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Assessing the relationship and influence of black carbon on distribution status of organochlorines in the coastal sediments from Pakistan

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ABSTRACT

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 eighteen coastal sites ($n = 285$) along the Arabian Sea from Pakistan. Results showed that the total concentration of TOC, BC, $\sum$OCPs and $\sum_{26}$PCBs ranged between 0.3 and 2.9% dw, 0.1–0.2% dw, 0.9–110 ng g^{-1} dw and 6.2–1200 ng g^{-1} dw, respectively. Correlation analysis of BC ($r = 0.26$–0.89) and TOC ($r = 0.06$–0.69) revealed a stronger association with studied compounds. The sedimentary depositional fluxes (D) for $\sum$OCPs and $\sum_{26}$PCBs were calculated as 1.7 and 4.9 tons yr^{-1}, respectively. In the coastal belt of Pakistan, sedimentary mass inventories (I) indicated the presence of 13 and 37 metric tons of $\sum$OCPs and $\sum_{26}$PCBs, respectively.

1. Introduction

Organochlorines (OCs) including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) 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 (Feng et al., 2011; Hu et al., 2009; Zhang et al., 2013). Their unique properties make them persistent in the environment, where they can exert chronic toxic effects on humans and wildlife (Lin et al., 2012a; Liu et al., 2012). Yet, these toxic pollutants have been used globally for industrial and agricultural purposes from several decades (Barakat et al., 2013).

Sediments are usually considered as ultimate sink for persistent organic pollutants and are considered as one of the best media for their long term monitoring (Ali et al., 2014; Malik et al., 2014). Investigation of OCPs and PCBs in coastal sediments therefore, provides important baseline data for assessment of POPs (Pazi et al., 2012). Significant amount of these toxic contaminants accumulate in the coastal sediments because of their hydrophobicity, low water solubility and sorption to particulate matter (Kucuksezgin and Tolga Gonul, 2012). 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 (Sánchez-García et al., 2010). Sorption is one of the key phenomena that affects the fate and behavior of contaminants in the sediments. Amorphous organic matter relatively homogenous, lipophilic and gel like matrix (Cornelissen et al., 2005) is one of the responsible agents for the absorption of contaminants in sediments (Accardi-Dey and Gschwend, 2002). Another form of organic matter of glassy and condensed type, generally termed as carbonaceous geosorbents (CG), is involved in the adsorption of hydrophobic contaminants (Semple

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et al., 2013). 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 (Sun et al., 2008). 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 (Hung et al., 2006; Jonker and Koelmans, 2002). 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 (Masiello and Druffel, 1998). 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 (Ahrens and Depree, 2004; Huang et al., 2003; Jonker and Koelmans, 2002; Koelmans et al., 2006).

Coastal areas of Pakistan are highly exposed to industrial and anthropogenic activities. In these areas, 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 (Mumtaz, 2002). 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 (Mumtaz, 2002). It is generally noted that the Sindh belt is more polluted than Balochistan belt due to the diverse range of industrial and anthropogenic activities developed in the former (Mumtaz, 2002).

Two main rivers, Malir and Lyari contribute with sedimentary loads from river Indus to the Arabian Sea. These are thus the main sources of sedimentary pollution attributed to upstream and industrial wastes to shelf regions. Malir River receives 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 (Hasnie and Qureshi, 2002; Siddique et al., 2009). 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.

Therefore, a detail study was conducted to assess the environmental distribution of OCs in 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 and depositional flux of OCs in the 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.

