnal tides and wave action with a mesomacrotidal setting (2.5- to 7-m amplitude). Hydrology of these coastal systems presents a cyclic pattern, characterized by a large amount of flow and ebb tides and rip and long shore currents (Sarkar et al. 2004). Sampling station Jambu Island represents a typical marine site not directly influenced by the main flux of Hooghly River.

### 2.2.2 Sampling Strategy and Analytical Protocol

During winter months (November–December 2005), cores of 30-cm length were collected with the help of a steel corer (40 cm length and 5 cm diameter) by gently intruding it into the sediments, dug out, and capped and frozen upon return to the laboratory. Unfortunately, sediment dating was not possible since samples were collected from mesomacrotidal environments which create bioturbational churning and loss of the uppermost cores (Binelli et al. 2007). The core length size differs between the stations due to variations in nature of the substratum. The upper 40 cm of each core was sliced into 4-cm fractions (subsamples) with the help of PVC (polyvinyl chloride) spatula. Prior to sample collection, all glassware for the collection and storage of sediment samples were thoroughly cleaned with acid (10 % $HNO_3$) and then rinsed in double-distilled (Milli-Q) water before each use. Core fractions were stored in labeled polyethylene bags in iceboxes and transported to the laboratory, where they were frozen to −20 °C. Within 2 days, a portion of each sample was placed in a ventilated oven at a very mild temperature (max. 40 °C). Dried samples were disaggregated and divided into two aliquots. One aliquot was used for measuring the sediment quality parameters (organic carbon, pH, percentage silt, clay, and sand) and the other part was sieved through 63 μm metallic sieves, stored in pre-cleaned, inert polyethylene bags, and kept at −20 °C until analyses. All visible marine organisms, coarse shell fragments, and sea grass leaves and roots, when present, were removed manually with the help of stainless-steel forceps.

### *2.2.3 Reagents and Standards*

All solvents were pesticide grade. Florisil adsorbent for chromatography (100–200 mesh) and anhydrous sodium sulfate were obtained from Fluka (Steinheim, Germany). Silica gel for column chromatography (70–230 mesh) was supplied by Sigma-Aldrich (Steinheim, Germany). The deuterated internal standard pp′ DDE D8 (100 ng $\mu L^{-1}$) and pesticide standard solutions (Mix 164, containing p,p′ DDT, p,p′ DDD, p,p′ DDE, o,p′ DDT, o,p′ DDD, and o,p′ DDE; and Mix 11, containing hexachlorobenzene and α, β, δ, and γ-HCHs) were from Dr. Ehrenstorfer (Augsburg, Germany) and the solvent of standards was iso-octane.

### *2.2.4 Extraction and Cleanup Procedure*

Samples (about 1 g) were spiked with deuterated internal standard pp′ DDE D8 and extracted for 12 h using a 100-mL acetone/*n*-hexane (1:1 v/v) mixture in a cold Soxhlet apparatus (FALC Instruments, Lurano, Italy). Samples were then dried using a rotary evaporator (RV 06-LR; IKA, Staufen, Germany) and under nitrogen flow to about 1 mL of final volume. Cleanup was performed using a multilayer column (40 × 1.5-cm I.D.) composed of 10 g of silica gel (activated overnight at 130 °C, then deactivated with water, 5 % w/w), followed by 10 g of Florisil (activated for 16 h at 650 °C), 1 g of anhydrous sodium sulfate, and approximately 0.5 cm of activated powdered copper at the top. The column was washed with *n*-hexane/acetone/dichloromethane (8:1:1 v/v). Elution was carried out by collecting first 50 mL of *n*-hexane (fraction 1) and then 50 mL of 1:1 *n*-hexane/dichloromethane (v/v) (fraction 2). p,p′-DDT, o,p′-DDT, p,p′-DDE, o,p′-DDE, HCB (hexachlorobenzene), and HCHs were recovered in fraction 1, while p,p′-DDD and o,p′-DDD were eluted in fraction 2. One milliliter of isooctane was added to each fraction and then concentrated by rotavapor to 10 mL and, afterward, gently to 1 mL under nitrogen flow.

### 2.2.5 Instrumental Analysis

An aliquot of 1 mL of the two fractions was injected into a GC chromatograph (TRACE GC; Thermo Electron MS/ MS, USA) equipped with an AS 2000 autosampler (Thermo Electron) and a programmed temperature vaporizer (PTV) injector and coupled with a Polaris*Q* Ion Trap mass spectrometer. We used sylanized glass liners (2 mL of volume), which were changed after 60–70 injections and resylanized with Sylon CT (Supelco, Bellefonte, PA, USA). Samples were injected into a Rtx-5MS (Restek, Belle-fonte, PA, USA) capillary column (30-m length, 0.25-mm I.D., 0.25 μm $d_f$) under the following conditions: PTV in solvent split mode (split flow = 20 mL $min^{-1}$); splitless time of 2 min; carrier gas helium at 1 mL $min^{-1}$; surge pressure of 100 kPa; and initial oven temperature starting at 100 °C and maintained for 1 min, then ramped to 180 °C (no hold time) at 20 °C $min^{-1}$, to 200 °C (no hold time) at 1.5 °C $min^{-1}$, to 250 °C (no hold time) at 3 °C $min^{-1}$, and, finally, to 300 °C (held 5 min) at 30 °C $min^{-1}$. Samples were analyzed using the following instrumental conditions: EI (Electron Impact) mode with a standard electron energy of 70 eV; transfer line maintained at 270 °C; damping gas, at 1 mL $min^{-1}$; and ion source, at 250 °C. Quantitative analyses were performed using the Excalibur software (Thermo Electron) and by external calibration curves ranging from 1 to 25 μg $L^{-1}$, according to environmental levels found in sediments.

### 2.2.6 Quality Assurance (QA) and Quality Control (QC)

A procedural blank was run in parallel with every batch of four samples using anhydrous sodium sulfate (heated for 6 h at 550 °C) and then extracted in a manner identical to that of the samples. No OCs was found in blanks. Samples and blanks were spiked with 2 ng of deuterated internal standard pp′-DDE D8 (0.5 μg $mL^{-1}$) prior to solvent extraction to monitor methodological analyte losses. Recoveries >75 % were accepted. Method performance for chlorinated pesticides was evaluated using SRM river sediment 1939a (NIST, Gaithersburg, MD, USA). The recoveries for all the considered compounds were always >80 % with respect to the reference value. Limits of detection (LODs) were estimated by the signal-to-noise ratio (3:1): 0.1 ng $g^{-1}$ dry weight (d.w.) for op′ DDT and pp′ DDT, and 0.05 ng $g^{-1}$ d.w. for the other OCs. In addition, organic carbon ($C_{org}$) content in sediment was determined following a rapid titration method (Walkey and Black 1934) and pH with the help of a deluxe pH meter (model 101E) using a combination glass electrode manufactured by M.S. Electronics (India) Pvt. Ltd. Mechanical analyses of sediment were done by sieving in a Ro-Tap Shaker (Krumbein and Pettijohn 1938) manufactured by W. S. Tyler Company (Cleveland, OH, USA) and statistical computation of textural parameters was done using formulae of Folk and Ward (1957).

### *2.2.7 Statistical Analyses*

Significant differences among sampling sites were checked by main effects analysis of variance (ANOVA) using HCH, DDT, and HCB as variables and station and depth profile as different factors, and cluster analysis was used for grouping seven sampling stations. The raw data were classified objectively using factor analysis. The purpose of factor analysis is to reduce the complexity within the similarity matrix of a multivariate data collection and transform it into a simpler and more easily interpreted factor matrix. All statistical analyses were carried out using the software package STATISTICA 6.0.

## 2.3 Results and Discussion

### *2.3.1 Sediment Characteristics*

Sediment characteristics such as organic carbon content ($C_{org}$ %) and percentages of sand, silt, and clay obtained in different profiles of the seven sampling stations are listed in Table 2.1. The sediment core samples show a variable admixture of sand (1.7–100 %), silt (0–88.2 %), and clay (0–74.6 %), with an overall size range from sandy to clayey very fine. The three stations (Lot 8, Kakdwip, and MG Ghat) morphologically belong to the intertidal mudflats of a macrotidal setting of the Hooghly River estuary and showed a general homogeneity, with dominant silty clay to clayey very fine material. The overall fine textural properties of the sediments in the core samples of the three stations indicate deposition from suspended and resuspended fine particles in a semidiurnal macrotidal regime. In a similar manner, core sediments of stations Canning, Dhamakhali, and Sandeshkhali showed suspensional finer deposits from the Matla-Bidyadhari tidal drainage complex in a macrotidal setting with a dominant silty clay composition associated with a subordinate sand fraction (maximum of 36.32 %) compared to that of the former sampling stations (Table 2.1). The sand fractions in the sediments in these stations may be attributed to its mesotidal settings together with the higher influx of sand carried by flood tide from the mouth of the Matla systems. The absolute dominance of sand in the core sediments of Jambu Island may be referred to its relatively high-energy intertidal beach setting influenced by wave and long shore currents. The textural properties seem to have a direct control on the adsorption capacity of the OCPs compounds as reported in Table 2.2a–g.

### *2.3.2 Levels of OCPs in Core Sediments*

Vertical distribution of ΣHCH, HCB, and ΣDDT in core sediment samples revealed a wide range of variations within the core and between stations, as reported in Table 2.2a–g. The concentration of various pesticides was in the following range

**Table 2.1** Values of pH, percentages organic carbon, sand, silt, and clay, and texture in sediment profiles of the seven sampling stations in the Sundarban mangrove environment

| Stations | Layer (cm) | Organic carbon (%) | Sand (%) | Silt (%) | Clay (%) | Texture |
|---|---|---|---|---|---|---|
| Kakdwip | 0–4 | 0.59 | 1.7 | 30.2 | 68.1 | Clayey very fine |
| | 4–8 | 0.59 | 2.3 | 58.2 | 39.5 | Silty clay loam |
| | 8–12 | 0.58 | 2.6 | 47 | 50.5 | Silty clay |
| | 12–16 | 0.49 | 2 | 61.7 | 36.3 | Silty clay loam |
| | 16–20 | 0.36 | 1.8 | 27.6 | 70.6 | Clayey very fine |
| | 20–24 | 0.49 | 3 | 27.2 | 69.8 | Clayey very fine |
| Lot 8 | 0–4 | 0.19 | 12.4 | 46.1 | 41.5 | Silty clay |
| | 4–8 | 0.53 | 7.4 | 88.2 | 4.4 | Silty |
| | 8–12 | 0.45 | 26.9 | 50.3 | 22.9 | Fine loamy |
| | 12–16 | 0.36 | 22.64 | 40.3 | 37 | Clay loam |
| | 16–20 | 1.06 | 17.8 | 30.5 | 51.7 | Clay loam |
| | 20–24 | 1.87 | 22.44 | 29.1 | 48.5 | Clayey fine |
| MG Ghat | 0–4 | 0.53 | 2.6 | 34.2 | 63.2 | Clayey very fine |
| | 4–8 | 0.55 | 3.4 | 26 | 70.2 | Clayey very fine |
| | 8–12 | 0.57 | 2.6 | 58.1 | 39.3 | Silty clay loam |
| | 12–16 | 0.57 | 3.3 | 53.7 | 43 | Silty clay |
| | 16–20 | 0.61 | 2.6 | 45 | 52.5 | Silty clay |
| | 20–24 | 0.55 | 3.4 | 32.9 | 63.8 | Clayey very fine |
| | 24–28 | 0.55 | 4.2 | 38 | 57.7 | Clayey very fine |
| Jambu Island | 0–4 | 0.48 | 98.6 | 1.4 | – | Sandy |
| | 4–8 | 0.09 | 100 | 0.03 | – | Sandy |
| | 8–12 | 0.12 | 100 | 0.04 | – | Sandy |
| | 12–16 | 0.06 | 99.9 | 0.08 | – | Sandy |
| | 16–20 | 0.08 | 100 | 0.04 | – | Sandy |
| | 20–24 | 0.09 | 100 | – | – | Sandy |
| Canning | 0–4 | 0.63 | 36.3 | 24.4 | 39.3 | Clayey fine |
| | 4–8 | 0.92 | 22.2 | 22.4 | 55.3 | Clayey fine |
| | 8–12 | 0.63 | 26 | 46.2 | 27.8 | Fine loamy |
| | 12–16 | 0.74 | 25.4 | 37.2 | 37.4 | Clay fine |
| Dhamakhali | 0–4 | 0.66 | 20.2 | 52.9 | 26.8 | Fine loamy |
| | 4–8 | 0.74 | 16 | 33 | 51 | Clayey fine |
| | 8–12 | 0.61 | 24.6 | 26 | 49.4 | Clayey fine |
| | 12–16 | 0.83 | 10.5 | 35.9 | 53.5 | Clayey fine |
| | 16–20 | 0.89 | 18.7 | 35.1 | 46.2 | Clayey fine |
| | 20–24 | 0.96 | 10.1 | 42.4 | 47.5 | Silty clay |
| Sandeshkhali | 0–4 | 0.85 | 12.2 | 31.8 | 55.9 | Clayey fine |
| | 4–8 | 0.88 | 9.8 | 28.6 | 61.6 | Clayey very fine |
| | 8–12 | 0.92 | 10.8 | 48.2 | 41 | Silty clay |
| | 12–16 | 0.79 | 14 | 29.4 | 56.6 | Clayey fine |
| | 16–20 | 0.98 | 12.1 | 37 | 50.9 | Clayey fine |

(continued)

**Table 2.1** (continued)

| Stations | Layer (cm) | Organic carbon (%) | Sand (%) | Silt (%) | Clay (%) | Texture |
|---|---|---|---|---|---|---|
| | 20–24 | 1 | 8 | 17.4 | 74.6 | Clayey very fine |
| | 24–28 | 1.17 | 3.5 | 39.7 | 56.8 | Silty clay |

(pooled mean values): ΣHCHs, from 0.05 to 12.40 ng $g^{-1}$; HCB, from 0.05 to 1.39 ng $g^{-1}$; and ΣDDTs, from 0.05 to 11.47 ng $g^{-1}$ showing extreme spatial heterogeneity in their distribution pattern. The prevalent distribution of ΣHCHs and ΣDDTs exhibit good resemblance among the three stations (Lot 8, Kakdwip, and MG Ghat) located along the mainstream of the Ganges estuary where the maximum values of these compounds were recorded (Table 2.2a–c). A similar closeness of elevated ΣDDT values is noticed in Dhamakhali and Sandeshkhali, located in the eastern part of the wetland, beside the Bidyadhari River. These are due to the comparatively poor seawater exchange at these two sites coupled with the huge untreated sewage discharge from the metropolitan megacity Calcutta. In contrast, the Canning station shows a moribund nature without being fed by any major sewage system. An overall low contamination was marked at Jambu Island due to its position in the offshore Bay of Bengal, where pollutants are dispersed by high wave activities. The site behaves as a functional component of virgin mangrove forest in a semi-sheltered situation. The mass fractions of four important isomers of HCHs (α, β, γ, and δ) in sediment cores reveal a heterogenic nature of distribution, and the total HCH concentrations in sediment cores are in the range of 0.08–6.89 ng $g^{-1}$ (pooled mean value). The proportion of HCH isomers (α-, β-, γ-, δ-) in the technical mixture is as follows: 55–80 % α-HCH, 5–14 % β-HCH, 8–15 % γ-HCH, and a minor proportion of δ-isomer (Li et al. 2006). Lindane is almost pure γ-isomer (γ-HCH > 90 %). The ratio of α-HCH to γ-HCH ranged between 4 and 15 in technical HCH mixtures and between 0.2 and 1 for lindane (Wurl et al. 2006). The mean percentage compositions of α-, β-, and γ-HCH to the ΣHCH mass fraction were recorded as 19.5 %, 21 %, and 20.4 %, respectively. An overall dominance of β-HCH was recorded, which might be explained by the lower vapor pressure and less degradable property of this isomer compared to other HCHs (Willett et al. 1998). The transformation of α- and γ-HCH to β-HCH may be the reason for the predominance of β-HCH in sediments (John et al. 1998; Senoo and Wada 1989). The relatively low percentage composition of α-HCH in this study is because this congener has a high vapor pressure and Henry's law constant and therefore is readily lost. Dominance of β-HCH in surficial sediment samples was also recorded by Zhang et al. (2003) from the Minjiang River estuary, southeastern China. It can be noted that β-HCH is always higher than γ-HCH, confirming the characteristic feature of more stability and resistance to microbial degradation (Rajendran and Subramanian 1997).

In industrial HCHs, the constituent distribution of the four isomers is α-HCH (65–70 % > δ-HCH (12–14 %) > β-HCH (5–6 %), while γ-HCH is >99 % in lindane. The value of α-HCH/δ-HCH is 4.64–5.83 for industrial HCHs and 0 for lindane,

**Table 2.2** Concentration of HCHs, HCB, and DDTs (ng g$^{-1}$ d.w.) in sediment profiles at seven stations—(a) $S_1$, (b) $S_2$, (c) $S_3$, (d) $S_4$, (e) $S_5$, (f) $S_6$, and (g) $S_7$—located in the Sundarban wetland

(a) $S_1$ (Kakdwip): ng g$^{-1}$ of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 |
|---|---|---|---|---|---|---|
| α-HCH | 1.05 | 1.14 | 1.53 | 1.02 | 1.25 | 0.83 |
| β-HCH | 1.43 | 2.53 | 6.37 | 2.21 | 2.18 | 2.97 |
| γ-HCH | 2.13 | 2.39 | 2.75 | 1.67 | 1.41 | 2.00 |
| δ-HCH | 0.84 | 0.66 | 1.75 | 0.58 | 0.28 | 0.77 |
| $\Sigma_4$HCHs | 5.45 | 6.71 | 12.40 | 5.49 | 5.12 | 6.57 |
| HCB | 0.50 | 0.39 | 0.81 | 0.88 | 0.99 | 0.45 |
| o,p′ DDE | <0.05 | <0.05 | 0.08 | 0.05 | <0.05 | 0.10 |
| p,p′ DDE | 0.42 | 0.47 | 0.35 | 0.46 | 0.33 | 1.81 |
| o,p′ DDD | 0.08 | 0.15 | 0.18 | 0.30 | 0.37 | 0.12 |
| p,p′ DDD | 0.12 | 0.09 | 0.16 | 0.59 | 0.20 | 0.11 |
| o,p′ DDT | 0.10 | 0.15 | 0.14 | 0.83 | 0.12 | <0.10 |
| p,p′ DDT | <0.10 | 0.20 | 0.28 | 0.25 | 0.66 | 0.15 |
| $\Sigma_6$DDTs | 0.72 | 1.06 | 1.19 | 2.48 | 1.68 | 2.29 |

(b) S2 (Lot 8): ng g$^{-}$1 of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 |
|---|---|---|---|---|---|---|
| α-HCH | 0.56 | 0.35 | 0.48 | 0.08 | 0.06 | 0.64 |
| β-HCH | 2.98 | 0.27 | 0.75 | 0.44 | 0.61 | 2.35 |
| γ-HCH | 2.09 | 0.28 | 0.43 | 0.34 | 0.26 | 1.60 |
| δ-HCH | 1.26 | 0.04 | 0.23 | 0.15 | 0.32 | 0.94 |
| $\Sigma_4$HCHs | 6.89 | 0.94 | 1.89 | 1.00 | 1.25 | 5.53 |
| HCB | 0.42 | 0.86 | 0.19 | 0.09 | 0.06 | 0.25 |
| o,p′ DDE | 0.11 | <0.05 | <0.05 | <0.05 | 0.07 | <0.05 |
| p,p′ DDE | 1.15 | 0.37 | 0.19 | 0.27 | 0.63 | 0.31 |
| o,p′ DDD | 0.21 | 0.13 | 0.12 | 0.17 | 0.18 | 0.32 |
| p,p′ DDD | 0.46 | 0.20 | 0.30 | 0.19 | 0.20 | 0.27 |
| o,p′ DDT | 0.50 | 0.37 | 0.33 | 0.26 | 0.34 | 0.38 |
| p,p′ DDT | 1.00 | 0.49 | 0.61 | 0.74 | 0.51 | 0.83 |
| $\Sigma_6$DDTs | 3.44 | 1.56 | 1.55 | 1.63 | 1.94 | 2.11 |

(c) S3 (Mayagoalinir Ghat): ng g$^{-}$1 of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 | 24–28 |
|---|---|---|---|---|---|---|---|
| α-HCH | 0.43 | 0.45 | 1.66 | 0.28 | 0.18 | 1.56 | 4.58 |
| β-HCH | 0.80 | 0.89 | 0.56 | 0.65 | 1.38 | 4.83 | 0.65 |
| γ-HCH | 0.73 | 1.07 | 1.30 | 0.34 | 2.45 | 1.24 | 0.44 |
| δ-HCH | 0.75 | 0.36 | 0.34 | 0.24 | 1.14 | 0.46 | 0.21 |
| $\Sigma_4$HCHs | 2.71 | 2.77 | 3.86 | 1.51 | 5.15 | 8.10 | 5.88 |
| HCB | 1.39 | 0.19 | 0.44 | 0.10 | 0.28 | 0.33 | 0.47 |
| o,p′ DDE | 0.10 | 0.07 | 0.09 | 0.10 | 0.13 | 0.05 | 0.07 |
| p,p′ DDE | 2.01 | 0.96 | 0.66 | 0.60 | 0.23 | 0.10 | 0.06 |
| o,p′ DDD | 0.09 | 0.16 | 0.18 | 0.06 | 0.26 | 0.17 | 0.17 |

(continued)

**Table 2.2** (continued)

(c) S3 (Mayagoalinir Ghat): ng g$^{-}$1 of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 | 24–28 |
|---|---|---|---|---|---|---|---|
| p,p′ DDD | 0.24 | 0.27 | 0.26 | 0.36 | 0.32 | 0.27 | 0.39 |
| o,p′ DDT | 0.56 | 0.43 | 0.43 | 0.34 | 0.43 | 0.55 | <0.10 |
| p,p′ DDT | 8.48 | 1.39 | 0.90 | 0.61 | 0.37 | 0.40 | 0.31 |
| $\Sigma_6$DDTs | 11.47 | 3.28 | 2.53 | 2.07 | 1.73 | 1.53 | 0.99 |

(d) S4 (Jambu Island): ng g$^{-1}$ of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 |
|---|---|---|---|---|---|---|
| α-HCH | 0.06 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| β-HCH | 0.15 | <0.05 | 0.05 | <0.05 | <0.05 | <0.05 |
| γ-HCH | 0.14 | <0.05 | <0.05 | 0.05 | <0.05 | <0.05 |
| δ-HCH | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| $\Sigma_4$HCHs | 0.35 | – | 0.05 | 0.05 | – | – |
| HCB | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| o,p′ DDE | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| p,p′ DDE | 0.26 | 0.05 | 0.05 | 0.07 | 0.06 | <0.05 |
| o,p′ DDD | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| p,p′ DDD | 0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| o,p′ DDT | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| p,p′ DDT | <0.10 | <0.10 | <0.10 | <0.10 | 0.16 | <0.10 |
| $\Sigma_6$DDTs | 0.31 | 0.05 | 0.05 | 0.07 | 0.22 | – |

(e) $S_5$ (Canning): ng g$^{-1}$ of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 |
|---|---|---|---|---|
| α-HCH | <0.05 | <0.05 | <0.05 | <0.05 |
| β-HCH | 0.29 | 0.19 | 0.19 | 0.22 |
| γ-HCH | 0.13 | 0.12 | 0.05 | 0.07 |
| δ-HCH | 0.09 | 0.11 | 0.09 | 0.07 |
| $\Sigma_4$HCHs | 0.51 | 0.42 | 0.33 | 0.36 |
| HCB | <0.05 | <0.05 | <0.05 | <0.05 |
| o,p′ DDE | <0.05 | <0.05 | <0.05 | <0.05 |
| p,p′ DDE | 0.38 | 0.31 | 0.21 | 0.31 |
| o,p′ DDD | 0.06 | 0.09 | 0.06 | 0.05 |
| p,p′ DDD | 0.11 | 0.16 | 0.10 | 0.11 |
| o,p′ DDT | 0.15 | 0.12 | 0.16 | 0.12 |
| p,p′ DDT | 0.23 | 0.25 | 0.15 | 0.46 |
| $\Sigma_6$DDTs | 0.93 | 0.93 | 0.68 | 1.05 |

