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Freely dissolved Organochlorine Pesticides (OCPs) and Polychlorinated Biphenyls (PCBs) along the Indus River Pakistan: Spatial pattern and Risk assessment

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Capsule: The study highlighted the LRAT of POPs into northern colder areas Pakistan and highlighted the re-emission of POPs into Indus River System

Abstract

Freely dissolved OCPs and PCBs were measured by using polyethylene passive samplers at 15 sites during 2014 throughout the stretch of Indus River to investigate spatial pattern and risk assess. Levels (pg/L) of dissolved ∑OCPs and ∑PCBs ranged from 34–1600 and 3–230. Among the detected OCPs, dissolved DDTs (*p, p′*-DDE, followed by *p, p′*-DDT) predominated with levels of 0.48 to 220 pg/L. The order of occurrence for other studied OCPs was as follows; HCB, Endosulfans, Chlordanes, and HCHs. Spatially, dissolved (pg/L) ∑OCPs varied ($p < 0.05$) as: surface water of Alluvial Riverine Zone (ARZ) showed highest levels (114) followed by Frozen Mountain Zone (FMZ) (52.9), Low Lying Zone (LLZ) (28.73) and Wet Mountain Zone (WMZ) (14.43) respectively. However, our zone wise PCBs data did not exhibit significant differences ($p > 0.05$). Principal component analysis/Multilinear Regression results showed that pesticides usage in crop/orchard fields and health sector, electric & electronic materials, and widespread industrial activities as the main source of OCPs and PCBs along Indus River. Our results showed that OCPs and PCBs contaminated water intake, played an important role towards the considerable cancer/non-cancer risk (HI and CR values) along the Indus River Flood-Plain.

Keywords: OCPs, PCBs, passive sampling, Indus River.

Introduction

Persistent organic pollutants (POPs) including organochlorine pesticides (OCPs) are widely used as pesticides for the crop protection and in health sector for malarial control (Ahad et al. 2010, Ali et al. 2014, Eqani et al. 2012b). Whereas industrial applications of polychlorinated biphenyls (PCBs) are included in paints and cements as plasticizers, in polyvinyl chloride (PVC) coatings as stabilizing additives, in reactive flame retardants, pesticide extenders and sealants for caulking, adhesives and coolants in electronic/electric industry (Sweetman &Jones 2000, Zhao et al. 2017). Other sources of PCBs contamination included open burning of e-waste, electrical manufacturing, e-waste, use in transformers, and leakage during transportation. Pakistan has also been reported to have major POPs hotspots (e.g. demolished DDT manufacturing units, obsolete pesticides stores, outdated pesticide burying grounds etc.), with the possibility of higher contribution towards global POPs emission. In recent years, studies have reported high OCP residues in the surrounding soils of different historical pesticides' stockpiles (Ahad *et al.,* 2010; Alamdar *et al.,* 2014; Khwaja *et al.,* 2006; Syed & Malik, 2011). Due to wide scale of POP usage, these chemicals are expected to be emitted into the surrounding environment including water bodies (e.g. lakes, rivers, marine ecosystem etc.) via surface runoff, and causing severe health impacts into aquatic/marine organisms and associated wildlife (Abbasi et al. 2015, Eqani et al. 2012b, Khan et al. 2017, Malik et al. 2011) Nawab et al., 2020). Several OCPs and PCBs possess high water/octanol (K_{ow}) values, which translates into great affinity/potential to magnify into the food chain due to their lipophilic characteristics. There is hence a high propensity to accumulate in many aquatic organisms (i.e., fish) and cause variety of adverse health impacts (Eqani et al. 2013, Gulland 1995, Sanpera et al. 2003). Additionally, some aquatic organisms represent a major part of the human diet, and pass on the accumulated toxic contaminants into

human beings via dietary intake. Many studies reported that POPs-contaminated fish poses enhanced health risks to the exposed human populations in various parts of the world (Dougherty et al. 2000, Eqani et al. 2013, Kalyoncu et al. 2009, Olsson et al. 2000). Human beings are exposed to POPs via several routes, which include the contaminated air inhalation, dust ingestion/inhalation, water and food (especially fish) (Ali et al. 2013, Dirtu & Covaci 2010, Eqani et al. 2012b, Maes et al. 2008, Whitehead et al. 2015). Exposure to POPs may also be implicated in severe human health impacts, which includes endocrine disruption, reproductive disorder, carcinogenic, neurological and immunological problems and birth defects (Bertazzi et al. 1998, Johnson-Restrepo et al. 2005, Kortenkamp 2008, Lee et al. 2010, Taylor et al. 2013).

OCPs and PCBs are also well known semi-volatile organic compounds (SVOCs), which have the potential to volatilize and re-emit from secondary sources (from previously contaminated environments), undergo long-term and short-term atmospheric transport (in semi-arid/arid areas), and be ultimately deposited into remote colder and/or high altitudinal locations, in particular north, south and third pole environment (Himalayan mountains) (Nasir et al. 2014, Wania &Haugen 1999). The process of transport of such SVOCs to long distances mainly occurs due to temperature and altitudinal variation and is well known as “Long Range Atmospheric Transport (LRAT)” and confirmed by many studies (Cincinelli &Dickhut 2011, Daly & Wania 2005, Davidson et al. 2003). Moreover, studies have also confirmed that remote colder areas acts as repositories of these chemicals, and in context of climate change, these repositories become highly active for remobilizing the chemicals in air and to the freshwater resources, which resulted in a major threat to human and wild life being through bio-accumulation processes (Khairy & Lohmann 2012, 2013, Sacks & Lohmann 2011). Additionally, open burning of e-waste has also been reported to release PCBs and other flame

retardants (Novel brominated flame retardants (NBFRs) and organophosphorus flame retardants (OPFRs) (Gioia et al. 2011, Tang et al. 2010, Wong et al. 2007). It is well known that E-waste such as electronic waste consists of heterogeneous mixture containing flame retardants (FRs), polychlorinated biphenyls (PCBs), and various other hazardous compounds (Robinson, 2009). However, (Iqbal et al. 2015, Iqbal et al. 2017) have pointed out that there is lack of the reliable data, inventories and research studies addressing e-waste issues in Pakistan.

Many studies have described the use of novel passive samplings i.e., low density polyethylene (LPDEs), for detecting/measuring POPs in various compartments of environment for exposure monitoring and evaluating POPs risk to human and wild-life at regional and global scales. Passive sampling gained considerable attention for its integrative sampling of contaminants from the environment and ability to catch episodic exposure in water (Schäfer et al. 2008, Shaw & Mueller 2009). However, studies along the Indus River in Pakistan are still scarce, and no study so far has relied on passive sampling of water to measure dissolved POPs in surface waters. Similarly, the authenticated data from Pakistan on dissolved fraction of POPs is also needed as previously studies followed questionable method of water sampling and/or they collected the water samples including the suspended particulate material, which overestimate the levels of “dissolved” POPs. The problem can be overcome by following few recent studies from USA and European labs, which have described the use of these novel passive samplings (i.e., LPDEs and PS, PUFs) for detecting/measuring POPs in different water bodies (Harner et al. 2006, Levy et al. 2009, Lohmann & Muir 2010).

