BLACK CARBON AND ORGANOCHLORINES IN COASTAL SEDIMENTS FROM PAKISTAN: LEVELS, SOURCES, RELATIONSHIP AND MASS INVENTORY

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Master of Philosophy

In

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APPROVAL CERTIFICATE

This is to certify that the dissertation entitled **"Black Carbon and Organochlorines in Coastal Sediments from Pakistan: Levels, Sources, Relationship and Mass Inventory"** submitted by **Usman Ali** is accepted in its present form by the Department of Environmental Sciences, Quaid-i-Azam University Islamabad, Pakistan, as satisfying the dissertation requirement for the degree of M. Phil in **Ecotoxicology**.

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ACKNOWLEDGEMENT

Table of Contents

List of Tables

List of Figures

List of Appendices

List of Abbreviations

Abbreviation	Word
POPs	Persistent Organic Pollutants
OCs	Organochlorines
OCPs	Organochlorine Pesticides
PCBs	Polychlorinated Biphenyls
BC	Black Carbon
TOC	Total Organic Carbon
I	Mass Inventory
D	Deposition Flux
SQGs	Sediment Quality Guidelines
ERL	Effect Range Low Value
ERM	Effect Range Medium Value
TEL	Threshold Effects Level
PEL	Probable Effects Level

Abstract

Black carbon (BC) is considered as carbonaceous geosorbent which may play a major role in the fate and distribution of organic pollutants. Levels of total organic carbon (TOC) and black carbon (BC) were determined together with those of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the selected coastal sites along the Arabian Sea from Pakistan. The results showed that the total concentration of TOC, BC, $\sum$OCPs and $\sum_{26}$PCBs were ranged between 0.3–2.9 % dw, 0.06–0.25 % dw, 0.9–107 ng g^{-1} dw and 6.2–1206 ng g^{-1} dw, respectively. Pearson Correlation Analysis revealed stronger association of BC (r=0.26–0.89) with OCPs and PCBs instead of TOC (r=0.06–0.69). Moreover, regression analysis showed that BC is a better descriptor of sedimentary concentrations of $\sum$HCHs (57 %), $\sum$DDTs (70 %), heptachlor (64 %), HCB (78 %), tri-CBs (70 %), tetra-CBs (81 %), penta-CBs (79 %), hexa-CBs (69 %) and hepta-CBs (61 %) while TOC did not show any role in describing organochlorine contaminants in the study area. Black carbon burial fluxes (F$_{burial}$) were found in the range of 183–766 µg cm^{-2}yr^{-1}. The sediment deposition fluxes (D) for $\sum$OCPs and $\sum_{26}$PCBs were 1.7 and 4.9 t yr^{-1}. While the sediment mass inventories (I) indicated the presence of 13.1 and 37 metric tons of $\sum$OCPs and $\sum_{26}$PCBs, respectively in the coastal belt of Pakistan. Risk assessment using internationally established sediment quality guidelines indicated significant ecotoxicological risks of organochlorines for coastal area of Pakistan.

Keywords: Organochlorines, black carbon, distribution status, mass inventories, coastal sediments, Pakistan

INTRODUCTION

1.1.   Preliminary Remarks

Organochlorines (OCs) including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are hydrophobic and ubiquitous group of persistent organic pollutants (POPs) and are still being used in developing countries due to their low cost and versatility [1-3]. Their unique properties make them persistent in the environment, where they can exert chronic and toxic effects on humans and wildlife [4, 5]. Yet, these toxic pollutants have been used globally for agricultural and industrial purposes from several decades [6].

Sediments are usually considered to be the ultimate sink for POPs and are considered as one of the best media for their long term monitoring. Investigation of OCPs and PCBs in coastal sediments therefore provides important baseline data for assessment of persistent organic pollutants [7]. Significant amount of these toxic contaminants accumulate in the coastal sediments due to their hydrophobicity, low water solubility and sorption to particulate matter [8]. Several factors are involved in affecting the occurrence of these contaminants in the coastal sediments including composition of sediments, chemical properties, partitioning processes and pattern of deposition of contaminants in the sediments [9]. Sorption is one of the important key phenomena that affects the behavior and fate of contaminants in the sediments. Amorphous organic matter, exhibiting gel like matrix, relatively homogenous and lipophilic [10] is one of the responsible agents for the absorption of contaminants in sediments. Another form of organic matter of glassy and condensed type, generally termed as carbonaceous geosorbents (CG), is involved in the adsorption of hydrophobic contaminants [11]. In particular, black carbon (BC) is an important type of CG involved in affecting the overall behavior of OCs in sediments, partially due to its porous nature [12]. Understanding the relationship between BC and OCs in sediments is essential for determining the fate and behavior of OCs in coastal environments.

BC influences the retention of contaminants in sediments and associated health risks of these compounds [13, 14]. Primarily, BC deposits near the source of emission but it can travel hundreds to thousands of kilometers in the atmosphere reaching even remote sites. In sediments, their residence time could reach up to several millions of years [15]. Organic pollutants strongly bind to BC particles through the occlusion into the carbon condensed structure, conditioning their transport to that of BC particles and limiting their bioavailability [13, 16-18].

Coastal areas of Pakistan are highly exposed to industrial and anthropogenic activities. In these coasts, discharge of domestic and untreated industrial effluent into shallow seawater is a common practice. Pakistan coastal belt (approximately 1000 km) stretches from southeast (Run of Kuch) near the Indian border to northwest (Gwadar) near the Iranian border along the Arabian Sea. The whole area is administratively divided into the Balochistan and Sindh coastal belts. Both belts lie in the tropical region and show varying shelf geometry and slope due to interplay of tectonics of different magnitudes [19]. Sedimentation in the area is active owed to long shore currents of varying intensity and wave actions that cause variable erosion of rocks and sediments [19]. It is generally noted that the Sindh belt is more polluted than Balochistan due to the diverse range of industrial and anthropogenic activities developed in the former [19].

Two main rivers, Malir and Lyari contribute with sedimentary loads from river Indus to the Arabian Sea. These are thus the main sources of sediment pollutants attributed to upstream and industrial wastes to shelf regions. Malir River receives a huge amount of industrial waste from Korangi Industrial Trading Estate (KITE), in addition to sewage and domestic wastes at various places from north south to southwest in the eastern part of Karachi city. Tanneries, textile, detergents, paints, dyes, pharmaceuticals, plastics, metallurgy, oil, food and beverages, lubricants, cement and auto-engineering works are the main industries that contribute to the pollution load from Karachi city to Arabian Sea [20, 21]. Lyari River receives high industrial waste load from the Sindh Industrial Trading Estate (SITE), besides urban wastes of cities such as domestic waste eventually pouring into the Arabian Sea. In

addition to riverine discharge, diffuse contamination from the widespread use of agricultural and industrial activities contributes to the deposition and accumulation of organic pollutants in the coastal sediments.

1.2.   Literature Overview

1.2.1. Historical background and legislation of POPs in Pakistan

In Pakistan, the use of persistent pesticides has decreased gradually and significantly over the years [22, 23]. Pesticides have been used in Pakistan since 1954 with the import of 250 metric tons [24]. The overall pesticide consumption in the country reached from seven thousand tons per annum in 1960 to seventy eight thousand one hundred and thirty two tons per annum in 2003 [22, 23, 25]. Khan, et al. [26] reported that a 100 times increase in pesticide use has been observed in Pakistan during 1980-2002. In the green revolution period (late 1960s and early 1970s), pesticides in thousands of tones were imported from USA and European countries for locust control, malaria eradication and for handling crop pest infestation in Pakistan [27].

Pesticide ordinance and rules were implemented in 1971 and 1973 respectively [27] but even after the adoption of these legislations, there existed no strategy for outdated pesticides and banned stockpiles in government custody. These include DDTs which was banned in 1994 but still found in chemical warehouses along with other obsolete persistent pesticides [28]. In this way, Pakistan contained obsolete pesticides stock piles as one of the world's largest stock piles. It is also reported that Pakistan has a stock of estimated above 5000 tons of expired pesticides and in different provinces outdated pesticides are quantified to be 2,016 tones in Sindh, 3,805 tons in Punjab, 128 tons in Balochistan and 179 tons in KPK [29].

The regulations and rules in Pakistan regarding pesticides manufacturing, import, sale and monitored were first established by the Agricultural Pesticide Ordinance, 1971 and Agriculture Pesticide Rules, 1973 under the guidelines of FAO. Later on the ordinance was amended in favor of importers because Pakistan is heavily relay on imported pesticides. The ordinance also provide registration scheme for

pesticides but the procedure of registration was complicated and time consuming in Pakistan. In 1999, Pakistan signed the Rotterdam Convention and became the 67th member country of this convention at United Nations in New York. The aim of this Convention was to share the chemicals and pesticides trade information following international rules and regulations [30]. Pakistan also ratified the Stockholm Convention and being the party of the Convention since July, 2000. Apart from environmental legislation on POPs in the country, yet there is a huge gap between legislation and implementation. Although environmentally harmful persistent pesticides are banned in the country but still available in the market including DDT, aldrin and dieldrin [31]. It is also reported by Baloch [32] that some banned persistent pesticides are available in the market, despite the fact that these are officially banned in the country. Malik [33] and Bhambhro [34] also reported lack of coordination among regulatory bodies and the poor implementation of Agricultural Pesticide Ordinance, 1971. In this scenario, both government regulatory bodies and private sector should take initiatives for proper implementation of environmental legislation regarding POPs in the country.

1.2.2. Organochlorines (OCs) in sediments

Sediments is an environmental matrix which is considered as the ultimate sink for POPs [35] and is considered as the best media for contaminants long term monitoring [36]. Sediments are mainly comprised of organic, inorganic particles and detritus which are relatively heterogeneous in terms of biological, physical and chemical characteristics [35]. The applied POPs make their way to sediments through surface runoff, leaching, vapor phase and ultimately accumulation and settling in sediments [37] for a long period of time due to their long half-life [38]. Glaciers are one of the major sources of POPs as they transport huge amounts of rock debris and sediments in their load [39]. During the water runoff from glaciers, high amount of sediments moves in plains and rivers. These sediments contain some POPs in high concentration as compared to water based on hydrophobic properties of POPs i-e, the level of HCH concentration was fairly low in water when contrast to sediments [37]. According to Sujatha, et al. [40] the transport of OCs from nonpoint or point sources

to the aquatic environment and sediments is strongly regulated by leaching, precipitation, surface erosion, solubilization, volatilization, sorption, complication and most importantly, the water-solubility. It is a general phenomenon that if any persistent organic compound is more water soluble then it has greater mobility towards long routs in sediments.