(f) $S_6$ (Dhamakhali): ng g$^{-1}$ of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 |
|---|---|---|---|---|---|---|
| α-HCH | 0.27 | 0.81 | 0.60 | 0.94 | 0.90 | 0.93 |
| β-HCH | 0.77 | 0.97 | 1.23 | 1.14 | 0.84 | 0.64 |
| γ-HCH | 0.84 | 1.61 | 1.63 | 1.90 | 1.31 | 1.03 |
| δ-HCH | 0.08 | 0.29 | 0.25 | 0.31 | 0.21 | 0.09 |
| $\Sigma_4$HCHs | 1.96 | 3.68 | 3.71 | 4.28 | 3.27 | 2.68 |

(continued)

**Table 2.2** (continued)

(f) $S_6$ (Dhamakhali): ng $g^{-1}$ of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 |
|---|---|---|---|---|---|---|
| HCB | 0.09 | 0.41 | 0.22 | 0.38 | 0.44 | 0.48 |
| o,p′ DDE | <0.05 | 0.06 | 0.05 | 0.06 | 0.06 | 0.05 |
| p,p′ DDE | 0.39 | 0.78 | 0.49 | 1.28 | 0.53 | 0.51 |
| o,p′ DDD | 0.08 | <0.05 | 0.09 | 0.09 | <0.05 | 0.06 |
| p,p′ DDD | 0.09 | 0.09 | 0.17 | 0.09 | 0.15 | 0.15 |
| o,p′ DDT | <0.10 | <0.10 | <0.10 | 0.14 | <0.10 | <0.10 |
| p,p′ DDT | 0.42 | 0.14 | 0.32 | 0.25 | 0.26 | 0.34 |
| $\Sigma_6$DDTs | 0.98 | 1.18 | 1.15 | 1.91 | 1.02 | 1.15 |

(g) $S_7$ (Sandeshkhali): ng $g^{-1}$ of pollutant

| | 0–4 | 4–8 | 8–12 | 12–16 | 16–20 | 20–24 | 24–28 |
|---|---|---|---|---|---|---|---|
| α-HCH | 1.14 | 0.27 | 0.24 | 0.24 | 0.08 | 0.25 | 0.37 |
| β-HCH | 2.06 | 0.69 | 0.75 | 0.49 | 0.51 | 0.53 | 1.19 |
| γ-HCH | 0.21 | 0.67 | 0.51 | 0.41 | 0.16 | 0.43 | 0.54 |
| δ-HCH | 1.49 | 0.31 | 0.19 | 0.23 | 0.30 | 0.25 | 0.49 |
| $\Sigma_4$HCHs | 4.90 | 1.95 | 1.70 | 1.36 | 1.06 | 1.45 | 2.59 |
| HCB | 0.28 | 0.12 | 0.10 | 0.11 | 0.05 | 0.09 | 0.12 |
| o,p′ DDE | 0.15 | <0.05 | 0.17 | <0.05 | <0.05 | 0.16 | 0.09 |
| p,p′ DDE | 2.29 | 0.17 | 1.67 | 0.10 | 0.54 | 1.06 | 0.50 |
| o,p′ DDD | 0.05 | 0.14 | 0.29 | 0.12 | 0.13 | 0.16 | <0.05 |
| p,p′ DDD | 0.35 | 0.27 | 0.26 | 0.13 | 0.22 | 0.22 | 0.14 |
| o,p′ DDT | 0.70 | 0.58 | 0.62 | <0.10 | 0.43 | 0.44 | 0.41 |
| p,p′ DDT | 0.79 | 0.70 | 1.01 | 0.15 | 0.79 | 0.64 | 0.33 |
| $\Sigma_6$DDTs | 4.33 | 1.90 | 4.02 | 0.59 | 2.15 | 2.67 | 1.49 |

respectively. In this study, the ratio of α- to γ-isomers ($\alpha/\gamma$ ratio) ranged from 0.43 to 1.21 (pooled mean values of cores), well below these in the technical mixture (i.e., 4–7). The low $\alpha/\gamma$ ratio in the sediment samples might be due to sources of purified lindane in the area, corresponding to the low values previously recorded by Guzzella et al. (2005) from the surface sediments of this wetland. Since the highest values were measured near the agricultural nonpoint sources (Lot 8, Kakdwip, MG Ghat), HCH contamination might have occurred through atmospheric transport from other parts of India, where a large amount of technical HCHs is still being used and high concentrations were found in biota (Ramesh et al. 1992). Unlike HCH and DDTs, the mass fraction of HCB in sediments did not show sharp spatial variations. The maximum value of HCB was recorded at Mayagoalinir Ghat (1.39 ng $g^{-1}$), revealing a probable recent input of this compound generated as a by-product during the production and usage of several agrochemical and industrial chemicals together with atmospheric deposition and other emission sources. The value is lower than SQG (Sediment Quality Guidelines) protecting marine and estuarine aquatic life in California (>1.4 ng $g^{-1}$; apparent effect threshold for bivalve larva abnormality), British Washington (230 ng $g^{-1}$; oyster larva toxicity), and Canada (100 ng $g^{-1}$; sediment quality criteria). Bailey (2001) reports that a large amount of HCB was also emitted by manufacturing (9500 kg $year^{-1}$) and combustion

(23,000 kg/year) as well as pesticide application (6500 kg year$^{-1}$). HCB is not only contained as a contaminant in several pesticides (such as technical HCH, pentachlorophenol, and dimethyl tetrachloroterephthalate), but also is formed as by-products from the manufacture of chlorine-containing pesticides, from the metal industry, and from incomplete combustion. Previously, a maximum HCB value of 0.98 ng g$^{-1}$ in surface sediments was recorded at a site in the upper stretch of the Hooghly estuary located close by, in the western part of the megacity Calcutta (Guzzella et al. 2005). However, very poor mass fractions of HCB in all the sediment cores were encountered at Jambu Island and Canning, which might be attributed to the limited sources and volatile nature of this compound.

Among the OCPs analyzed in this study, DDT and its degradation products, DDD and DDE, are the major components (Table 2.2a–g). The dominance of DDTs in the sediment was also reported by Pandit et al. (2002) in the coastal environment of Mumbai, western part of India. This may be attributed to the slow degradation of DDTs or recent input of DDTs in this environment (Travers et al. 1999). Comparable residue levels of these pesticides have been reported earlier in Indian marine environments (Sarkar and SenGupta 1987, 1988). The contribution of each metabolite in the sediment core was very erratic, in which the two homologues pp′ DDT and pp′, DDE were the dominant and shared major part (16–53 % and 20–53 %, respectively) of DDTs. The maximum mass fraction of 11.48 ng g$^{-1}$ was recorded in the top layer at Mayagoalinir Ghat where pp′ DDT and pp′ DDE contributed 74 % and 18 %, respectively. Dominance of the parent compound denotes current input of fresh DDT to the aquatic ecosystem of the Sundarban delta as a result of agricultural runoff (Kannan et al. 1995) along with atmospheric deposition (Kennish 1997) and discharges in storm waters. The dominance of pp′ DDT or both pp′ DDT and pp′ DDE in sediments was also recorded by Guruge and Tanabe (2001) on the west coast of Sri Lanka and by Booij et al. (2001) on the northwestern coast of Java, Indonesia. The significant mass fraction of pp′ DDE in coastal sediments may be due to the presence of various species of marine benthic organisms, which can accelerate the biodegradation process and the alkaline nature of marine systems, which is highly favorable for such types of transformations (Pandit et al. 2001). Preferential atmospheric transport of pp′ DDE compared to other DDT compounds (Iwata et al. 1994a, b) would explain the high percentages of pp′ DDE but not the high percentages of pp′ DDD in the area. The ratio of pp′ DDT and pp′ DDE can be used to estimate whether recent inputs of technical DDT exist. Generally, a ratio of ≤0.33 is considered an aged mixture, while a relatively high pp′ DDT/pp′ DDE ratio implies a recent input (Stranberg et al. 1998). The observed ratios (0.41–2.70) were well above 0.33 for all the stations, indicating recent pp′ DDT influxes and, by implication, ongoing insecticide use throughout this coastal environment. It is generally accepted that the atmosphere represents an important sink for organic contaminants (Atlas and Giam 1981). DDT is still used to eradicate contagious disease (such as malaria and dengue) in tropical countries and is then globally redistributed throughout the atmosphere (Sharpe 1995). Nearly 85 % of the DDT produced in India is used for mosquito control (Ahmed et al. 1996); therefore, the levels of ΣDDT observed could be attributed to municipal wastewater inflow from residential areas to the adjoining riverine systems.

The presence of HCH isomers and DDT metabolites can be attributed to the use of these pesticides in agricultural and antimalaria sanitary activities, used throughout the country due to their cost benefits, bioefficacy potential, and popularity among the farmers. HCH pesticide has been used for agricultural purposes to control insects in cotton, rice, and vegetable crops and is still used in some developing countries around the tropical belt (Doong et al. 2002). The average ΣHCH mass fractions were lower than ΣDDTs at Canning and Sandeshkhali. This may be due to a lower discharge and/or to their differences in physicochemical and biological properties, with HCHs having higher water solubility, vapor pressure, and biodegradability compared to DDTs (Lognathan and Kannan 1994). Residue of HCH isomers was recorded at all the sampling sites, which may be attributed to the heavy use of these pesticides in Indian agriculture until recently (Pandit et al. 2001). This indicates that the tropical environment is better suited for decontamination of such pesticide residue. Distribution of HCH isomers, HCB, and DDT metabolites in all the sediment cores at seven stations did not follow any uniform trend, either from top to bottom or vice versa. The erratic distribution of these compounds might be due to particular hydrological characteristics of Sundarban wetland being severely influenced by the south-east monsoon and mesomacrotidal regime (Goodbred 2003) as well as non-homogenous inputs from point and nonpoint sources of these chemicals. The dispersion process is also influenced by estuarine mixing and resuspension processes in this typical mesomacrotidal environment. Enrichment of these compounds in surface/subsurface layers was located at few sites, namely, Lot 8, Sandeshkhali, and Jambu Island, as well as in the deeper layers (16–24 cm) at sites Canning Dhamakhali and MG Ghat.

### 2.3.3 Ecotoxicological Concerns

The sediment quality guidelines (SQG) specified by the USEPA (U.S. Environment Protection Agency 1997) and by the Canadian Council of Ministers of the Environment (CCEM 2002) were used to assess the potential ecotoxicological impacts of organic contaminants. Effects range-low (ER-L) and effects range-medium (ER-M) values are used to predict potential impacts of contaminants in sediments, as devised by Long et al. (1995), whereas ER-L values correspond to the lowest 10 percentile and ER-M values to median values, when the chemical mass fractions of a contaminant in marine sediments are sorted according to the degree of their effect levels. ER-L represents the value at which toxicity may begin to be observed in sensitive marine species, whereas ER-M value represents the mass fraction below which adverse effects are expected to occur only rarely. Besides the threshold effect level (TEL), the probable effect level (PEL) is used as the criterion for the prediction of toxicity and corresponds to a level above which adverse effects are frequently expected. Sediment quality criteria and mass fraction ranges of major organochlorine contaminants are summarized in Table 2.3.

**Table 2.3** Minimum, maximum, and average concentrations (C) of major organochlorine contaminants (ng $g^{-1}$) and corresponding sediment quality criteria

| DDT metabolite | $^{C}min$ | $^{C}max$ | $^{C}avg$ | ER-L | % above ER-L | ER-M | % above ER-M | TEL | % above TEL | PEL | % above PEL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| p,p′ DDT | <0.10 | 8.48 | 0.61 | 1 | 7.14 | 7 | 2.38 | 1.19 | 4.76 | 4.77 | 2.38 |
| p,p′ DDD | <0.05 | 0.59 | 0.19 | 2 | 0.00 | 20 | 0.00 | 1.22 | 0.00 | 7.18 | 0.00 |
| p,p′ DDE | <0.05 | 2.29 | 0.56 | 2.2 | 2.38 | 27 | 0.00 | 2.07 | 2.38 | 374.17 | 0.00 |
| ∑DDT | 0.05 | 11.47 | 1.74 | 0.50 | 64.28 | 6 | 2.38 | 2.26 | 21.43 | 4.79 | 2.38 |
| γ-HCH | <0.05 | 2.75 | 0.87 | – | – | – | – | 0.32 | 66.67 | 0.99 | 40.48 |

*Note*: *ER-L* effect range-low value, *ER-M* effect range-medium value, *% above ER-L/ER-M* percentage of sample above ER-L/ER-M, *TEL* threshold effect level, *PEL* probable effect level

For ΣDDT the levels at all sample locations exceed the ER-L value but are lower than the ER-M values, leading to an intermediate ranking of sediment toxicity. For γ-HCH the threshold value (TEL) is much higher than the certified value and the ecotoxicological impacts to marine environment. The PEL value of γ-HCH also exceeds the PEL value, indicating that there is every chance of contamination of the marine environment and the habitants inhabiting the sediment.

### 2.3.4 Statistical Evaluations and Interpretations

To establish the variation of the ΣHCHs at the seven studied stations, a one-way analysis of variance (ANOVA) was undertaken using mass fraction of ΣHCHs as cases with stations and depth profiles as different factors; significant values were obtained for ΣHCHs with stations ($F=9.1514$, $p=0.00005$) over the depth profiles ($F=0.455$, $p=0.836$). Similar observation was also noticed in the case of ΣDDTs for stations ($F=6.6443$, $p=0.046$) and depth profiles ($F=0.867$, $p=0.528$). As evidenced by the correlation matrix, it is evident that there exist positive correlations between ΣDDTs and clay ($r=0.75$, $p=0.05$) and silt ($r=0.69$, $p=0.09$) and, similarly, between ΣHCHs and clay ($r=0.66$, $p=0.01$) and silt ($r=0.65$, $p=0.11$). In contrast, negative correlation values were noticed for all the organochlorines with sand, which reveals that coarse particles have less adsorption capacity for OCPs, as expected. It is interesting to find that there is a positive correlation between RHCHs and ΣDDTs, suggesting similar sources of these micropollutants in this region, as well as similar environmental behavior (Iwata et al. 1995).

The results of sorted rotated factor loading scores along with eigenvalues, percentage variances, and cumulative variances are reported in Table 2.4. The sorted rotated factor-loading pattern of all seven stations extracts four factors, which account for a total cumulative variance of only 73.3 %, of which factor 1 is responsible for 21.6 %, which implies positive loadings by HCH isomers, DDT metabolites (except op′ DDT and pp′ DDT), and clay. Organic carbon and sand, on the other hand, have negative loadings, along with two metabolites of DDT. Considering the above observations, factor 1 can be termed the “clay factor.” Factor 2 shows a variance of about

**Table 2.4** Results of factor analysis (after varimax rotation) considering sediment quality parameters and HCH isomers and DDT metabolites

| Variable | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| % sand | –0.380 | –0.538 | –0.208 | 0.652 |
| % silt | 0.179 | 0.720 | –0.024 | –0.269 |
| % clay | 0.404 | 0.174 | 0.324 | –0.722 |
| α-HCH | 0.551 | 0.225 | –0.124 | –0.157 |
| β-HCH | 0.881 | 0.173 | 0.097 | –0.009 |
| γ-HCH | 0.864 | 0.120 | 0.031 | –0.165 |
| δ-HCH | 0.757 | 0.188 | 0.426 | –0.037 |
| o,p′DDE | 0.280 | 0.193 | 0.723 | –0.174 |
| p,p′ DDE | 0.136 | 0.017 | 0.876 | –0.214 |
| o,p′ DDD | 0.357 | 0.707 | 0.015 | –0.170 |
| p,p′ DDD | 0.218 | 0.848 | 0.273 | –0.089 |
| o,p′ DDT | –0.016 | 0.747 | 0.524 | –0.039 |
| p,p′-DDT | –0.124 | 0.136 | 0.704 | –0.013 |
| % variance | 21.6 | 20.2 | 17.8 | 13.7 |
| % cumulative variance | 21.6 | 41.8 | 59.6 | 73.3 |

20.2 %, where all the variables except sand have positive loadings. As finer particles of sediment can adsorb more chemical species, this factor can be termed the “mud factor.” Factor 3, which explains 17.8 % of the total variance has a strong positive loading on variables like op′ DDE, pp′ DDE, op′ DDT, pp′ DDT, clay, and δ-HCH, along with organic carbon. As more and more recent anthropogenic inputs of DDT and other OCPs are responsible for accumulation of their metabolites in sediments, this factor can be termed the “anthropogenic factor.” Factor 4 shows a variance of 13.7 %, with a major positive influence from sand only. So this factor can be termed the “sand factor.” A cluster analysis was carried out to identify any analogous behavior pattern among the seven sampling sites. Figure 2.1 shows two prominent clusters, with cluster 2 forming a clearly differentiated group by Jambu Island and Canning. This might be due to the very low concentration of pesticides in sediments for both stations. The pattern of clustering between Kakdwip and Dhamakhali followed by Sandeshkhali, MG Ghat, and Lot 8 in cluster 1, based on Euclidean distance (similarity measurement), clearly demonstrates different contamination due to respective anthropogenic factors coupled with differential geomorphological setup.

### 2.3.5 *Comparative Account of OCPs in Coastal Regions of India*

To evaluate the relative degrees of OCPs contamination in coastal sediments in India, we compared the present data against the available data reported in other Asian countries (Table 2.5). Mass fractions of HCH and DDT were generally low in comparison

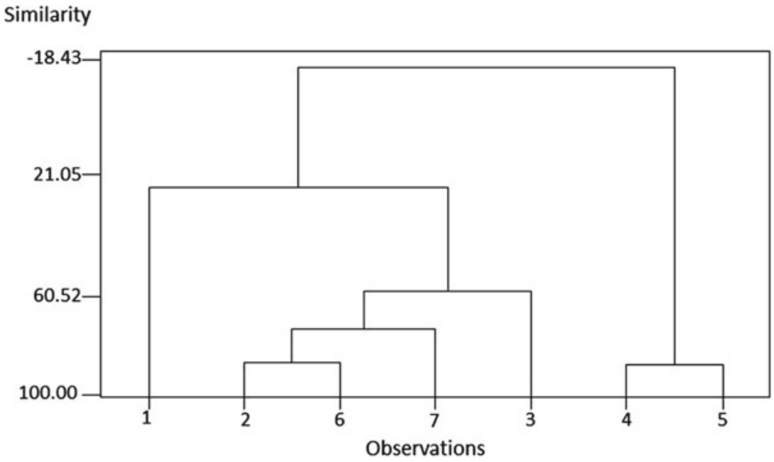

**Fig. 2.1** Dendrogram showing the relationship among sediment samples from seven cores collected from Sundarban region using Ward's method

**Table 2.5** Comparison of OCPs concentrations in sediments from coastal areas in Asia: ng $g^{-1}$ dry weight

| Location | Year | ΣDDTs | ΣHCH | Reference |
|---|---|---|---|---|
| Mason Bay, Korea | 1997 | 0.2–80.2 | nd-1.3 | Hong et al. (2003) |
| Minjiang River Estuary, China | 1999 | 1.6–13.1 | 3–16.2 | Zhang et al. (2003) |
| West and east coast of India | 1995–1997 | nd-364 | 1.5–1053 | Pandit et al. (2001) |
| Ulsan Bay, Korea | 2001 | 0.02–41.9 | 0.02–4.55 | Khim et al. (2001) |
| Daya Bay, China | 1999 | 0.10–20.3 | 0.3–4.2 | Zhou et al. (2001) |
| Wu-Shi Estuary, Taiwan | 2002 | nd-11.4 | – | Doong et al. (2002) |
| Yangtze Estuary, China | 2001 | nd-0.6 | – | Liu et al. (2001) |
| Singapore, Coast | 2003 | 2.2–11.9 | 3.3–46.2 | Wurl and Obbard (2005) |

*Note*: *nd* not detectable

with those in other coastal environments countries, indicating that the Sundarban wetland was not grossly polluted by these organic contaminants. The finding is also in agreement with the observation of Agnihotri et al. (1996) in the upper stretch of the Ganga River. Cavanagh et al. (1999) also endorsed that volatilization of persistent organic compounds such as organochlorine occurs in the warmer climate of tropical regions. Hence, it is possible that the major loss of many OCPs used in India occurs through volatilization. However, a dramatic increase in HCH and DDT has been noticed compared to previous reports such as that by Guzzella et al. (2005) on surface sediments in Sundarban wetland. This might be due to excessive agricultural application, industrial pollution discharge, and difficulty of degradation of these organochlorines.

## 2.4 Conclusion

This study has provided a comprehensive evaluation of selected OCPs in core sediments from Indian Sundarban—a UNESCO World Heritage Site. The mass fraction of OCPs revealed relatively low to moderately high values, with an erratic distribution in the sediment cores, either top to bottom or vice versa, reflecting non-homogenous input of these compounds. The mesomacrotidal phenomenon allows mechanisms of penetration and redistribution of these POPs by swinging effects. Due to a diversity of inputs such as agricultural runoffs, wastewater and sewage discharges, and agricultural wastes, maximum concentrations of OCPs were recorded at sites located along the mainstream of the Hooghly (the Ganges) estuary. Among the HCHs and DDTs, β-HCH and DDE predominate, respectively, as the former is more resistance to degradation and most DDT has been transformed to DDE. From an ecotoxicological point of view, the impacts of DDT and γ-HCH are very much pronounced as they exceeded the ER-L and TEL certified values, respectively. The findings point to the urgent need to establish a reliable monitoring program for POPs including organochlorines, so that any mass fractions exceeding environmental quality standards can be detected and appropriate actions can be taken. New legislation is required for the protection of illegal use of such products, and better education of the public will also play a central role in the implementation of such measures.

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# Chapter 3
# Congener Profiles of Polychlorinated Biphenyls (PCBs) in Sediment Cores from Sundarban Wetland

## 3.1 Introduction

Polychlorinated biphenyls (PCBs) are among the most important industrial contaminants in marine ecosystems estimating more than $1.5 \times 10^6$ t as world production (excluding the former USSR and China) between 1929 and 1988 (Koppe and Keys 2002). PCBs are a group of synthetic halogenated aromatic hydrocarbons that have been linked to a number of environmental and public health concerns. Despite their ban or restricted use (UNEP Stockholm Convention 2003), PCBs and organochlorine pesticides are among the most prevalent environmental pollutants and can be found in various abiotic (air, water, sediments, soil) and biotic (from plankton to humans) compartments (de Voogt et al. 1990; Jones and de Voogt 1999; de Boer et al. 2000, 2001). Theoretically, there are 209 PCB congeners with one to ten chlorine atoms bound to the phenyl rings. They are very resistant to decomposition and have an excellent insulating property as well as a high heat capacity. Their properties have led to many industrial applications but also make PCBs one of the major environmental pollutant classes. These are readily accumulated in benthic organisms and have the potential for trophic magnification ultimately affecting fish, wildlife, and human populations (Safe 1994; Metcalfe and Metcalfe 1997). Moreover, PCBs can affect a wide variety of endocrine systems by directly affecting the components of the endocrine system such as hormones, metabolic enzymes, carrier proteins, receptors, endocrine glands, and feedback regulation systems. Effects of these components can lead to alterations in neuro-development, reproduction, and in induction of endocrine-sensitive tumors (ATSDR 2000).

Commonly considered key representatives of the industrial pollutants, PCBs are used extremely in electrical transformers and capacitors as heat transfer fluids and in consumer products (Eduljee 1988; Harrad et al. 1994). They are ubiquitous in the environment and can enter the marine environment from a number of sources including direct deposition from the atmosphere, runoff from land and directly from industrial and waste water treatment plant discharges (Preston 1992; Broman et al.