The present study was conducted for reporting the levels, distribution and apportionment of emission sources of POPs (i.e., organochlorine pesticides (OCPs),

polychlorinated biphenyls (PCBs) into the Indus River, Pakistan. The study had the following main objectives. 1) To investigate the levels, compositional pattern, potential sources and 2) Risk assessment of POPs into the Indus water ecosystem of Pakistan via passive sampling.

Materials and Methods

Study Area and Field Strategies

The Indus flood-plain area is inhibited by more than 100 million human people and these areas is dependent on Indus River for agricultural activities and for fishing. The Indus River originates in the Tibetan plateau near the Lake Mansarovar, proceeds via the Ladakh region (Jammu and Kashmir), Gilgit Baltistan and then flows towards south direction along entire length of Pakistan and finally merges into Arabian Sea near Karachi, Sindh Pakistan. The Indus River is the largest as well as longest river that flows throughout the entire length from north to south of Pakistan and its catchment area possesses diverse ecological systems i.e., snow-capped northern areas, lower Himalayan mountainous valleys, agricultural plains in the south and coastal areas near Arabian sea. The Indus River also runs through the densely polluted and populated industrial cities of Punjab Province and the Khyber Pakhtunkhwa (KPK) Province, Pakistan, receiving a higher amount of pollutants from the industrial and municipal effluents through various streams and its tributaries such as Chenab River, Ravi River and Jhelum River.

After the preliminary survey of study area, fifteen sampling sites were selected along the entire stretch of Indus River, where the passive samples were installed during 2014. These sites include Gilgit, Hunza, Skurdu, Swat (Gullibagh, Kalam, Malamjaba), Swabi, Nowshera Mianwali, Bakkar, Layyah, D.G Khan, Sukkur, Khairpur and Hyderabad. The detailed description of each site is given as **Text S1** and **Table. S1.** Sites location was identified in the catchment using a GPS (Global Positioning System, Garmin) and mobile weather station was

used for recording the climatic data of each studied site. Low Density Polyethylene sheets (LDPE) were deployed in the surface waters for three weeks.

Passive sampling for water

First, a roll of about 2 cm wide, 60 cm long and 100 microns thick LDPE tubing was cut off and cleaned with hexane. They were treated twice for 24 h in graduated cylinder with 250 mL n-hexane and were cleaned from inside and dried in a nitrogen stream for 30 minutes. Subsequently, these tubes were welded (front and back twice) and put for storage in container. For the spiking, two performance reference compounds (PRCs) such as Tetrachlorometaxylene (TCmX) and PCB-29 were selected which are deuterated possible structural isomers of the substances. For this step, a polyethylene tube was put in 1.5 L bottle containing 1 L of water and then added 10 μg of deuterated substance.

These were first capped and clamped for 72 hours in over headed shaker (15 rpm speed). Discarded the solution and the tubes dried with the pulp and frozen till outdoor exposure. For the deployment, the polyethylene tubes were then placed in space provided by the grating and screwed. LDPE passive water samplers were deployed 1 m below the surface attached to small buoys. Each sampler was assembled at the deployment sites to avoid contamination during transportation. A photo was taken for documentation, quality assurance **(Fig. S4).** At the completion of the deployment period, the LPDE were retrieved, resealed and returned to Lohmann Lab, University of Rhode Island, for analysis. The detailed methods have been reported elsewhere (Schäfer et al. 2010). Sampling rates were calculated using the PRCs as follows:

$$f = exp\ (-Rs \times t / K_{LDPE-water} \times m_{LDPE}) \qquad (1)$$

Where f is the fraction of PRC retained in the passive sampler after deployment. Details on the PRC method have been described elsewhere (Booij et al., 2002; Khairy et al., 2014)

Extraction and Clean-up of passive water samples

Details of LDPE extraction can be found elsewhere (Khairy &Lohmann 2013). Briefly, the PE tubes were cold extracted twice in ethyl acetate each for 24 hours after spiking with 10 µL of surrogate standards mixture composed with labelled organochlorine pesticides (13C6-hexachlorobenzene and 13C12-p,p´-DDT, 5 ng.mL^{-1} in nonane) were added before extraction. The resulting extracts were combined and concentrated to 1 mL on a TurboVap, solvent exchanged to the hexane, and concentrated to ~50 µL using a gentle stream of ultrapure nitrogen. Injection standard was added for volume correction to all sample extracts prior to analysis.

Chromatographic Analysis

The target compounds were DDTs (*o, p′*-DDD, *p, p′*-DDD, *o, p′*-DDE, *p, p′*-DDE, *o, p′*-DDT, *p, p′*-DDT), HCB, HCHs (α-HCH, β-HCH, δ-HCH and γ-HCH), cis-chlordane (CC), trans-chlordane (TC) and trans nonachlordane (non-trans), Endosalfan I, Endosalfan II, Endosalfan salphate, Adlrin, Endrin, Methoxychlor, Heptachlor and Polychlorinated Biphenyl ($\sum_{31}$PCBs) PCB-11, PCB-28, PCB-58, PCB-74, PCB-70, PCB-44, PCB-49, PCB-37, PCB-60, PCB-66, PCB-77, PCB-82, PCB-87, PCB-101, PCB-123, PCB-118, PCB-114, PCB-126, PCB-105, PCB-153, PCB-187, PCB-169, PCB-156, PCB-128, PCB-166, PCB-158, PCB-183, PCB-198, PCB-195, PCB-189 and PCB-170) were analyzed using an Agilent GC 6890N with a DB-5 MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) equipped with a Quattro micro GC tandem MS (Waters). The injector temperatures were set to 250 °C. The initial temperature of oven were set at 150 °C for 3 min, and then raised to 290 °C at a rate

of 4 °C/min and held for 10 min. Persistent organic pollutants (POPs) were then determined in selected ion mode (SIM). MSD sources and quadruple temperature were 230 °C and 150 °C. The MS used in this case were in SIM mode having two ions monitored for each of the target compound group in a specific window. DDT inlet degradation was daily checked and control within the 15%. All the persistent organic pollutants (POPs) were quantified using HP-Chemstation to confirm the peaks.

Statistical Analysis

Analytical results were organized by using Excel software. Graphical representation of POPs data was made using Microsoft Excel 2016 and Arc-GIS (version 10.2) was used for showing various sampling locations on map and the spatial distribution of different chemicals. A level of $p < 0.05$ was considered statistically significant for multiple comparisons. A one-way ANOVA then followed by Tukey's HSD post hoc test were employed for making multiple comparisons among the different contaminants and zones. Principal component analysis/Multilinear Regression (PCA/MLR) by using SPSS Statistics (version 21) was then performed for investigating the qualitative source for target OCPs and PCBs measured in the water of Indus River, Pakistan. The detail of calculations of human health risk assessment is describes as **Text S3** in the supplementary material.