Attention has widely been made for organochlorines (OCPs and PCBs) assessment in coastal regions around the globe. At 34 sites from coastal Lake Qarun, Egypt, the concentration, sources, distribution and risk assessment of OCPs and PCBs were determined by Barakat, et al. [6]. Both OCPs and PCBs were widely found in sediments with concentrations ranges between 1.01 to 164.8 ng g^{-1} for 25 OCPs and 1.48 to 137.2 ng g^{-1} for 29 PCBs. The largest Egyptian coastal lake (Manzala Lake) was also found contaminated with OCPs and PCBs. The range for OCPs and PCBs were found to be 0.63-31.31 ng g^{-1} and 0.26-31.27 ng g^{-1} respectively [41]. Higher levels of OCs were geographically determined in areas influenced by municipal discharge. The contamination levels were found similar or lower in comparison with other regions of the world. A study by Kucuksezgin and Tolga Gonul [8] indicated contamination of OCPs and PCBs in Eastern Aegean coastal sediments. The total concentration for OCPs and PCBs ranged between BDL-17.8 and BDL-26.1 ng g^{-1} respectively. Izmir Inner Bay was found most contaminated than other sites under study. The established sediment quality guidelines indicated that heptachlor, PCBs and DDTs were concerned contaminants for ecotoxicological risk in Eastern Aegean. El Nemr, et al. [42] reported PCBs, HCHs and DDTs at 17 sites along Red Sea in a range from 0.40 to 6.17, 0.01 to 0.09 and n.d. to 0.46 ng g^{-1} respectively. The levels of 10 PCBs and 20 OCPs were investigated by El Nemr, et al. [43] along Egyptian Mediterranean coast. The levels of PCBs, HCHs, DDTs were ranged between 0.31-1.95, 0.09-3.31, 0.08-3.31 ng g^{-1} dy weight respectively. Pazi, et al. [7] studied OCPs and PCBs in surface sediments of Candarli Gulf and the concentration ranged between 10.2-57.3 ng g^{-1} and 2.8-205 ng g^{-1} respectively.

Among South Asian region, OCPs residues from sediments of the Bay of Bengal (India) were monitored by Sarkar and Sen Gupta [44]. Aldrin was recorded in highest

concentration (μg/g) range of 20-530 followed by γ-HCH (10-210), dieldrin (50-510) and DDTs (20-790). Agricultural runoff from several rivers along the east coast of India mainly including Hugli, Mahanadi, Godavari, Krishna, Vamsodhara, Palar and Pennar were the main sources of POPs in the Bay. Concentration (0.04 to 4.79 ng g^{-1}) reported by Rajendran, et al. [45] is 670×10^{3} times lesser than reported by Sarkar and Sen Gupta [44] in the Bay of Bengal. This decreasing trend during the last 10 years was due to less DDT usage in India as a result of restrictions imposed by the Indian government against POPs. Such situations can also observe in coastal areas of Pakistan when compared the results of Bano, et al. [46] and Khan, et al. [23] with a gap of 19 years. In 1991, Bano, et al. [46] indicated higher concentrations of POPs from different Pakistani rivers. After a huge gap, Khan, et al. [23] reported lower DDT levels which reflect the negligible DDT discharges in the area. This might also be due to the strict restrictions being taken and implemented by Pakistani Government regarding the use of DDT. Sarkar, et al. [47] reported the concentration ranges (ng/g) of HCHs, DDTs, endrin, aldrin and dieldrin to be 0.8-7.8, 47-25.1, 0.4-0.9, 0.10-0.3, and 0.70-3.33 respectively in different estuaries of Indian west coast whereas in offshore sediments of the ranges were 0.10-6.2, 1.14-17.6, 0.09-0.26, 0.39-0.78, 0.09-0.26 and 0.20-1.41, respectively.

The variation of POPs in marine and estuary sediments was due to various reasons including elevated rates of contaminants influx to the estuaries, abiotic degradation of POPs by several physicochemical characteristics of sediments and the microbiological degradation. The retaining capacity of the sediments also plays a major role by holding large quantity of contaminants as the sediments having high amount of clay minerals can hold high quantity of POPs as compared to those with sandy silt or sandy clay rich sediments. From Pakistan, in west coast of Arabian Sea at Karachi harbor, Khan, et al. [23] reported higher concentrations of DDT along with its metabolites including DDD and DDE in most of the samples. 95 % samples were contaminated with *p´,p´*-DDE suggesting historic DDTs input. The level of DDTs was 0.04-0.24 ng/g. HCHs, HCBs and cyclodienes were found in lower concentrations. Overall, it was concluded by this study that the concentration of POPs in Karachi

harbor and adjoining area was lower than concentrations reported from neighboring and regional countries. The authors suggested the existence of lower concentration of POPs as a result of discharge of untreated industrial effluents and domestic waste discharge into harbor area through Lyari River.

The spatial distribution of POPs at different locations in sediments is significantly different. Rajendran, et al. [45] reported elevated levels of PCBs in sediments away from the discharge point while Khan, et al. [23] contradictory reported high OCPs concentration at the discharge point. Sarkar and Sen Gupta [44] also reported elevated levels of dieldrin, HCHs and DDTs from mouth of the Hooghly, Mahanadi and Palar rivers rather than at central part of river. Sarkar, et al. [47] reported considerable high OCs concentration in estuarine as compared to offshore sediments. The concentration (ng/g) ranges of aldrin, HCHs, dieldrin and DDTs were 0.10 to 0.27, 0.85 to 7.87, 0.70 to 3.33 and 1.47 to 25.17 in estuarine sediments while 0.09 to 0.26, 0.10 to 0.60, 0.20 to 1.41 and 1.41 to 17.55 respectively in offshore sediments.

1.2.3. Black Carbon (BC)

The term, "Black carbon (BC)" which has no universally accepted definition [48], covers a range of carbonaceous materials formed only in combustion of carbon based fuels [49]. This term is collectively used for partly charred plant residues to highly graphitized soot particles as a result of incomplete combustion [50]. The most widely used definitions are based upon the (i) chemical or physical properties of BC; or (ii) the measurement method [48]. According to Andreae and Gelencsér [51], BC is actually a "soot carbon" and "an impure form of near elemental carbon with graphite like structure". BC received increasing attention from scientific community owing to its importance in global biogeochemical processes such as fire history, radiative heat balance of earth, pollutants carrier and also due to their potential role in global warming [52]. The major challenge in developing of global BC inventories global BC is affected by the analytical measurement of black carbon in natural matrices. A number of analytical methods such as microscopic, thermal, spectroscopic, chemical, optical and molecular markers are defined and available in scientific literature for BC

measurements. This huge variation in detection methods of BC is due to its aromatic structure and analytical complexity [53, 54]. The main properties of different BC forms is summarized in Table 1.

1.2.4. BC-Hydrophobic Contaminant Interaction in Sediments

Hydrophobic organic contaminants such as OCs are highly influenced by BC. There are number of factors that affect the fate of contaminants in the sediments, the most important of which is considered as organic matter. Organic matter provides the most important binding sites for the organic contaminants [55]. A partly degraded polymer type of organic matter, termed amorphous organic matter, consist of amino acids, lignin, lipids and exhibits a structure which is homogenous, gel like matrix and lipophilic. This amorphous organic matter is thought to be responsible for organic contaminants adsorption [10]. On the other hand, apart from absorption, adsorption is most likely to be occurred on glassy and condensed type of organic matter and may refer to the term generally used as "carbonaceous geosorbents" [11].   One sub-domain of these carbonaceous geosorbents is BC that includes kerogen, soot, unburned coal, fly ash, char coal and biochar. Figure 1 shows the conceptual model for behavior of organic contaminants sorption-desorption in sediments.

As, the black carbon exhibits aromatic and condensed structure [18, 56], organic contaminants have shown extensive sorption with BC including PCBs, PAHs [13, 57-60], pesticides [61-64] and other contaminants of ecotoxicological concern [65]. The physic-chemical properties of black carbon fluctuate because of different source, combustion conditions, weathering state and mode of BC formation [66]. This would leads to the inferences for sorption of hydrophobic organic contaminants. Nevertheless, less studies in literature provides comparative sorption behavior of different forms of black carbon including their intrinsic properties [67]. Furthermore, in comparison with amorphous organic matter, sorption of organic contaminants with BC has shown 10-1000 times stronger [10, 57]. This is because of the sediment water distribution coefficients at higher levels [68].

Table 1: Summarized characteristics of black carbon

BC Type	Source	Formation	Configuration	Surface Area $(m^2\,g^{-1})$
Soot	Fossil fuels; biomass	Incomplete combustion; Condensation of acetylenic and aromatic molecules in the gas phase	Spherules/aciniform agglomerates; onion-like structure; Sub-µm in size	63
Chars	Fossil fuels; biomass	Incomplete combustion	Less structured particles with identifiable pre-combustion features; 1–100 µm size	201
Charcoal		Oxidation of carbon on solid fuel surfaces	Microporous network structure; graphitic sheets in a highly disordered organization; 1–100 µm size	
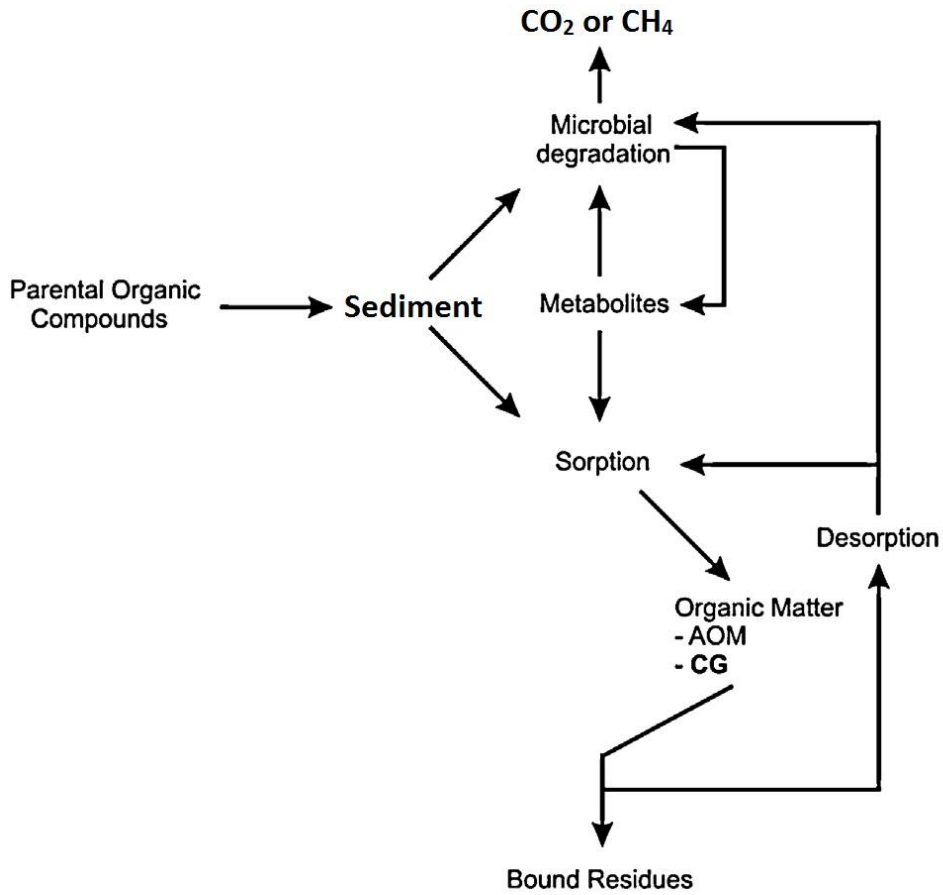
Figure 1: Conceptual model showing behavior of organic contaminants sorption-desorption in sediments

The sorption of organic contaminants with amorphous organic matter is usually linear, reversible and fast. Further the sorption-desorption mechanism of hydrophobic organic chemicals with amorphous organic matter is systematically well-defined by normalized partition co-efficient (K_{OC}) which indicates the rapid sorption-desorption of organic contaminants with amorphous organic matter. In comparison, BC showed slow sorption and desorption [16, 68] because of elevated non-linearity [57] as a result of which there is strong sorption of organic contaminants with BC. These processes are characterized and explained by different models such as Freundlich model, Langmuir model [16, 62], or computer models as well as multiple interruption tests for determination of rate limiting steps in adsorption processes of organic contaminants with BC. However, the exact process of molecular interactions of organic contaminants with BC that governs strong sorption is still unclear [11].