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1996; Thompson et al. 1996). They are hydrophobic and upon entry into the aquatic environment, they rapidly associate with suspended particulate material and sediments. Their ultimate fate depends on a variety of physical, chemical and biological interactions including biotic uptake, abiotic degradation, volatilization and burial in bottom sediments (Hong et al. 1999; Calamari 2002). PCBs are of environmental concern because they resist degradation by physical, chemical, or biological pathways, bioaccumulate through the food web (Muir et al. 1988; Thomann 1989) and pose a risk causing adverse effects on the environment and human health (Jones and de Voogt 1999; Focant et al. 2003); Perusal of literature reveals that PCBs are readily accumulated in benthic organisms and have the potential for trophic biomagnification finally affecting fish, wildlife, and human population (Safe 1994; Metcalfe and Metcalfe 1997). Concentrations of contaminants in sediments can provide a good indication of the level of environmental stress to ecosystems. A preliminary account of the distribution of organochlorine pesticides and other persistent organic pollutants (POPs) including PCBs in surface sediments has been recorded in Sundarban mangrove wetland by Bhattacharya et al. (2003) and Guzzella et al. (2005). These reports reveal some interesting features of contamination status. Hence, the present work has been undertaken to redress the lack of information to highlight the spatial distribution of PCBs in intertidal core sediments with reference to available sediment quality guidelines and examines the potential input mechanisms of these compounds to the sediments.

## 3.2 Methodology

### *3.2.1 Study Area and Sampling Sites*

The Indian Sundarban wetland represents an important ecological, economical, and recreational resource for the coastal inhabitants. This coastal environment suffers from environmental degradation due to rapid human settlement, tourist activities, deforestation, and increasing agricultural and aquaculture practices. A significant ecological change is pronounced in this delta due to huge discharges of untreated domestic and industrial effluents carried by the rivers, disposal of contaminated mud from harbor dredging. The delta has become vulnerable to chemical pollutants such as heavy metals, organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and polybrominated diphenyl ethers which may have changed the estuary's geochemistry and affected the local coastal environment (Sarkar et al. 2002, 2004, 2007; Guzzella et al. 2005; Binelli et al. 2007).

Seven sampling sites, namely Lot 8, Kakdwip, Mayagoalinir Ghat, Jambu Island, Canning, Dhamakhali, and Sandeshkhali, that have been chosen in Sundarban wetland belong to different tidal environments and have different wave energy fluxes and distances from the sea (the Bay of Bengal; Fig. 3.1). The first three stations are located on the mainstream of the River Ganges while the last three sites are located further east of the wetland. These sites belong to lower

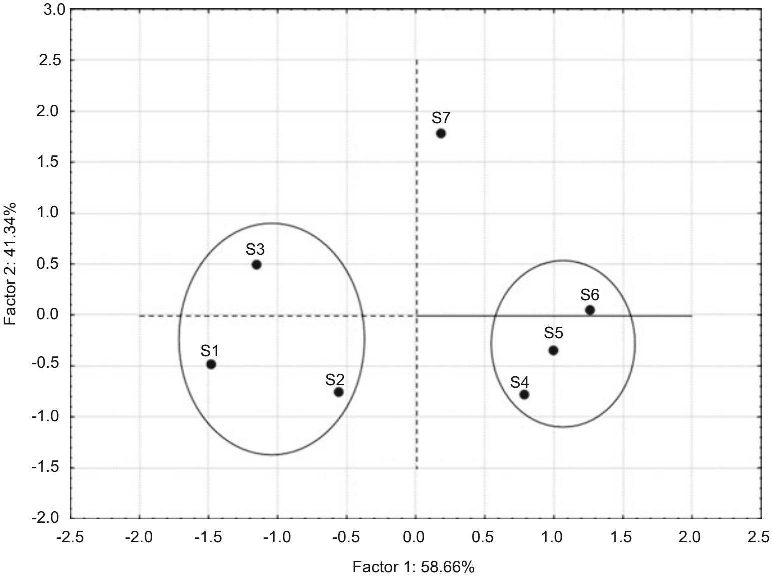

**Fig. 3.1** Principal component analysis (PCA) of the seven sampling sites

deltaic plain experiencing intense semidiurnal tides and wave action with a mesomacrotidal setting (2.5–7 m amplitude). Sampling station Jambu Island and represents a typical marine site not directly influenced by the main flux of Hooghly River. Hydrology of these coastal systems presents a cyclic pattern, characterized by large amount of flow and ebb tides rip and long shore currents (Sarkar et al. 2004).

### 3.2.2 *Sample Collection and Preservation*

During winter months, cores of 30 cm length were collected with the help of a steel corer (40 cm in length and 5 cm in diameter) by gently pushing it into the sediments and dug out, capped, and frozen on return to the laboratory. The core length size differs between the stations due to variations in nature of the substratum. Each core was sliced into 4 cm fractions (subsample) with the help of a PVC spatula, dried in a ventilated oven at 40 °C. Dried samples were then disaggregated using an agate mortar and pestle, sieved through 63 μm metallic sieve and individually transferred in tissue papers contained into pre-cleaned inert polypropylene bags and stored at −20 °C for subsequent extraction and chemical analyses. All utensils used in the collection were thoroughly washed and rinsed with acetone and hexane between sampling sites to minimize the likelihood of cross-contamination. The sediment samples were characterized for particle size distribution, pH, and organic carbon. Detailed experimental procedures are present elsewhere (Chatterjee et al. 2007).

Unfortunately, sediment dating was not possible since samples were collected from mesomacrotidal environments, which create bioturbational churning, and the loss of the uppermost cores (Binelli et al. 2007).

### 3.2.3 *Chemicals and Reagents*

All solvents used were pesticide grade. Florisil adsorbent for chromatography (100–200 mesh) and anhydrous sodium sulfate were obtained from Fluka (Steinheim, Germany). Silica gel for column chromatography (70–230 mesh) was supplied by Sigma-Aldrich (Steinheim, Germany). The internal standard decachlorodiphenyl (CB-209) was purchased from AccuStandard Inc. (New Haven, CT, USA), while PCB standard was obtained adding 23 single CB congeners included between tri- to octa-chlorinated classes (PCBs 28, 52, 81, 101, 110, 118, 128, 129, 136, 138, 141, 149, 151, 153, 170, 174, 177, 180, 183, 187, 194, 196, 201) supplied by Dr. Ehrenstorfer (Augsburg, Germany).

### 3.2.4 *Extraction and Cleanup*

Samples (about 1 g of dry weight) were spiked with 2 ng of recovery standard (CB-209) and extracted for 12 h using 100 mL acetone/*n*-hexane (1:1 v/v) mixture in a cold soxhlet apparatus (FALC Instruments, Lurano, Italy). Samples were dried using a rotary evaporator (RV 06-LR, IKA, Staufen, Germany) and then under nitrogen flow to about 1 mL of final volume. Cleanup was performed using a multilayer column (40× 1.5 cm i.d.) composed by 10 g of silica gel (activated overnight at 130 °C, then deactivated with water, 5 % w/w), followed by 10 g of Florisil (activated for 16 h at 650 °C) and approximately 0.5 cm of activated powdered copper at the top. The column was washed with *n*-hexane/acetone/dichloromethane (8:1:1 v/v). Elution was carried out first by collecting 50 mL of *n*-hexane and then 50 mL of 1:1 *n*-hexane/dichloromethane (v/v). 1 mL of isooctane was added to final sample that was concentrated by rotary evaporator to 10 mL and then to 1 mL under nitrogen flow.

### 3.2.5 *Instrumental Analysis*

An aliquot of 2 μL of the two fractions was injected into a GC chromatograph (TRACE GC, Thermo-Electron, Texas, USA) equipped with a programmed temperature vaporizer (PTV) injector and coupled with a Polaris *Q* Ion Trap mass spectrometer (Thermo Electron), using an AS 2000 autosampler (Thermo Electron) and a Rtx-5MS (Restek, Bellefonte, PA, USA) capillary column (30 m length, 0.25 mm i.d., 0.25 μm *df*). We used sylanized glass liners (1 mL of volume) which were changed after 60–70 injections and re-sylanized with Sylon CT (Supelco, Bellefonte, PA, USA). PTV was set in solvent split mode (split flow = 20 mL $\text{min}^{-1}$); splitless time at 2 min; carrier gas helium at 1 mL $\text{min}^{-1}$; surge pressure of 100 kPa; initial oven temperature starting at 100 °C and maintained for 1 min, then ramped to 180 °C (no hold time) at 20 °C $\text{min}^{-1}$, to 200 °C (no hold time) at 1.5 °C $\text{min}^{-1}$, to 250 °C (no hold time) at 3 °C $\text{min}^{-1}$ and finally to 300 °C (held 5 min) at 30 °C $\text{min}^{-1}$. Samples were analyzed using MS/MS spectrometry under the following instrumental conditions: EI mode with standard electron energy of 70 eV; the transfer line was maintained at 270 °C, the ion source at 250 °C, and the damping gas was set at 1 mL $\text{min}^{-1}$.

### *3.2.6 Quality Control (QC) and Quality Assurance (QA)*

A procedural blank was run in parallel with every batch of four samples using anhydrous sodium sulfate (heated for 6 h at 550 °C) and then extracted in a manner identical to that of the samples. No PCBs was found in blanks. Samples and blanks were spiked with internal standard (CB-209) at 2.0 ng $\text{g}^{-1}$ prior to solvent extraction to monitor methodological analyte losses. The selection of this internal standard is due to the lack of CB-209 in the contamination pattern found by a previous research in Sundarban wetland (Guzzella et al. 2005). Recoveries over than 80 % were accepted. Method performance for PCB congeners was evaluated using SRM river sediment 1939a (NIST, Gaithersburg, MD, USA). Results for the reference material were within the range of certified values specified for the target compounds. Quantitative analyses were performed using the Excalibur software (Thermo Electron) and by external calibration curves ranging from 2 to 40 μg $\text{L}^{-1}$, according to environmental levels of PCBs found in sediments. The limit of detection (LOD; signal/noise = 3) was 0.02 ng $\text{g}^{-1}$ dry weight for each congener, in accordance with Guzzella et al. (2005).

### *3.2.7 Statistical Analyses*

Principal components analysis (PCA) was carried out using the average of $\Sigma_{23}$PCBs measured in all layers from the seven sampling sites. Significant differences among sampling sites were checked by main effects analysis of variance (ANOVA) using $\Sigma_{23}$PCBs as variables, while stations and depth profiles as different factors followed by the multistage *post hoc* test of Newman–Keuls ($p < 0.05$). The homogeneity of variance was performed by Levene's statistic. Correlation matrix and regression analyses between selective dominant congeners were carried out to verify their possible correlations and to check eventual correlations between PCBs and other pollutants measured in the same survey. All statistical analyses were carried out by the software package STATISTICA.

## 3.3 Result and Discussion

### *3.3.1 Level of PCBs*

Levels of $\Sigma_{23}$PCBs measured at seven sampling sites from Sundarban mangrove wetland range between 0.47 and 26.84 ng $g^{-1}$ d.w. (Table 3.1) with pooled mean value of 0.01–2.88 ng $g^{-1}$ d.w. Marked variations in relative contribution of individual congeners together with sharp spatial heterogeneity between eastern and western flank of the wetland have been recorded. Based on the prevalent contamination, four distinct individual groups could be identified: (1) Sandeshkhali the localized hot spot where sharp synchronous elevated levels of majority of the PCB congeners were recorded reaching maximum value of 26.84 ng $g^{-1}$ d.w. at 4–8 cm depth. This is about nine times greater than deeper profile (24–28 cm), and this might be attributed to the recent deposition of PCBs, (2) Lot 8, Kakdwip, and Mayagoalinir Ghat, constituting the moderate group of contamination with an overall uniform distribution in core, suggesting a similarity in sources and/or post-depositional behavior (3) Canning and Dhamakhali, comparatively less polluted sites where $\Sigma_{23}$PCBs (ranging from 1.13 to 2.48 ng $g^{-1}$ d.w.) is reasonably lower than Sandeshkhali and (4) Jambu Island representing the lowest polluted station coupled with less number of PCB congeners and confirms a dispersion of PCBs moving seaward. This pattern of contamination is shown well by the PCA analysis (Fig. 3.1).

Core sediments of Canning and Dhamakhali showed suspensional finer deposits from the Matla-Bidyadhari tidal drainage complex in a macrotidal setting with a dominant silty clay composition. The fairly high concentration of PCBs at Sandeshkhali might be attributed to the huge discharge of untreated urban sewage sludge through the sewage disposal canal of the metropolitan city, about 15 km upstream of the affected site. Moreover, the diesel-powered electrical generators used for agriculture act as local anthropogenic sources of PCBs and thus help for the elevated concentration (Montone et al. 2001). Presence of fine-grained particles, dominated by clayey fractions also facilitate in adsorbing the compounds.

The three stations (Lot 8, Kakdwip, and Mayagoalinir Ghat), morphologically belong to the intertidal mudflat of a macrotidal setting of the Hooghly River estuary, showed a general homogeneity with silty clay to clayey very fine materials (Table 3.2). The overall fine textural properties of the sediment in the core samples of the three stations indicate deposition from suspended and resuspended fine particles in a semidiurnal macrotidal regime. The moderately high values at these sites might be attributed to the huge discharge of untreated or partially treated industrial waters (e.g., paper, plastics, leather) from the upstream part of the Hooghly estuary (as shown in Fig. 1.1). In addition, intense dredging operations, agricultural runoffs, dumping of industrial wastes and atmospheric depositions further aggravate the PCB pollution. Moreover, there is high density of shipping activities along the mainstream of Hooghly estuary and hence high PCB levels in sediments are related to potential discharges from the ships. Other important sources of PCBs in this wetland may include volatilization from previously contaminated sediments followed by atmospheric

**Table 3.1** Concentration of PCB congeners (ng $g^{-1}$ dry weight) in core sediments at seven sampling sites in Sundarban mangrove wetland

| Station | Layer (cm) | 28 | 52 | 101 | 81 | 136 | 110 | 151 | 149 | 118 | 153 | 141 | 138 | 129 | 187 | 183 | 128 | 174 | 177 | 180 | 170 | 201 | 196 | 194 | ΣPCBs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lot 8 | *0–4* | 0.17 | 0.17 | 0.29 |  | 0.04 | 0.06 | 0.06 | 0.16 | 0.15 | 0.19 | 0.07 | 0.37 | 0.05 | 0.06 | 0.02 | 0.03 | 0.06 | 0.07 | 0.14 | 0.04 | 0.02 | 0.03 | 0.02 | 2.26 |
|  | *4–8* | 0.03 | 0.10 | 0.68 |  | 0.16 | 0.14 | 0.46 | 0.93 | 0.34 | 1.25 | 1.00 | 2.33 | 0.09 | 0.34 | 0.25 | 0.14 | 0.35 | 0.38 | 0.53 | 0.16 |  | 0.06 | 0.03 | 9.74 |
|  | *8–12* | 0.10 | 0.15 | 0.85 | 0.02 | 0.18 | 0.19 | 0.77 | 1.54 | 0.57 | 2.22 | 1.43 | 4.13 | 0.19 | 0.71 | 0.45 | 0.29 | 0.85 | 0.92 | 1.14 | 0.25 | 0.07 | 0.11 | 0.04 | 17.17 |
|  | *12–16* | 0.12 | 0.10 | 1.02 | 0.02 | 0.25 | 0.16 | 0.66 | 1.30 | 0.45 | 1.57 | 0.96 | 2.61 | 0.11 | 0.41 | 0.28 | 0.19 | 0.52 | 0.41 | 0.62 | 0.15 | 0.03 | 0.06 |  | 12.01 |
|  | *16–20* | 0.07 | 0.12 | 0.57 |  | 0.11 | 0.09 | 0.36 | 0.90 | 0.40 | 1.32 | 0.82 | 1.98 | 0.09 | 0.28 | 0.24 | 0.13 | 0.35 | 0.28 | 0.43 | 0.12 | 0.04 | 0.02 | 0.02 | 8.73 |
|  | *20–24* | 0.26 | 0.36 | 1.25 |  | 0.21 | 0.20 | 0.84 | 1.40 | 0.66 | 1.72 | 1.16 | 2.27 | 0.06 | 0.37 | 0.17 | 0.19 | 0.51 | 0.58 | 0.69 | 0.23 | 0.05 | 0.10 | 0.02 | 13.30 |
| Kakdwip | *0–4* | 0.08 | 0.08 |  |  |  | 0.02 | 0.03 | 0.06 | 0.04 | 0.06 | 0.08 |  |  |  |  |  | 0.02 | 0.03 |  |  |  |  | 0.08 | 0.59 |
|  | *4–8* | 0.14 | 0.45 |  | 0.10 | 0.07 | 0.14 | 0.24 | 0.19 | 0.29 | 0.13 | 0.32 | 0.02 | 0.05 |  | 0.04 | 0.05 | 0.08 | 0.09 | 0.04 |  |  |  | 0.14 | 2.57 |
|  | *8–12* | 0.12 | 0.16 | 0.40 |  | 0.04 | 0.12 | 0.19 | 0.23 | 0.13 | 0.24 | 0.08 | 0.25 | 0.02 | 0.03 | 0.03 | 0.02 | 0.04 | 0.04 | 0.09 | 0.02 |  |  |  | 2.29 |
|  | *12–16* | 0.08 | 0.14 | 0.66 |  | 0.12 | 0.15 | 0.70 | 1.06 | 0.37 | 1.58 | 0.77 | 1.73 | 0.05 | 0.31 | 0.20 | 0.14 | 0.08 | 0.30 | 0.18 | 0.13 | 0.03 | 0.06 |  | 8.84 |
|  | *16–20* | 0.25 | 0.25 | 1.60 |  | 0.27 | 0.35 | 1.12 | 2.29 | 0.85 | 0.95 | 1.60 | 4.28 | 0.15 | 0.78 | 0.51 | 0.38 | 0.81 | 0.86 | 0.18 | 0.31 | 0.09 | 0.07 | 0.03 | 17.99 |
|  | *20–24* | 0.16 | 0.11 | 0.54 |  | 0.09 | 0.11 | 0.14 | 0.31 | 0.25 | 0.40 | 0.22 | 0.46 | 0.02 | 0.05 | 0.05 |  | 0.08 | 0.04 | 0.12 | 0.05 | 0.02 |  |  | 3.25 |
| MG Ghat | *0–4* | 0.14 | 0.21 | 0.29 | 0.22 |  | 0.06 | 0.07 | 0.17 | 0.18 | 0.14 | 0.07 | 0.25 | 0.02 | 0.04 | 0.03 | 0.02 | 0.05 | 0.04 | 0.08 | 0.03 |  |  |  | 2.11 |
|  | *4–8* | 0.15 | 0.24 | 0.90 |  | 0.18 | 0.15 | 0.51 | 1.01 | 0.43 | 1.14 | 0.67 | 1.83 | 0.07 | 0.25 | 0.20 | 0.12 | 0.31 | 0.33 | 0.46 | 0.13 | 0.03 | 0.05 | 0.06 | 9.23 |
|  | *8–12* | 0.18 | 0.35 | 0.86 |  | 0.12 | 0.17 | 0.61 | 1.28 | 0.57 | 1.92 | 1.08 | 3.66 | 0.19 | 0.60 | 0.43 | 0.28 | 0.87 | 0.80 | 1.12 | 0.34 | 0.09 | 0.12 | 0.05 | 15.70 |
|  | *12–16* | 0.17 | 0.24 | 1.14 |  | 0.25 | 0.21 | 0.77 | 1.69 | 0.76 | 2.51 | 1.81 | 4.44 | 0.20 | 0.78 | 0.50 | 0.35 | 0.94 | 0.84 | 0.99 | 0.26 | 0.06 | 0.09 | 0.04 | 19.04 |
|  | *16–20* | 0.38 | 0.49 | 1.22 |  | 0.14 | 0.20 | 0.65 | 1.01 | 0.52 | 1.12 | 0.62 | 1.86 | 0.09 | 0.22 | 0.20 | 0.15 | 0.33 | 0.32 | 0.03 | 0.19 | 0.05 | 0.12 | 0.10 | 1 |
|  | *20–24* | 0.19 | 0.44 | 1.25 |  | 0.15 | 0.29 | 0.80 | 1.73 | 0.82 | 2.70 | 1.65 | 5.52 | 0.17 | 0.86 | 0.65 | 0.45 | 1.23 | 1.22 | 1.59 | 0.48 | 0.08 | 0.19 | 0.07 | 22.54 |
|  | *24–28* | 0.19 | 0.53 | 1.00 | 0.18 | 0.15 | 0.20 | 0.76 | 1.17 | 0.51 | 1.61 | 0.99 | 2.63 | 0.10 | 0.40 | 0.27 | 0.20 | 0.53 | 0.45 | 0.68 | 0.19 | 0.05 | 0.08 | 0.06 | 12.94 |

(continued)