Quality assurance & Quality control (QA/QC)

For QA/QC, the instruments were daily calibrated with the calibration standards. Three solvent blanks, five field blanks and five procedural blanks were analysed by using the same procedure as for the real samples. OCPs and PCBs concentrations in LDPE sheets were corrected by surrogate standard recoveries and blank subtracted using the field blank relevant to the sampling location. For every batch, internal standards were then injected into Gas Chromatogram before

the sample injection. Recoveries of 13C6-HCB and 13C12-p,p'-DDT were 66 + 13 % and 80 + 16 % in the water samples. There was no significant difference between selected OCPs and PCBs concentrations in the field and laboratory blanks, indicating negligible contamination during transport, storage and analyses. The limit of detection (LOD) was calculated as the average laboratory blanks plus three times the standard deviation. DiBB (2,5 dibromobiphenyl), TeBB (2,2'5,5' tetrabromobiphenyl), PeBB (2,2',4,5',6 pentabromobiphenyl) and ACN added before GC-MS analysis as an internal standard. The processing of data acquisition was controlled by Agilent MSD Productivity Chemstation software version G1701EA E.02.02.1431. All the chemicals were of analytical grade and were purchased from the Merck, Germany. All solvents used in this study, redistilled for purifying solvents to reduce any interference effects of solvents. All glassware used in this study were baked (450 ^{o}C) for 6 hours prior to use.

Results and Discussion

Freely dissolved OCPs and PCBs

Sampling rates (Rs) for water passive samplers are given in **(Table S2).** The sampling rates of the polyethylene passive water samplers ranged from 9.0 to 91 L/day at all sampling sites. These values of sampling rate were consistent with the sampling rate of study done from water at wetland mountain sites of S-SE Brazil (Meire et al. 2016). Rs value for Hyderabad site (S-15) of low-lying zones (LLZ) showed highest values (91 L/day) while Gilgit site (S-2) of frozen mountain zones (FMZ) showed low sampling rate i.e., 9.0 L/day.

Freely dissolved OCPs levels ranged from 34-1600 pg/L throughout Indus River as shown in **Table 1 & Fig 1.** Among the studied OCPs (pg/L), DDTs (0.48-220) dominated, followed by endosulfan (0.20-14), HCBs (0.23-6.4), chlordane (0.09-4.58) and HCH (BDL-2.64). *p, p'*-DDE accounted for higher frequency among the studied OCPs at most of the studied

site locations**.** In contrast, trans nonachlor (0.09 pg/L) was among the less frequently detected pesticides in the surface water of the Indus River. The freely dissolved levels of OCPs in various zones showed the following trends; Alluvial Riverine zone (ARZ) ranged from (19.28-259.70 pg/L) > Frozen mountain zone (FMZ) (2.77-201.80 pg/L) > Low lying zone (LLZ) (1.67-58.05 pg/L) and > Wet mountain zone (WMZ) (1.35-42.24 pg/L) in descending order, respectively **(Table.1).** The levels of OCPs measured at WMZ and FMZ similar to those reported in water of Glacial-fed lakes, Ice melting-fed lake and Rain-fed lake in remote alpine lakes located in Himalayas, Pakistan (Nawab et al. 2020) and the valley of Kashmir (Ullah et al., 2019). The current OCPs values were much lower than those detected from the previously studied surface water samples from River Chenab (Eqani et al. 2012b), and River Ravi, Pakistan (Baqar et al. 2018). In previous studies conducted at Pakistan, the authors (Baqar et al. 2018, Eqani et al. 2012b) documented the active water sampling followed by the liquid-liquid extraction method, which reflected both dissolved and suspended particulate material associated POPs level.

Historically, DDTs has been reported to be widely used OCPs for controlling the crop pests and malarial outbreaks in Pakistan (Eqani et al. 2012a, Malik et al. 2011). Along the Indus River, DDT and its metabolites (*p, p′*-DDE) were frequently detected as shown in **Fig 2a.** The freely dissolved concentration of DDTs ranged from 0.48–220 pg/L. Moreover, the dissolved *p, p′*-DDE concentration ranged from BDL–150 pg/L (mean: 30) and consistent with already reported values of *p, p′*-DDE in Lake Erie (19 pg/L) (Blanchard et al. 2008). Other DDTs followed the occurrence order in descending order as; *p, p′*-DDT (0.12-35.34; mean: 9.47), *p, p′*-DDD/ *o, p′*-DDT (0.04-17.43; 4.0), *o, p′*-DDE (0-12.21; 2.11) and *o, p′*-DDD (0.06-8.88; 1.90). Our DDTs levels were relatively higher than those of wetland mountain region of S-SE Brazil (0.2–0.3 pg/L) (Meire et al. 2016). (Schreiber et al. 2013) reported the analogous DDTs levels to

current study, as dissolved *p, p′*-DDEs fraction in the upland surface water of the River Xanaes in the Central Argentina was measured as 70-340 pg/L. Nevertheless, various ratios between parent compound and their metabolites were reported into the literature, to track/fingerprint the possible sources, their age and usage patterns at specific areas/region (Jiang et al. 2009). It has been documented that dechlorination of DDTs may convert their isomers to its metabolites e.g., *p, p′*-DDT into *p, p′*-DDE in the presence of aerobic condition and reductively converted into the *p, p′*-DDD in the presence of anaerobic conditions (Zhang et al. 2006). Hence, DDT/(DDD+DDE)<1, showed the historical usage of DDTs whereas value higher than unity indicated fresh/current usage (Gao et al. 2013, Jiang et al. 2009). In present study, *p, p′*-DDT /(*p, p′*-DDE + *p, p′*-DDD) value is lower than unity at most of the studied location with few exceptions included the sites of swat, hunza and gilgit of FMZ, where DDTs diagnostic ratios indicating the current as well historical usage of this banned pesticide **(Fig.S2).** Additionally, the values for the DDD/DDE ranging from 0.09-5.95 (with mean value of 0.65). Generally, all the sites showed the values below unity reflected the aerobic degradation of DDTs in these areas which might be due to the frequent ploughing/crop cultivation in the agricultural field. In contrary, the Hunza site showed the DDD/DDE as 5.95, indicating that the DDT in the soil is metabolized in anaerobic environment, which could be explained by high organic matter contents and its microbial degradation in these forests covered areas. The *o, p′*-DDT/ *p, p′*-DDT ratio has reported to assess the usage of dicofol as possible additional source of DDTs in the environment. The ratio of the *o, p′*-DDT / *p, p′*-DDT ranged from 0.2 to 0.3 in the technical DDT and is 7.0 ± 2.2 in dicofol (Qiu et al. 2005). In the current study, ratio of the *o, p′*-DDT / *p, p′*-DDT ranged from 0.23 to 0.98 and highlighted that the major usage of technical DDT in the Indus flood plain **(Fig. S2)**.

Among the HCHs, γ-HCH contributed significantly among all dissolved HCHs and ranged from 0-2.64 pg/L. The dominance of γ-HCH in the surface water of Indus water can be explained by the higher water solubility of γ-HCH. Moreover, lindane (containing 90% of γ-HCH) has also been reported to be used in current study areas (Eqani et al. 2012a, Eqani et al. 2012b) which would have reached the aquatic ecosystem through surface runoff. In contrary to this, the other HCHs (β-HCH and α-HCH) have more affinity (K_{ow} ~ 3.8 and 3.72) to bind/adsorb onto the surface of suspended particulate material and finally deposit into the bed sediments (Eqani et al. 2011). The concentrations of HCHs were consistent with those observed in the Great Lakes, USA, (4 pg/L) in earlier studies (Khairy et al. 2014). The current values were lower than those detected in the surface water of River Chenab (Eqani et al. 2012b), and River Ravi, Pakistan (Baqar et al. 2018) and Chinese fresh water resources (Luo et al. 2004, Tang et al. 2008) and from Kolleru Lake, India (Sreenivasa Rao &Ramamohana Rao 2000).