A term, sorption-desorption hysteresis for kinetics of organic contaminants and BC is used. Actually, the desorption rates of organic contaminants from non-linear black carbon is much slower than linear amorphous organic matter. This resistance to desorption may increase the contact time of organic contaminants with BC, as a result of which, BC indorses ageing [69]. In a sorption-desorption hysteresis process, the isotherm related to desorption has overall larger capacity as compared to the isotherm determined for sorption process [16]. The mechanism of sorption-desorption hysteresis is explained better where organic compounds entrapped in BC pore spaces undergo collapse during desorption (Figure 2). Though, further research is still needed to completely understand and explain the phenomena for sorption capacity of large hydrophobic organic compounds with BC and associated sorption and desorption hysteresis process.

1.3.   Objectives

A detail study was conducted in order to assess the environmental distribution of OCs in the coastal areas of Pakistan and to understand, how geosorbent BC may influence this environmental behavior in the study area. This study was designed with specific objectives of (i) analysis, spatial distribution, mass inventory,

depositional flux and risk assessment of OCs in coastal areas of Pakistan; (ii) BC analysis and its burial flux in coastal areas of Pakistan and (iii) influence and relation of BC with hydrophobic OCs (OCPs and PCBs) by using regression and correlation analysis. This study provides baseline data for the sedimentary distribution of OCs and BC in the coastal sediments from Pakistan as well as calculation of burial fluxes in this region.
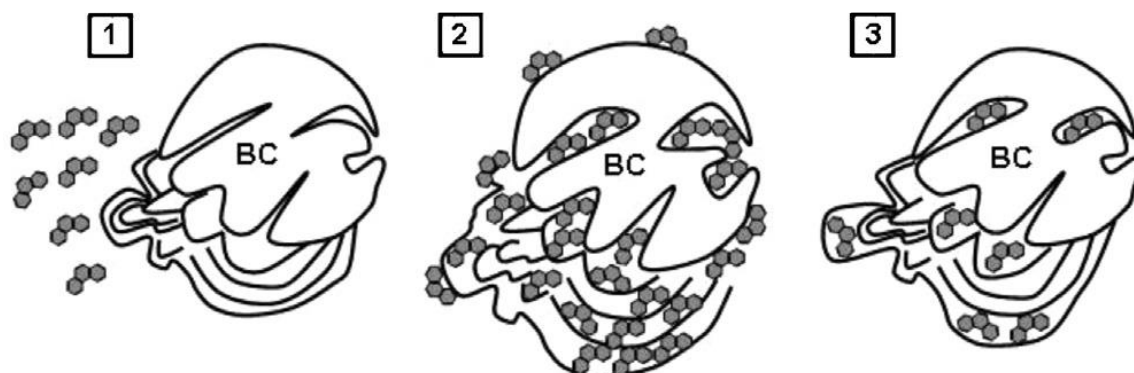
Figure 2: Schematic depiction of the mechanism invoked to explain sorption–desorption hysteresis.

(1) BC in original form prior to sorption;

(2) Sorption causes the matrix to swell and accommodate sorbate molecules in newly formed/enlarged pores;

(3) Upon desorption sorbate molecules become trapped within the collapsed matrix 'scaffold' and so: % desorbed < % originally sorbed.

Materials and Methods

2.1.   Study area and sediments sampling

A total of eighteen (18) sites were chosen from west to east along the coastal belt (960 km long) of Pakistan covering the whole territorial area by taking samples from Dasht River Estuary (DRE), Jiwani (JW), Old Marine Base Jiwani (OMB), Ganz Beach Area (GBA), Gwadar Port (sites GP-1 and GP-2), Gwadar Bay (GB), Pasni (PS), Pasni Bay Jetti (PBJ), Astola Island (sites AI-1 and AI-2), Ormara Turtle Beaches (OTB), Hingol River Estuary (HRE), Somiani Miani Hor (sites SMH-1 and SMH-2), Ibrahim Haidri (IH), Rohri Goth (RG) and Port Qasim (PQ). The pollution load along the coast varies from place to place depending on influx of pollution load due to anthropogenic activities. Among these sites, GP-1 and GP-2 are potentially exposed to developing activities and sites IH, RG and PQ are highly rendering with industrial activities (Figure 3 & Table 2). Sediment samples were collected in January, 2012 at different depths (Table 3). Samples were selected in composite with five sub samples. Hand trowel was used for taking all sediment samples. They were then kept in polyethylene bags, brought to laboratory and stored frozen at -4 °C till final analysis.

2.2.   Analysis of OCs and quality assurance

All sediment samples (20 g) were extracted using Soxhlet extraction with DCM (purchased from Merck and Co., Inc.) for 24 hr. Prior to extraction, a mixture of surrogate standards of 2,4,5,6–tetrachloro–m–xylene (TCmX), PCB-30, PCB-198 and PCB-209 were added to each of the sediment sample. For the removal of sulphur content, activated copper granules were added into the collection flasks. The extract was concentrated and solvent exchanged to hexane (purchased from Merck and Co., Inc.). It was then purified using 8 mm i.d. alumina/silica column packed from bottom to top with neutral alumina (3 cm/3 % deactivated), neutral silica gel (3 cm/3 % deactivated), 50 % sulphuric acid silica (3 cm) and anhydrous sodium sulphate (1 cm). Prior to use for purification purpose, the neutral alumina, neutral silica gel and anhydrous sodium sulphate were also Soxhlet extracted with DCM for 48 hr and then baked for 12 hr at 180, 250 and 450 °C respectively. Finally, the column was eluted

Table 2: Sampling codes and sites mentioned in the study

S. No.	Site Code	Name	Latitude	Longitude
1	AI-1	Astola Island-1	25° 02´ 079´´	63° 81´ 913´´
2	PS	Pasni	25° 10´ 968´´	63° 43´ 373´´
3	GP-1	Gwadar Port-1	25° 00´ 25´´	62° 37´ 694´´
4	OMB	Old Marine Base Jiwani	24° 92´ 067´´	61° 78´ 826´´
5	GP-2	Gwadar Port-2	25° 11´ 365´´	62° 23´ 342´´
6	PQ	Port Qasim	24° 56´ 718´´	67° 09´ 789´´
7	SMH-1	Somiani Miani Hor-1	25° 37´ 228´´	66° 53´ 789´´
8	SMH-2	Somiani Miani Hor-2	25° 45´ 274´´	66° 20´ 168´´
9	JW	Jiwani	24° 97´ 092´´	61° 72´ 115´´
10	OTB	Ormara Turtle Beaches	25° 07´ 025´´	64° 63´ 622´´
11	DRE	Dasht River Estuary Jiwani	25° 07´ 841´´	61° 66´ 605´´
12	HRE	Hingol River Estuary	25° 27´ 254´´	65° 50´ 764´´
13	RG	Rohri Goth Karachi	24° 69´ 443´´	66° 92´ 274´´
14	GB	Gwadar Bay	24° 93´ 563´´	62° 30´ 855´´
15	AI-2	Astola Island-2	25° 02´ 798´´	63° 90´ 894´´
16	GBA	Ganz Beach Area	25° 00´ 006´´	61° 86´ 621´´
17	PBJ	Pasni Bay Jetti	25° 20´ 006´´	63° 48´ 385´´
18	IH	Ibrahim Haidri	24° 70´ 253´´	66° 64´ 668´´
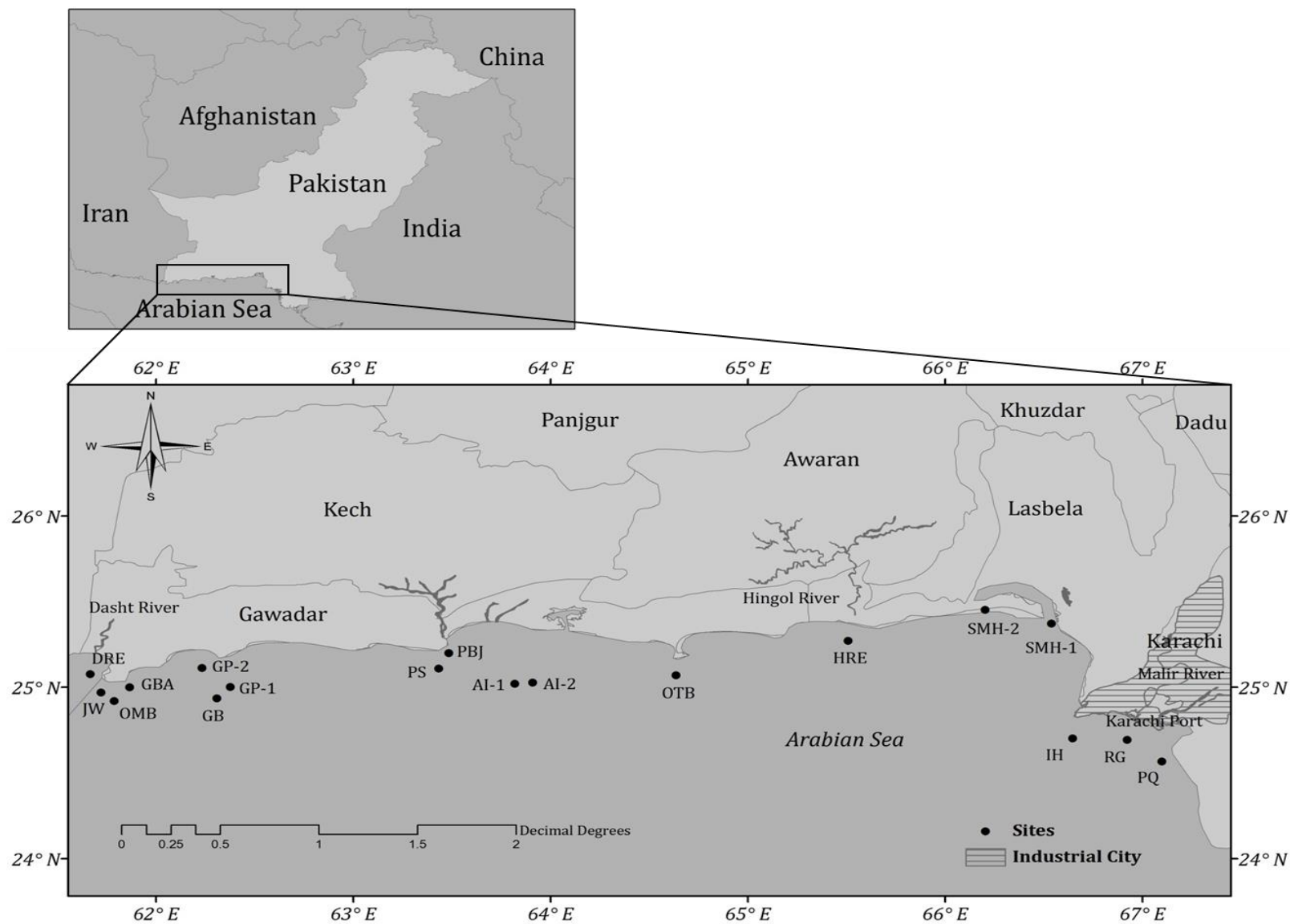
Figure 3: Map of the study area, showing the eighteen sampling sites in coastal belt of Pakistan

with 50 ml of DCM/hexane (1:1). The fraction was concentrated to 0.2 ml under gentle high purity nitrogen stream after adding 25 μL of dodecane. In all samples, a known quantity of PCB-54, as internal standard, was added before analysis.