**Table 3.1** (continued)

| Station | Layer (cm) | 28 | 52 | 101 | 81 | 136 | 110 | 151 | 149 | 118 | 153 | 141 | 138 | 129 | 187 | 183 | 128 | 174 | 177 | 180 | 170 | 201 | 196 | 194 | ΣPCBs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Jambu Island | *0–4* | 0.05 | 0.05 | 0.09 |  |  | 0.02 | 0.02 | 0.06 | 0.05 | 0.09 | 0.04 | 0.10 |  |  |  | 0.04 |  | 0.02 | 0.03 |  |  |  |  | 0.72 |
|  | *4–8* |  | 0.02 | 0.13 |  |  | 0.02 |  | 0.06 | 0.03 | 0.07 | 0.03 | 0.09 |  |  |  |  |  | 0.02 | 0.03 |  |  |  |  | 0.60 |
|  | *8–12* | 0.02 |  | 0.12 |  |  |  | 0.02 | 0.05 | 0.03 | 0.07 | 0.03 | 0.07 |  |  |  |  | 0.02 |  | 0.03 |  |  |  |  | 0.52 |
|  | *12–16* | 0.02 | 0.02 | 0.11 |  |  |  | 0.03 | 0.05 | 0.03 | 0.07 | 0.04 | 0.09 |  |  |  |  | 0.02 | 0.02 | 0.03 |  |  |  |  | 0.58 |
|  | *16–20* |  | 0.02 | 0.11 |  |  | 0.02 |  | 0.04 | 0.04 | 0.06 | 0.04 | 0.08 |  |  |  |  | 0.02 |  |  |  |  |  |  | 0.47 |
|  | *20–24* | 0.02 | 0.02 | 0.14 |  |  | 0.02 | 0.03 | 0.05 | 0.03 | 0.09 | 0.03 | 0.09 |  |  |  |  |  |  |  |  |  |  |  | 0.57 |
| Canning | *0–4* | 0.09 | 0.06 | 0.38 |  | 0.02 | 0.06 | 0.07 | 0.00 | 0.13 | 0.28 | 0.08 | 0.37 | 0.02 | 0.05 | 0.02 | 0.05 | 0.06 | 0.07 | 0.09 | 0.04 | 0.02 |  |  | 1.97 |
|  | *4–8* | 0.05 | 0.02 | 0.31 |  |  | 0.02 | 0.05 |  | 0.14 | 0.18 | 0.08 | 0.20 |  | 0.03 |  | 0.03 | 0.05 | 0.03 | 0.10 | 0.04 |  |  |  | 1.39 |
|  | *8–12* |  | 0.03 | 0.24 |  |  | 0.04 | 0.06 | 0.11 | 0.07 | 0.18 | 0.08 | 0.23 |  | 0.02 | 0.03 |  | 0.06 | 0.06 | 0.08 | 0.05 |  |  |  | 1.36 |
|  | *12–16* | 0.03 |  | 0.27 |  | 0.02 | 0.03 | 0.03 | 0.07 | 0.08 | 0.13 | 0.06 | 0.17 |  | 0.02 | 0.02 | 0.02 | 0.03 | 0.04 | 0.06 | 0.03 |  |  |  | 1.13 |
| Dhamakhali | *0–4* | 0.10 | 0.19 | 0.23 |  | 0.03 | 0.06 | 0.07 | 0.13 | 0.08 | 0.13 | 0.07 | 0.14 |  | 0.02 |  | 0.03 | 0.03 | 0.03 | 0.04 | 0.02 |  |  |  | 1.39 |
|  | *4–8* | 0.31 | 0.35 | 0.35 |  |  | 0.09 | 0.11 | 0.20 | 0.12 | 0.20 | 0.08 | 0.20 |  | 0.03 |  |  | 0.03 | 0.04 | 0.04 | 0.03 |  |  |  | 2.21 |
|  | *8–12* | 0.14 | 0.13 | 0.26 |  | 0.03 | 0.04 | 0.04 | 0.16 | 0.10 | 0.15 | 0.07 | 0.14 |  | 0.02 |  |  | 0.04 |  | 0.05 | 0.02 |  |  |  | 1.42 |
|  | *12–16* | 0.29 | 0.32 | 0.32 |  | 0.09 | 0.05 | 0.08 | 0.16 | 0.14 | 0.19 | 0.09 | 0.20 |  | 0.03 | 0.02 |  | 0.03 | 0.03 | 0.05 | 0.02 |  |  |  | 2.12 |
|  | *16–20* | 0.26 | 0.21 | 0.51 |  | 0.13 | 0.08 | 0.12 | 0.26 | 0.17 | 0.21 | 0.09 | 0.24 |  | 0.03 | 0.03 |  | 0.00 | 0.04 | 0.07 | 0.03 |  |  |  | 2.48 |
|  | *20–24* | 0.19 | 0.30 | 0.36 |  | 0.11 | 0.07 | 0.08 | 0.19 | 0.12 | 0.17 | 0.05 | 0.19 |  | 0.04 | 0.03 | 0.02 | 0.05 | 0.03 | 0.07 |  |  |  |  | 2.10 |
| Sandeshkhali | *0–4* | 0.34 | 0.45 | 1.00 | 0.02 | 0.09 | 0.27 | 0.26 | 0.54 | 0.57 | 0.65 | 0.30 | 1.02 | 0.09 | 0.10 | 0.11 | 0.15 | 0.22 | 0.20 | 0.37 | 0.15 | 0.06 | 0.09 | 0.06 | 7.11 |
|  | *4–8* | 0.22 | 0.18 | 1.63 |  | 0.11 | 0.43 | 1.21 | 2.55 | 1.23 | 3.87 | 2.14 | 6.08 | 0.20 | 0.72 | 0.55 | 0.70 | 1.21 | 1.23 | 1.64 | 0.53 | 0.14 | 0.16 | 0.07 | 26.84 |
|  | *8–12* | 0.19 | 0.14 | 1.81 |  | 0.17 | 0.49 | 1.25 | 2.45 | 1.27 | 4.36 | 2.04 | 5.52 | 0.21 | 0.94 | 0.61 | 0.48 | 1.12 | 1.03 | 1.44 | 0.54 | 0.14 | 0.14 | 0.07 | 26.41 |
|  | *12–16* | 0.13 | 0.14 | 1.31 |  | 0.02 | 0.24 | 0.70 | 1.19 | 0.57 | 1.68 | 0.93 | 2.26 | 0.12 | 0.08 | 0.25 | 0.26 | 0.49 | 0.44 | 0.80 | 0.31 | 0.03 | 0.08 | 0.03 | 12.04 |
|  | *16–20* | 0.15 | 0.05 | 1.05 |  | 0.07 | 0.22 | 0.46 | 1.04 | 0.54 | 1.83 | 0.72 | 1.96 | 0.10 | 0.25 | 0.19 | 0.22 | 0.39 | 0.38 | 0.54 | 0.20 | 0.04 | 0.02 | 0.03 | 10.45 |
|  | *20–24* | 0.05 | 0.09 | 0.76 |  | 0.05 | 0.19 | 0.16 | 0.32 | 0.28 | 0.54 | 0.20 | 0.57 | 0.04 | 0.07 | 0.06 | 0.11 | 0.14 | 0.13 | 0.24 | 0.14 |  | 0.02 | 0.04 | 4.21 |
|  | *24–28* | 0.07 | 0.08 | 0.78 |  | 0.03 | 0.12 | 0.14 | 0.31 | 0.28 | 0.36 | 0.17 | 0.45 |  | 0.06 | 0.05 | 0.08 | 0.11 | 0.09 | 0.11 | 0.09 |  | 0.02 | 0.03 | 3.45 |

**Table 3.2** Sediment quality characteristics of the 42 samples from the seven sampling sites of Sundarban mangrove wetland

| Sample | Layer cm | $C_{org}$ % | Sand % | Silt % | Clay % | Texture |
|---|---|---|---|---|---|---|
| Lot 8 | 0–4 | 0.59 | 1.7 | 30.2 | 68.1 | Clayey very fine |
| | 4–8 | 0.59 | 2.3 | 58.2 | 39.5 | Silty clay loam |
| | 8–12 | 0.58 | 2.6 | 47 | 50.5 | Silty clay |
| | 12–16 | 0.49 | 2 | 61.7 | 36.3 | Silty clay loam |
| | 16–20 | 0.36 | 1.8 | 27.6 | 70.6 | Clayey very fine |
| | 20–24 | 0.49 | 3 | 27.2 | 69.8 | Clayey very fine |
| Kakdwip | 0–4 | 0.19 | 12.4 | 46.1 | 41.5 | Silty clay |
| | 4–8 | 0.53 | 7.4 | 88.2 | 4.4 | Silty |
| | 8–12 | 0.45 | 26.9 | 50.3 | 22.9 | Fine loamy |
| | 12–16 | 0.36 | 22.64 | 40.3 | 37 | Clay loam |
| | 16–20 | 1.06 | 17.8 | 30.5 | 51.7 | Clay loam |
| | 20–24 | 1.87 | 22.44 | 29.1 | 48.5 | Clayey fine |
| MG Ghat | 0–4 | 0.53 | 2.6 | 34.2 | 63.2 | Clayey very fine |
| | 4–8 | 0.55 | 3.4 | 26 | 70.6 | Clayey very fine |
| | 8–12 | 0.57 | 2.6 | 58.1 | 39.3 | Silty clay loam |
| | 12–16 | 0.57 | 3.3 | 53.7 | \43 | Silty clay |
| | 16–20 | 0.61 | 2.6 | 45 | 52.5 | Silty clay |
| | 20–24 | 0.55 | 3.4 | 32.9 | 63.8 | Clayey very fine |
| | 24–28 | 0.55 | 4.2 | 38 | 57.7 | Clayey very fine |
| Jambu Island | 0–4 | 0.48 | 98.6 | 1.4 | – | Sandy |
| | 4–8 | 0.09 | 100 | 0.03 | – | Sandy |
| | 8–12 | 0.12 | 100 | 0.04 | – | Sandy |
| | 12–16 | 0.06 | 99.9 | 0.08 | – | Sandy |
| | 16–20 | 0.08 | 100 | 0.04 | – | Sandy |
| | 20–24 | 0.09 | 100 | – | – | Sandy |
| Canning | 0–4 | 0.63 | 36.3 | 24.4 | 39.3 | Clayey fine |
| | 4–8 | 0.92 | 22.2 | 22.4 | 55.3 | Clayey fine |
| | 8–12 | 0.63 | 26 | 46.2 | 27.8 | Fine loam |
| | 12–16 | 0.74 | 25.4 | 37.2 | 37.4 | Clay loam |
| Dhamakhali | 0–4 | 0.66 | 20.2 | 52.9 | 26.8 | Fine loamy |
| | 4–8 | 0.74 | 16 | 33 | 51 | Clayey fine |
| | 8–12 | 0.61 | 24.6 | 26 | 49.4 | Clayey fine |
| | 12–16 | 0.83 | 10.5 | 35.9 | 53.5 | Clayey fine |
| | 16–20 | 0.89 | 18.7 | 35.1 | 46.2 | Clayey fine |
| | 20–24 | 0.96 | 10.1 | 42.4 | 47.5 | Silty clay |
| Sandeshkhali | 0–4 | 0.85 | 12.2 | 31.8 | 55.9 | Clayey fine |
| | 4–8 | 0.88 | 9.8 | 28.6 | 61.6 | Clayey very fine |
| | 8–12 | 0.92 | 10.8 | 48.2 | 41 | Silty clay |
| | 12–16 | 0.79 | 14 | 29.4 | 56.6 | Clayey fine |
| | 16–20 | 0.98 | 12.1 | 37 | 50.9 | Clayey fine |
| | 20–24 | 1 | 8 | 17.4 | 74.6 | Clayey very fine |
| | 24–28 | 1.17 | 3.5 | 39.7 | 56.8 | Silty clay |

transport and deposition (Galassi et al. 1992; Kallenborn et al. 1998). Phytoplankton may also play an important role in the transfer and distribution of PCBs as emphasized by Konat and Kowalewska (2001) from Odra estuary.

Concerning the PCB congeners, tri-chlorinated biphenyls (tri-CB) to octa-CB were detected in the sediment samples. An overall decreasing order of seven dominant PCB congeners' contribution to the total load was: CB 138 > 153 > 149 > 101 > 1 18 > 141 > 151. This order can be explained by the fact that lightly chlorinated PCBs are less persistent, have lower *n*-octanol/water coefficient ($k_{\mathrm{ow}}$), and are more volatile than heavily chlorinated PCBs. Therefore, heavily chlorinated PCBs are more accumulative in the sediments, whereas lightly chlorinated PCBs are degraded and further volatilized as interpreted by Toan et al. (2007), while working on PCBs in surface soils from Hanoi, Vietnam. The observed finding of congener distribution toward more highly chlorinated compounds is consistent with previously published data recorded along the lower stretch of the Ganges (Hooghly) estuary (Guzzella et al. 2005). This indicates the preferential retention of these less volatile and more lipophilic compounds in the marine environment (de Voogt et al. 1990). Differences in congener composition in the aquatic systems may also be attributed to a decline in the proportion of less chlorinated PCBs that are more susceptible to losses through volatilization, sedimentation, and possibly microbial degradation (Brown et al. 1987; Quensen et al. 1988; MacDonald et al. 1992). Moderately and high chlorinated PCBs may, therefore, remain persistent in the aquatic environment because they are less volatile and more soluble in lipids, adsorb more readily to sediments, and are more resistant to microbial degradation (Shiu and Mackay 1986; Connell et al. 1998; Tyler and Millward 1996).

Uniformity in the sequence of decreasing order of dominant PCB congeners (CB 138 > 153 > 149) was evident at three sites, namely Lot 8, Mayagoalinir Ghat, and Sandeshkhali, and to some extent at Kakdwip, whereas CB 101 > 138 > 153 was pronounced at Jambu Island, Canning, Dhamakhali which is evident in Fig. 3.2 showing the distribution of the seven dominant congeners. The major contributors, CB 138 and CB 153, share 22.1 % to 9.5 % and 14.2 % to 9.0 % of the $\Sigma_{23}$PCBs, respectively. These two hexachlorobiphenyls dominated the PCB profiles also in sediment cores corresponding to the finding of Toan et al. (2007) from Hanoi, Vietnam, and in surface sediments by Guzzella et al. (2005) in a previous campaign carried out in the Sundarban wetland. The major presence of tetrachlorobiphenyls (CB 52 and CB 81) pentachlorobiphenyls (CB 101, CB 110, CB 118, and CB 136) and hexachlorobiphenyls (CB 128, CB 129, CB 138, CB 141, CB 149, CB 151, and CB 153) suggests a contribution from the commercial mixtures, which have been widely used in transformers, electrical equipment, and other industries (Barakat et al. 2002).

Comparisons among the average percentages of different chlorinated classes of PCBs found in all sediment layers (Table 3.3) showed some differences among the seven sampling stations. Notwithstanding that hexa-PCBs were the major chlorinated class found in all sites (37–58 %), Dhamakhali pointed out a different contamination pattern with levels of tri-(11 %) and tetra-substituted (13 %) congeners much higher than the negligible percentages found in the other sites. Since these lower chlorinated congeners reached the 24 % of the total PCB load, this site can be inter-

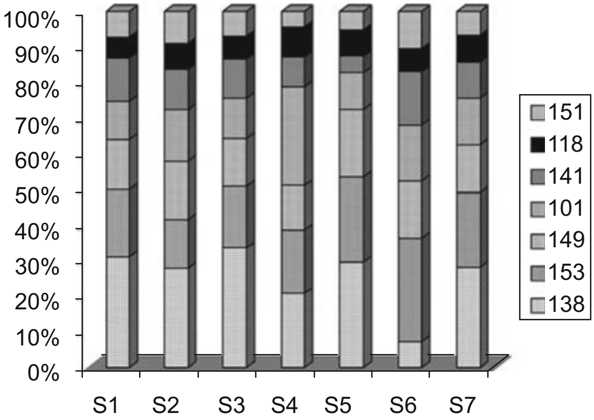

**Fig. 3.2** Profile of seven dominant PCB congeners of the seven sampling sites

**Table 3.3** Average percentages (%) of different chlorination classes at the seven sampling stations

| Classes | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ |
|---|---|---|---|---|---|---|---|
| Tri-CBs | 2 | 3 | 2 | 4 | 3 | 11 | 2 |
| Tetra-CBs | 2 | 5 | 6 | 4 | 2 | 13 | 2 |
| Penta-CBs | 16 | 38 | 16 | 30 | 31 | 30 | 22 |
| Hexa-CBs | 58 | 51 | 55 | 49 | 44 | 37 | 54 |
| Hepta-CBs | 20 | 14 | 20 | 12 | 18 | 9 | 19 |
| Octa-CBs | 1 | 1 | 1 | 2 | 2 | 1 | 2 |

$S_1$ Lot 8, $S_2$ Kakdwip, $S_3$ MG Ghat, $S_4$ Jambu Island, $S_5$ Canning, $S_6$ Dhamakhali, $S_7$ Sandeshkhali

ested by mechanism of contamination different in comparison with the other stations. Although Dhamakhali is located close to the highest polluted Sandeshkhali, the different pattern of contamination is probably due also to different sedimentation rates into the Vidyadhari River which is a tidal river system heavily contaminated by the outfall from a 20 km long sewage canal from Calcutta. No uniform temporal trend in PCB levels was recorded (Table 3.1) probably due to the particular hydrological characteristics of Sundarban wetland, which are severely influenced by southeast monsoon and the macrotidal regime (Bhattacharya et al. 2003; Goodberg 2003). Fluctuations in PCB levels may also arise from non-homogenous inputs from point and from nonpoint sources of these xenobiotic compounds. PCB distribution in sediment core at Lot 8, Kakdwip, Mayagoalinir Ghat, and Sandeshkhali reveals most erratic pattern while rest of the stations maintain almost uniform trends associated with less number of PCB congeners and their individual concentration. The observed distributional variability of PCBs clearly reflects source differences, which in most cases can be attributed to local point sources. However, atmospheric transport of the lower chlorinated species and the specific association of lower chlorinated congeners with the sand-size fractions and of highly chlorinated congeners with the finest fraction (Pierard et al. 1996) may also partly account for the different pattern as recorded between the sites of Sundarban.

In a marine environment with intense aquacultural and shipping activities such as Hooghly estuary, with many different sources of PCB inputs, both point and diffusive, it is difficult to pinpoint precisely a clear source–occurrence relationship. Furthermore, the sediment resuspension from tidal movement in the estuary may promote chlorination dependent different transport further masking source-concentration matches (Tyler and Millward 1996). Again, the hydrological characteristics of the Hooghly River estuary (HRE), such as macrotidal effect and seasonal fluctuation in flow rate due to performed impact of southwest monsoon (annual rainfall 1600 mm), can influence the distribution of these compounds in sediments especially at Lot 8, Kakdwip, and Mayagoalinir Ghat. In the present study, sediment quality characteristics ranged from silty clay to clayey (Table 3.2), but texture was non-homogenous in different core layers, corroborating the very particular hydrological conditions of the HRE and Sundarban wetland tidal system.

### *3.3.2 Statistical Evaluation and Interpretation*

PCB species sorbed on sediments can suffer degradation and desorption processes, the latter being strongly influenced by physicochemical characteristics of the sediment such as grain size or organic of seven stations, a main effect ANOVA was performed using the mean of $\Sigma_{23}$PCB measured in all layers as variables ($n = 161$) and stations and layers as factors. It has been revealed that the variation of concentration levels between chemicals and stations are highly significant ($F = 7.38$; $p < 0.0001$) but variations between depths are insignificant ($F = 0.35$; $p = 0.919$). The multistage post *hoc* test of Newman–Keuls matter content. Because of their high hydrophobicity, PCBs were expected to be associated with organic-rich particles. However, low correlation ($r = 0.12$, $p < 0.44$, $n = 42$) between $\Sigma_{23}$PCBs and organic carbon was recorded, corroborating the previous study by Guzzella et al. (2005) that failed to correlate sediment characteristics and levels of organochlorines and PAHs which may be due to the combined effect of transport, mixing, and deposition. Guzzella et al. (2005) suggested that the productive and varying benthic communities at different stations (e.g., Canning, Dhamakhali, Sandeshkhali) in mangrove wetlands increase organic carbon levels in sediments, masking any relationship between PCBs and organic carbon as suggested by Guinan et al. (2001). Lack of correlation between PCBs and organic carbon in sediments was also recorded by Wafo et al. (2006) from Cortious creek, France. However, significant correlation between $\Sigma_{23}$PCBs and clay particles as observed in the present study implies role of the fine-grained particles in the transportation and redistribution of these compounds. To establish the variation of the PCB congeners over (Table 3.4) confirmed the presence of different contamination groups since the three stations located on the mainstream of River Hooghly are significantly different ($p < 0.05$) from the eastern sites Canning and Dhamakhali (excepted MG Ghat with Dhamakhali). The most polluted site Sandeshkhali is significantly different ($p < 0.05$) from Jambu Island, Canning, and Dhamakhali, while its PCB contamination seems to be similar to those stations (Lot 8, Kakdwip, MG Ghat) situated in the western side of the wetland.

Results of correlation coefficient ($r$) values show that there exist strong positive correlations among the seven dominant PCB congeners (CBs 138, 153, 149, 101, 177,

**Table 3.4** Levels of significance (main-effect ANOVA, Newman–Keuls post hoc test, $p<0.05$) among the seven sampling sites in Sundarban mangrove wetland

| Stations | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ |
|---|---|---|---|---|---|---|---|
| $S_1$ | – | | | | | | |
| $S_2$ | 0.938 | – | | | | | |
| $S_3$ | 0.997 | 0.999 | – | | | | |
| $S_4$ | <0.01** | <0.01** | <0.05* | – | | | |
| $S_5$ | <0.001*** | <0.001*** | <0.001*** | 0.112 | – | | |
| $S_6$ | <0.05* | <0.05* | 0.075 | 0.440 | 0.055 | – | |
| $S_7$ | 0.956 | 0.990 | 0.983 | <0.05* | <0.001*** | <0.05* | – |

*$S_1$* Lot 8, *$S_2$* Kakdwip, *$S_3$* MG Ghat, *$S_4$* Jambu Island, *$S_5$* Canning, *$S_6$* Dhamakhali, *$S_7$* Sandeshkhali
*$p<0.05$, **$p<0.01$, ***$p<0.001$

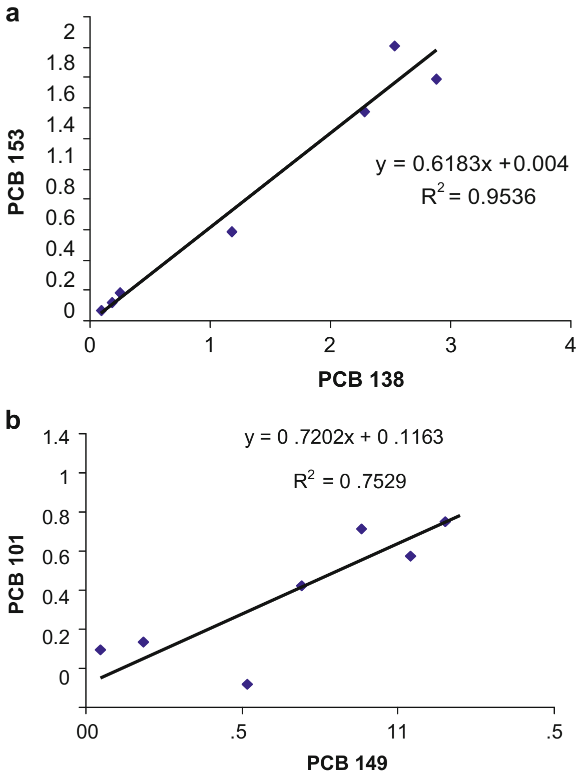

**Fig. 3.3** Correlation between concentrations of four dominant PCB congeners in the seven sampling sites

141, and 110). Results suggested that these congeners might come from the similar sources and have similar environmental behaviors (Iwata et al. 1994). It is interesting to find that there are strong positive correlations among the four dominant congeners of PCBs (CB 138, 153 and CB 101 and 149) suggesting a similar trend for those pollutants. The regression lines along with the equations, as evidenced in Fig. 3.3a, b also exhibit a very good fit. The average value of PCBs was also compared both with the mean of the six DDT homologues and 14 polybrominated ethers measured during the same monitoring campaign (Binelli et al. 2007; Sarkar et al. 2008). Since no significant correlation was found either with the sum of the well-known organochlorine insecticide and its homologues ($r^2=0.41$, $p=0.12$) or the flame retardants ($r^2=0.45$, $p=0.09$), the PCBs seem to have a different environmental behavior.

### 3.3.3 Comparison with Other Studies

To evaluate the relative degrees of PCB contaminations in coastal sediments in India, we compared the present data against the available data reported elsewhere (Table 3.5). Although we recognize that the direct compatibility is somewhat compromised by the fact that different studies consider different PCB congeners, still it is important to evaluate the quantitative patterns of PCB contamination to get a sense of regional similarity. The prevalent contamination was higher than those detected in the West coast of Sri Lanka and similar to those found in the Hanoi region in Vietnam, but lower than the levels found in the early 1990s in Mandovi estuary, India (170 ng $g^{-1}$ d.w., Iwata et al. 1994). The concentrations of $\Sigma_{23}$PCB in this study are comparable with those in Chinese and to some extent Korean coastal sediments. In contrast, the Japan and Singapore coastal regions reveal many fold increase than the present observation. Our data were also compared with PCB levels in Sundarban wetland found in a previous research carried out in 2003 (Guzzella et al. 2005) where 14 different PCB congeners (Table 3.5) were measured in surface sediments (0–5 cm) at ten different sampling sites. Two of them (Canning and Dhamakhali) are the same of our research, and the latter is very close to Sandeshkhali, while other two (Gangasagar and Kachuberia) are close to Mayagoalinir Ghat and to Lot 8 and Kakdwip, respectively. The general temporal trend of PCB contamination seems to increase since the sum of the same congeners measured in either monitoring campaigns in the surface sediments from these eight sites ranges between 0.2 and 2.3 ng $g^{-1}$ d.w. in 2003 and from 0.5 to 5.2 ng $g^{-1}$ d.w. in 2006 survey. These data can point out new PCB inputs from the basin during the last years.