Freely dissolved chlordanes (trans-, cis-, and trans-nonachlor isomers) were detected at many instances (>50 % of total samples) along the Indus River. Levels of trans-chlordane were slightly higher than cis-chlordane and the ratio of TC/CC >1 were taken generally to be indicative of recent usage of chlordanes. Trans-nonachlor (TN)/TC ratio in technical chlordane is reported as 0.42 and the ratio TN/TC is 0.52 in Indus River indicating the lower concentration of trans-nonachlor as compared to trans-clordane. The concentration of freely dissolved total chlordane (0.96 pg/L) into the Indus River was lower than those from Lake Erie (56 pg/L) (Khairy et al. 2014).

In Pakistan, the wide scale application of endosulfan has been reported for crop protection, which can cause a variety of health abnormalities (Eqani et al. 2012a, Islam et al. 2018). In our study, ∑endosulphans ranged from BDL–12.83 pg/L in the dissolved fraction throughout the

Indus River. Among the various zones, WMZ (6.41 pg/L) showed higher concentration of dissolved endosulfan followed by ARZ (2.31 pg/L) > FMZ (1.28 pg/L) > LLZ (1.27 pg/L). In general, endosulphans compositional trends showed the dominance of endosulfan-I and endosulfan sulphates and reflected the current as well as aged use of this insecticide (Weber et al. 2010). However, our measured levels were much lower than those found in Pakistani water bodies (Ahad et al. 2006, Baqar et al. 2018, Eqani et al. 2012b) and in mountain water and snowpack sample of the Western USA National Park (44-1500 pg/L) (Blais et al. 1998, Blais et al. 2001).

Similarly, HCB was also detected at most of the sampling sites throughout the studied stretch of the Indus River, Pakistan and its levels (pg/L) ranged from 0.23 to 6.41. The mean values of HCB in various studied zones followed the trends as; ARZ (3.11 pg/L) followed by > FMZ (2.89 pg/L) > WMZ (0.50 pg/L) > LLZ (0.45 pg/L) in descending order. These HCB levels were consistent with the HCB level in the South Atlantic (1.9-3.3 pg/L), and South Pacific (0.4-0.8 pg/L) open water transects (Zhang &Lohmann 2010). However, these HCB values were relatively lower than those reported from River Chenab, Pakistan (0.29–87 ng/L and 0.43–87 ng/L during summer and winter seasons, respectively) (Eqani et al. 2012b). These concentrations were also lower than those from the Baiertang waters, China and Yellow river, China (Luo et al. 2004, Tang et al. 2008) and from Kolleru Lake, India (Sreenivasa Rao &Ramamohana Rao 2000). Moreover, these HCB level were also much lower as compared to the levels reported in the South American freshwater bodies i.e. 1000-10,000 ng/L (UNEP, 2002).

In the Indus River water, total freely dissolved concentration (pg/L) of $\sum_{21}$ PCBs measured at FMZ as 7.44-226 (average value: 95.36) followed by at WMZ as 41.91-199 pg/L (120.54), at ARZ 30.88-144.96 (82.02) and at LLZ as 3.02-26.69 (14.86). The descriptive statistic of total

concentration of freely dissolved $\sum_{21}$ PCBs are given in **Table 2**. The occurrence trends of different PCBs homologues in the Indus River followed the order as: tri-CBs (~29–71%) > penta-CB (~3–9%) > tetra-CB (~3–8%) > octa-CBs (~3–6%) > hexa-CBs (~2–3%) > hepta-CBs (~1–2%) **(Fig. 2b).** Tri-chlorinated biphenyls were among dominant homologs at the bhakkar site of ARZ followed by gulibagh site of FMZ, swabi at WMZ and sukkar at LLZ. Tetra-chlorinated biphenyls levels were higher at bhakkar at LLZ followed by sukkar at LLZ, kalam swat at FMZ and swabi at WMZ. Regarding penta CBs, still higher concentration at bhakkar site followed by gilgit, swat, nowshera and hyderabad. Other PCBs like hexa-chlorinated biphenyls were higher in gilgit, hepta and octa-chlorinated biphenyls at skardu of FMZ. These distributions are consistent with tri-, and tetra-chlorinated biphenyls being released from longer range transport sources, due to the greater volatile nature of these lower chlorinated biphenyls. In contrast, penta-, hexa and hepta- chlorinated biphenyls due to their lower volatility, were released from more local sources. The present study has shown that levels of PCBs at FMZ, WMZ and ARZ were consistent with the levels reported for Lake Erie (52–330 pg/L) and Lake Ontario 110–190 pg/L (Anderson et al. 1999, Khairy & Lohmann 2013) and high-mid altitude remote areas of Himalayas, Pakistan (Nawab et al. 2020). The concentration of $\sum_{21}$ PCBs (7.44-226) were relatively lower than those reported for River Chenab, Pakistan (Eqani et al., 2012), Minjiang Estuary, China (203.9–2473 ng/L) (Zhang et al. 2003), Tonghui River, China (31.58–344.9 ng/L) (Zhang et al. 2004) and Daya Bay, China (91.1–1355.3 ng/L) (Zhou et al. 2001). The current compositional profiles from the Indus River were similar to the commercial PCBs formulation of Aroclor-1242 -1260, -1262 and 1248 **(Fig. S3).** These Aroclors were used in different settings to enhance insulation, and improving physical and chemical resistance. They were also used as plasticizers, lubricants, coolants, and in electrical transformers, electrical

capacitors, vacuum pumps and gas transmission turbines, and might still be in use in transformers and capacitors. However, current evidences suggest that presently the major source of these Aroclor may be a recycling of what was previously introduced into the environment, involving evaporation and redeposition. The $\sum_7$dioxin like PCBs levels ranged from 0.07–0.81 pg/L (median: 0.35 pg/L) with higher value found into the urban areas of ARZ (nearby D.G Khan) due to extensive urbanization and industrial activities in this region. Fingerprinting of these contaminants has suggested to be very important because of their tetrachlorodibenzo -p-dioxins (TCDDs) like carcinogenic properties (Eqani et al. 2012b, Zhao et al. 2006). WHO_{05}-TEQs of the mono-ortho dioxins like PCBs (-105, -114, -118, and -156) and non-ortho dioxin like PCBs (-77, - 126, -169) were calculated which ranged from 9×10^{-6}- 4.3×10^{-5} (median: 1.2×10^{-5}) and 9×10^{-6}- 3.2×10^{-4} (median: 1.5×10^{-4}) pg TEQ/L into all samples **(Table S5)**. Among the individual mono-ortho DL-PCBs and the non-ortho DL- PCBs, PCB-105 and -169 contributed very significantly toward total calculated TEQs. Higher TEQs for mono-ortho DL-PCBs were calculated at ARZ followed by LLZ, FMZ and WMZ which showed the higher industrial activity at ARZ.

