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## Significance of black carbon in the sediment–water partitioning of organochlorine pesticides (OCPs) in the Indus River, Pakistan

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### ABSTRACT

This study was conducted with the aim of assessing the levels and black carbon mediated sediment–water partitioning of organochlorine pesticides (OCPs) from the Indus River.  $\Sigma$ OCPs ranged between 52–285 ng L<sup>-1</sup> and 5.6–29.2 ng g<sup>-1</sup> in water and sediment samples respectively. However, the ranges of sedimentary fraction of total organic carbon ( $f_{\text{TOC}}$ ) and black carbon ( $f_{\text{BC}}$ ) were 0.82–2.26% and 0.04–0.5% respectively. Spatially, OCPs concentrations were higher at upstream sites as compared to downstream sites. Source diagnostic ratios indicated the technical usage of HCH ( $\alpha$ -HCH/ $\gamma$ -HCH > 4) and significant presence of DDT metabolites with fresh inputs into the Indus River as indicated by the ratios of (DDE+DDD)/ $\Sigma$ DDTs (0.27–0.96). The partitioning of OCPs between the sediments and water can be explained by two carbon Freundlich adsorption model which included both organic carbon and black carbon pools as partitioning media.

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### 1. Introduction

Organochlorine pesticides (OCPs) are an important group of persistent organic pollutants (POPs) which are toxic, persistent, bio-accumulative and have the ability of long-range transport potential (Ali et al., 2014b; Lohmann et al., 2007). These chemicals are widely known for causing adverse and toxic effects in humans including immunological, carcinogenic and reproductive disorders (Sanpera et al., 2003). Therefore, use of these chemicals was generally prohibited in the early 1970s (Zhang et al., 2011). Though Pakistan also holds several legislations regarding the control or phasing out of OCPs, still there exists a huge gap between legislation and its proper implementation (Ali et al., 2014b). Recent studies (Ali et al., 2015a, 2015b) conducted in the Indus River Basin of Pakistan showed higher levels of POPs owing to the increasing industrial and agricultural activities being presently developed in the region. Indus River plays a critical role in the agricultural sector of the country. It has a unique ecological importance in the region. The escalating anthropogenic activities along the Indus

River may seriously pollute the region with POPs. Application of banned pesticides on the surrounding fields and untreated domestic and industrial effluents could be the possible sources of OCPs in the study area. As a result, this study was performed in order to assess the pollution status of the area in terms of OCPs.

Sorption is a key process in environmental fate of organic chemicals in the sediments (Zhang et al., 2008). Previously, fraction of organic carbon or total organic carbon ( $f_{\text{OC}}$ ) was considered as a key factor responsible for controlling the sorption of hydrophobic nonionic organic compounds in the sediments (Chiou et al., 1979; Karickhoff, 1981). But this traditional paradigm has now been changed with publications of a number of recent studies that indicated the significant role of black carbon (BC) as better adsorbent than organic carbon for hydrophobic nonionic organic chemicals in the sediments (Accardi-Dey and Gschwend, 2002, 2003; Ali et al., 2014a; Cornelissen et al., 2004). The elevated sorption capacity of BC may be owing to the difference in physical–chemical characteristics of organic carbon and BC such as elemental composition, surface area and association of functional groups etc. (Zhang et al., 2008). The presence of strongly sorbing BC particles may be responsible for the reduced availability of nonionic organic compounds and associated ecotoxicity in the aquatic systems (Accardi-Dey and Gschwend, 2002; Zhang et al.,

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2013). Therefore, such relationships have now been proposed that may improve the correlations between solid and aqueous phase concentrations of the nonionic organic compounds by considering both OC and BC (Werner et al., 2009).

So far, no study was conducted that provides the BC mediated OCPs partitioning and distribution status for aquatic system of the Indus River, Pakistan. Therefore, this study was planned to investigate the significance of BC in sediment–water partitioning of OCPs in the Indus River. The objectives of this study were to: (1) provide the levels, sources and distribution of OCPs in water and sediments at major barrages of the Indus River, (2) analyze the sedimentary levels and sources of black carbon and (3) study the influence of sedimentary characteristics (i.e., black carbon) on water concentration of OCPs through sediment–water partitioning.

## 2. Materials and methods

### 2.1. Study area and sampling

The study area lies on the Indus River, covering an approximate stretch of 500 km. Indus River has a length of 3180 km with total drainage area of 1,165,000 km<sup>2</sup> and annual flow of 207 billion cubic meters (Nasir and Akbar, 2012; Waqas et al., 2012). Four stations were selected (SI Fig. 1) for water ( $n=37$ ) and sediments ( $n=37$ ) sampling i.e. Taunsa (TAU;  $n=7$ ), Kot Mithan (KM;  $n=6$ ), Guddu (GUD;  $n=13$ ) and Sukkur (SUK;  $n=11$ ). Water samples were collected at a depth of 0–5 cm in 1.5 L pre-cleaned bottles from the selected sites. Sampling bottles were pre-washed with acetone to avoid contamination. After collection, samples were placed in ice containing cooler and transferred immediately to Environmental Biology and Ecotoxicology Laboratory, where it was stored at  $-4^{\circ}\text{C}$  until further analysis. Sediment samples (0–20 cm)

were collected by using stainless steel hand trowel. After that, samples were kept in polyethylene bags, labeled and transported to Environmental Biology and Ecotoxicology Laboratory for further analysis. The detailed description of the study area, sites and sample collection, duration of sampling and general description during the sampling period is presented in the supporting information and SI Table 1.