### 3.3.4 Ecotoxicological Concerns

The sediment quality guidelines (SQG) specified by US EPA (1997) and by Canadian Council of Ministers of the Environment (CCME 2002) were used to assess the potential ecotoxicological impacts of organic contaminants measured in surface sediments of Sundarban mangrove wetland. Effects range low (ERL) and effects range median (ERM) values are used to predict potential impacts of contaminants, whereas ERL values correspond to the lower 10% and ERM values to median values, when the chemical concentration of a contaminant in marine sediments are sorted according to the degree of their effects levels. ERL represents the value at which toxicity may begin to be observed in sensitive marine species, whereas ERM represents the concentration

**Table 3.5** Comparative data on total PCB levels (ng $g^{-1}$ d.w.) in sediments

| Location | Year | ΣPCBs | References |
|---|---|---|---|
| Osaka Bay, Japan | 1990 | 63–240[a] | Iwata et al. (1994) |
| Hong Kong | 1997/1998 | n.d.–97.9[a] | Richardson and Zheng (1999) |
| Mason Bay, Korea | 1997 | 1.2–41.4[b] | Hong et al. (2003) |
| North Coast of Vietnam | 1997 | 1.1–66.4[c] | Nhan et al. (1999) |
| Minjiang River Estuary, China | 1999 | 15.8–57.9[d] | Zhang et al. (2003) |
| Daya Bay, China | 1999 | 0.9–11.2[c] | Zhou et al. (2001) |
| Yangtze Estuary, China | 2001 | n.d–19.0[e] | Liu et al. (2003) |
| Pearl River Estuary, China | 1996 | 0.2–1.8 | Hong et al. (1999) |
| Pearl River Delta, China | 2015 | 0.198–1.11[f] | Lai et al. (2015) |
| Singapore | 2003 | 1.4–329.6[g] | Wurl and Obbard (2005) |
| Sri Lanka (West Coast) | 1996 | 0.45–4.4 | Guruge and Tanabe (2001) |
| Kuwait | 2005 | 0.4–8.2 | Gevao et al. (2006) |
| Sundarban wetland India | 2003 | 0.18–2.33[h] | Guzzella et al. (2005) |
| Sundarban wetland, India | 2006 | 0.47–26.84 | Binelli et al. (2009) |

[a] PCB mixture basis (Aroclors)

[b] 2× $\Sigma_{18}$PCB; twice the sum of PCB congeners 8, 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 170, 180, 187, 195, 206, and 209

[c] 5× $\Sigma_6$PCB; sum of six PCB congeners 28, 52, 101, 138, 153, and 180 multiplied by a factor of 5 for 209 PCB mixture basis

[d] Sum of PCB congeners 1, 5, 28, 29, 47, 49, 77, 97, 101, 105, 118, 138, 153, 154, 169, 171, 180, 200, and 204

[e] Sum of PCB congeners 1, 11, 29, 47, 121, 136, and 187

[f] Sum of 7 PCB congeners 28, 52, 101, 118, 153, 138, and 180

[g] Sum of PCB congeners 18, 28, 31, 33, 44, 49, 53, 70, 74, 82, 87, 95, 99, 101, 105, 118, 128, 132, 138, 153, 156, 158, 169, 170, 171,177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208, and 209

[h] Sum of 14 PCBs (18, 28+31, 52, 44, 101 149, 118, 153, 138, 180, 170, 194, 209)

below which adverse effects are expected to occur only rarely. Besides the threshold effect level (TEL), the probable effect level (PEL) is used as the criterion for the prediction of toxicity and corresponds to a level above which adverse effects are frequently expected. In the present study, $\Sigma_{23}$PCB concentration above ERL (22.7 ng $g^{-1}$ d.w.) and TEL (21.6 ng $g^{-1}$ d.w.) were pronounced in only 4.8 and 7.1 % of the total cases. However, no concentration exceeded that of ERM (180 ng $g^{-1}$ d.w.) and PEL (188.8 ng $g^{-1}$ d.w.) values. Thus, it can be inferred that toxicity of PCBs in Sundarban sediments can be ranked as intermediate.

## 3.4 Conclusion

It is evident from the present study that PCBs occur in relatively low to moderately high values in sediments of Sundarban mangrove wetland, a UNESCO World Heritage Site. The erratic distribution in sediment profiles denotes non-homogenous input of these organic compounds. The spatial distribution of PCBs is related to a combination of factors including point source input, organic carbon content, wave action, and atmospheric inputs. The present PCB levels were exceeding the lower limit of SQGs in few cases. The present findings point to the need to establish a reliable monitoring programme for these persistent pollutants, so that any overtaking in concentration over environmental quality standard can be detected and remedial measures could be taken. It is worthwhile to mention that the coastal region has undergone rapid changes over the last two decades, and it is expected that further changes in population and industrial and agricultural activity will occur. For the protection of human health and the marine ecosystems, analyses of representative edible species could be taken into consideration.

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# Chapter 4
# Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment Cores from Sundarban Wetland

## 4.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of lipophilic xenobiotic contaminants that is widespread in the environment. This class of organic compounds has been widely studied (Neff 1979; McElory et al. 1989; Tolosa et al. 1996) because of its carcinogenic and mutagenic properties (Lehr and Jerina 1977; Yan 1985; White 1986). PAHs are derived mainly from anthropogenic inputs and are the result of fossil oil discharges and incomplete combustion of organic matter. The latter include combustion of fossil fuels, waste incineration, coke production, carbon black, coal tar pitch, asphalt, and petroleum cracking (McCready et al. 2000). Numerous studies have shown PAHs to be capable of inducing dioxin-like responses in vitro in both fish (Behrens et al. 2001; Jung et al. 2001; Villeneuve et al. 2002) and mammalian cell lines (Willet et al. 1997; Clemons et al. 1998). PAHs have also been shown to induce ethoxyresorufin-*O*-deethylase (EROD) activity in vivo (Gerhart and Carlson 1978; Brunstrom et al. 1991; Blanchard et al. 1999; Basu et al. 2001). Three PAHs—benzo[a]pyrene, chrysene, and benz[a]anthracene—have been reported to elicit estrogenic responses in vitro (Clemons et al. 1998).

The PAH study in the coastal environments is of great importance as these areas are biologically important, and productive system possess high socioeconomic values. They receive considerable pollutant inputs from land-based sources via coastal discharges, thus potentially threatening the biological resources, among other negative effects. The Indian Sundarban wetland (as shown in Fig. 1.1) is one of the most sensitive but complex ecosystems in the world and suffers from environmental degradation due to rapid human settlement, tourism and port activities, operation of excessive number of mechanized boats, deforestation, and increasing agricultural and aquaculture practices (Bhattacharya 2008). The ongoing degradation is also related to huge siltation, flooding, storm runoff, atmospheric

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deposition, and other stresses resulting in changes in water quality, depletion of fishery resources, choking of river mouth and inlets, and overall loss of biodiversity as evident in recent years (Bhattacharya and Sarkar 2003; Sarkar et al. 2007). A significant ecological change is pronounced in this area due to huge discharges of untreated or semi-treated domestic and municipal wastes as well as effluents from multifarious industries (as shown in Fig. 1.1) carried by rivers as well as contaminated mud disposal from harbor dredging. Recent studies on the pollution status of Sundarban have revealed the presence of both inorganic and organic pollutants in sediments, such as heavy metals, organochlorine pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), which may have changed the estuary's geochemistry and affected the local coastal environment (Sarkar et al. 2002, 2004; Guzzella et al. 2005; Binelli et al. 2007).

The objective of this study was the assessment on the distribution and origin of PAH contamination in core sediments of Sundarban mangrove wetland. To this end, four sediment cores were collected in this region and were analyzed for 18 parent PAHs and some alkylated derivatives in order to identify their origin and evaluate their ecotoxicological significance.

## 4.2 Methodology

### *4.2.1 Study Area and Sampling Sites*

The Indian Sundarban is a mangrove wetland belonging to the low-lying coastal zone, formed at the estuarine phase of the Hugli River. It is a tide-dominated estuarine wetland set on the lower deltaic plains of the Ganges and Brahmaputra rivers. The wetland is characterized by a complex network of tidal creeks, which surround hundreds of tidal islands exposed to different elevations at high and low semidiurnal tides. Geomorphologically, mangrove swamp, tidal marsh, intertidal mudflats, sandy beaches, tidal creeks, and inlets characterize the estuarine wetland. A number of southerly flowing rivers (viz., Hugli, Baratala, Saptamukhi, Jamira, Bidyadhari, Matla, and Gosaba, as shown in Fig. 1.1) traverse the wetland from the west to the east (Bhattacharya 2000). Reclamation of land, deforestation, and industrial and agricultural wastes impart variable degrees of anthropogenic stresses leading to concentrations of both heavy metals and persistent organic pollutants (POPs). The four sampling sites, namely, Gangadharpur, Lothian Island, Jharkhali, and Gosaba (as shown in Fig. 1.1), have been chosen taking into consideration the representative locales of the variable environmental and energy regimes of the wetland, which cover a wide range of substrate behavior, wave-tide climate, intensity of bioturbation (animal–sediment interaction), geomorphic–hydrodynamic regimes, and distances from the sea.

### 4.2.2 *Sample Collection and Preservation*

Cores of 30 cm length were collected in the winter season (January–February) with the help of a steel corer (40 cm long and 5 cm in diameter) by gently pushing it into the sediments and dug out, capped, and frozen on return to the laboratory. The core length size differs among the stations due to variations in nature of the substratum. Each core was sliced into 4-cm fractions (subsample) with the help of a PVC spatula. Sliced samples were then oven dried at 50 °C (Zuloaga et al. 2009) and then gently disaggregated, sieved through 63 μm metallic sieves, and individually transferred into pre-cleaned inert polypropylene bags and stored at −20 °C for subsequent extraction and chemical analyses. The sediment samples were characterized for particle size, pH, and organic carbon; the experimental procedures are presented elsewhere (Kwokal et al. 2008). Sediment cores were not dated because they were not well preserved, as commonly found in river influenced coastal sediments.

### 4.2.3 *Chemicals and Reagents*

A PAH mixture containing phenanthrene (P), anthracene (A), fluoranthene (Fl), pyrene (Py), benz[a]anthracene (BaA), chrysene (C), benzo[b]fluoranthene (BbFl), benzo[k] fluoranthene (BkFl), benzo[a]pyrene (BaPy), indeno[1,2,3-cd]pyrene (IPy), dibenz[a,h] anthracene (DBA), and ben-zo[ghi]perylene (BPer) at 10 mg $L^{-1}$ each in cyclohexane was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Individual standards such as 1-methylphenanthrene (99 %) (MP) and 3,6-dimethylphenanthrene (97 %) (DMP) were obtained from Ultra Scientific (North Kingstown, Rhode Island, USA). The following perdeuterated standards, used as surrogates, were obtained from Cambridge Isotope Laboratories (Andover, Massachusetts, USA): naphthalene-d8 (99 %), anthracene-d10 (98 %), pyrene-d10 (98 %), and benzo[a]pyrene-d12 (98 %). Decafluorobiphenyl, used as internal standard, was from Merck (Hohenbrunn, Germany). Suprasolv-grade acetone, hexane, and dichloromethane were obtained from Merck (Darmstadt, Germany). Silica gel 40 (0.063–0.200 mm) for column chromatography was also obtained from Merck. Anhydrous sodium sulfate for analysis and aluminum oxide 90 active neutral (0.063–0.200 mm) for column chromatography were also obtained from Merck.

### 4.2.4 *Sample Extraction and Fractionation*

Samples were spiked with the surrogates (naphthalene-d8, anthracene-d10, pyrene-d10, benzo[a]pyrene-d12, and benzo[a]anthracene-d12). Then, samples were extracted with a Pressurized Solvent Extraction apparatus from Applied Separations

(Allentown, Pennsylvania, USA) with hexane–acetone (1:1) in a 11-mL stainless-steel extraction cell [1 g Hydromatrix (bottom), sample (3 g dry weight sample) (middle), and 4 g of washed sea sand (top)]. Extraction was performed at 100 °C and 140 bar for 10 min in three cycles. Finally, the extraction cell is flushed under pressure using a combination of solvent (5 s) and nitrogen gas (3 min). The recovered extracts were then carefully evaporated to near dryness for further fractionation into aliphatic and aromatic hydrocarbons.

Fractionation was performed by adsorption chromatography in an open glass column (45 cm × 1.2 cm) packed with 1 g anhydrous sodium sulfate (top), 6 g neutral alumina (middle) (activated at 400 °C, 5 % water deactivated), and 6 g silica gel (bottom) (activated at 120 °C and 5 % deactivated). Two fractions were collected: (1) aliphatic hydrocarbons eluting with 20 mL of *n*-hexane and (2) polycyclic aromatic hydrocarbons with 50 mL of *n*-hexane:dichloromethane (80:20, v:v). The collected extracts were concentrated with a rotary evaporator until 1 mL.

Analysis of the aliphatic and aromatic fractions was accomplished with a TRACE-MS Thermo-Finnigan TRACE-GC gas chromatography (Manchester, UK) in the electron impact (EI) mode at 70 eV. A 30-m 9 0.25-mm-inner diameter capillary column coated with 0.25 lm of ZB-5MS stationary phase was obtained from Phenomenex Zebron (Torrance, California, USA). The carrier gas was helium, with a constant flow rate of 1.2 mL $\text{min}^{-1}$. The injector, in the splitless mode, temperature was held at 280 °C, and the purge valve was activated 50 s after the injection. Column temperature was held at 60 °C for 1 min, then the temperature was increased to 200 at 10 °C min and finally to 320 at 4.8 °C $\text{min}^{-1}$, holding that temperature for 10 min. Transfer line and ion source temperatures were held at 250 and 200 °C, respectively. Data were acquired in the full-scan mode from 50 to 350 amu (10 scan $\text{s}^{-1}$) with 6 min of solvent delay and processed by the X-calibur Thermo Finnigan software (San Jose, California, USA).

### 4.2.5 Quantitation

Quantitation of parent and alkylated PAHs was performed from the reconstructed ion chromatograms obtained from the molecular ion by the internal standard procedure by using decafluorobiphenyl. Using external calibration $R^2>0.996$ were obtained for all of the target analytes. The limit of quantification (LOQ) in the full-scan mode ranged from 0.25 to 0.29 ng $\text{g}^{-1}$. Internal laboratory reference materials and quality control charts were used to assess the accuracy of the analytical procedure used for the PAH determination.

### 4.2.6 Statistical Analyses

Significant differences among sampling sites were checked by main effects of analysis of variance (ANOVA) using $\sum_{16}$PAHs as variables and stations and depth profiles as different factors. The dataset was analyzed with principal component analysis (PCA), which is often used as an explorative tool to extract components needed to explain variance of observed data. All statistical analyses were carried out by the software package STATISTICA 6.0.

## 4.3 Results and Discussion

### 4.3.1 *Sediment Geochemistry and PAH Accumulation*

The sediment quality parameters (pH, organic carbon, and textural properties) of the different samples vary among them, as depicted in Table 4.1. Values of pH range from slightly acidic to basic (pH 6.5–8.4); the acidic nature is mainly found in Gangadharpur and Jharkhali partly due to the oxidation of $FeS_2$ and FeS to $SO_4^{2-}$ and partly results from the decomposition of mangrove litter and hydrolysis of tannin in mangrove plants releasing various kinds of organic acids (Liao 1990). Organic carbon ($C_{org}$) values were below 1 % in all stations except at Lothian. Very low organic carbon values in the intertidal zone sediments of Sundarban wetland were also recorded in previous studies

**Table 4.1** Distribution profile of the sediment quality characteristics at four sampling sites of the Sundarban wetland

| Stations | Depth (cm) | pH | $C_{org}$ (%) | Sand (%) | Silt (%) | Clay (%) |
|---|---|---|---|---|---|---|
| Gangadharpur | 0–4 | 6.5 | 0.81 | 13.04 | 68.36 | 18.6 |
| | 4–8 | 6.6 | 0.87 | 7.72 | 27.56 | 64.72 |
| | 8–12 | 6.7 | 0.81 | 9.36 | 22.18 | 68.46 |
| | 12–16 | 7.1 | 0.73 | 9.96 | 37.68 | 52.36 |
| | 16–20 | 7.1 | 0.66 | 13.84 | 67.3 | 18.86 |
| | 20–24 | 7.4 | 0.83 | 16.12 | 32.42 | 51.46 |
| Lothian Island | 0–4 | 8.4 | 1.16 | 1.92 | 86.32 | 11.78 |
| | 4–8 | 8.3 | 1.57 | 2.52 | 67.44 | 30.04 |
| | 8–12 | 8.2 | 1.2 | 1.24 | 81.32 | 17.44 |
| | 12–16 | 8.1 | 1.2 | 1.04 | 33.18 | 65.78 |
| | 16–20 | 7.9 | 0.92 | 1.4 | 32.62 | 65.98 |
| Jharkhali | 0–4 | 6.5 | 0.85 | 0.48 | 40.1 | 59.42 |
| | 4–8 | 6.6 | 0.65 | 0.16 | 43.3 | 56.54 |
| | 8–12 | 7.2 | 0.83 | 0.28 | 33.96 | 65.76 |
| | 12–16 | 7.5 | 0.9 | 0.32 | 37.62 | 62.06 |
| | 16–20 | 7.5 | 0.87 | 1.2 | 37.14 | 61.66 |
| | 20–24 | 7.7 | 0.87 | 0.24 | 43.24 | 56.52 |
| | 24–28 | 7.9 | 0.87 | 0.28 | 31.58 | 68.14 |
| Gosaba | 0–4 | 6.5 | 0.73 | 0.4 | 44.9 | 54.7 |
| | 4–8 | 7.9 | 0.73 | 2.4 | 66.56 | 31.04 |
| | 8–12 | 8.1 | 0.61 | 0.6 | 51.7 | 47.7 |
| | 12–16 | 7.7 | 0.83 | 0.4 | 35.94 | 63.66 |
| | 16–20 | 7.7 | 0.63 | 1.28 | 38.16 | 60.56 |

(Sarkar et al. 2004; Chatterjee et al. 2007). These low values of organic carbon are probably related to the poor absorbability of organics on negatively charged quartz grains, which predominate in the intertidal sediments of this estuarine environment (Bhattacharya and Sarkar 2003; Sarkar et al. 2004). Regarding textural composition, the four stations also exhibit wide variations: silty clay at Jharkhali and Gosaba with differences in the proportions of silt and clay content, fine silty to silty clay at Gangadharpur and clayey silty to silty clay at Lothian. Textural differences might be attributed to vigorous estuarine mixing, suspension–resuspension, and flocculation–deflocculation processes. These variations mighty influence the PAH accumulation in the core sediments (Table 4.2), where the processes involved are quite complex in nature. Other important factors are the chemical properties of the compounds, especially their water solubility, sediment composition, and organic carbon content.

### 4.3.2 Surface Distribution of Individual PAHs

In general, the spatial distribution of PAHs in surface sediments is controlled by the hydrodynamic conditions of the wetland, including the following factors: (1) textural composition and depositional rate of sediments, (2) input rate of PAHs, (3) differential resuspension and redeposition of sedimentary PAHs, (4) vertical mixing due to physical or biological processes, and (5) microbial degradation of PAHs (Boonyatumanond et al. 2006).

The occurrence of PAHs was observed at the four sites, exhibiting the following trend: Lothian > Gangadharpur ~ Gosaba > Jharkhali (Table 4.2). An overall enrichment of all components, with a relative predominance of three- to five-ring PAHs was evidenced at the Lothian site, where the maximum concentration of P16PAHs was recorded (2938 ng $g^{-1}$ at 12–16 cm). The distribution at Gangadharpur was similar but depleted in the three-ring PAHs, whereas at locations Jharkhali and Gosaba, the five-ring PAHs were distinctly predominant (Fig. 4.1a & b). A slight increase of alkylated derivatives (MPs) was also observed in these locations.

The elevated levels of PAHs at Lothian site indicate a situation in which tidal recycling of sediments at the mouth of the Saptamukhi River (as shown in Fig. 1.1) plays the dominant role in the sedimentation processes. Although designated as a river, the hydrodynamic regime of Saptamukhi is that of a tidal inlet where the mixing of ebb and flood flows due to tidal asymmetry bring the sediments to resuspension for longer time. This local resuspension and recycling processes might account for the higher concentration of most of the components. In addition, the fine-sediment particle size (silty clay) together with high organic matter content (1.20 %) facilitates the absorption and accumulation of PAHs in this location.

The enrichment of high-molecular-weight (HMW) PAHs at stations Jharkhali and Gosaba, compared with Gangadharpur and Lothian, could be explained by the lower mobility of these PAHs and their deposition in proximity to the source. Chemical and biological removal processes appear to be unimportant once the PAHs were delivered to surface waters and sediments.

**Table 4.2** Distribution profile of 16 PAH congeners and total PAH concentration (ng $g^{-1}$ dry weight) in core sediments at four sampling sites of the Sundarban wetland

| | Layer (cm) | Phe | Anth | Mphe | DMPhe | DBT | Flu | Pyr | B[a]A | Chry | B[b]F | B[k]F | B[a]P | Per | Inpy | DB[ah]A | B[ghi] P | Total PAH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gangad-harpur | 0–4 | 36 | 7 | 27 | 14 | 5 | 74 | 50 | 24 | 34 | 55 | 21 | 27 | 89 | 34 | 6 | 38 | 498 |
| | 4–8 | 77 | 22 | 72 | 21 | 11 | 240 | 160 | 79 | 87 | 59 | 26 | 46 | 92 | 33 | 7 | 47 | 987 |
| | 8–12 | 23 | 8 | 21 | 13 | 4 | 73 | 49 | 20 | 25 | 32 | 11 | 20 | 101 | 22 | 4 | 30 | 420 |
| | 12–16 | 44 | 12 | 30 | 14 | 6 | 120 | 70 | 28 | 34 | 52 | 14 | 29 | 90 | 19 | 4 | 22 | 546 |
| | 16–20 | 126 | 23 | 41 | 17 | 14 | 232 | 131 | 53 | 56 | 66 | 20 | 35 | 94 | 22 | 5 | 23 | 900 |
| | 20–24 | 24 | 8 | 25 | 10 | 4 | 91 | 55 | 20 | 24 | 36 | 12 | 22 | 87 | 15 | 3 | 17 | 417 |
| Lothian | 0–4 | 248 | 32 | 59 | 68 | 17 | 251 | 174 | 79 | 110 | 106 | 38 | 70 | 71 | 68 | 12 | 101 | 1376 |
| | 4–8 | 206 | 21 | 99 | 103 | 18 | 183 | 130 | 59 | 83 | 128 | 42 | 60 | 49 | 58 | 14 | 61 | 1109 |
| | 8–12 | 103 | 13 | 25 | 26 | 8 | 90 | 60 | 31 | 44 | 63 | 20 | 38 | 44 | 30 | 7 | 33 | 585 |
| | 12–16 | 397 | 64 | 181 | 57 | 43 | 391 | 299 | 213 | 288 | 372 | 119 | 202 | 96 | 196 | 42 | 218 | 2938 |
| | 16–20 | 56 | 3 | 14 | 11 | 4 | 25 | 14 | 6 | 8 | 12 | 4 | 6 | 45 | 5 | 1 | 6 | 195 |
| Jharkhali | 0–4 | 46 | 5 | 30 | 7 | 4 | 27 | 15 | 6 | 8 | 12 | 5 | 5 | 99 | 5 | 1 | 5 | 241 |
| | 4–8 | 28 | 2 | 27 | 12 | 2 | 24 | 14 | 6 | 8 | 12 | 5 | 5 | 96 | 4 | 1 | 4 | 209 |
| | 8–12 | 33 | 4 | 13 | 6 | 3 | 13 | 9 | 3 | 5 | 12 | 4 | 4 | 102 | 4 | 1 | 5 | 203 |
| | 12–16 | 26 | 3 | 11 | 7 | 3 | 14 | 9 | 3 | 5 | 9 | 3 | 4 | 105 | 4 | 1 | 6 | 195 |
| | 16–20 | 16 | 2 | 16 | 6 | 2 | 11 | 8 | 4 | 5 | 11 | 4 | 5 | 89 | 5 | 1 | 5 | 166 |
| | 20–24 | 98 | 6 | 29 | 21 | 8 | 14 | 11 | 3 | 3 | 24 | 7 | 3 | 139 | 6 | 1 | 8 | 329 |
| | 24–28 | 8 | 0 | 9 | 9 | nd | 4 | 5 | 2 | 3 | 11 | 3 | 3 | 84 | 3 | 0 | 4 | 132 |
| Gosaba | 0–4 | 75 | 5 | 56 | 56 | 6 | 43 | 29 | 10 | 18 | 48 | 14 | 17 | 150 | 18 | 4 | 22 | 457 |
| | 4–8 | 31 | 0 | 23 | 23 | 2 | 19 | 13 | 5 | 8 | 15 | 4 | 8 | 103 | 8 | 1 | 14 | 232 |
| | 8–12 | 109 | 12 | 35 | 35 | 9 | 143 | 95 | 41 | 51 | 87 | 25 | 47 | 86 | 37 | 9 | 42 | 795 |
| | 12–16 | 35 | 3 | 21 | 21 | 4 | 29 | 24 | 10 | 15 | 29 | 8 | 13 | 107 | 12 | 2 | 12 | 313 |
| | 16–20 | 67 | 14 | 27 | 27 | 5 | 206 | 164 | 77 | 124 | 168 | 53 | 133 | 148 | 77 | 15 | 87 | 1338 |

*nd* not detectable

Among the individual components, perylene deserves special attention. It was found to be present in all samples but at similar orders of magnitude (71–150 ng $g^{-1}$), with a relative contribution increasing from 5 % (Lothian) to 41 % (Jharkali) of the total sedimentary PAHs, conversely to the total PAH concentrations. This might reflect the natural terrestrial input in the region. A concentration of perylene >10 % of the total pentacyclic aromatics] (e.g., benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene) indicates a probable diagenetic input, whereas those <10 % indicate a probable pyrolytic origin (Baumard et al. 1998).