PCA/MLR based source appointment for OCPs and PCBs in the surface water of Indus River

Principal component analysis/multiple linear regression (PCA/MLR) was performed on the data of OCPs and PCBs for individual metabolites of DDTs, HCHs and PCBs homologues (i.e., tri-CB, tetra-CB, penta-CB, hexa-CB, hepta-CB and octa-CB) using varimax rotation method **(Fig. S7).**

In the frozen mountain zone (FMZ), the PCA extracted four components (explaining 33, 26, 24 and 13 variability, respectively), which is also shown as **Table S8.** The PC-1 accounted for 33.33 % variance and highlighted the *p, p′*-DDD, *o, p′*-DDT, *o, p′*-DDE, and *p, p′*-DDE. In

the past, DDTs were used for agricultural purposes and malarial control program and PCA/MLR has also indicated the historical as well as current illegally use of DDTs in agriculture and health sector in the studied area. Diagnostic ratio for DDTs in these areas has also indicated its fresh and/or aged uses of DDTs in these areas. Moreover, wet and dry deposition of atmospheric dust particles through the process of altitudinal fractionation can also justify the DDTs contamination in these areas (Khan et al. 2017, Sohail et al. 2018). Atmospheric DDT fallout into the freshwater ecosystem has also been reported worldwide as >150 Kg yr^{-1}. ΣDDT dust borne contamination has been estimated to the Great Lakes, USA due to wet and dry deposition (Hoff et al. 1996). The PC-1 also dominated by various polychlorinated biphenyles including octa-CB, hepta-CB and penta-CB, which reflected the long range dust borne PCBs contamination into this area (Eqani et al. 2012b). The PC-2 was accounted for 26.18% of the total variance and dominated by HCBs, hexa-CB and tri-CB. HCB act as intermediate product used in preparation of the OCPs and other industrial activities (Tolosa et al. 2010, Zhao et al. 2010). In the studies area, HCB might find their way into surface water via run off from contaminated soils and/or via dry and wet deposition of long range atmospheric particulate material. The PC-2 has also highlighted the hexa-CB and tri-CB and indicated the dry and wet deposition of long range atmospheric particulate material from surrounding countries (China and India and low-lying areas of Pakistan) into these high altitudinal areas as source of these pollutants. The presence of lower molecular weight PCBs can be linked through the gaseous deposition of these contamination via cold trapping process (Ali et al. 2017). The PC-3 accounted for 23.80 % of the total variance and dominated by octa and penta-CB, which are industrial chemicals used for paints, plastics, electronic goods such as capacitors and transformer oil and can present into these areas due to

long term dust particles deposition from nearby regions. The PC-4 accounted for 13.02 % of the total variance and dominated by *p, p′*-DDT and indicated fresh usage of DDTs in these areas.

PCA/MLR results for the wet mountain zone (WMZ) showed that only one factor explained > 90 % of the variation in data and highlighted the DDTs metabolites, HCBs and all CBs, originating from the common source and shown as **Table S9**. As mentioned earlier that lower Himalayans areas are historically receiving POPs/metals contaminated dust from the Indus floodplain and low-lying areas, which had built up POPs/metals levels, and now in context of rapid urbanization these contaminants are continually emitted into the environment (Alamdar et al. 2016, Eqani et al. 2016). Moreover, rapid urbanization in these mountainous areas is also associated with various environmental problems and wide range of chemicals are being used in these areas for industrial purposes and emit PCBs and HCBs from painted surfaces, electrical appliances, plastics, PVC materials etc. (Khan et al. 2017, Sohail et al. 2018). DDTs emission in these areas may also be the consequence of urbanization and emitted via dry/wet depositional from nearby areas, where the usage of these chemicals are suspected for different purposes including malarial control, protection of timber and indoor environments (Ali et al. 2014, Nasir et al. 2014, Sohail et al. 2018). Moreover, the historical usage of DDTs and the presence of obsolete pesticide stockpiles and abandoned DDT factories in these areas may have also contributed towards the high levels of its metabolites (DDD, DDE) entering the Indus river via surface run off (Sohail *et al.*, 2018).

For the alluvial riverine zone (ARZ), two extracted components (PC-1 and PC-2) accounted 93 % of the total variance in the POPs data from the Indus River, which are also shown in **Table S10**. PC-1 factor accounted 54.0 % of the total variance and was dominated by *p, p′*-DDE, followed by *o, p′*-DDE, *p, p′*-DDT, *p, p′*-DDD/ *o, p′*-DDT, and *o, p′*-DDD and

highlighted the current and/or aged usage of DDTs in these well-known agricultural areas. Moreover, hepta-CBs highlighted by PC1 and points the industrial activities in these areas, which resulted into contamination of Indus river via various local drains and posed several ecological risks to Indus river ecosystem. The PC-2 has accounted 39 % of the total variance and highlighted tri-CB, tetra-CB, penta-CB, octa-C and HCBs and reflected the industrial activities in these areas as major sources of these chemicals.

For the low-lying zone (LLZ), we considered PC-1 which explained more than 90% of the variance in data obtained from the Indus River and highlighted a mixed source containing of pesticides and electronics, which is shown as **Table S11**. Agricultural application of pesticides as well as industrial activities are the main reasons for the contamination of this zone. All districts included in LLZ zones are characterized by harsh climatic conditions (i.e. wind storms, high temperature, less vegetation cover and low rainfall) and historical agricultural background. Moreover, these low-lying areas are also receiving industrial, agricultural and urban waste from other parts of the country via local stream network and Indus river system, which may further flush out into Arabian sea or re-emitted through *volatilization* (Eqani *et al.* 2016).

Toxicity assessment due to OCPs and PCBs

Toxicity assessment showed that PCB and DDTs metabolites are well below the Criterion Continuous Concentration (CMC) and Criterion Continuous Concentration (CCC) values for all the studied zones **(Table. S4).** Similarly, none of the other OCPs isomers exceeded the established Maximum admissible concentrations (MAC) and Annual Average concentrations (AA) values by the European Council **(Table. S4),** suggesting low ecological risk associated with the levels of OCPs/PCBs into the Indus River. However, it is well known that these chemicals have potential to bioaccumulate due to their lipophilic characteristics (log K_{ow}) and

even at very low levels into the fresh water system, contributed significantly towards the total body burdens into the aquatic organisms (fish) (Moses, S. K *et al*., 2015) and subsequent food chain and finally associated humans

We calculated the chemical daily intake (CDI) estimates for the assessment of intake of chemicals via various routes (i.e., ingestion and dermal) contact into the associated human body. Using values of dissolved OCPs and PCBs in the Indus River, CDI (pg/person/day) for oral and dermal exposure for *p, p′*-DDD ranged from 1.26−12.65 and 0.003−0.03, for *p, p′*-DDE 6.51−97.49 and 0.01−0.23, for *p, p′*-DDT 3.51−23.97 and 0.008−5.82, for γ-HCH/lindane 1.28 and 0.003, for ΣChlordane 0.99−3.15 and 0.002−0.007 and for ΣPCBs 28.89−233.33 and 0.07−0.57 **(Table. 3).** The Hazard Quotient (HQ) for OCPs and PCBs exposure were taken by dividing the CDIs value with reference doses (Rf_oDs) and for cancer risk (CR) multiplying CDIs value by SFs (USEPA, 2011). HI and CR were well below guidelines, indicating no elevated risk **(Table S6 and S7).** Moreover, this study highlighted the contribution of water matrix via non-carcinogenic and carcinogenic risk, which in addition to dust, soil and biota (diet), may pose several health problems to associated human population.