### 2.2. Extraction and cleanup

Prior to extraction, all water samples (1000 ml) were filtered through Whatman 42 filter paper in order to eliminate debris and other tiny particles. The sediment samples were air-dried, sieved through 2 mm sieve and then transferred to Guangzhou China and stored frozen until further analysis. Liquid–liquid extraction method was used for the extraction of water samples (Eqani et al., 2012). 1 L of filtered water sample was added in a separatory funnel and a known quantity of 2,4,5,6-tetrachloro-*m*-xylene (TCmX) was added in each sample as surrogate standard. 75 ml of dichloromethane (DCM) was added to each sample, shaken vigorously for 2–4 min and allowed to settle down for 10 min to get two layers. Lower transparent layer of organic solvent containing pollutants was collected on anhydrous Na<sub>2</sub>SO<sub>4</sub> placed on glass wool. The extract was concentrated via rotary evaporator and the solvent phase was changed from DCM to hexane. The extracts were then evaporated to almost 2–3 mL and then eluted with 30 mL of hexane and DCM mixture (3:2 v/v) to purify via chromatographic column of deactivated alumina/silica gel (1:2 v/v). Eluates were concentrated to 0.2 ml under a nitrogen stream and spiked with an internal standard of PCB-209 before instrumental analysis (Eqani et al., 2012).

The sediment samples (20 g for each sample) were Soxhlet-extracted for 48 h with DCM. A mixture of TCmX was added as a surrogate standard in each sample prior to extraction. The extract

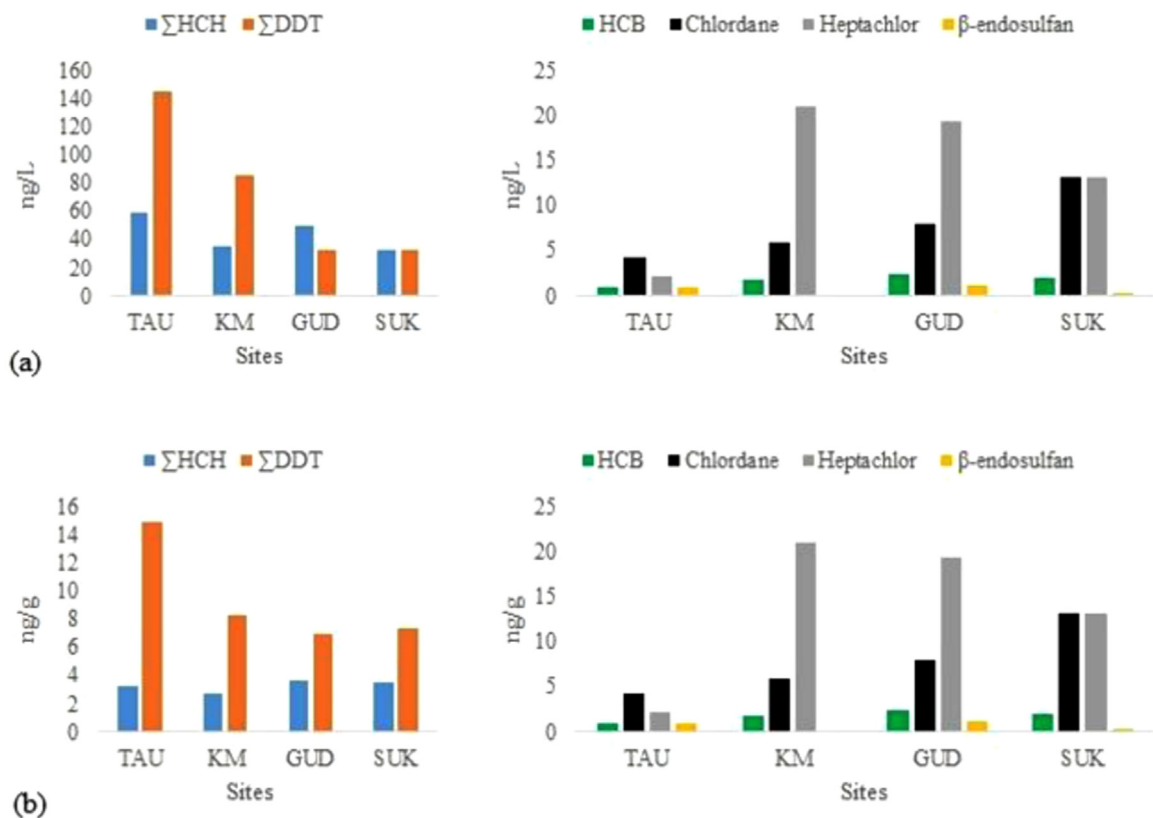


Fig. 1. : Spatial distribution of OCPs in water and sediments of the Indus River.

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