### 4.3.3 Variations of PAH Profiles in Sediment Cores

The median distributions of PAHs down to the sediment cores parallel those of the surface samples (Fig. 4.1) and in other Asian coastal regions (Khim et al. 1999; Yang 2000; Yamashita et al. 2000). As shown in Table 4.2, the vertical distribution

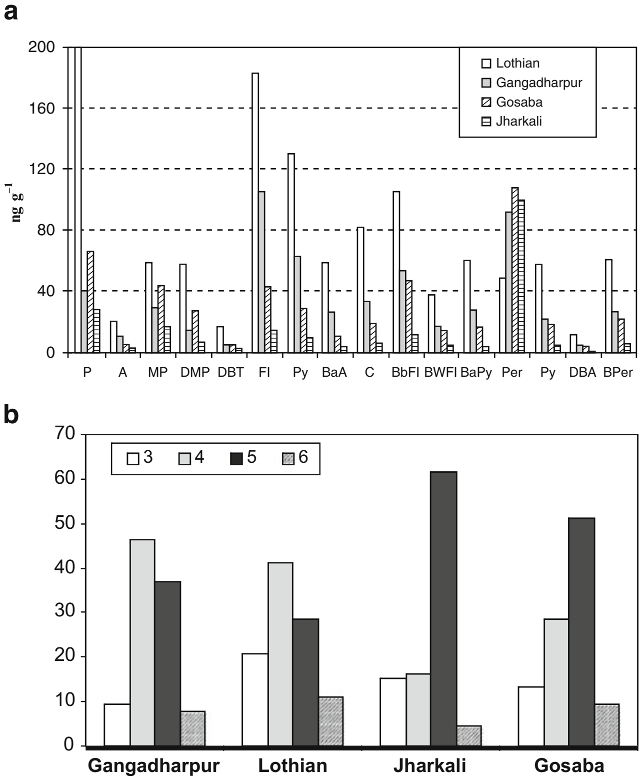

**Fig. 4.1** Spatial distributions of (**a**) individual compounds and (**b**) three-, four-, five-, and six-ring PAHs compounds in core sediments (median values expressed in ng $g^{-1}$ dry weight) of the four sampling. Sites of the Sundarban wetland

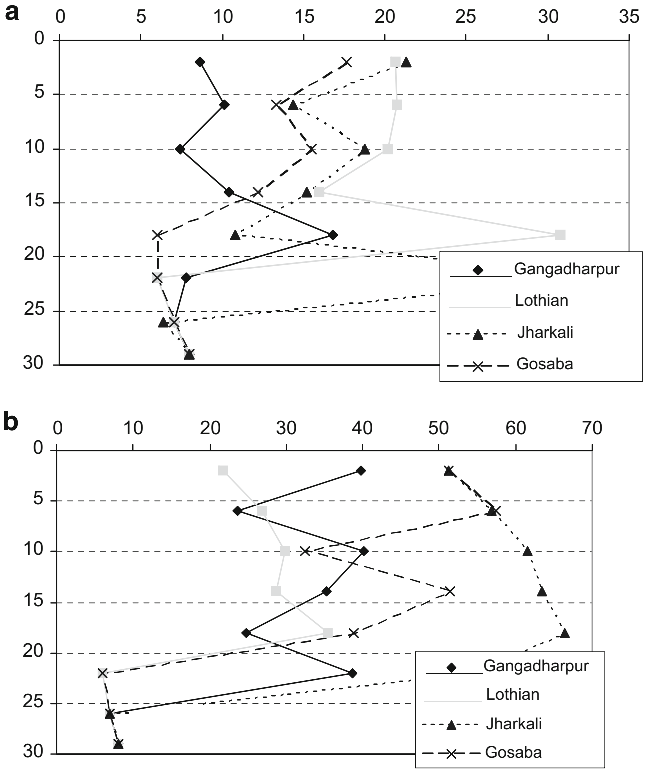

**Fig. 4.2** Vertical profiles of (**a**) three-ring and (**b**) five-ring PAHs (%) of the four sampling sites of the Sundarban wetland

of concentrations of $\sum_{16}$PAHs measured at the four sampling stations (Gangadharpur, Lothian Island, Jharkhali, and Gosaba) exhibited a wide range of values, the minimum being 132 ng $g^{-1}$ at Jharkhali at 28–30 cm depth and the maximum 2938 ng $g^{-1}$ at 12–16 cm depth at Lothian. The prevalent spatial variations in PAH concentrations in sediment core samples might be ascribed to differences in hydrodynamic regimes related to river discharge and tidal influx, changes in sediment particle size characteristics in individual core and non-homogenous inputs from point sources and non-point-sources of POPs in this region.

The depth profiles of individual PAHs are complex and did not follow any consistent trend, as it was also found in the region for other organic and inorganic pollutants like PBDEs (Binelli et al. 2007) and heavy metals (Chatterjee et al. 2007). However, an overall decreasing trend of total PAHs from top to lower levels of the core seems to occur and this is more evident in the case of three-ring PAHs, which attain their maximum values at 20–30 cm depth (Fig. 4.1a). Perylene was present at all levels of the core samples, showing a more uniform profile, probably associated to its diagenetic origin.

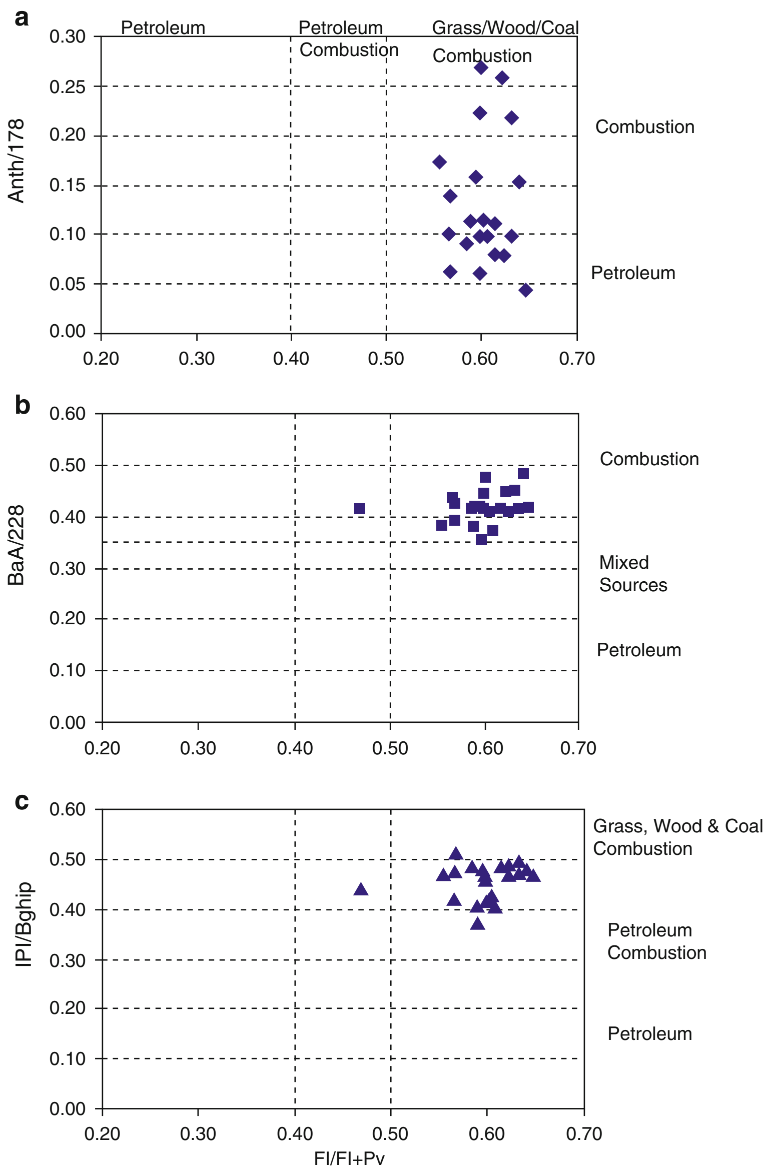

**Fig. 4.3** PAH cross-plots for the ratios of (**a**) Ant/178 versus Flu/(Flu+Pyr), (**b**) BaA/228 versus Flu/(Flu+Pyr), and (**c**) IPy/(IPy+BPer) versus Fl/(Fl+Pyr) ratios in the sediment cores from the Sundarban wetland

The prevalent erratic vertical distribution of PAHs might be mainly related to the non-homogenous textural composition of the different sediment core layers resultant from the particular hydrological conditions of the Hooghly estuary and adjoining Sundarban wetland situated under a mesomacrotidal setting and seasonal flow rate fluctuations. The PAH accumulation patterns and in situ degradation or metabolism by benthic communities could also have contributed to the dispersion of the profiles.

To establish variation of the 16 PAHs in the four stations, two-way analysis of variance (ANOVA) was undertaken using total PAHs as variables and stations and depth profiles as different factors. Significant values were obtained between PAHs ($F = 22.3$; $p < 0.00001$) and between stations ($F = 5.4$; $p < 0.001$), but variation between depths was insignificant ($F = 0.77$; $p < 0.59$). The results of correlation matrix reveal significant correlations between the following five- and six-ring aromatic ring PAHs for all the stations: benzo[a]pyrene, benzo[ghi]perylene, dibenzo[a,h]anthracene, benzo[k]fluoranthene, and benzo[b]fluoranthene, indicating their identical behavior during transport in the estuarine environment. A good correlation exists between the benzo[a]pyrene level and the total PAH concentration, making this compound a potential molecular marker for PAH pollution. PCA revealed that the first common factor (PC1) accounts for 62.1 % of total variance (Table 4.3). This factor has positive loadings on perylene, clay, and mud (i.e., percent material <63 μm) and negative loadings on the rest of the PAH molecules, organic carbon, and sand. Based on this composition, PC1 is essentially a biogenic component of diagenetic origin, the abundance and distribution of which is controlled by grain size distribution. The second component (PC2, 10.9 % of total variance) has positive loadings with petrogenic PAH (P, MP, DMP, DBT), pH, organic carbon, silt, and mud. Therefore, PC2 is controlled by petrogenic PAHs, the abundance and distribution of which is determined by sediment organic carbon and grain size. The third component (PC3, 8.6 % of the total variance) has significant positive loading for clay and insignificant positive loadings for petrogenic and pyrolytic PAH compounds (P, A, MP, DBT, C, BbFl, BkFl, BaPy, Per, IPy, DBA, BPer, and total PAHs), which indicates that clay (or smaller grain size) is the dominant controlling factor in distribution of PAH compounds in Sundarban wetland.

High-molecular-weight PAHs (benzo[k]fluoranthene, benzo[b]fluoranthene, and dibenz[a,h]anthracene) showed an overall similar distribution in three locations [Gangadharpur, Jharkhali, and Gosaba, excepting Lothian], suggesting that these compounds possess identical sources.

### 4.3.4 Sources of PAH in Sediment Cores

The PAH fingerprints can be used to differentiate between pyrolytic and petrogenic sources. These are characterized by using molecular indexes based on the concentration ratios of selected PAHs (Colombo et al. 1989). However, one difficulty in identifying the PAH origin is the possible coexistence of several contamination sources and the transformation processes that PAHs can undergo before deposition in the analyzed sediments (Butler and Crossley 1981). The ratio of the sum of methylphenanthrenes to phenanthrene (MP/P) has frequently been used to distinguish petrogenic from pyrogenic PAHs (Yunker et al. 2002; Hwang et al. 2003; Kannan et al. 2005). Typically, MP/P ratios range from 2 to 6 for petrogenic PAHs and generally

**Table 4.3** Results of PCA: Eigen analysis of the correlation matrix

| Eigenvalue | 14.911 | 2.625 | 2.076 |
|---|---|---|---|
| Proportion | 0.621 | 0.109 | 0.086 |
| Cumulative | 0.621 | 0.731 | 0.817 |
| Variable | PC1 | PC2 | PC3 |
| Depth | 0.076 | −0.097 | 0.100 |
| Phe | −0.221 | 0.189 | 0.082 |
| Anth | −0.235 | −0.068 | 0.032 |
| Mphe | −0.222 | 0.021 | 0.127 |
| DMPhe | −0.206 | 0.221 | 0.106 |
| DBT | −0.233 | 0.060 | 0.056 |
| Flu | −0.247 | −0.134 | −0.056 |
| Pyr | −0.251 | −0.119 | −0.020 |
| B[a]A | −0.251 | −0.100 | −0.004 |
| Chry | −0.251 | −0.082 | 0.009 |
| B[b]F | −0.250 | −0.042 | 0.074 |
| B[k]F | −0.253 | −0.047 | 0.077 |
| B[a]P | −0.249 | −0.083 | 0.024 |
| Per | 0.046 | −0.329 | 0.321 |
| Inpy | −0.252 | −.039 | 0.051 |
| DB[ah]A | −0.253 | −0.023 | 0.080 |
| B(ghi)P | −0.249 | −0.032 | 0.051 |
| Total | −0.255 | −0.051 | 0.076 |
| pH | −0.068 | 0.410 | 0.043 |
| $C_{org}$% | −0.101 | 0.402 | −0.021 |
| Sand | −0.092 | −0.365 | −0.422 |
| Silt | −0.095 | 0.325 | −0.403 |
| Clay | 0.120 | −0.212 | 0.503 |
| Mud | 0.046 | 0.332 | 0.469 |

lower than 1 for pyrogenic origin (Garrigues et al. 1995; Budzinski et al. 1997). In this study, the said ratios ranged from 0.24 to 1.11 throughout the core (Table 4.4), showing that the PAHs in the sediment were mainly of pyrolytic origin. In addition, the ratios of phenanthrene to anthracene (P/A) and fluoranthene to pyrene (Fl/Py) have also been applied to assess the contribution of petrogenic or pyrolytic sources of PAHs. A P/A ratio lower than 10 and an Fl/Py ratio higher than 1 have also been evidenced in the majority of cases, which strongly support the pyrogenic origin of PAHs (Sicre et al. 1987; Baumard et al. 1998). This endorsed the previous findings of Guzzella et al. (2005) in the surface sediments along the lower stretch of the Hooghly estuary where the values of P17PAH ranged from 2.5 to 1081 ng $g^{-1}$, indicating low to moderate PAH pollution. Saha et al. 2009 also ascertained the strong pyrogenic signature to the PAH in sediments from India, where most industries use coal, coal products, and wood as sources of energy (almost 74 % of total energy consumption) and use very little crude oil and petroleum (17 % of the total energy consumption) (Saha et al. 2009). The wide range of PAH pair ratios found in the

**Table 4.4** Characteristic values of selected molecular ratios for pyrolytic and petrogenic PAHs

| | This study | | | | Source | | |
|---|---|---|---|---|---|---|---|
| Ratio | Gangadharpur | Lothian | Jharkhali | Gosaba | Pyrolytic | Petrogenic | References |
| P/A | 4.1 | 7.6 | 11.3 | 9.4 | <10 | [15 | Baumard et al. (1998) |
| Fl/Py | 1.2 | 1.4 | 1.5 | 1.5 | >1 | <1 | Baumard et al. (1998) |
| MP/P | 0.65 | 0.37 | 0.52 | 0.65 | <1 | 2–6 | Budzinski et al. (1997) |
| LMW/HMW | 0.27 | 0.41 | 0.55 | 0.32 | Low | High | Budzinski et al. (1997) |

Sundarban wetland sediments (Table 4.4) might suggest that the signature of PAHs could be altered by biological (e.g., bacterial degradation), chemical (e.g., oxidation and reduction), and/or physical (e.g., air mass mixing and sediment resuspension) processes during transport and postdepositional phases in sediments as endorsed by Bicego et al. 2006 from the Santos and Sao Vicente estuarine system, Brazil.

Isomer pair ratios A/178, BaA/228, and IPy/(IPy + BPer) have been plotted against Fl/(Fl + Py) to show how PAHs are distributed relative to their possible sources (Fig. 4.3, based on Yunker et al. 2002). The A/178 isomer pair ratios show that PAHs are derived primarily from combustion (A/178 >0.10 in all sites), with no occurrence of PAHs originating from petroleum (Fig. 4.3). The combustion of crude oil is possibly the major source of PAHs in sediments because the study region is situated in an area of intense shipping traffic at the mouth of the Hooghly estuary. The Fl/(Fl + Py) isomer pair ratios showed that no PAH was introduced directly from petroleum or its derivatives but mainly was derived from biomass and coal combustion. The industrial complex, which uses large quantities of coal in its activities, is the source of combustion-derived PAHs. The IPy/(IPy + BPer) isomer pair ratios showed that PAHs are derived from petroleum combustion. Although distinct sources might be inferred from PAH isomer ratios, it is well documented that in urban and industrial areas, PAHs might originate from a variety of sources and be transported by different pathways.

Moreover, the PAH source fingerprints were similar for the four sampling sites, which support that PAH sources to this wetland sediments were similar. The large amount of fossil fuels burned for domestic cooking, preparing molasses, and husking rice by the local inhabitants using coal, charcoal, wood, and so forth (Chatterjee et al. 2009) and coal-fired power plants located in the upstream of the estuary could contribute to a local atmospheric source of PAHs. Furthermore, river discharges and urban runoff, automotive sources, and automobile emissions are other important potential sources of PAHs in the coastal sediments. The automobile emissions as potential source of PAHs in the sediments of Guanica Bay, Puerto Rico, have also been reported by Pait et al. (2008).

**Table 4.5** Worldwide concentration ranges of PAHs in sediments (ng $g^{-1}$ dry weight) from different countries

| Locations | Average | Maximum | References |
|---|---|---|---|
| Guba Pechenga, Barents Sea, Russia | 76 | 208 | Savinov et al. (2003) |
| Todos Santos Bay, Mexico | 96 | 813 | Macías-Zamora et al. (2002) |
| Yalujiang River, China | 290 | 1,500 | Wu et al. (2003) |
| Deep Bay, China | 409 | 726 | Zhang et al. (2004) |
| Minjiang River Estuary, China | 433 | 887 | Zhan et al. (2004) |
| Lingding Bay, China | 560 | 1,006 | Mai et al. (2002) |
| Bohai Sea, Yellow Sea, China | 877 | 5,734 | Ma et al. (2001) |
| Zhujiang River China | 2,432 | 10,811 | Mai et al. (2002) |
| Tokyo Bay, Japan | 631.1 | 2,010 | Yamashita et al. (2000) |
| Masan Bay, Korea | 353 | 1,100 | Khim et al. (1999) |
| Izmit Bay, Turkey | NA | 25,000 | Tolun et al. (2001) |
| Kiel Harbor, Germany | 8,000 | 30,000 | Baumard et al. (1999) |
| Mailing Bay, Taihu Lake | 2,563 | 4,754 | Qiao et al. (2005) |
| NA not available | | | |

Table 4.5 summarizes previous studies on the PAH levels in sediments collected from different coastal regions of the world. The direct compatibility is somewhat compromised by the fact that PAH patterns differ in different cases, still it is important to evaluate the quantitative data of PAH contamination to get a sense of regional similarity. In comparison with literature data, core sediments from the Sundarban wetland seem to be ranging from low to moderately polluted by PAHs, and they fully reflect contaminant levels found in other Asian coastal environments, such as that of the Yellow Sea (Mai et al. 2002), but much lower than those reported in the Izmit Bay, Turkey (Tolun et al. 2001) and Kiel Harbor, Germany (Baumard et al. 1999).

## 4.3.5 *Assessment of Sediment Quality Using Environmental Quality Thresholds*

The effects range low (ERL) and the effects range median (ERM) values were used for impact assessment on aquatic sediment with a ranking of low to high impact values (Long et al. 1995; Khim et al. 1999). The measured concentrations of PAHs were compared with the existing ERL and ERM values. Results showed that the total PAH concentrations at the three sites were below the ERL of 4000 ng $g^{-1}$. Among the 16 PAHs, only phenanthrene in Lothian Island exceeded the ERL value of 240 ng $g^{-1}$. Hence, concentration of this PAH is of great concern because this might have adverse effects on the flora and fauna of this wetland, such as growth impairments of halophytic plants (Vane et al. 2009), biochemical disruptions and cell damage in animals (Eisler 2000), toxicity in fish and birds (Payne et al. 2003; Albers 2003), as well as negative health impacts in human beings (Rylander et al. 2009).

### 4.3.6 Risk Assessment

Comparisons among the concentrations of specific pollutants detected in sediments and their corresponding sediment quality values (i.e., concentrations below which adverse effects in the marine ecosystem were unlikely) were performed in the present investigation. The levels of risks posed by certain chemicals in the sediments were characterized by the risk quotients, which were calculated using risk quotient (RQ) =

$$\text{Concentration of chemical X in sediment} / \text{Sediment quality value} \tag{4}$$

In most cases, sediment quality values are not single numbers but are often represented in ranges of values, which have both lower and upper limits. These two values could be used to calculate risk quotients under the best-case (RQbcs) and worst-case (RQwcs) scenarios:

$$\begin{aligned}\text{RQbcs} &= \text{Lowest measured concentration of chemical} \\ &\quad \text{in sediment} \times \text{Upper limit of sediment quality value}\end{aligned} \tag{4}$$

And

$$\begin{aligned}\text{RQwcs} &= \text{Highest measured concentration of chemical} \\ &\quad \text{in sediment} \times \text{Lower limit of sediment quality value}\end{aligned} \tag{4}$$

The calculation of RQbcs and RQwcs provides a simple way to distinguish chemicals, which might or might not require further analysis. In principle, RQbcs $> 1$ would indicate that the chemical in question would require attention, and probably some control measure and remedial action is needed. In contrast, if RQwcs $< 1$, the chemical is probably of little concern and thus should be accorded a lower priority in terms of management actions. In situations where RQbcs $< 1$ or RQwcs $> 1$, a more refined risk assessment should be undertaken to ascertain the risks due to the specific chemicals.

An assessment of potential environmental risks associated with PAHs measured in the present study was conducted and the results are summarized in Table 4.6. Sediment quality values used in the calculation of risk quotients included the Hong Kong Interim Sediment Quality Value (HK-ISQV) and Canadian Sediment Quality Guidelines (CSQG). Sediment quality values are not available for certain PAHs in the HK-ISQV and, in those cases, ERL and ERM guideline values from the US National Oceanic and Atmospheric Administration (NOAA) were used [(http://response.restoration.noaa.gov/cpr/sediment/squirt/ squirt. html)] (Burton 2002). Only contaminants for which sediment quality values are available were assessed in this study. Concentrations of contaminants recorded in the sediment samples are taken as the measured environmental concentrations (MECs).