Conclusion

This is the first study reporting concentrations of dissolved OCPs and PCBs measured through passive water sampling by using polyethylene sheets (LPDE) throughout the Indus River, Pakistan. In general, the Indus River water was moderately contaminated with OCPs and PCBs when compared with the other water bodies throughout the world. Our results also highlighted the LRAT of POPs into northern colder areas Pakistan and highlighted the re-emission of POPs from their repositories (via historical cold trapping) at various colder sites. These POPs likely entered the Indus via melting of glaciers and ice masses and which also continually volatilizing

the POPs into ambient air of these pristine areas. Nevertheless, local sources also contributed towards the recent emission of these toxic chemicals (especially DDTs), which are being used for agricultural and industrial purposes and transported/deposited into the entire geographic zones along Indus river ecosystem by wet/dry deposition process.

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Competing of Interest

None

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Author contribution

Muhammad Sohail, Syed Ali Musstjab Akber Shah Eqani, Habib Bokhari, and Muhammad Zaffar Hashmi develop idea, wrote and supervise the research, Nadeem Ali, Ambreen Alamdar, Joel E Podgorski, Dave Adelman, and Rainer Lohmann wrote, provided technical support and improved the manuscript.

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Availability of data and materials

The study was conducted in Pakistan and data was analyzed properly.

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Table 1

Freely Dissolved OCPs (pg/L)		Studied Zone				
		FMZ	WMZ	ARZ	LLZ	Overall
HCBs	Mean± Std	2.9±2.1	0.50±0.22	3.11±0.63	0.45±0.31	2.26±1.77
	Min-Max	0.71-6.41	0.34-0.66	2.62-3.98	0.23-0.67	0.23-6.41
γ-HCH	Mean± Std	<BDL	<BDL	0.66±1.32	<BDL	0.19-0.71
	Min-Max	<BDL	<BDL	0-2.64	<BDL	<BDL - 2.64
Transchlordane	Mean± Std	0.19±0.30	0.51±0.72	1.03±0.76	0.34±0.17	0.50±0.58
	Min-Max	<BDL - 0.65	<BDL - 1.02	0.22-2.05	0.22-0.46	0-2.05
Cischlordane	Mean± Std	0.40±0.64	<BDL	<BDL	0.17±0.14	0.20±0.44
	Min-Max	<BDL - 1.42	<BDL	<BDL	0.06-0.27	<BDL - 1.42
Transnonachlor	Mean± Std	0.18±0.29	<BDL	0.59±0.43	0.10-0.14	0.26±0.36
	Min-Max	<BDL - 0.69	<BDL	0.09-1.11	<BDL - 0.19	0-1.11
Dieldrin	Mean± Std	<BDL	<BDL	4.61±9.22	<BDL	1.32±4.93
	Min-Max	<BDL	<BDL	0-18.45	<BDL	<BDL - 18.45
α-Endosulfane	Mean± Std	0.91±1.53	6.41±9.07	2.31±1.16	1.27±0.90	3.53±0.94
	Min-	<BDL -	<BDL -	0.80-5.22	<BDL -	0-12.83

	Max	3.69	12.83		1.80	
Endosulfane	Mean±					
Sulfate	Std	0.26±0.34	0.43±0.61	0.30±0.61	0.10±0.14	0.27±0.41
	Min-	<BDL -	<BDL -	<BDL -	<BDL -	<BDL -
	Max	0.83	0.87	1.22	0.20	1.22
	Mean±					
o, p′-DDE	Std	1.35±2.58	0.29±0.41	4.67±5.52	1.13±1.59	2.11±3.43
	Min-	<BDL -	<BDL -	1.28-	<BDL -	
	Max	6.57	0.58	12.21	2.25	0-12.21
	Mean±	29.31±60.		50.14±67.	17.67±24.	29.89±52.7
p, p′-DDE	Std	82	3.35±4.74	44	63	1
	Min-	0.36-	<BDL -	8.18-	0.26-	<BDL -
	Max	152.96	6.70	150.38	37.09	152.96
	Mean±					
o, p′-DDD	Std	1.74±2.30	0.45±0.63	3.52±3.83	0.61±0.77	1.90±2.63
	Min-	<BDL -	<BDL -			<BDL -
	Max	5.96	0.90	0.27-8.88	0.06-1.15	8.88
p, p′-DDD/ *o, p′*-	Mean±					
DDT	Std	4.24±5.04	0.65±0.55	6.51±7.79	1.58±2.19	4.00±5.33
	Min-	0.16-		0.63-		
	Max	12.75	0.27-1.04	17.43	0.04-3.13	0.04-17.43
	Mean±	11.50±13.		12.30±15.		
p, p′-DDT	Std	46	1.84±2.00	96	5.31±7.34	9.47±12.20
	Min-	0.29-		1.46±35.3	0.12-	
	Max	34.75	0.42-3.25	4	10.51	0.12-35.34
	Mean±	48.14±75.		77.13±99.	26.31±36.	47.37±71.9
DDTs	Std	24	6.58±8.33	73	53	5
	Min-	0.81-		11.82-	0.48-	0.48-
	Max	197.89	0.69-12.47	224.24	52.14	224.24
	Min-	2.77-	1.35-	19.28-	1.67-	
∑OCPs	Max	201.80	42.24	259.70	58.05	