Twenty six (26) PCB congeners (PCB-28, -37, -44, -49, -52, -60, -66, -70, -74, -77, -82, -87, -99, -101, -105, -118, -126, -128, -138, -153, -166, -170, -179, -180, -183 and -187) were analyzed together with 13 OCPs (α-HCH, β-HCH, γ-HCH, *o,p'*- and *p,p'*-DDE, -DDD and -DDT, *trans*-chlordane (TC), *cis*-chlordane (CC), HCB and Heptachlor). All of these compounds were analyzed using GC-MS system (Agilent 7890/7000 GC-MS/MS). The specifications of the capillary column were: VARIAN, CP-Sil 8 CB, 50 m, 0.25 mm, 0.25 μm. The MS was operated with an EI source (-70 eV) in multiple reaction monitoring mode. The temperatures of transfer line, injector interface and ion source were set at 280 °C, 250 °C and 230 °C, respectively. The GC oven temperature program was set at 80 °C for 0.5 min, then 20 °C/min to 160 °C, 4 °C/min to 240 °C, and finally 10 °C/min to 295 °C, and hold for 10 min. 1 μL of sample was injected in splitless mode. Helium was used as carrier gas at the flow rate of 1 mL/min. Collision induced dissociation gas and quench gas in collision cell were nitrogen and helium at the flow rate of 1.5 mL/min and 2.25 mL/min, respectively.

Stringent quality assurance and control was maintained throughout the analytical procedure. For this purpose, blank samples including procedural blank, spiked blank (consist of all chemicals) and also a duplicate sample were run with each batch of ten samples in order to evaluate potential contamination during the whole analytical procedure and repeatability of the analysis. It was observed no significant difference between analytes concentration in the laboratory, transportation and field blanks which indicates negligible contamination of samples during transport, storage and analysis. Average surrogate recoveries for TCmX and PCB-209 were calculated to be 73±6% and 81±5 % for the sediment samples. Further, the instrumental detection limit (IDL) values were calculated from the lowest standards, extrapolating to the corresponding amount of analytes that would generate a signal to noise ratio of 3:1. The studied compounds lies under the IDLs, were considered as non-detected (n.d.). The method detection limits (MDLs) were considered as the average values of blanks,

with 3 standard deviations of blank values. When there was no compound detection in the blanks, then a standard of 3 times the IDLs was used for calculating the MDLs. Reported values were corrected according to the recovery ratios and blank values.

2.3.   Total organic carbon and black carbon (CTO-375 method)

Multi N/C 3100 Analytik Jena TOC analyzer was used for the determination of total organic carbon (TOC). For black carbon (BC) detection, the chemo-thermal oxidation (CTO-375) method described elsewhere [70-72] was used. Briefly, the dried sediment samples (2-3 g) were exposed to thermal oxidation (375 °C, 18 h) in a muffle furnace under constraint air flow. They were then digested with 1 N HCL [72]. The residual organic carbon content was determined as BC by using a Multi N/C 3100 Analytik Jena TOC analyzer.

2.4.   Depositional flux and mass inventory of OCs

The deposition flux of OCs was estimated based on OCs concentrations (ng g^{-1}), area (territorial; 21335 km^2) and mass accumulation rate (g cm^{-2} yr^{-1}). Sedimentation rate (cm yr^{-1}) via density (g/cm^3) of the dry sediment samples was used for the calculation of mass accumulation rate. Then, depositional flux was calculated by using following formula [73]:

$$D = \frac{\sum_{i=1}^{n} ARi \times [OCs]_i}{n} \times A$$

Here, AR$_i$ is the accumulation rate at the site from where the sample i was taken; [OCs]$_i$ is the OCs content in sample i; n is the total number of samples (18) and A represents the territorial area.

Furthermore, sedimentary mass inventories for OCs were calculated in order to assess the potential of sediments as a new contamination source for marine environments [74]. The mass inventory was calculated by using following formula [75, 76]:

$$I = C.A.d.\rho$$

Here, C is the median value of concentration of OCs compounds of interest in coastal sediments, A is the territorial area (21335 km^2), d is the density (1.5 g/cm^3) and ρ is the mean sediment depth (5.5 cm).

2.5.   Sedimentary BC burial flux

For estimating BC burial fluxes numerous properties of sediments must be taken into account. The next equation was used [77]:

$$F_{burial} = C.d.\omega. \ (1\text{-}\phi)$$

Where F_{burial} (µg/cm^2.yr) is the calculated burial flux, C is the BC concentration (µg/g), d is the density of dry coastal sediments (g/cm^3), ω is the sedimentation rate (cm/yr) and ϕ is the porosity of the coastal sediments. The sedimentation rate was calculated using the empirical relationship described by Middelburg, et al. [78] between sedimentation rate and coastal depth. For the determination of porosity, a central value (0.75±0.05) of a range (0.7-0.8) was used which is typically found in sediment mixing layer around the world [52]. Sediment particle density was measured by the method described by Dewis and Freitas [79].

Results and Discussion

3.1.   Organochlorines: Levels, distribution and global comparison

Descriptive statistics for concentration profiles of OCs in coastal sediments is presented in Table 3. Total concentrations of OCPs ranged from 0.9–107 ng g^{-1}. Mean levels of OCPs were observed in the following order: ∑DDT>∑Chlordane>HCB> ∑HCHs>Heptachlor. Among all OCPs, ∑DDT (*o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT) were dominant compound (Appendix I), contributing 58.2 % of the total OCPs. Among DDTs metabolites, the concentration of *p,p'*-DDE was the highest with 46.4 % of total DDTs. Concentrations of ∑HCHs (*α*-HCH, *β*-HCH, *γ*-HCH) ranged from 0.1–7.3 ng g^{-1}. Among HCHs isomers, *β*-HCH was the dominant metabolite (38.6 %) followed by *α*-HCH (31.2 %) and *γ*-HCH (30.2 %) (Appendix I). Concentrations of ∑Chlordane (*cis*- and *trans*-Chlordane), HCB and heptachlor were 0.4–8.4 ng g^{-1}, 0.05–19 ng g^{-1} and 0.08–2.3 ng g^{-1}, respectively (Table 3). The total concentration of PCBs (26 congeners) ranged from 6.2–1200 ng g^{-1} with a mean value of 108 ng g^{-1}. Among analyzed PCBs, maximum average levels correspond to tri- and tetra-PCBs homologous (Appendix II), accounting for 59 % and 33 % of the total PCBs, respectively. Penta- and hexa- PCBs exhibited low concentrations which have low to medium toxicity levels [6] while hepta PCBs were detected at the lowest levels.

Spatial distribution of OCs showed different spatial trends with respect to sampling stations (Figure 4a & 4b) that may be attributed to different input sources, degradation rate, sediment texture and desorption or preferential sedimentation [80]. Generally, elevated levels of OCs were observed at the southern coast in the samples collected near from metropolitan city Karachi, owed to industrial and developmental activities. Higher levels of ∑DDTs were determined at sites IH and RG which are close to urban and industrial settlements and receive high amount of sewage, ship and industrial wastes [81], while higher concentrations of ∑HCHs were observed at sampling site RG.

Table 3: Descriptive statistics of organochlorines levels (ng g^{-1}) in the coastal sediments from Pakistan