2. Materials and methods

2.1. Sediment 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 285 subsamples including Dasht River Estuary (DRE; $n = 19$), Jiwani (JW; $n = 16$), Old Marine Base Jiwani (OMB; $n = 15$), Ganz Beach Area (GBA; $n = 18$), Gwadar Port (sites GP-1; $n = 11$ and GP-2; $n = 12$), Gwadar Bay (GB; $n = 15$), Pasni (PS; $n = 17$), Pasni Bay Jetti (PBJ; $n = 16$), Astola Island (sites AI-1; $n = 14$ and AI-2; $n = 17$), Ormara Turtle Beaches (OTB; $n = 11$), Hingol River Estuary (HRE; $n = 18$), Somiani Miani Hor (sites SMH-1; $n = 19$ and SMH-2; $n = 19$), Ibrahim Haidri (IH; $n = 18$), Rohri Goth (RG; $n = 15$) and Port Qasim (PQ; $n = 15$). 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 (Fig. S1 & Table S1). Sediment samples were collected in January, 2012 at different depths (Table 1). All sediment samples were taken by using a hand trowel, kept in polyethylene bags and brought to the laboratory, stored frozen at −4 °C until further analysis.

2.2. Analyses of OCs and QA/QC

A total of 26 PCB congeners (PCB-28, PCB-37, PCB-44, PCB-49, PCB-52, PCB-60, PCB-66, PCB-70, PCB-74, PCB-77, PCB-82, PCB-87, PCB-99, PCB-101, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-166, PCB-170, PCB-179, PCB-180, PCB-183 and PCB-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). Detailed analytical procedures and QA/QC data were provided in the Supporting Information (S1: Analysis and QA/QC). Briefly, after adding surrogates, sediments (20 g) were Soxhlet extracted with DCM. Clean-ups were done by column chromatography, and the measurement was conducted using an Agilent 7890/7000 GC–MS/MS. The specific multiple reaction monitoring (MRM) parameters for the target compounds are shown in Tables S2 and S3. All reported values were corrected by the blanks values and surrogate recovery.

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

Total organic carbon (TOC) was determined by TOC analyzer (Multi N/C 3100 Analytik Jena). For black carbon (BC) detection, the chemo-thermal oxidation (CTO-375) method described elsewhere (Elmquist et al., 2008, 2007; Gustafsson et al., 2001) 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 (Elmquist et al., 2007). The residual organic carbon content was determined as BC by using a TOC analyzer (Multi N/C 3100 Analytik Jena).

2.4. Depositional flux and mass inventory of OCs

The depositional flux of OCs was estimated based on OCs concentrations (ng g^{-1}), mass accumulation rate (g cm^{-2} yr^{-1}) and area (territorial; 21,335 km^2). Mass accumulation rate was calculated by using the sedimentation rate (cm yr^{-1}) via density (g cm^{-3}) of the dry sediment samples. Then, depositional flux was calculated by using following formula (Bouloubassi et al., 2012):

$$D = \frac{\sum_{i=1}^{n} AR_i \times [OCs]_i}{n} \times A \quad (1)$$

Here, AR_i is the mass 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 (metric tons) for OCs were calculated in order to assess the potential of sediments as a new contamination source for marine environments (Chen et al., 2006). The mass inventory was calculated by using following formula (Lin et al., 2009; Qin et al., 2011):

$$I = C \cdot A \cdot d \cdot \rho \quad (2)$$

Here, C is the median concentration of OCs compounds of interest in coastal sediments, A is the territorial area (21,335 km^2), d is the density (1.5 g cm^{-3}) and ρ is the mean sediment depth (5.5 cm).

Table 1
Mean depth (cm) and descriptive statistics of organochlorines levels (ng g^{-1} dw) in the coastal sediments from Pakistan.

Compound (ng g^{-1})	Mean	SD	Range
Depth	5.5	–	3–7
∑HCHs	1.1	1.8	0.1–7.3
∑DDTs	9.9	24	0.07–78
∑Chlordane	3.9	2.7	0.4–8.3
Heptachlor	0.41	0.49	0.08–2.2
HCB	1.6	4.6	0.06–19
∑OCPs	17	30	0.9–110
Tri-CBs	63	170	2.3–720
Tetra-CBs	36	92	2.2–390
Penta-CBs	7.3	21	0.16–88
Hexa-CBs	0.87	2.2	0.01–9.2
Hepta-CBs	0.47	0.96	0.03–4
$\sum_{26}$PCBs	110	280	6.2–1200