Interestingly, all of the RQbcs estimated were below 0.1, and this might suggest that the pollutants under investigation pose little hazard to the ecosystem. Pyrene and benzo[a]pyrene had RQwcs $< 0.1$, based on both the HK-ISQV and CSQG. These results indicate that the concentrations of these chemicals in the sediments posed few

**Table 4.6** Estimated RQs based on the concentrations of PAH contaminants measured in the sediment samples of Sundarban mangrove wetland (SMW) using the HK-ISQV and CSQG

| | | HK-ISQVs (ng g$^{-1}$) | | CSQG (ng g$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|
| Pollutants | SMW | Lower limit | Upper limit | Thresh-old | Probable | 0.01 < RQwcs <0.1 | 0.1 < RQ wcs < 1 |
| Phe | 8–379 | 240 | 1,500 | 86.7 | 86.7 | | ○● |
| Ant | 0–64 | 85.3 | 1,100 | 46.9 | 46.9 | | ○● |
| Flu | 4–391 | 600 | 5,100 | 113 | 113 | | ○● |
| Pyr | 8–299 | 665 | 2,600 | 153 | 153 | ○ | ● |
| Chry | 3–288 | 384 | 2,800 | 108 | 108 | | ○● |
| B[a]P | 2–213 | 430 | 1,600 | 88.8 | 88.8 | ○ | ● |
| ΣPAH | 132–2,938 | 4,022 | 44,792 | / | / | | ○● |

*Note*: Only worst-case RQs (RQwcs) are shown. All best-case RQs were <0.1. RQs were calculated based mainly on two sediment quality criteria (*open circle* = HK-ISQV; *filled circle* = CSQG). ERL and ERM guideline values from the NOAA [(http://response.restoration.noaa.gov/cpr/sediment/squirt/squirt.html);59] were used because the corresponding HK-ISQVs were not available

risks to the local aquatic system. Other contaminants, such as anthracene, fluoranthene, chrysene, and total PAHs, had RQwcs < 1 only for one of the sediment quality criteria (Table 4.6).

It is noteworthy that the CSQG is, in general, more stringent that the HK-ISQV. The question here is which criteria should be adopted in India or, more specifically, in the Sundarban wetland. Indeed, it might be more desirable to derive system-specific criteria for the region. In the absence of criteria specific to the PAH contamination in the Indian Sundarban wetland, the approach adopted in this study involved using both the CSQG and HK-ISQV to assess risks under the best- and worst-case scenarios. This type of preliminary assessment provides a simple and useful means of screening pollutants of concern and assists in prioritizing management efforts.

### *4.3.7 Assessment of Sediment Toxicity Based on the Total Concentrations of PAHs*

Benzo[a]pyrene is the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor among all known potentially carcinogenic PAHs (Peters et al. 1999). The toxic equivalency factors (TEQ$^{\text{carc}}{}_{\text{S}}$) were used to quantify the carcinogenicity of other PAHs relative to benzo[a]pyrene and to estimate benzo[a]pyrene-equivalent doses [BaP$_{\text{eq}}$ dose]. Nadal et al. (2004) calculated toxic equivalent factors (TEFs) forbenz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, dibenz[a,h] anthracene, and chrysene are 0.1, 1, 0.1, 0.1, 0.1, 1, and 0.001, respectively (USEPA 1993).

In this study, we converted the above-mentioned seven PAH concentrations into the corresponding total toxic benzo[a]pyrene equivalents (TEQ$^{\text{carc)}}$ for each site as follows: TEQ$^{\text{carc}}{}_{\text{S}}$ = ($C_{\text{i}}$ 9 TEF$^{\text{carc}}$), where $C_{\text{i}}$ is the concentration of the PAH (in ng $g^{-1}$). Total $TEQs^{carc}$ values calculated for all the samples varied from 6.95 ng $g^{-1}$ $TEQ^{carc}{}_{S}$ to 119 ng $g^{-1}TEQ^{carc}{}_{S}$, with an average of 59 ng $g^{-1}$ dry weight $TEQ^{carc}{}_{S}$. The maximum total $TEQ^{carc}{}_{S}$ value was recorded at the Lothian site. These values were lower than those of other literature-reported sites, such as surface sediments of Meiliang Bay, China (Qiao et al. 2005), Ariake Sea, Japan (Nakata et al. 2003), Northwest Mediterranean sediments (Catalonia, Spain) (Eljarrat et al. 2001), and coastal lagoons in central Vietnam (Giuliani et al. 2008).

## 4.4 Conclusion

The data provide a baseline characterization of the spatial distribution and potential sources of PAHs in sediment cores of the Sundarban wetland, which would be helpful in its effective management. Relative to other urbanized coastal areas worldwide, the prevalent PAH content of the Sundarban sediments can be considered low to moderately contaminated, resulting from the impact of the rapid economic development of the surrounding regions for the last two decades. The pooled mean values of PAHs ranged from 264 to 1421 ng $g^{-1}$ dry weight. Sediment containing high organic carbon content might favor accumulation of PAHs. Spatial variations and variations within the core are very much pronounced, which are directly related to automobile exhaust emission, combustion of coal and wood, transport, and intensive fishing by mechanized boats.

From an ecotoxicological point of view, the study sites appear to be moderately polluted by two triaromatic compounds (fluorene and phenanthrene). The PAH diagnostic ratios indicated that the PAHs in the sediment cores were mainly of pyrolytic origin, mainly transported by surface runoffs. The data provide background information that should be useful in designing future strategies for environmental protection of the wetland, with special focus on the area at Lothian Island.

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# Chapter 5
# Accumulation of Micropollutants in Representative Biota of Sundarban Wetland

## 5.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are non-iconic hydrophobic contaminants ubiquitously present in coastal areas that arise from numerous anthropogenic activities. This type of compounds has been widely studied (Neff 1979; McElory et al. 1989) due to its carcinogenic and mutagenic properties (Lehr and Jerima 1977; Yan 1985; White 1986). Organisms have been used as bioindicators of chemical contaminants such as PAHs, since due to the hydrophobicity of such pollutants, they are found at higher concentrations than those in the water column. For instance, the Mussel Watch project in the USA and the OSPAR in Europe have been developed using mussels and oysters to monitor spatial and temporal trends of contaminant concentrations in coastal and estuarine regions (Farrington et al. 1983; Claisse et al. 1992; O'Connor 1996; Besada et al. 2002; Webster et al. 2006).

The interest in using organisms to monitor pollution arose from the fact that some bivalve molluscs might accumulate and "record" the contaminants present in water column and/or in sediments, whereas the contaminants in the water column may not be recorded in the sediments. Besides, analysis of bivalve tissues gives an indication of the bioavailable fraction of environmental contamination and of direct exposure to chemicals. The characteristics of the sedimentary environment where organisms live in and parameters specific to the organisms (their feeding behavior and their habitat) can influence sediment-adsorbed contaminant bioavailability. The organisms in close contact with the sediment phase (deposit-feeding bivalves, burrowing organisms, organisms living in high water turbidity zones) accumulate PAHs to a great extent (Lake et al. 1990; Hickey et al. 1995). Mussels, which accumulate contaminants from the surrounding seawater, are also resistant to a wide range of contaminants and are most commonly used as sentinel organisms (Cossa 1989; Varanasi et al. 1989; O'Connor 1996; Baumard et al. 1998, 1999). Moreover, persistent organic pollutants (POPs) have a lipophilic nature, and the highest lipid content in bivalves may have accounted for the highest levels of POPs in their tissues compared

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to other organism of less lipid values (Wei et al. 2006). By virtue of their wide geographic distribution, sufficiently long-lived and of a reasonable size, marine bivalves molluscs have been used as essential organisms in many countries for marine pollution monitoring, e.g., in "Mussel Watch Programmes," since the late 1970s. Hence, the present investigation especially concentrates on bioaccumulation of POPs by this specific macrozoobenthos considering the following bivalve species: *Sanguinolaria acuminata* (clam) (Family Psammobiidae), *Meretrix meretrix* (clam) (Family Veneridae), and *Macoma birmanica* (mussel) (Family Tellinidae).

Sediment properties marked by high organic carbon content are known to reduce the bioavailability of hydrophobic organic compounds (Knezovich et al. 1987). Grain-size variations in sediments which act as a parameter for pollutant concentrations should be taken into account. The hydrophobic compound distribution varies with different grain-size fractions, where the high-molecular-weight PAHs tend to concentrate in the finest fractions (Prahl and Carpenter 1983; Readman et al. 1984; Raoux and Garrigues 1991). Bivalves can filter and adsorb the smallest particles and are not active in all the sediment fractions. Recent studies on the pollution status of the Sundarban delta have revealed the presence of high concentrations of heavy metals (Zn and Cu) (Chatterjee et al. 2007), as well as POPs such as organochlorine pesticides, polychlorinated biphenyls (PCBs), PAHs, and polybrominated diphenyl ethers (PBDEs) in sediments (Guzzella et al. 2005; Binelli et al. 2007, 2008). This environmental scenario has stimulated the idea of undertaking a collaborative research on the occurrence of PAHs in the three intertidal bivalves with the following objectives: (a) determining PAH distributions, trends, and their possible sources in Sundarban wetland, by using these macrobenthos as a function of biological characteristics (diet, trophic level, etc.); (b) evaluating the effectiveness of the bivalve species as biomonitors by selecting sampling sites bearing different source materials; (c) understanding PAH distribution patterns in individual bivalve tissues; and (d) evaluating ecotoxicological risk of the bivalves to the biota of higher trophic levels. These species are the major macrozoobenthos of the coastal region, widely distributed along the eastern and western part of Sundarban, tolerant to a wide range of temperature and salinity, and readily distinguishable from other species. All these characteristics enhance their value as index species for biomonitoring. To the best of our knowledge, this is the first report on the detailed characterization of PAH contamination in intertidal bivalves in this tropical coastal Indian environments.

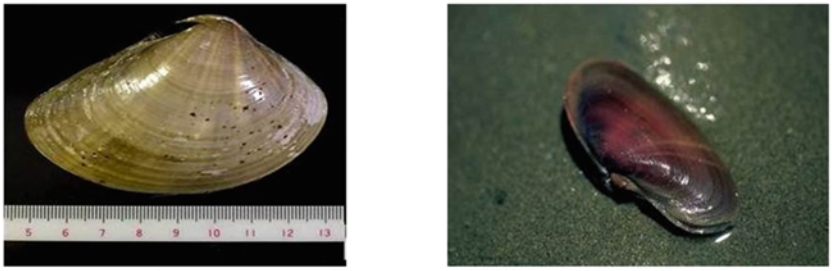
## 5.2 Methodology

### *5.2.1 Study Sites, Sample Collection, and Preservation*

During January–February 2006, the bivalve molluscs were sampled manually at low tide level from the intertidal estuarine mudflats of three different study sites in Sundarban mangrove wetland, namely, Canning, Chemagari, and Gangasagar (as shown in Fig. 1.1) under typical tropical mesomacrotidal setting. The sampling sites belong to the northern and southern extremities of Sundarban and can be differentiated from each other in terms of river discharge, erosion, flocculation, and atmospheric deposition. They have diverse human interferences with a variable degree of heavy metals and trace organic contamination. The details of the geomorphological setup of these sampling stations have already been described in the previous publications (Sarkar et al. 2008; Chatterjee et al. 2009).

Three representative bivalve species were chosen as they provided different exposure levels of contaminant uptake: *M. meritrix* (of two different size groups, small, 3.54–6.28 cm length and large, 5.2–7.28 cm) from Canning is a deposit feeder, and the other two bivalves (*M. birmanica* collected from Chemagari and *S. acuminata* of Family Psammobidae from Gangasagar) are suspension-filter feeders. Representative of the bivalve species from Sundarban intertidal regions has been shown in Fig. 5.1. The sampling stations were chosen so that the samples collected had various types of contaminant sources. The bivalve species range from 3.54 to 7.28 cm length and 6.28 to 18.41 g weight. All analyses were carried out on composite samples of 25 specimens of a similar size group (except for *M. meretrix* for which two size groups were sampled) to reduce possible variations in PAH concentrations due to size and age (NAS 1980).

The specimens were transported to the laboratory in acid-washed plastic containers (Moody and Lindstrom 1977). The bivalves were promptly cleaned of incrustations, washed in distilled water, and they depurated to avoid measurement variations of the total organic contaminants in the tissues, as endorsed by Wallner-Kersanach et al. (1994) for heavy metals in biota. Twenty-five species of each bivalve were weighed, measured



**_Meretrix meretrix_ : Family Veneridae** **_Sanguinolaria acuminata_ : Family Psammobiidae**

**_Pelecyora trigona_ : Family Veneridae** **_Anadara granosa_ : Family Arcidae**

**Fig. 5.1** Representative of Bivalve molluscs inhabiting in the mudflat of Sundarban mangrove wetland (shell length in terms of the longest shell dimension by Vernier Calipers), and dissected into five tissue fractions, i.e., visceral mass (stomach, digestive diverticula, intestine, rectum, and heart), mantle, gill, adductor muscle, and podium with stainless steel instruments taking necessary measures in order to avoid contamination of the tissue samples. These tissues were thoroughly washed with deionized water. Shells were also washed in a jet of distilled water, individually treated with 50% (w/v) hydrogen peroxide in the ratio of 1 $cm^3$ $g^{-1}$ shell weight and were gently heated at 60 °C. The tissue samples were thawed, macerated, weighed, and dried at 70 °C for 48 h in a hot air oven before digestion (Fourie and Peisach 1977).

Simultaneously, sediment samples of the adjacent habitats were collected with the help of a stainless steel spade, stored in polyethylene bags, and transported to the laboratory. Samples were oven-dried at 50 °C and were divided into two parts: one for physicochemical analysis and the other for PAH analysis.

### 5.2.2 Analytical Methods

The organic carbon ($C_{org}$) content of the soil was determined following a rapid titration method (Walkey and Black 1934) and the pH by means of a deluxe pH meter (model no. 101E). Mechanical analysis of sediment was done by sieving in a Ro-Tap shaker (Krumbein and Pettijohn 1938), and statistical computation of textural parameters was calculated by using the formulae of Folk and Ward (1957).

The analyses of PAHs in sediments and biota were performed as optimized elsewhere (Bartolomé et al. 2005; Navarro et al. 2006). Briefly, ~1.0 g of dry sediment or ~2.0 g of dry biota sample was weighed and submitted to microwave-assisted extraction in 15 mL of acetone at 21 psi for 15 min and at 80% of microwave power in a MDS-2000 microwave (CEM, Matthews, NC, USA), after 25 μL of a mixture of acenaphthene-$d_{10}$, chrysene-$d_{12}$, and phenanthrene-$d_{10}$ at 20 μg $mL^{-1}$ in acetone was added as surrogates. The extract was concentrated under a gentle stream of nitrogen and loaded onto a 1-g (sediments) or 5-g (biota) Florisil® cartridge (Supelco, Walton-on-Thames, UK) for further cleanup of the extract. PAHs were eluted in a (4:1) *n*-hexane/toluene mixture. The elutes were concentrated to dryness redissolved in 500 μL of isooctane and kept in the dark at −18 °C until analysis. The extracts were analyzed in a 6890N Agilent gas chromatograph coupled to a 5973N Agilent mass spectrometer (Agilent Technologies, Avondale, PA, USA) with a 7683 Agilent autosampler. Two microliters of sample were injected in the splitless mode at 270 °C into a (30 m × 0.25 mm, 0.25 μm) HP-5 capillary column (Agilent Technologies Inc., Palo Alto, CA, USA). The method summarized above was validated in the laboratories using the certified reference materials NIST 1944 (marine sediment) and NIST 2977 (mussel tissue; Gaithersburg, MD, USA). The results obtained were within the uncertainties of the reference values. Blank samples were processed together with samples, and Limits of Detection (LODs) were estimated as the average signal of the blanks plus three times the standard deviation of the signal of the blanks. LODs in the 0.07–19.8 and 0.23–25.5 ng $g^{-1}$ were obtained for sediment and biota, respectively. Deuterated analogues were used for both recovery and quantification corrections. Recoveries were higher than 50 % in all the cases, except for naphthalene which showed lower recoveries in some samples (>25 %). The analysis of the samples was repeated in triplicate, and relative standard deviations were within 1–20 % in all the cases.

## 5.3 Results and Discussion

### *5.3.1 Sediment Geochemistry*

The sediment quality parameters at the three sampling stations (pH, organic carbon, and textural properties) are significantly different from each other, and these variations are reflected on the PAH levels in the sediments (Table 5.1), as well as in PAH accumulation pattern of individual bivalve species (Tables 5.2, 5.3, and 5.4). Values of pH ranged from slightly acidic to basic (6.8–8.2). The acidic nature is mainly observed in Canning, partly due to the oxidation of $FeS_2$ and FeS to $SO_4^{2-}$ and partly due to the decomposition of mangrove litter and hydrolysis of tannin in mangrove plants that release various types of organic acids (Liao 1990). Low organic carbon ($C_{org}$) values were recorded at all the three stations, with a minimum concentration at Gangasagar (0.12 %) and a maximum at Canning ($S_1$; 0.81 %), while Chemagari sediments showed a 0.36 % of organic carbon. The prevalent low $C_{org}$ values might be the result of sedimentation and mixing processes at the sediment–water interface where the rate of delivery, as well as the rates of degradation by microbial-mediated processes, can be high (Canuel and Martens 1993). Very low organic carbon values

**Table 5.1** Concentration of PAH congeners in sediments (expressed in ng $g^{-1}$ dry wt.) of the three station of Sundarban

| PAHs | Canning | Chemaguri | Gangasagar |
|---|---|---|---|
| NAP | 42.75 | 22.98 | 79.13 |
| Acy | 7.34 | 10.01 | 1.63 |
| Ace | 16.53 | 36.25 | 8.4 |
| Flu | 7.57 | 32.25 | 2.76 |
| Phe | 33.38 | 83.33 | 0.91 |
| Ant | 2.81 | 7.71 | 4.76 |
| Flr | 46.88 | 70.97 | 4.73 |
| Pyr | 44.09 | 59.84 | 7.33 |
| B[*a*]A | 14.74 | 14.1 | 1.58 |
| Chr | 16.2 | 18.89 | 2.16 |
| B[*b*]F | 10.27 | 8.18 | <LOD |
| B[*k*]F | 13.03 | 12.9 | <LOD |
| B[*a*]P | 10.8 | 8.14 | 1.48 |
| D[*ah*]A | 15.6 | 17.79 | 1.81 |
| B[*ghi*]P | 11.01 | 20.15 | 2.38 |
| Ind | 23.98 | 38.18 | 2.73 |
| ∑PAH | 316.98 | 533.67 | 121.79 |

**Table 5.2** Concentrations of PAH congeners in body tissues of the bivalve mollusk *M. meritrix* (expressed in ng $g^{-1}$ dry wt.) of two different size groups collected from the sampling site Canning of Sundarban

| | Organs of large-size group | | | | | | Organs of small-size groups | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PAHs | Shell | Gill | Mantle | Vis. mass | Podium | Ad. muscle | Shell | Gill | Mantle | Vis. mass | Podium | Ad. muscle |
| Nap[a] | <25.5 | 105 | 51.9 | 87.4 | 43.5 | 37.4 | <25.5 | 154 | 39.7 | 53.3 | 71.5 | 454 |
| Acy[b] | <2.1 | 5.5 | 2.2 | 9.9 | 2.7 | 2.5 | 4.1 | 8.7 | 2.5 | 7.1 | 3.8 | 7 |
| Ace[c] | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 |
| Flu[d] | <5.03 | 19.8 | 8.7 | 26.2 | 11 | 10.4 | <5.03 | 46.5 | 11.9 | 17.1 | 21 | 14.8 |
| Phe[e] | 9.5 | 46.3 | 36.2 | 88.8 | 32.6 | 31.9 | 14 | 203 | 60.1 | 78.38 | 88.2 | 43.1 |
| Ant[f] | 1.2 | 6.2 | 2.8 | 9.3 | 2.3 | 2.7 | 1.2 | 4.6 | 3.5 | 10.5 | 3 | 3 |
| Flr[g] | 4.7 | 37.5 | 27.3 | 10.1 | 34.3 | 31.4 | 7.4 | 83.3 | 58.9 | 132 | 53.5 | 27 |
| Pyr[h] | 8.1 | 34.8 | 22.4 | 85.2 | 17.9 | 26.4 | 7.7 | 68.9 | 25.7 | 52.1 | 86.2 | 26.3 |
| BaA[i] | <2.3 | 15.1 | 3.4 | 15.7 | 3.4 | <2.3 | <2.3 | 16.8 | 5.1 | 14.7 | 6.7 | 4.3 |
| Chr[j] | 4.6 | 34.2 | 14.2 | 37.4 | 14.4 | 10.3 | 4 | 9.2 | 18.3 | 37.2 | 4.8 | 8.5 |
| BbF[k] | 2.2 | 12.6 | 4.6 | 9.9 | 7.5 | <1.8 | <1.8 | 70.6 | 19.2 | 13.1 | <1.8 | <1.8 |
| Bkf[l] | <0.9 | 12.8 | <0.9 | 5.9 | 3.7 | <0.9 | <0.9 | 64.2 | 13.5 | 12.1 | <0.9 | <0.9 |
| BaP[m] | 1.7 | 9.4 | 3 | 7.3 | 3.3 | <1.4 | <1.4 | 18.2 | 7.2 | 12.4 | <1.4 | <1.4 |
| DahA[n] | 1.3 | 7.6 | 2.2 | 11.6 | 2.7 | 0.8 | 0.9 | 18.3 | 8.1 | 13.8 | 2.3 | <0.4 |
| BghiP[o] | 4.4 | 3.9 | 5.6 | 10.1 | 3.6 | 3.9 | 4 | <0.6 | 12.3 | 7.9 | <0.6 | <0.6 |
| Ind[p] | 5.7 | 19.4 | 7.5 | 35.8 | 9.3 | 3.7 | 3.9 | 51.9 | 20.3 | 43.2 | 12.4 | <0.9 |
| ΣPAHs | 43.3 | 370 | 192 | 541 | 192 | 161 | 47 | 818 | 306 | 204 | 253 | 588 |

**Table 5.3** Concentration of PAH congeners in *M. birmanica* (expressed in ng g$^{-1}$ dry wt.) collected from Chemagari Site, Sundarban

| PAHs (ng g$^{-1}$) | Shell | Gill | Mantle | Vis mass | Podium | Ad. muscle | Siphon |
|---|---|---|---|---|---|---|---|
| Nap | <25.5 | 117 | 40.8 | 89 | 43.1 | 93.3 | 93 |
| Acy | <2.1 | 2.3 | 1.3 | 6.5 | <2.1 | 4.3 | 3.8 |
| Ace | <12.8 | 13 | <12.8 | <12.8 | <12.8 | <12.8 | <12.8 |
| Flu | <5.03 | 9.2 | <5.03 | 29.7 | <5.03 | 5.2 | 9 |
| Phe | <5.9 | 44.2 | 16.7 | 148 | 14.7 | 9.8 | 22.7 |
| Ant | 0.8 | 6 | 1.4 | 15.6 | 2.06 | 1.2 | 3.4 |
| Flr | 2.8 | 72.5 | 25.4 | 13.6 | 20.9 | 14.12 | 31.4 |
| Pyr | 4.4 | 62.9 | 22.3 | 56.3 | 31.6 | 15.4 | 28.9 |
| BaA | <2.3 | 7.7 | <2.3 | 7 | <2.3 | <2.3 | <2.3 |
| Chr | 3.5 | 28.7 | 8.7 | 39 | 6.7 | 5.6 | 9 |
| BbF | 1 | <1.8 | <1.8 | 14 | <1.8 | <1.8 | <1.8 |
| BkF | <0.9 | <0.9 | <0.9 | 11.3 | <0.9 | <0.9 | <0.9 |
| BaP | <1.4 | <1.4 | <1.4 | 18.9 | <1.4 | <1.4 | <1.4 |
| DahA | 0.9 | <0.4 | 0.5 | 6.8 | 0.8 | 0.8 | 0.4 |
| BghiP | 4.1 | <0.6 | 2.3 | 11.43 | 3.9 | 3.8 | 1.8 |
| Ind | 3.9 | <0.9 | 2.2 | 19.1 | 3.8 | 3.7 | 1.8 |
| ΣPAHs | 21.4 | 363.5 | 121.53 | 608.81 | 127.45 | 157.42 | 204.97 |

**Table 5.4** Concentration of PAH congeners in *S. acuminata* (expressed in ng g$^{-1}$ dry wt.) collected from Gangasagar Site, Sundarban

| PAHs (ng g$^{-1}$) | Shell | Gill | Mantle | Vis mass | Podium | Ad. muscle | Siphon |
|---|---|---|---|---|---|---|---|
| Nap | <25.5 | 160 | 38.8 | 112 | 108 | 84.2 | 79.3 |
| Acy | 2 | 3.5 | 1.7 | 38.2 | 17 | 15.7 | 10.8 |
| Ace | <2.1 | <2.1 | <2.1 | 55.3 | <2.1 | 21.1 | <2.1 |
| Flu | <5.0 | 12.6 | 7.6 | 128 | 11.1 | 7.5 | 7.2 |
| Phe | <5.9 | <5.9 | 76.2 | 1051 | 95.5 | 25.7 | 52.2 |
| Ant | 0.8 | <0.4 | 12.4 | 203 | 18.2 | 3.1 | 9.3 |
| Flr | 5.6 | 174 | 139 | 1433 | 128 | 35 | 69 |
| Pyr | 7.9 | 156 | 115 | 1043 | 101 | 29.2 | 57.5 |
| BaA | <2.3 | 68.5 | 30.3 | 355 | 38.6 | 12.1 | 24.5 |
| Chr | 4.7 | 104 | 53.9 | 537 | 57.8 | 18.8 | 47.7 |
| BbF | 1 | 70.1 | 15.7 | 175 | 28 | <1.8 | 12.2 |
| BkF | <0.9 | 66.8 | 14.2 | 205 | 23.3 | <0.9 | 16.4 |
| BaP | <1.4 | 86 | 17.1 | 197 | 51.3 | <1.4 | 14.9 |
| DahA | 0.9 | 44.4 | 5 | 114 | <0.4 | 80.5 | 0.6 |
| BghiP | 4.2 | <0.6 | 6.1 | 46.1 | 0.7 | <0.6 | 2.9 |
| Ind | 4 | 86.7 | 20.5 | 227 | <0.9 | 139 | 2.8 |
| ΣPAHs | 31.12 | 1033.62 | 552.75 | 5919.2 | 678.37 | 471.89 | 407.51 |

in intertidal zone sediments in Sundarban were also recorded in previous works (Sarkar et al. 2004; Chatterjee et al. 2007) and are related with the poor adsorbability of organics on negatively charged quartz grains, which predominate in the siliciclastic sediments in this estuarine environment.