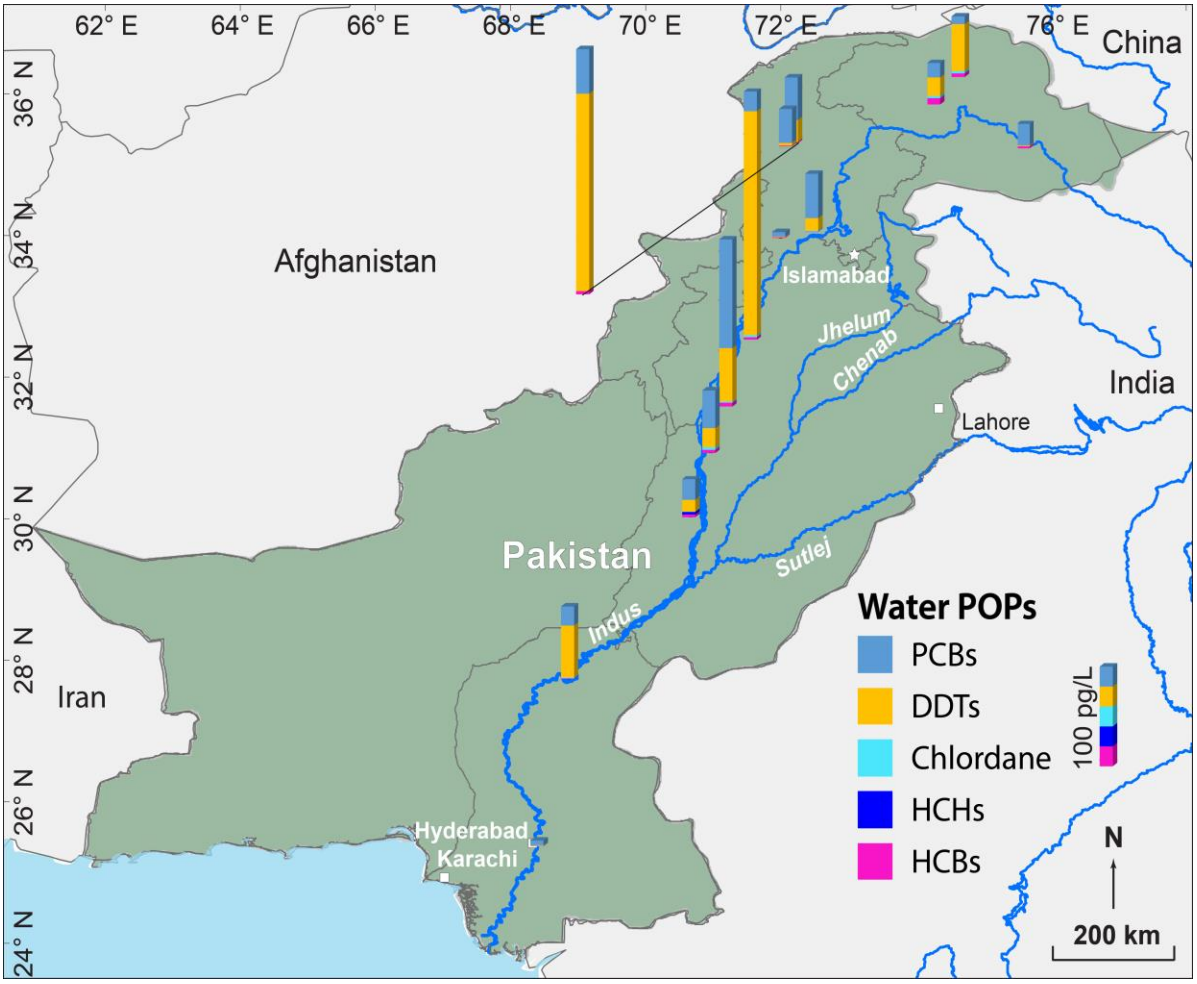
Table 2

Freely dissolved PCBs		Studied Zones FMZ	WMZ	ARZ	LLZ	Overall
PCB-8	Mean±	1.85±2.03	0.84±0.92	2.27±3.20	0.36±0.08	1.61±2.12
	Min-	0.14 -	0.20 - 1.49	0.49 - 7.06	0.30 -	0.14 - 7.06
PCB-11	Mean±	3.76±4.00	5.08± 6.27	8.97± 9.61	1.41±	5.10± 6.17
	Min-	0.29-9.42	0.65-9.51	1.04±	0.84-1.98	0.29-22.86
PCB-18	Mean±	1.69±	0.89± 1.05	1.11± 1.09	0.24±	1.20± 1.42
	Min-	0.23-4.76	0.14-1.63	0.48-2.75	0.17-0.31	0.14-4.76
PCB-28	Mean±	2.48±	1.79± 2.53	4.81± 4.73	1.37±	2.89± 3.01
	Min-	0.48-4.84	<BDL -	1.37-11.71	0.46-2.28	<BDL -
PCB-44	Mean±	0.07±	0.03± 0.04	0.07± 0.14	0.01±	0.06± 0.11
	Min-	<BDL -	<BDL -	<BDL -	<BDL -	<BDL -
PCB-66	Mean±	0.7±0.61	0.39±0.55	1.83±1.04	1.38±1.69	1.07±0.98
	Min-	0.25-1.88	<BDL -	0.90-3.26	0.18-2.57	<BDL -
PCB-101	Mean±	0.72±0.51	1.19±0.06	1.57±0.84	0.09±0.13	0.94±0.73
	Min-	<BDL -	1.14-1.23	0.49-2.49	<BDL -	<BDL -
PCB-123	Mean±	<BDL	<BDL	0.07±0.13	0.09±0.12	0.03±0.08
	Min-	<BDL	<BDL	<BDL -	<BDL -	<BDL -
PCB-118	Mean±	0.22±0.15	<BDL	0.46±0.19	0.43±0.54	0.29±0.26
	Min-	<BDL -	<BDL	0.24-0.71	0.04±0.81	<BDL -
PCB-105	Mean±	0.08±0.10	0.08±0.11	0.08±0.10	0.02±0.02	0.07±0.09
	Min-	<BDL -	<BDL -	<BDL -	<BDL -	<BDL -
PCB-126	Mean±	0.01±0.02	<BDL	<BDL	<BDL	<BDL
	Min-	<BDL -	<BDL	<BDL	<BDL	<BDL -

PCB-153	Mean±	0.22±0.29	0.20±0.28	0.11±0.22	0.03±0.05	0.16±0.23
	Min-	<BDL -	<BDL -	<BDL -	<BDL -	<BDL -
PCB-138	Mean±	0.21±0.13	0.22±0.31	0.44±0.27	0.32±0.45	0.29±0.24
	Min-	0.04-0.41	<BDL -	0.14-0.77	<BDL -	<BDL -
PCB-128	Mean±	0.02±0.05	<BDL	<BDL	<BDL	0.01±0.03
	Min-	<BDL -	<BDL	<BDL	<BDL	<BDL -
PCB-156	Mean±	<BDL	<BDL	0.05±0.15	<BDL	0.02±0.08
	Min-	<BDL	<BDL	<BDL -	<BDL	<BDL -
PCB-169	Mean±	<BDL	<BDL	<BDL -	<BDL	<BDL
	Min-	<BDL	<BDL	<BDL -	<BDL	<BDL -
PCB-187	Mean±	0.58±1.34	0.16±0.23	0.06±0.08	0.06±0.09	0.30±0.87
	Min-	<BDL -	<BDL -	0.00-0.16	<BDL -	<BDL -
PCB-180	Mean±	0.06±0.06	0.14±0.19	0.24±0.19	0.10±0.06	0.13±0.14
	Min-	<BDL -	<BDL -	<BDL -	0.06-0.14	<BDL -
PCB-170	Mean±	0.04±0.09	<BDL	0.02±0.03	0.04±0.06	0.03±0.06
	Min-	<BDL -	<BDL	<BDL -	<BDL -	<BDL -
PCB-195	Mean±	1.07±2.29	1.24±1.75	1.22±1.12	0.01±0.01	0.98±1.65
	Min-	<BDL -	<BDL -	<BDL -	<BDL -	<BDL -
PCB-206	Mean±	81.6±91.7	108.30±97.	58.63±38.	8.92±11,6	68.47±72.
	Min-	3.54-	39.70-	20.53-	0.67-	0.67-
∑PCBs	Mean± Std	95.36±92.7	120.54±11.2	82.02±51.90	14.86±16.73	83.65±76.83
	Min-Max	7.44-226.40	41.91-199.17	30.88-144.96	3.02-26.69	3.02-226.40