Location	Depth (cm)	∑HCHs	∑DDTs	∑Chlordane	Heptachlor	HCB	∑OCPs	Tri-CBs	Tetra-CBs	Penta-CBs	Hexa-CBs	Hepta-CBs	∑$_{26}$PCBs
AI-1	6	0.44	2.99	5.67	0.51	0.48	10.1	67.1	29.9	4.32	0.50	0.13	102
PS	7	0.56	0.61	8.39	0.46	0.55	10.6	13.2	7.71	0.84	0.08	0.09	21.9
GP-1	4	0.31	0.14	0.42	0.08	0.06	1.0	5.14	5.14	0.61	0.07	0.11	11.1
OMB	5	0.38	0.21	6.24	0.36	0.28	7.5	16.0	7.09	0.94	0.17	0.19	24.4
GP-2	6	3.48	11.3	5.84	0.41	0.25	21.2	26.2	13.2	4.01	1.36	1.53	46.3
PQ	3	1.02	4.27	7.16	0.41	0.13	13.0	4.37	3.50	0.35	0.05	0.08	8.4
SMH-1	4	0.29	0.48	6.19	0.32	0.12	7.4	5.45	2.21	0.16	0.01	0.12	8.0
SMH-2	5	1.69	1.99	5.60	0.39	0.16	9.8	86.3	26.4	0.77	0.09	0.11	113.7
JW	5	0.35	1.71	5.10	0.24	0.12	7.5	5.38	3.46	0.36	0.06	0.14	9.41
OTB	5	0.60	3.47	1.73	0.15	0.12	6.1	3.70	3.86	0.78	0.12	0.08	8.5
DRE	5	0.25	0.08	1.26	0.14	0.33	2.1	12.3	7.11	0.76	0.05	0.08	20.3
HRE	6	0.46	0.29	1.78	0.29	0.50	3.3	17.8	7.47	0.82	0.16	0.22	26.5
RG	7	7.32	71.1	1.69	0.74	5.81	86.7	129	117	22.1	2.45	1.05	271.6
GB	6	0.35	0.56	1.34	0.16	0.41	2.8	21.9	17.1	3.61	0.51	0.07	43.2
AI-2	7	0.31	0.52	5.69	0.21	0.07	6.8	2.30	2.62	0.66	0.28	0.34	6.2
GBA	7	0.19	0.48	0.51	0.12	0.14	1.4	5.09	5.23	1.30	0.31	0.13	12.1
PBJ	7	0.10	0.07	0.56	0.09	0.11	0.9	4.17	3.01	0.40	0.05	0.03	7.7
IH	4	2.23	77.5	5.54	2.25	19.4	107	718	387	88.2	9.2	4.00	1206
Mean	**5.5**	**1.13**	**9.87**	**3.93**	**0.41**	**1.61**	**17**	**63.48**	**36.06**	**7.28**	**0.87**	**0.47**	**108.16**
Median	**–**	**0.41**	**0.58**	**5.32**	**0.30**	**0.20**	**7.43**	**12.74**	**7.10**	**0.80**	**0.14**	**0.12**	**21.10**
SD	**–**	**1.77**	**23.62**	**2.67**	**0.49**	**4.64**	**29.7**	**166.84**	**91.56**	**20.83**	**2.19**	**0.96**	**281.62**
Range	**3–7**	**0.1–7.3**	**0.07–77.5**	**0.4–8.3**	**0.08–2.2**	**0.06–19.4**	**0.9–107**	**2.3–718**	**2.21–387**	**0.16–88**	**0.01–9.2**	**0.03–4**	**6.2–1206**
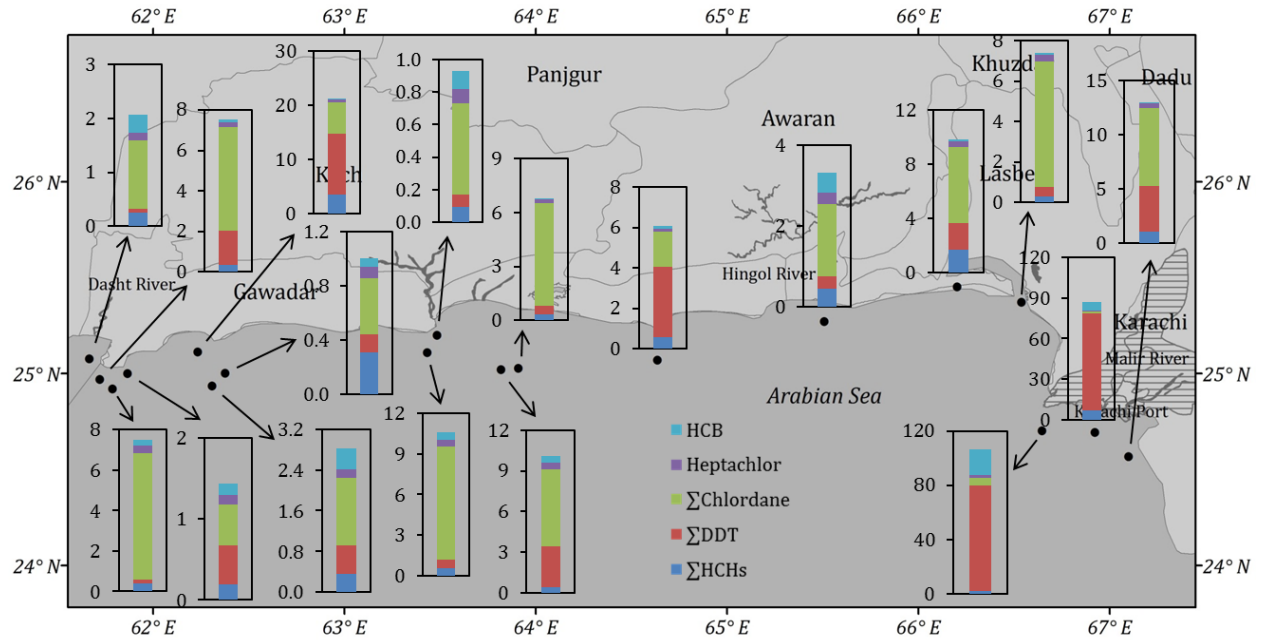
(a)
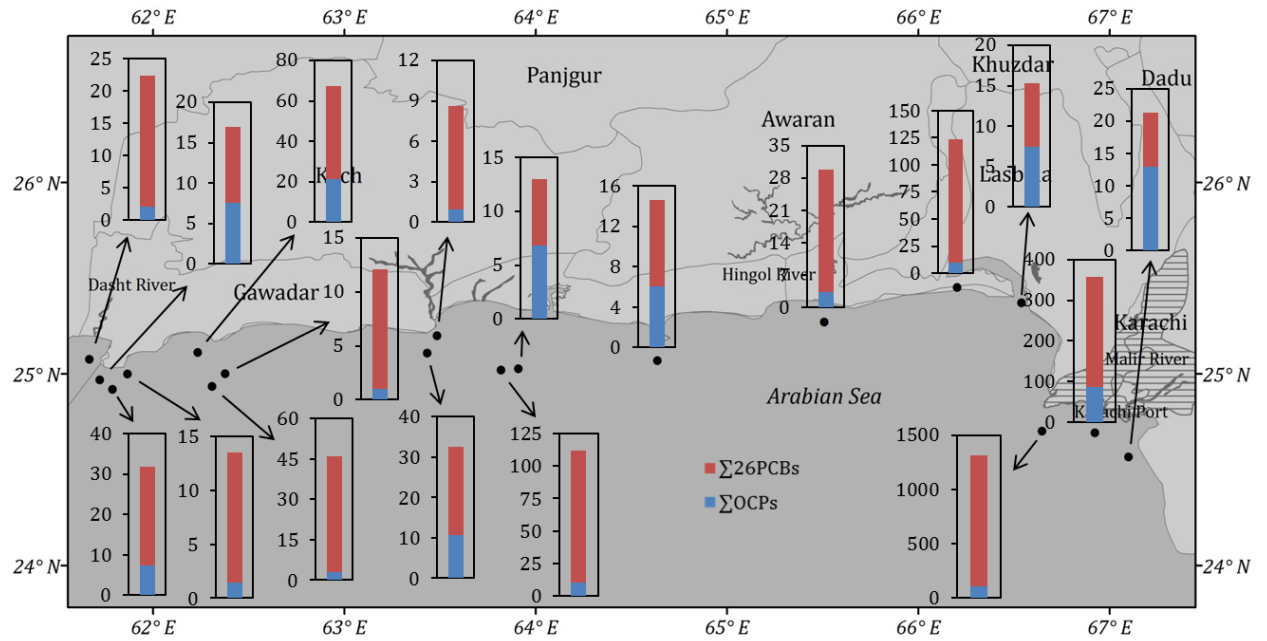
(b)

Figure 4: Spatial distribution of (a) OCPs and (b) PCBs in coastal sediments of Pakistan (ng g^{-1})

PCBs distribution patterns showed that sampling sites close to urban settlements and recreational points contained much higher levels as compared to other sampling sites. Sampling site IH contained the highest levels of PCBs which is closer to the thermal power station followed by RG, SMH-2 and AI-1. These areas are relatively closed to industrial, municipal, recreational and ship manufacturing facilities and all these industries are the main input sources of PCBs in coastal area of Pakistan. Although, PCBs are globally banned, but the historic use of these persistent chemicals in ship painting, transformers and electrical equipments was common due to which still PCBs are released and found in sedimentary matrix. This area (sites IH and RG) contains three main coastal industries near the port with elevated amounts of effluents discharging from power plants, steel mill and refineries. According to Hameed, et al. [81], highly polluted wastes from these industries discharged irrationally into water bodies. It is also estimated that 90,000 tons of oily waste is discharged every year into the Karachi port located at southern coast in Karachi city limits with prior treatment facilities [81].

Global comparison of OCs, including ∑DDTs, ∑HCHs and ∑PCBs is given (Table 4). Levels of ∑DDT calculated in current study are lower than those of marine sediments from Vietnam [82, 83] and Masan Bay, Korea [84]. In contrast, ∑DDT values in this study are higher than those reported from coastal sediments of Gulf of Aden [85] and Sea Lots Trinidad [86]. The levels of ∑HCH reported in our study are higher than those presented from most of the coastal regions including Korea [87], Vietnam [82] and Baltic Sea [88]. This suggests a potential contamination of the Pakistan coasts in terms of OCs. In case of global comparison of PCBs, 17 sites from a total of eighteen sites were selected. Sampling site Ibrahim Haidri (IH) was excluded during the comparison as it contained a number of outlier values. The concentration range (7.2 to 370 ng g^{-1}) for the rest of the site (except site IH) were higher than other areas of the world including Black Sea, Turkey; Casco Bay, Maine, USA and Lower Mekong river basin of Laos and Thailand [89-91] (Table 4). However, PCBs levels coastal sediments of Pakistan were found lower than those reported by Mohammed, et al. [86] in Sea Lots, Trinidad and Barakat, et al. [41] in Alexandria Harbor, Egypt.

3.2.   TOC and BC levels

Descriptive statistics of TOC and BC in the coastal sediments are shown in Table 5. Sediments showed TOC concentrations varying from 0.28 to 2.9 % dw within the range of those reported values from different marine areas in the world such as de Mora, et al. [92] reported TOC contents in the Caspian Sea, Lin, et al. [5] measured values in the East China Sea, and Hu, et al. [1] described levels in the Bohai Sea. While comparatively higher values were measured in the Black Sea region of Turkey [93], in Vietnam [82] and in Marseille, France [94].

As for BC, coastal sediments showed soot concentrations (as derived from the CTO-375 method) ranging 0.06–0.25 % dw and amounting to 5.3–28.8 % TOC. These results are in agreement with those presented by different studies in the literature. Guo, et al. [95] reported BC contents obtained with the same CTO–375 method ranging 0.1–17 % TOC in Arctic sediments. Other studies of regional frame using the same analytical approach reported sedimentary BC ranging 3–6 %TOC in the Gulf of Maine [96], 3–6 % TOC in the NW Atlantic shelf [96], 12–18 % TOC in Palos Verdes, CA NE Pacific Shelf [96], or 2–47% TOC in the Swedish Continental Shelf [9]. With a different analytical approach consisting in an acidic digestion (H_2CrO_4/H_2SO_4), Lim and Cachier [97] determined BC concentrations of 5–38 % TOC in sediments from the Western Mediterranean Sea. In current study, highest concentration of BC was determined in RG (0.22 % dw; 18.2 % TOC) and IH (0.25 % dw; 8.8 % TOC), where industrial activity of Karachi city results in higher emission loads.

Table 4: Comparison of OCs (ng g^{-1}) in sediments from other studies

Location	∑HCHs	∑DDTs	∑PCBs (Congeners)	References
Coastal areas, Pakistan	0.1–7.3	0.07–77	6–1206 (26)	This study
Gulf of Aden, Yemen	n.d.–0.06	n.d.–0.74	0.4–4.23 (101)	Mostafa, et al. [85]
Sea Lots, Trinidad	0.7–1.8	6.1–29	62–601 (136)	Mohammed, et al. [86]
Baltic Sea	0.002–0.36	0.13–0.5	0.01–6.2 (7)	Pikkarainen [88]
Coast of Korea	n.d.–5.5	0.01–135	0.17–371 (18)	Hong, et al. [87]
Singapore	3–46	2–12	1–330 (37)	Wurl and Obbard [98]
Hugli Estuary, West Bengal, India	0.11–0.4	0.18–1.93	0.18–2.33 (13)	Guzzella, et al. [36]
Bay of Bengal, India	0.17–1.56	0.04–4.8	0.02–6.6 (54)	Rajendran, et al. [45]
Egyptian Mediterranean coast	0.09–3.31	0.08–3.31	0.31–1.95 (10)	El Nemr, et al. [43]
Egyptian coast of Red Sea	0.009–0.086	0.003–0.457	0.40–6.17 (10)	El Nemr, et al. [42]
Hanoi, Vietnam	<0.2–36	4.4–1,100	1.3–384	Hoai, et al. [83]
Lake Qarun, Egypt	0.13–62.6	n.d.–5.88	1.48–137.2 (29)	Barakat, et al. [6]
Norwegian Arctic	0.21–7.0	0.23–5.4	0.18–13 (15)	Jiao, et al. [99]
Estuarine and marine sediments, Vietnam	n.d.–1.0	0.31–274	0.04–18.71 (22)	Hong, et al. [82]
Lower Mekong River Basin, Laos and Thailand	0.005–9.9	0.027–52	0.18–310 (62)	Sudaryanto, et al. [91]
Casco Bay, Maine, USA	n.d.	0.0–455.5	0.3–148 (18)	Wade, et al. [90]
Masan Bay, Korea	n.d.–1.03	0.28–89.2	1.24–41.4	Hong, et al. [84]
Alexandria Harbou (Egypt)	<0.25–6.0	0.25–885	0.9–1210	Barakat, et al. [100]
Black Sea (Turkey)	0.08–1.1	0.2–7.2	0.4–4.4	Fillmann, et al. [89]

n.d.: not detected

Table 5: Total organic carbon (TOC), black carbon (BC), sedimentation rate (ω) and BC burial flux (F_{burial}) in the coastal sediments from Pakistan