Regarding textural composition, the three stations also exhibit wide variations, silty at Canning, very fine clayey at Chemagari, and sandy at Gangasagar, which are related to vigorous estuarine mixing, suspension, resuspension, and flocculation processes. The sampling station Canning belongs to the upstream stretch of the moribund Matla River, where the recirculatory tidal currents play an important role in the depositional behavior of finer silty particles (89.79 %). At Chemagari site, the semidiurnal macrotidal situation helps the settling down of finer suspended particles with mud (clay 67.3 % and silt 24.2 %) as the major component. In contrast, Gangasagar, being situated at the sea face (Bay of Bengal), experiences high wave and tidal energy. The sediments deposited here indicate a typical beach environment with sand as the major component (98.57 %), facilitating the typical habitat for *S. acuminata*. The insignificant percentage of fine silt and clay that are mixed with the main muddy component from tidal suspension are generally washed out or cleaned by repeated swash backwash effects in this low-gradient beach face (Bhattacharya 1993).

### 5.3.2 Distribution of PAH Congeners in Sediments

Levels of the sum of the 16 USEPA PAHs in sediment at the 3 sampling stations from Sundarban ranged from 534 (in Chemagari) to 122 ng $g^{-1}$ (in Gangasagar). Canning and Chemagari, a dominance of the high-molecular-weight (HMW) PAHs was observed, accounting to 65.18 % and 78.91 %, respectively, while dominance of low-molecular-weight (LMW) PAHs was recorded in Gangasagar, mainly due to the elevated level of naphthalene (79.1 ng $g^{-1}$), accounting approximately 80.1 % of the total PAHs. The processes controlling the level of PAHs at the sediment are however complex. Among different factors, the chemical properties of the compound (especially their water solubility) and the sediment composition, notably the organic carbon and clay contents (Yang et al. 1998) are important. The low level of PAHs in Gangasagar might be related to low organic carbon content in the sediments as stated earlier. The present study indicates that the organic carbon content of sediment plays an important role in the control of the PAH level in the sediment (Yang 2000). Moreover, as mentioned earlier, the sediments at this site are predominated by sand which does not show a high adsorptive capacity (Zanardi et al. 1999) for PAH.

### 5.3.3 Variations of PAH Congener Residues in Bivalve Tissues

The individual tissue burden of total PAHs in the three bivalves from Sundarban wetland differs widely, ranging from 21.3 (in shell of *Macoma birmanica*) to 5919 ng $g^{-1}$ (in visceral mass of *S. acuminata*), which reveals that the organisms have a different selectivity for a range of PAH congeners. These variations might be ascribed to the following factors: (a) different degrees of bioavailability of the compounds, (b) variable capacities of the bivalves to metabolize them, and (c) biotransformation capacities of the organism (Kennish 1997). Moreover, fluctuation in PAH levels arise from non-homogenous inputs from point and nonpoint sources of these compounds that are related to the results observed. A preferential LMW and HMW PAHs were evident both in hard and soft tissues of *S. acuminata*, reaching their maximum values of 1588 and 4332 ng $g^{-1}$, the 26.8 % and 73.2 % of the total PAHs, respectively. In contrast, comparative low values were recorded in *M. meretrix* and *M. birmanica*, exhibiting an overall similar trend of distribution of PAHs in bivalves and sediments. Small variations of total PAHs in these two sites could be produced by different physiological conditions in the mussel population (Guinan et al. 2001).

In the case of bivalve mollusks exposed to both particulate and dissolved contaminants, mussels still preferentially accumulated the LMW compounds, but in the turbid area at Gangasagar, the HMW compounds (penta- and hexaaromatics) were accumulated to a moderately greater extent than the rest. The site experiences high turbidity (transparency value ~1–1.8 cm) throughout the year due to dual effects of wave swash and backwash from the open sea and tidal current of macrotidal amplitude. The other two stations, namely, Chemagari and Canning, located off the coast of Bay of Bengal, lie in succession towards more and more northeast and thus experience less turbidity, together with the influence of a meso- to microtidal amplitude and insignificant wave activity. As a result, the inhabiting *S. acuminata* is directly in contact with the sediment and, therefore, may have absorbed some particles from resuspended sediment, as well as the dissolved fraction of the PAHs (Baumard et al. 1999). In contrast, due to its location at the mouth of estuary, Gangasagar station lies in close vicinity to an international shipping line and in direct influence to pollution sources throughout the year. As a consequence, a high concentration of PAHs in *S. acuminata* is observed compared to the other two stations' bivalves sampled away from the point sources.

Concentration of individual PAH congeners in the organs of bivalves revealed a wide range of variations, as shown in Tables 5.2, 5.3, and 5.4. Interestingly, maximum values of all the 16 congeners (except for naphthalene) were recorded in *S. acuminata* inhabiting close to pollution sources (e.g., Baumard et al. 1999). The abundance of HMW PAHs in *S. acuminata* was also typically encountered in atmospheric particles and urban aerosols (Muel and Saguem 1985; Sicre et al. 1987), due to their low water solubility, low microbial degradation rate (Readman et al. 1982), and high particulate affinity, compared with LMW PAHs. However, it should be noted that naphthalene was the most abundant LMW PAH, followed by phenanthrene. The former showed a relatively high level in the soft tissues of all the bivalves (maximum value of 454 ng $g^{-1}$ in adductor muscle of *M. meretrix*), as well as in adjacent sediments, reaching a maximum value of 79.1 ng $g^{-1}$ at Gangasagar. This is in good agreement with the findings of Wu et al. (1999) who found that the abundance of naphthalene series accounted for ~10 % of the PAH in sediments of the northern part of the South China Sea. Venkatesan and Kaplan (1982) also found relatively high levels (10–20 ng $g^{-1}$) of naphthalene in the Beaufort Sea and Cook Inlet sediments and suggested that this compound was derived mainly from anthropogenic activities.

Fluoranthene was the most abundant compound in soft tissues of all the three bivalves and adjacent sediments, reaching a maximum value of 1433 ng $g^{-1}$ in visceral mass of *S. acuminata* and 71.0 ng $g^{-1}$ in sediments at Chemagari. A predominance of four-ring compounds in sediment has also been documented elsewhere (Foster and Wright 1988; Pruell et al. 1990; Pereira et al. 1996). Fluoranthene and pyrene fluctuated in three bivalves, with an over-enrichment in *S. acuminata* at the site Gangasagar. This may be explained by the mixing of marine and riverine sediments, together with additional inputs from various parts of the estuary. Readman et al. (1984) in Tamar estuary also found a secondary maximum of PAH concentration located off Plymouth, and this high concentration was supposed to be associated with urban discharge, including sewage outfalls, an oil jetty terminal, and the dockyard. Among the tri-aromatics, all the bivalves accumulated preferentially phenanthrene, the water-soluble compound, which reached a maximum value in visceral mass of *S. acuminata* (1051 ng $g^{-1}$), as well as in the adjacent sediments (83 ng $g^{-1}$) at Gangasagar.

Chrysene, an aromatic compound of natural origin, is the best-accumulated congener in all the tissues of the bivalves and reached a maximum value of 537 ng $g^{-1}$ in the visceral mass of *S. acuminata*. Chrysenes are more resistant to degradation than naphthalenes, dibenzothiophenes, phenanthrenes, and fluoranthenes (Wang et al. 1998) and bear higher $K_{ow}$s (octanol/water partitioning coefficients), which may favor bioaccumulation (Francioni et al. 2007).

In all the studied bivalves, especially in *M. meretrix* and *M. birmanica*, comparatively low bioaccumulation of five- to six-ring PAH was observed, which is supposed to be due to the following factors: (a) these heavy PAH are introduced principally via atmospheric deposition of soot particles, which are too small (10–100 nm) to be retained by filter feeders (Dame 1996) and have no nutritional value and (b) PAH from oil released directly in water may undergo partitioning into the abundant organic particulate matter of nutritional value present in the estuary (Rebello et al. 1998). Interestingly, small-sized *M. meretrix* exhibited supremacy over the large-sized group in PAH accumulation in both hard and soft tissues. This is difficult to explain due to lack of information on PAH accumulation in body tissues in bivalves as a function of size.

### 5.3.4 Variations of PAHs in Individual Organs

An overall trend of organ-specificity against accumulation of PAHs was observed (with a few exceptions). Maximum accumulation of PAH was obtained in visceral mass (1433 ng $g^{-1}$) followed by adductor muscle (454 ng $g^{-1}$), gill (203 ng $g^{-1}$), mantle (139 ng $g^{-1}$), podium (128 ng $g^{-1}$), siphon (93 ng $g^{-1}$), and shell (<25.5 ng $g^{-1}$). The important accumulation of PAHs in gill, mantle, and digestive glands could be related to the functions of these organs. Unfortunately, there is a complete lack of data pertaining to accumulation of PAH congeners in bivalve tissues, and hence, it becomes difficult for sound interpretation. However, elevated levels of heavy metals (Cu, Pb, and Zn) in gill and mantle were also recorded in marine bivalves (Sarkar et al. 2008), and this is mainly due to the presence of mucous layers covering these organs, facilitating rapid accumulation because of its ion-exchange properties and their close contact with the surrounding water, giving place to a greater and faster accumulation (Pringle et al. 1968). The digestive diverticula present in visceral mass is actively involved in the digestion and adsorption of food and excretion, which can justify the maximum value of the total PAHs in all the bivalves (except for small-sized *M. meretrix*, where gill showed a maximum value of 818 ng $g^{-1}$). These observations suggest that the food pathway predominate in the accumulation of PAHs for these intertidal organisms. It is worth mentioning that the digestive gland plays an important role in heavy metal metabolism and contributes to their detoxification (Viarengo 1989). The podium, siphon, and adductor muscle were found to be poor reflectors of PAHs in the environment (except for a sole case where adductor muscle of small-sized *M. meretrix* accumulated maximum values of naphthalene, 454 ng $g^{-1}$); these organs have no absorptive or secretary function, and lower levels of PAHs were recorded when compared to other tissues. Interestingly, an overall poor accumulation of the HMW PAHs was observed in the adductor muscle in all the bivalves.

Unlike the soft tissues, shell shows a very poor accumulation of PAHs, which was also observed by Sarkar et al. (2007) in the accumulation of heavy metals by the bivalves (*M. meretrix*, *S. acuminata*, *Anadara granosa*, and *Pelecyora trigona*) in Sundarban wetland. The observed variations might be associated with the periostracum, either adsorbed to or as structural compounds of this thin organic layer (Foster and Chacko 1995). From the present dataset, it is revealed that bivalve shells are of no practical use in the monitoring of PAHs as endorsed by Foster and Chacko (1995) and Brix and Lyngby (1985) using bivalve shells *Patella vulgata* and *Mytilus edulis*, respectively, for heavy metal contamination.

### 5.3.5 Mussel PAH Concentration in Relation to Adjacent Sediments

Bioaccumulation factors (BAF) for each compound (i.e., 16 BAFs) and for each site were determined: $\text{BAF} = C_{\text{PAH}}/C_{\text{sed}}$, where $C_{\text{PAH}}$ is the concentration of PAHs in the bivalve tissues, and $C_{\text{sed}}$ is the concentration of PAHs in the adjacent sediments. The highest concentration factor was recorded in the visceral mass (48.60), followed by the gill (8.49) in *S. acuminata*. Consistent higher values were also pronounced for all the organs of this species, certifying its ability to accumulate PAHs in several orders of magnitude higher than the background medium. Similar elevated levels of BAF were recorded in gills and other soft tissues for heavy metals in the bivalve *Pelecyora trigona* of coastal regions of Sundarban (Sarkar et al. 2007).

### 5.3.6 Identifying the Source of PAHs

With the development of environmental geochemistry, some criteria, such as phenanthrene/anthracene and fluoranthene/pyrene ratio values, have been used in order to distinguish between PAHs of various origins (Sicre et al. 1987; Budzinski et al. 1997). These criteria are based on peculiarities in PAH composition and distribution pattern as a function of the emission source. Phenanthrene is a thermodynamically more stable tricyclic aromatic isomer than anthracene. Hence, petroleum contains more phenanthrene relative to anthracene. Therefore, the PAHs of petrogenic input are generally characterized by high phenanthrene/anthracene ratios. On the contrary, high temperature processes such as incomplete combustion of fossil fuel can result in low phenanthrene/anthracene ratios (Phe/Ant < 15; Wise et al. 1988; Benner et al. 1989, 1990). For the fluoranthene/pyrene ratios, values greater than 1 are obviously related to pyrolytic origins, whereas values less than 1 are attributed to petrogenic source (Sicre et al. 1987). Results from the present study showed that phenanthrene/anthracene ratio is <10 for most of the bivalve organs, except for small-sized *M. meretrix*, where the ratio showed a value higher than 15 for 3 organs (gill, mantle, and podium), suggesting a petrogenic origin with over-imposition of pyrolytic PAH sources. Moreover, the ratios of chrysene/benzo(*a*)anthracene and fluoranthene/pyrene are found to be higher and lower than 1, respectively, which is indicative of a strong petrogenic origin.

In addition, PAH fingerprints in all the bivalves together with the adjacent sediments (except for Gangasagar, $S_3$) showed an overall predominance of HMW PAHs like chrysene, benzo(*b*)fluoranthene, benzo(*a*)pyrene, benzo(*g*,*h*,*i*)perylene, and indene (1,2,3-*cd*) pyrene and lower for LMW PAHs (acenapthene, fluorene, anthracene) as evidenced in Tables 5.1, 5.2, 5.3, and 5.4. The predominance of HMW PAHs both for bivalves and sediments can be taken as an evidence of the strong influence of petrogenic sources for the contaminants in Sundarban wetland. However, a reverse picture of pyrogenic origin in two sites of Sundarban wetland has been earmarked recently (Binelli et al. 2008).

For sediments, considering the diagnostic ratios as referred above, it is revealed that sources are of pyrolytic origin, except for the site of Gangasagar where the values of fluoranthene/pyrene (0.64) and LMW/HMW PAH (4.03) strongly suggest petrogenic origin. The percentage of LMW PAH at this site goes as high as 80 %, whereas at Canning and Chemagari, the same analytes contribute only 34.8 % and 21.1 %, respectively. The contamination of sediment at this site by crude oil is supported by the prevalent higher value of naphthalene (79.1 ng $g^{-1}$) of all the three stations and the highest concentration of the 16 congeners at this site. Naphthalene often constitutes a significant fraction of crude oils and petroleum products with lighter fractions and, hence, is used to detect PAH input from these sources (Sporstøl et al. 1983). Exhausts of the small boats, trawlers, and launches used extensively either in fishing activities or transportation are significant factors that can be coupled with the influence of frequent leakages of crude oil and petroleum products from the oil terminals situated in the upstream of the estuary.

### *5.3.7 Assessment of Sediment Quality Using Biological Thresholds*

The effects range low (ERL) and the effects range median (ERM) values were used for assessment of aquatic sediment with a ranking of low to high impact values (Long et al. 1995). The measured concentrations of PAHs were compared with the ERL and ERM values. Results showed that the total PAH concentrations at the three sites were below the ERL of 4000 ng $g^{-1}$. Among the 16 congeners, only acenaphthylene (at Canning and Chemagari) and fluorene (exclusively at Chemagari) exceeded the respective ERL values of 16 and 19 ng $g^{-1}$. These findings indicate that these two sites have some potential biological impact, but should have no impairment.

Although PAH concentrations that may cause adverse effects in marine organisms are still incipiently reported, elevated concentrations of HMW PAHs recorded in *S. acuminata* raised concern. Concentrations in *S. acuminata* are above 1000 ng $g^{-1}$ for phenanthere, fluoranthene, and pyrene, which may lead to abnormalities in fish embryos (Crals et al. 2002). The risks associated to mussel consumption by human are difficult to estimate since there are no general regulations for most PAHs. The European Commission Regulation 208/2005 proposed the limit of 10 ng $g^{-1}$ for benzo(*a*)pyrene in edible mussels. Concentrations above this limit were observed in *S. acuminata* (in majority of the organs), followed by *M. birmanica* (only in visceral mass) and *M. meretrix* (only in gill) of the small-size group. It is worthy to mention that *M. meretrix*, widely distributed in Asian countries including India, is famous for its delicious meat and has important commercial values (Baojun et al. 2005).

### 5.3.8 Comparative Account of PAH Accumulation in Bivalve Molluscs

Table 5.5 summarizes previous studies on the levels of PAHs in different bivalves collected from different coastal regions of the world. However, the comparative account, to some extent, does not fully justify anything, since the PAH congeners differ in different cases, and the food and feeding habits of the bivalves also vary in different regions. Moreover, there is a complete lack of data on the accumulation of PAHs in individual organs of marine bivalves. Still, it is important to evaluate the quantitative patterns of PAH contamination to get a sense of regional similarity. The levels of PAHs detected in our study are comparable to those reported in bivalves from Pearl River Estuary (Wei et al. 2006), but lower than those reported in mussel in Guanabara Bay, Brazil (Francioni et al. 2005). The observed concentrations of total PAHs in bivalves are low in comparison with concentrations reported in the literature for contaminated sites (Baumard et al. 1998, 1999). It is, therefore, likely that differences in PAH concentrations observed between bivalves species are a result of differences in the conditions of the bivalve populations at each site rather

**Table 5.5** Summary of PAH concentration levels (ng $g^{-1}$ dry wt.) detected in bivalve mollusc from different parts of the world

| Locations and year | Range of PAH in ng $g^{-1}$ | References |
|---|---|---|
| East Coast, China, 2001 | 456.8–3496.0 in mussel | Fung et al. (2004) |
| Pearl River Estuary, China, 2003 | 27.8–1041.0 in shellfish | Wei et al. (2006) |
| Northern Irish Sea-Loughs, Ireland | 95–184 in mussel | Guinan et al. (2001) |
| Guanabara Bay, Brazil | 60–6000 in mussel | Francioni et al. (2007) |
| Mediterranean Sea | 25–337 in mussel | Baumard et al. (1998) |

than an indication of the contamination status. The three stations are different in terms of productivity. At the time of sampling, it is possible that variations in the concentrations of PAHs in the bivalves might be related to the different stages in their life cycle as observed elsewhere (Jacob et al. 1997; Law et al. 1999).

## 5.4 Conclusions and Recommendations

The nature, distribution, and origin of the 16 USEPA polycyclic aromatic hydrocarbons (PAHs) were analyzed in 3 representative bivalve mollusk species together with their host sediments in Indian Sundarban wetland. The PAH group profile in various organs of these bivalves substantiates an unprecedented predominance of HMW over LMW PAHs, whereas a reverse trend is encountered in sediments. A similar trend of PAH contamination in sediments due to pyrogenic sources was also previously endorsed by Binelli et al. (2008) in the same wetland. Variations in total PAHs in bivalves among the sites suggest that differences in prevalent concentration could be caused by different physiological conditions and feeding habits in the bivalve population along with the textural composition of sediments. The amount of carcinogenic compounds (benzo(*a*)phenanthrene, benzo(*k*)fluoranthene, benzo(*a*) anthracene) seems to dominate in visceral mass and gill of *Sanguinolaria acuminata* in Gangasagar site, and thus, it could be efficiently used as bioindicator of PAH contamination. The prevalent level of these PAHs draws immediate attention, as these are hazardous to health of many organisms feeding on them, especially shore birds. The year-round availability of this multicolored species together with its easy handling, ample biomass for chemical testing and unique bioaccumulation potential provided sound reasoning for its use as bioindicator species.

It is worthwhile to mention here that the coastal region of West Bengal has undergone rapid changes over the last two decades, and it is expected that further changes in population and industrial as well as agricultural activity will occur. For the protection of human health and wild lives, analysis of substantial number of more edible molluscan species including finfishes should be taken into consideration. The most significant observations which connote an urgent need for attention that organochlorine pesticide residues were also present in human blood (Subramaniam and Solomon 2006), mother's milk (Someya et al. 2010), and blubber of endangered gangetic dolphin (*Platanista gangetica gangetica*) (Tanabe et al. 1993) in various parts of India.

Keeping in view of the present grave scenario, authors strongly recommend to implement the following programme:

(a) A multidisciplinary integrated approach involving toxicology, epidemiology, physiology, and behavioral sciences to assess the hazards and plan the preventive strategies need to be developed.
(b) Strict implementation of various legislation, standards, and code of conducts for regulation of manufacturing, distribution, handling, and application of pesticides. New legislation for the banning of illegal use of POPs should be introduced and education of the public implementation of such measures

(c) An extensive awareness scheme for safe use of pesticides through all possible forms of media, i.e., radio, television, newspapers. The government and other allied agencies should educate farmers and agriculture managers on best management practices (BMP) as well as integrated pest management (IPM) for sustainable use of pesticide in agriculture.
(d) Establish a reliable monitoring programme for POPs including organochlorines, so that any mass fractions exceeding environmental quality standards can be detected for taking appropriate remedial action.

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