Table 3

Studied POPs	**FMZ**		**WMZ**		**ARZ**		**LLZ**	
	CDI oral	CDI dermal	CDI oral	CDI dermal	CDI oral	CDI dermal	CDI oral	CDI dermal
p, p′-DDD	8.26	0.02	1.26	0.003	12.65	0.03	3.07	0.007
p, p′-DDE	56.99	0.13	6.51	0.01	97.49	0.23	34.35	0.08
p, p′-DDT	22.36	0.05	3.57	0.008	23.91	5.82	10.32	0.02
γ-HCH/lindane					1.28	0.003		
ΣChlordane	1.49	0.003	0.99	0.0024	3.15	0.0076	1.18	0.0045
ΣPCBs	185.42	0.45	233.33	0.57	159.48	0.38	28.89	0.07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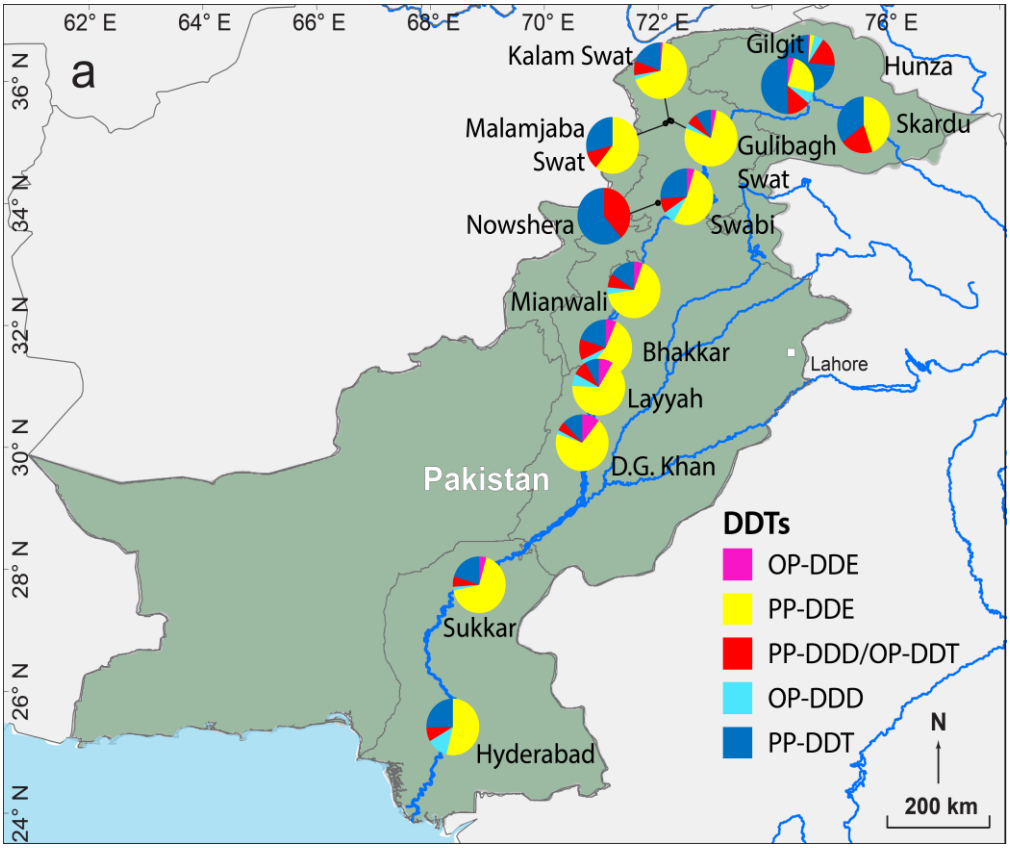
64° E
66° E
68° E
70° E
72° E
76° E
36° N
34° N
32° N
30° N
28° N
26° N
24° N
China
Afghanistan
Islamabad
Jhelum
Chenab
India
Lahore
Pakistan
Sutlej
Indus
Iran
Hyderabad
Karachi
Water POPs
PCBs
DDTs
Chlordane
HCHs
HCBs
100 pg/L
N
200 km

Figure 1.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62° E
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36° N
34° N
32° N
30° N
28° N
26° N
24° N
Kalam Swat
Gilgit
Hunza
Skardu
Malamjaba
Swat
Gulibagh
Swat
Swabi
Nowshera
Mianwali
Bhakkar
Lahore
Layyah
D.G. Khan
Pakistan
Sukkar
Hyderabad
DDTs
OP-DDE
PP-DDE
PP-DDD/OP-DDT
OP-DDD
PP-DDT
N
200 km

Fig 2 a.

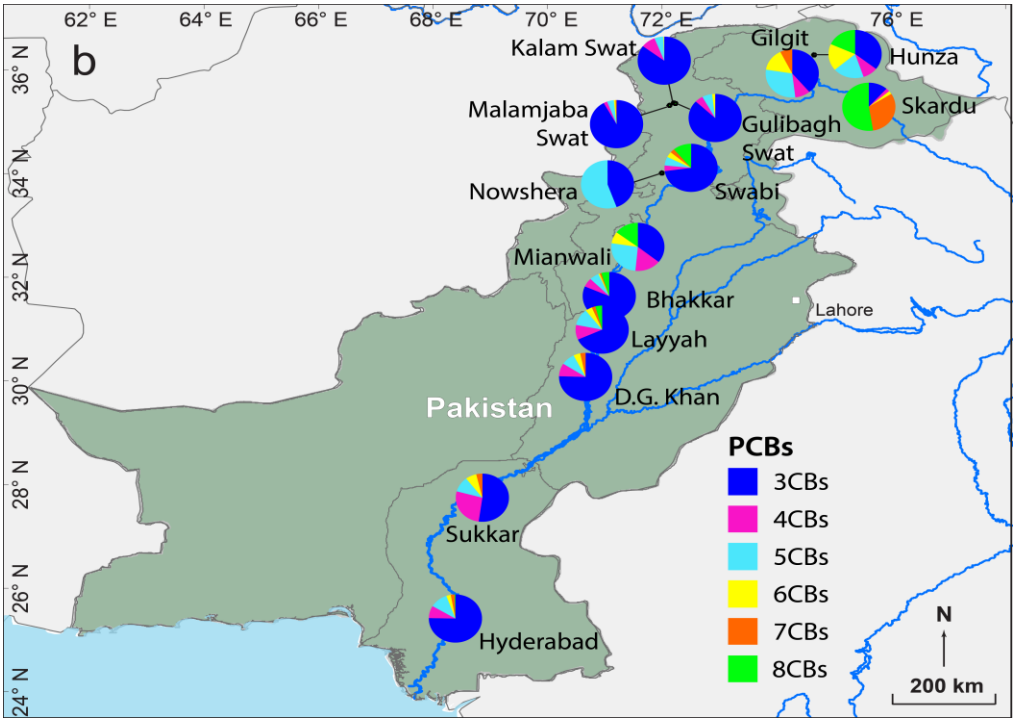
b
62° E
64° E
66° E
68° E
70° E
72° E
76° E
36° N
34° N
32° N
30° N
28° N
26° N
24° N
Kalam Swat
Gilgit
Hunza
Skardu
Malamjaba
Swat
Gulibagh
Swat
Swabi
Nowshera
Mianwali
Bhakkar
Lahore
Layyah
D.G. Khan
Pakistan
Sukkar
Hyderabad
PCBs
3CBs
4CBs
5CBs
6CBs
7CBs
8CBs
N
200 km

Fig 2 b.