Location	TOC	BC	BC	Sedimentation Rate	BC burial flux
	(% dw)	(% dw)	(% TOC)	(ω: cm/yr)	($\mu g/cm^2.yr$)
AI-1	0.54	0.12	22.3	0.4376	328
PS	0.82	0.09	11.0	0.4372	234
GP-1	1.03	0.06	5.8	0.4385	183
OMB	1.42	0.11	7.9	0.4381	324
GP-2	2.27	0.12	5.3	0.4376	346
PQ	1.25	0.10	7.7	0.4390	249
SMH-1	1.03	0.08	7.9	0.4385	212
SMH-2	0.52	0.13	24.9	0.4381	419
JW	0.28	0.08	28.8	0.4381	243
OTB	1.88	0.12	6.6	0.4381	355
DRE	1.08	0.09	7.9	0.4381	246
HRE	1.27	0.10	7.9	0.4376	290
RG	1.20	0.22	18.2	0.4372	663
GB	0.54	0.12	22.3	0.4376	355
AI-2	0.90	0.11	12.2	0.4372	308
GBA	1.34	0.08	6.0	0.4372	220
PBJ	0.88	0.07	7.9	0.4372	201
IH	2.86	0.25	8.8	0.4385	766
Mean	**1.17**	**0.11**	**12.19**	**0.44**	**330**
Median	**1.05**	**0.11**	**7.9**	**0.4378**	**299**
SD	**0.64**	**0.05**	**7.5**	**0.0005**	**155**
Range	**0.28–2.86**	**0.06–0.25**	**5.3–28.8**	**0.437-0.439**	**183–766**

3.3.   Role of BC–versus–TOC in explaining the OCs distribution

The sorption of hydrophobic organic contaminants to that of suspended particles in sediments is a key process that affects the transport, fate and ecological risks of OCs in the marine environment [101]. Hydrophobic contaminants including PCBs, pesticides and other substances having toxicological concerns may be dominated by extensive adsorption onto condensed carbonaceous geosorbents such as BC owing to its condense and aromatic structure [11]. Here, we hypothesize that the significant fraction of sedimentary TOC being composed of BC (5.3–28.8 %) may indicate that BC represents an important factor explaining the distribution of the hydrophobic pollutants studied (i.e. OCPs and PCBs) [18] in current study. In the present section, we perform a statistical analysis to discriminate the relative abilities of BC–versus–TOC in determining the concentration and spatial distribution of OCs.

A correlation analysis was performed between BC vs OCs and TOC vs OCs. The OCs data were box-cox transformed making it normally distributed by using Xlstat version of Microsoft Excel (2010) prior to correlation analysis. The next observations are extracted from the resulting statistics (Table 6): (i) BC showed significant correlations (r=0.76–0.88; *p value*: <0.0001) for HCH, DDT, heptachlor, HCB among OCPs. In contrast, chlordane did not show any correlation with BC. Among PCBs, all homolog groups (tri-, tetra-, penta-, hexa- and hepta-CBs) showed a linear positive correlation (r=0.78–0.89; *p value*: <0001) with BC. (ii) TOC did not show any significant correlation with OCPs and PCBs with lesser chlorine atoms (tri- and tetra-CBs). To some extent, TOC showed weak correlation with DDTs (r=0.49; *p value*: 0.039) and HCB (r=0.47; *p value*: 0.047) while significant with higher chlorine PCBs such as penta-CBs (r=0.53; *p value*: 0.023), hexa-CBs (r=0.56; *p value*: 0.015) and hepta-CBs (r=0.69; *p value*: 0.001). Overall it was concluded, that according to the Pearson correlation analysis, the spatial distribution of OCs in the Pakistan coastal sediments seems to be further governed by the sedimentary content of BC than TOC.

The regression analysis was performed to evaluate that how BC describes the OCs in Pakistan coast than TOC. The regression coefficients prescribed significant role

Table 6: Pearson correlation analysis (r) of organochlorines (OCs) against black carbon (BC) versus total organic carbon (TOC)

Compound	BC (% dw)		TOC (% dw)	
	R	*p-value*	*R*	*p-value*
∑HCHs	**0.76**	**< 0.0001**	0.44	0.066
∑DDTs	**0.83**	**< 0.0001**	**0.49**	**0.039**
∑Chlordane	0.26	0.295	0.06	0.804
Heptachlor	**0.79**	**< 0.0001**	0.43	0.074
HCB	**0.88**	**< 0.0001**	**0.47**	**0.047**
Tri-PCBs	**0.84**	**< 0.0001**	0.35	0.150
Tetra-PCBs	**0.89**	**< 0.0001**	0.40	0.098
Penta-PCBs	**0.89**	**< 0.0001**	**0.53**	**0.023**
Hexa-PCBs	**0.83**	**< 0.0001**	**0.56**	**0.015**
Hepta-PCBs	**0.78**	**< 0.0001**	**0.69**	**0.001**

of BC on the distribution of OCs. They furthermore explained the variation in a data set. By taking BC and TOC as independent variables while OCs as dependent variables, the linear regression model estimates the total variation caused by BC and TOC. Following extractions were extracted from regression analysis: (i) Among OCPs, BC explained 57 % concentration variation for ∑HCHs, 70 % for ∑DDTs, 64 % for heptachlor and 78 % for HCB (Figure 5a). In case of chlordane, BC did not explain any variation conceivably due to different source origins. For PCBs, BC explained 70 % concentration variation for tri-CBs, 81 % for tetra-CBs, 79 % for penta-CBs, 69 % for hexa-CBs and 61 % for hepta-CBs (Figure 5c); (ii) TOC did not show any significant concentration variation for both OCPs and PCBs (Figure 5b & 5d). Hence, from above mentioned regression results, it was concluded that BC perhaps appears to be a better descriptor than TOC for the studied OCs.

Some common conclusions may be extracted from the statistical analysis. First, it was reported that TOC may controls the sorption of hydrophobic organic compounds in soils and sediments [102], however from above statistical analysis, it is evidently clear that BC seems to be the principal factor in controlling the sorption of OCs than that of TOC in Pakistan coastal sediments. We found that BC exhibits high sorption affinity with up to three orders of magnitude for OCs than that for natural organic matter. The reason for this strong sorption of OCs with BC appears to be the spherules/aciniform agglomerates and onion like structure of BC with size in sub μm and surface area of approximately 63 $m^2\,g^{-1}$ [11] which makes it highly aromatic and condensed than that of TOC. Some of other reasons behind this stronger affinity of OCs for BC than for TOC may be the different degradability of both fractions. Overall, BC is considered to be one of the most inert fractions of TOC, whereas the non-BC organic carbon is relatively easy to degrade chemically and biologically over time, promoting desorption of OCs more quickly than BC. Another hypothesis is the co-formation of OCs and BC, that is that both compounds originates from combustion processes (pyrogenic) and get attached from source, being then dispersed together [9].

The mode of OCs fixation with BC can also be deduced from statistical results. Generally, there can be two modes of fixation of OCs onto BC particles: (i) physical
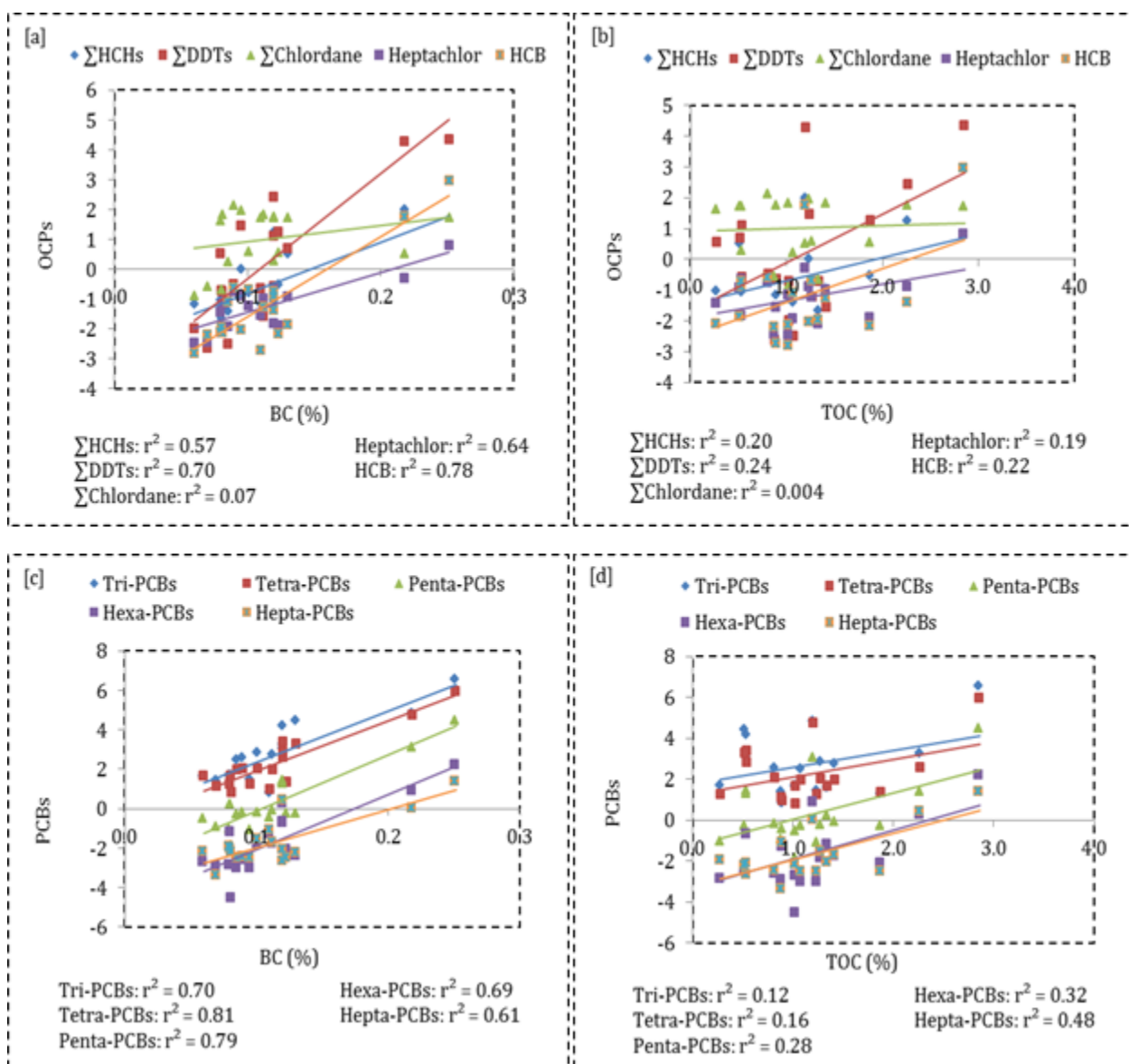
Figure 5: Regression analysis of organochlorines (OCs) against black carbon (BC) versus total organic carbon (TOC); [a] BC vs OCPs, [b] TOC vs OCPs, [c] BC vs PCBs, [d] TOC vs PCBs

occlusion of OCs inside restricted pores during formation of BC and (ii) reversible adsorption on pore or exterior surface after the formation of BC [18]. The results of our study support the first mode of fixation of OCs with BC in coastal areas of Pakistan, owing to high correlation values and better data variation by regression analysis.

Another important conclusion, in case of PCBs, was observed during statistical analysis. Staniszewska, et al. [103] reported PCB congeners with higher number of chlorine atoms being more strongly adsorbed onto BC in sediments, in agreement with Cornelissen, et al. [10] and Semple, et al. [11]. In contrast, Bucheli and Gustafsson [104] reported stronger sorption to BC of planar PCB compounds (with lower chlorine atom homolog groups) than non-planar PCB compounds (with higher chlorine atom PCB homolog groups), despite the lower hydrophobicity of the planar compounds. Apparently, this was due to the ability of penetration of planar compounds to narrow pores of BC, where they interact with $\pi-\pi$ forces along with aromatic pore walls [105]. However, non-planar PCBs experienced electronic interactions with pore walls as well as with surface of BC because of steric hindrance but due to the small pore size in BC, overall sorption is lowered [10, 11, 105]. In this study, PCBs showed a higher correlation of BC with planar congeners (i.e., tetra- PCBs as compared to higher ones (hexa- and hepta- PCBs) (Figure 5c). This behavior was probably due to the fact that planar compounds penetrate into narrow pores of BC and interact with aromatic and condense pore walls of BC through $\pi-\pi$ forces [105, 106].

3.4.   Genesis and composition

3.4.1. *OCs*

The compositional differences of DDTs and HCHs isomers indicate distinct sources of OCs in the environment [107] (Figure 6). (DDE+DDD)/∑DDT ratios were found in the range of 0.33–0.97 (Table 7), which indicated significant presence of DDT metabolites with slow degradation or fresh DDT inputs into the coastal sediments [108, 109]. Most of the sites showed historical usage of DDT (DDE+DDD/∑DDT>0.5). Biologically, in the environment, DDT could be either degraded into DDE or DDD under aerobic or anaerobic conditions respectively [110]. In our study, all coastal

sediment samples except for sites PQ and IH, DDE/DDD ratios were less than 1, suggesting the anaerobic type of degradation process in the coastal sediments of Pakistan. Further, compositionally technical DDT contains less *o,p'*-DDT and high *p,p'*-DDT with approximately 15 and 85 % respectively while dicofol shows the reverse pattern [111]. Our samples contained dicofol products as DDTs inputs in coastal sediments as the ratio of *o,p'*-DDT/*p,p'*-DDT in most of the samples were found to be more than 1.0.

HCH is commercially used and produced in two forms: (i) technical HCH which contains 60-70% α-, 5-12% β-, 10–12% γ-HCH and minor amounts of other isomers; (ii) Lindane which contains almost pure γ-HCH (>99 %) [6]. The ratio of α-HCH/γ-HCH indicates technical HCH source. The value of α-HCH/γ-HCH >4 indicates the presence of technical HCH while high percentage of γ-HCH indicates the lindane contamination in the environment [110]. In our samples, the α-HCH/γ-HCH ratio was determined at AI-1, GP-1, OMB, PQ, SMH-2, JW, OTB, HRE and GBA which indicate the use of technical HCH. Compositionally, high proportion (Figure 6) of β-HCH (38.6 %) was present in sediments followed by α-HCH (31.2 %) due to its relative stability and lower vapor pressure along with resistance to microbial degradation [6]. Therefore, presence of this HCH isomer in huge amounts is a clear indication of past usage of HCHs.

Homologue profile of PCBs provides valuable information on fate of processes of PCBs in the environment [112]. Technical mixture of PCBs contained 70 % of tri-, tetra- and penta-CBs having tri-CBs as dominating homologues. The results of this study indicated relatively higher proportion of lower CBs in the coastal sediments which might came from electronic waste, as electronic waste is potentially an important source of PCBs in developing countries [113]. Further, the compositional comparison of PCBs with Aroclor mixtures indicates technical mixture of PCBs in the area. In this study, the PCBs composition showed resemblance with Aroclor 1016, 1221, 1232 and 1242 (Figure 6).

Table 7: Ratios of metabolites of HCHs, DDTs and BC/TOC

| Location	α/γ-HCH	DDE+DDD/$\sum$DDT	o,p'-DDT/ p,p'-DDT	DDD/DDE	BC/TOC	% age of BC/TOC
AI-1	4.12	0.74	1.36	38.70	0.22	10.15
PS	2.61	0.65	6.78	11.15	0.11	5.02
GP-1	5.04	0.42	1.50	n.d.	0.06	2.66
OMB	4.57	0.34	0.09	3.34	0.08	3.61
GP-2	0.21	0.84	0.72	4.74	0.05	2.41
PQ	4.58	0.95	2.09	0.49	0.08	3.49
SMH-1	n.d.	0.86	22.71	18.67	0.08	3.61
SMH-2	7.80	0.87	4.56	36.85	0.25	11.34
JW	4.44	0.81	10.02	73.93	0.29	13.13
OTB	5.73	0.86	7.67	23.88	0.07	2.99
DRE	2.65	0.63	3.05	12.05	0.08	3.61
HRE	4.84	0.33	0.32	4.33	0.08	3.61
RG	0.65	0.86	3.76	2.43	0.18	8.29
GB	3.25	0.63	0.27	13.23	0.22	10.15
AI-2	1.94	0.70	0.39	13.77	0.12	5.58
GBA	4.01	0.57	0.70	37.39	0.06	2.74
PBJ	3.84	0.46	0.00	n.d.	0.08	3.61
IH	0.89	0.97	0.30	0.17	0.09	4.01
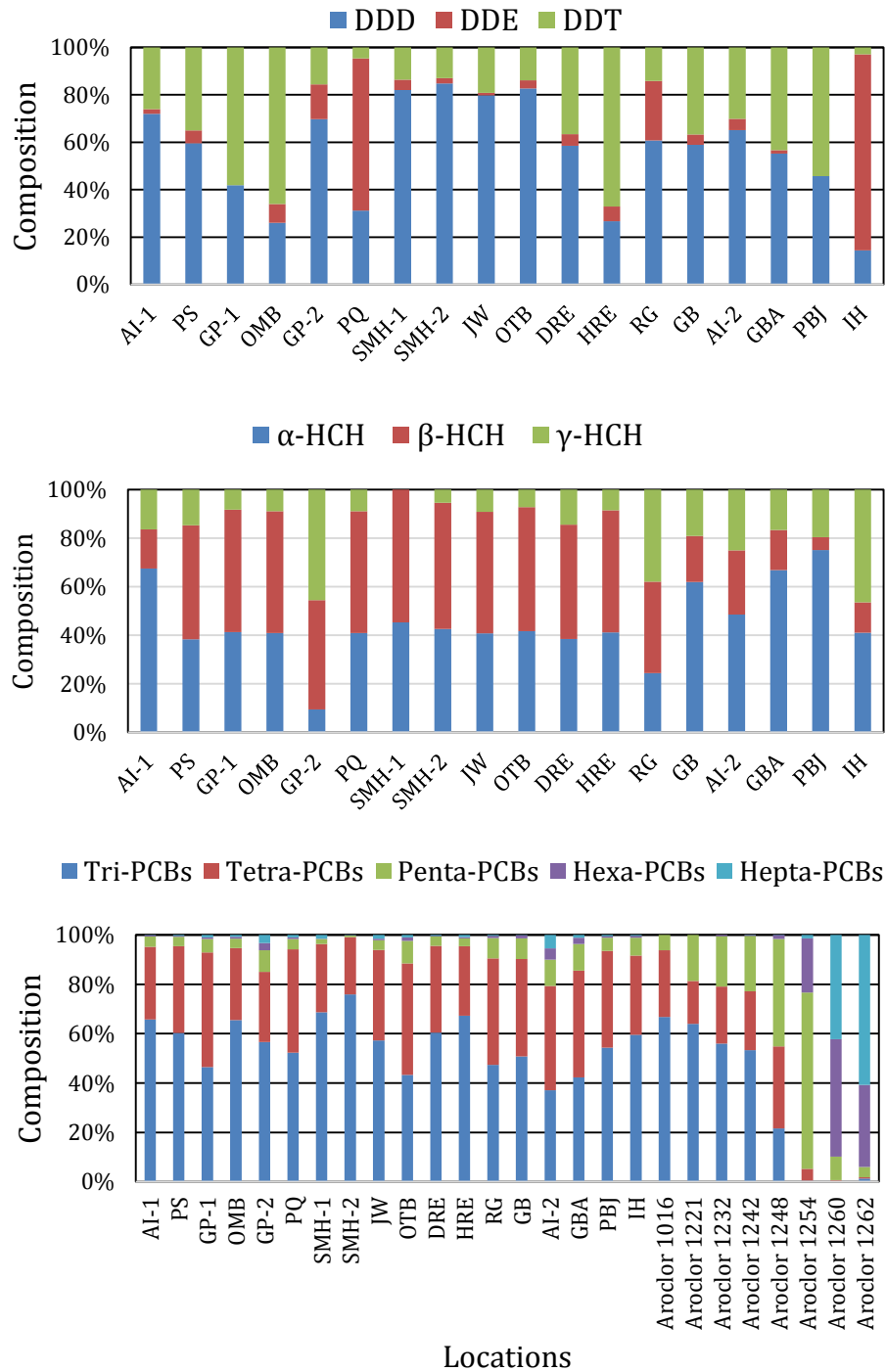
Figure 6: Compositional profile of the OCs (DDTs, HCHs & PCBs)

3.4.2. BC

Pyrogenic BC may derive from different sources: traffic pollution, industry, household coal consumption, incineration, biomass burning and acetylenic/aromatic molecules condensation in gas phase etc. The ratios of BC/TOC were widely accepted marker for BC source [114-116]. According to Muri, et al. [116], the low BC/TOC ratios (4 % and 8 %) are characteristic of remote alpine lakes and that much higher ratios (10 % and > 10 %) are found in urbanized areas. The values of BC/TOC in the present coastal sediments (2.4–13 %) suggested that BC is a significant component of TOC and are comparable to East and South China Sea (5–14 %; [117]), in harbor and gulf sediments of Norway (6.4–12.3 %; [118]), in Guanabara of Brazil (2.3–12.8 %) [119] and in Cadiz of Spain (3–16.5 %) [120]. Moreover, the value of BC/TOC<0.11 designates the incomplete biomass combustion for BC source while the value of BC/TOC approximately 0.5 indicates the fossil fuels burning, industrial and traffic emission as BC source [115]. The values for BC/TOC ratios in our study ranged from 0.05–0.29 with mean value of 0.12 (Table 7) which evidently specified the anthropogenic input of BC including mix sources of incomplete combustion of biomass and fossil fuel burning in coastal areas.

3.5.   Mass inventory and deposition flux of OCs

Mass inventory and deposition flux for organochlorines (OCPs and PCBs) is shown in Table 8. The sedimentary deposition fluxes (D) for $\sum$OCPs and $\sum_{26}$PCBs were 1.74 and 4.93 t year^{-1} in territorial area of Pakistan. This is the first calculated deposition flux for OCs in coastal region of Pakistan. Literature does not provide any record about annual deposition flux for OCs in coastal sediments from Pakistan. The same approach was used by Bouloubassi, et al. [73] for PAHs depositional flux in Gulf of Lions (Mediterranean Sea). The sedimentary mass inventories (I) indicated the presence of 13.1 and 37 metric tons of $\sum$OCPs and $\sum_{26}$PCBs respectively in the Arabian Sea coast of Pakistan which may be the potential contamination source for global oceans. By using the similar approach, previously Chen, et al. [74] reported the accumulation of 0.4 t OCPs in Pearl River Estuary and 1.4 t of OCPs in Northern South China Sea.

3.6.   Sedimentary BC burial flux

Sedimentary BC burial flux indicates how much BC is sequestered in the sediments. For this purpose the BC levels and sedimentation rates were used. The average sedimentation rate deduced from depth dependent empirical relationship was 0.44 cm/yr (Table 5). This value is in the range typically of coastal and continental shelf sediments. The BC burial flux in the eighteen coastal sites of Pakistan ranged between 183–766 µg/cm^2.yr with median value of 299±155 µg/cm^2.yr (Table 5). These burial flux values are higher and in some cases comparable with those calculated in similar coastal environments, e.g. Gulf of Cádiz; SW Spain (21–633 and 42–285 µg/cm^2.yr; using BPCAs as BC molecular markers, and a variant of the CTO method, respectively [52], inner shelf of northeastern USA (470–2300 µg/cm^2.yr) [96], inner shelf of Gulf of Maine Proper (86–194 µg/cm^2.yr) [96], or Gulf of Panama (100–300 µg/cm^2.yr; using a digestion with KOH/H$_2$O$_2$) [121].

3.7.   Risk assessment of OCs

To elucidate the potential ecotoxicological risks of OCs in the coastal areas of Pakistan, selected contaminant's concentration ranges from studied area is compared with widely used sediment quality guidelines (Table 9) for assessment of potential adverse biological impacts for coastal areas of Pakistan. The sediment quality guidelines such as Effect Range Low (ERL), Effect Range Medium (ERM), Threshold Effects Level (TEL) and Probable Effects Level (PEL) were used for elucidating the potential ecotoxicological risks associated with OCs in the studied area [5, 122]. The concentrations of DDTs and its metabolites (*p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT) were above the ERL values at 8 sampling sites. For ERM values, only two sites were potentially considered toxic for DDTs (sites RG and IH), one for *p,p'*-DDD (RG) and *p,p'*-DDE (IH) and none for *p,p'*-DDT. Considering TEL and PEL guidelines, 4 and 2 sites for DDTs, 5 and 1 for *p,p'*-DDD, 3 and 2 for *p,p'*-DDE and 1 and 0 were having adverse ecotoxicological effects. Overall for DDTs, two sites (RG and IH) were potentially at the highest risk in terms of ecotoxicological effects. Concentrations of *γ*-HCH were only above for TEL and PEL guidelines at 3 sites (GP-2, RG, IH). Similarly the heptachlor concentrations were also low as compared to DDTs. The

concentrations of heptachlor were only above for ERL values at 3 sites. For PCBs, 39, 6, 56 and 11 % sites are potentially at risk against ERL, ERM, TEL and PEL respectively (Table 9).

Table 8: Mass inventory (*I*) and depositional flux (*D*) for organochlorines (OCs) in territorial area of Pakistan coastal belt

Component	Mass Inventory (I)	Deposition flux (D)
	(Metric tons)	(t year^{-1})
∑HCHs	0.72	0.10
∑DDTs	1.02	0.14
∑Chlordane	9.36	1.33
Heptachlor	0.53	0.07
HCB	0.36	0.05
∑OCPs	13.1	1.74
Tri-PCBs	22.4	2.97
Tetra-PCBs	12.5	1.73
Penta-PCBs	1.4	0.20
Hexa-PCBs	0.25	0.04
Hepta-PCBs	0.21	0.03
∑$_{26}$PCBs	37	4.93

Table 9: Comparison of the OCs concentrations (ng g^{-1}) measured in this study to those specified by the sediment quality guidelines (SQGs) for potential ecotoxicological impacts

OC compound	SQGs Guidelines Values				This study: Range (mean)	Values Above Limits in this Study			
	ERL[a]	ERM[b]	TEL[c]	PEL[d]		ERL[a]	ERM[b]	TEL[c]	PEL[d]
p,p'-DDD	2	20	1.22	7.81	0.13-35.4 (3.94)	3 (GP-2, OTB, RG)	1 (RG)	5 (AI-1, GP-2, SMH-2, OTB, RG)	1 (RG)
p,p'-DDE	2.2	27	2.07	3.74	0.06-61.8 (16.5)	3 (PQ, RG, IH)	1 (IH)	3 (PQ, RG, IH)	2 (RG, IH)
p,p'-DDT	1	7	1.19	4.47	0.003-2.12 (0.34)	3 (GP-2, RG, IH)		2 (RG, IH)	
∑DDTs	1.58	46.1	3.89	51.7	0.07-77.5 (9.87)	8 (AI-1, GP-2, PQ, SMH-2, JW, OTB, RG, IH)	2 (RG, IH)	4 (GP-2, PQ, RG, IH)	2 (RG, IH)
γ-HCH			0.32	0.99	0.00-2.78 (0.34)	-	-	3 (GP-2, RG, IH)	3 (GP-2, RG, IH)
Heptachlor	0.5	6	2.26	4.79	0.08-2.25 (7.36)	3 (AI-1, RG, IH)			
∑PCBs	50	400	21.5	189	6-1206 (108)	7 (AI-1, SMH-2, RG, IH)	1 (IH)	10 (AI-1, PS, OMB, GP-2, SMH-2, HRE, RG, GB, IH)	2 (RG, IH)

[a] **Effects range low value**
[b] **Effects range medium value**
[c] **Threshold effects level**
[d] **Probable effects level**

Conclusion

This study presents the levels and distribution status of hydrophobic organochlorines and carbon contents (TOC and BC) in coastal sediments from Pakistan. Higher levels of organochlorines and carbon contents were found in southern region of coastal belt i.e., the metropolitan city Karachi and adjacent areas, possibly owing to escalating industrial and anthropogenic activities. Another aspect, in terms of role of carbon contents in fate and distribution of organochlorines was also elucidated in the present study, as by inference, literature reported strong sorption of hydrophobic organochlorines with black carbon. The Pearson correlation analysis and regression analysis proved that black carbon has a significant impact on the fate and distribution of organochlorines and is a better descriptor of organochlorines as compared to TOC. Further, levels of black carbon burial flux indicated the sequestration of huge amount of carbon in the form of black carbon in the Arabian Sea which can be used as a baseline data for further carbon sequestration studies. The sediment deposition fluxes (D) and mass inventories (I) indicated that presence of OCs at Arabian Sea coast of Pakistan may be the potential source of contamination for oceans around the globe. Risk assessment showed that most coastal sites are potentially at risk against any of the studied organochlorine contaminant. Further investigations are required to elucidate the sorption and partition behavior of OCPs and PCBs in relation to BC in the coastal sediments.

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Appendix I: Concentration of OCPs (along with metabolites of OCPs compounds) on each sediment sampling site

Location	α-HCH	β-HCH	γ-HCH	o,p'-DDD	p,p'-DDD	o,p'-DDE	p,p'-DDE	o,p'-DDT	p,p'-DDT	CC	TC	Heptachlor	HCB	∑OCPs
AI-1	0.29	0.07	0.07	0.34	1.81	0.06	n.d.	0.45	0.33	1.95	3.72	0.51	0.48	10.1
PS	0.22	0.26	0.08	0.18	0.18	0.03	n.d.	0.19	0.03	3.04	5.35	0.46	0.55	10.6
GP-1	0.13	0.16	0.03	0.06	n.d.	n.d.	n.d.	0.05	0.03	0.11	0.30	0.08	0.06	1.0
OMB	0.15	0.19	0.03	0.05	n.d.	0.02	n.d.	0.01	0.13	2.20	4.04	0.36	0.28	7.5
GP-2	0.33	1.57	1.58	1.23	6.62	0.12	1.54	0.74	1.02	1.92	3.91	0.41	0.25	21.2
PQ	0.42	0.51	0.09	0.72	0.61	0.17	2.57	0.13	0.06	2.48	4.68	0.41	0.13	13.0
SMH-1	0.13	0.16	0.00	0.17	0.22	0.02	n.d.	0.06	0.00	2.17	4.02	0.32	0.12	7.4
SMH-2	0.72	0.88	0.09	0.32	1.36	0.05	n.d.	0.21	0.05	1.89	3.71	0.39	0.16	9.8
JW	0.14	0.18	0.03	0.23	1.13	0.02	n.d.	0.30	0.03	1.76	3.34	0.24	0.12	7.5
OTB	0.25	0.31	0.04	0.64	2.23	0.06	0.06	0.42	0.06	0.59	1.14	0.15	0.12	6.1
DRE	0.09	0.12	0.04	0.05	n.d.	0.00	n.d.	0.02	0.01	0.43	0.83	0.14	0.33	2.1
HRE	0.19	0.23	0.04	0.08	n.d.	0.02	n.d.	0.05	0.15	0.57	1.21	0.29	0.50	3.3
RG	1.79	2.75	2.78	7.85	35.38	1.26	16.55	7.96	2.12	0.47	1.22	0.74	5.81	86.7
GB	0.22	0.07	0.07	0.20	0.13	0.02	n.d.	0.04	0.16	0.48	0.86	0.16	0.41	2.8
AI-2	0.15	0.08	0.08	0.20	0.14	0.02	n.d.	0.04	0.11	1.97	3.72	0.21	0.07	6.8
GBA	0.13	0.03	0.03	0.13	0.14	0.01	n.d.	0.09	0.12	0.13	0.38	0.12	0.14	1.4
PBJ	0.07	0.01	0.02	0.03	n.d.	n.d.	n.d.	n.d.	0.04	0.19	0.37	0.09	0.11	0.9
IH	0.92	0.28	1.04	9.95	1.20	2.30	61.80	0.52	1.73	0.69	4.85	2.25	19.42	107
Sum	6.34	7.84	6.12	22.43	51.17	4.17	82.51	11.28	6.17	23.06	47.63	7.36	29.06	305.2
Mean	0.35	0.44	0.34	1.25	3.94	0.26	16.50	0.66	0.34	1.28	2.65	0.41	1.61	17
SD	0.42	0.69	0.74	2.82	9.61	0.62	26.17	1.89	0.62	0.95	1.79	0.49	4.64	29.7
Range	0.07-1.79	0.005-2.75	0.00-2.78	0.03-9.95	0.13-35.4	0.004-2.30	0.06-61.8	0.01-7.96	0.003-2.12	0.11-3.04	0.3-5.35	0.08-2.25	0.06-19.42	0.9-107

n.d.: not detected

Appendix II: Concentration (ng g^{-1}) and descriptive statistics of PCBs data

Location	Tri-PCBs [a]	Tetra-PCBs [b]	Penta-PCBs [c]	Hexa-PCBs [d]	Hepta-PCBs [e]
AI-1	67.1	29.9	4.3	0.5	0.1
PS	13.2	7.7	0.8	0.1	0.1
GP-1	5.1	5.1	0.6	0.1	0.1
OMB	16.0	7.1	0.9	0.2	0.2
GP-2	26.2	13.2	4.0	1.4	1.5
PQ	4.4	3.5	0.3	0.1	0.1
SMH-1	5.5	2.2	0.2	0.0	0.1
SMH-2	86.3	26.4	0.8	0.1	0.1
JW	5.4	3.5	0.4	0.1	0.1
OTB	3.7	3.9	0.8	0.1	0.1
DRE	12.2	7.1	0.8	0.0	0.1
HRE	17.8	7.5	0.8	0.2	0.2
RG	128.5	117.0	22.1	2.4	1.1
GB	21.9	17.1	3.6	0.5	0.1
AI-2	2.3	2.6	0.7	0.3	0.3
GBA	5.1	5.2	1.3	0.3	0.1
PBJ	4.2	3.0	0.4	0.1	0.0
IH	717.7	387.1	88.2	9.3	4.0
Mean	63.5	36.1	7.3	0.9	0.5
SD	166.8	91.6	20.8	2.2	1.0
Min	2.3	2.2	0.2	0.0	0.0
Max	717.7	387.1	88.2	9.3	4.0

[a] **Sum of PCB 28,37**
[b] **Sum of PCB 44,49,52,60,66,70,74,77**
[c] **Sum of PCB 82,87,99,101,105,118,126,128**
[d] **Sum of PCB 138,153,166**
[e] **Sum of PCB 170,179,180,183,187**