

PAPER



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## Gaseous and soil OCPs and PCBs along the Indus River, Pakistan: spatial patterns and air–soil gradients†

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This study presents first-hand information on the occurrence of persistent organic pollutants (POPs) in the ambient air and surface soil along the Indus flood-plain, Pakistan. The sampling campaign was conducted at 15 site locations during 2014–15, along the Indus River (approximately 1300 km). Composite surface soil samples ( $N = 15$ ) and passive air samples ( $N = 15$ ) were collected for the estimation of gaseous POPs as well as air–soil exchange to evaluate the POP emission and distribution or dispersion patterns, source tracking, and contribution of the local and regional sources towards POP accumulation in the Indus River system. Among the studied POPs, levels of DDTs and PCBs were noticeably higher in ambient air (50–560 and 10–1100  $\text{pg m}^{-3}$ ) and in soil (0.20–350 and 1.40–20  $\text{ng g}^{-1}$ ), respectively. Regarding the spatial patterns, higher DDT concentrations ( $\text{ng g}^{-1}$ ) were detected in the air and soil samples collected from the wet mountain zone (WMZ) ( $p < 0.05$ ), followed by the alluvial riverine zone (ARZ), low-lying mountain zone (LLZ), and frozen mountain zone (FMZ). The PCB data did not exhibit significant differences ( $p > 0.05$ ) for the air samples, while PCB concentrations were significantly higher ( $p < 0.05$ ) in soil from the LLZ, which may be associated with rapid urbanization and industrial activities in this area. The air–soil exchange of DDTs and PCBs showed net volatilization at most of the studied sites except for a few samples from the FMZ and WMZ. Results of this study about air–soil exchange gradients indicate the long range regional atmospheric transport (LRAT) of POPs to the colder areas (FMZ) of Pakistan, where these act as a secondary source of POPs in these areas.

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### Environmental significance

Monitoring data of POPs into Indus floodplain areas shows the recent emission of DDTs and PCBs and also long range regional transport of POPs which reflected that, to what extent humans and environment have been exposed, which sites are contaminated and in future may pose high ecological risks. Pakistan is signatory to the Stockholm Convention (SC) on POPs since December 2001. Findings of this study will help policy makers specifically Ministry of Climate Change, Pakistan to take informed decisions on POPs management, take necessary actions on reported sites and inclusion of these sites under National Implementation Plan (NIP) to eliminate and reduce releases of POPs in Pakistan.

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## 1. Introduction

Persistent organic pollutants (POPs) like organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are widely reported toxic chemicals used historically in the industrial and agricultural sectors and are well known to cause several health abnormalities (such as cancer, endocrine disruption, immunological disorders *etc.*) due to their persistent nature and lipophilic properties.<sup>1–3</sup> Given that OCPs and PCBs are semi-volatile in nature, these chemicals have the capability for long-range atmospheric transport (LRAT) to remote colder areas and may pose several ecological risks to the wildlife and human populations of these areas.<sup>3,4</sup> Moreover, the impacts of climate change also greatly affect the global and regional atmospheric

air circulation, which ultimately influences the trans-boundary movement, fate, and transport of POPs in different environmental compartments at local, regional and global scales.<sup>3,5-7</sup> In 2001, the Stockholm Convention banned the usage and manufacturing of POPs, which was strictly followed in developed countries but may not have been in developing countries. For example, the Pakistan Environmental Protection Agency (EPA) still allowed the usage of DDTs and some other POPs for specific purposes (like malarial and dengue control). Similarly, there has also been illegal trade of these banned chemicals, which are reported to have been smuggled into Pakistan from neighboring countries namely India and Afghanistan.<sup>7,8</sup> Nevertheless, there is also little public awareness which prevents immediate inspection of the industries and implementation of the Stockholm Convention's strict regulations.

Besides the persistence and recent usage in the environment, secondary sources of POP chemicals are reported in the pristine environment throughout the world, as these chemicals have the potential to travel considerably long distances and end up accumulating in vegetation, soil and water bodies at high altitudes due to the global distillation phenomenon, particularly in the polar regions and Third Pole Environment (TPE) including the Himalayas and their associated areas of Pakistan.<sup>4,6</sup> As the climate warms, these repositories become active in remobilizing these chemicals into the atmosphere and associated freshwater bodies (e.g., the Indus River system), posing a major threat to wildlife and human beings *via* the bio-accumulation process.<sup>9-11</sup> On the other hand, many studies have reported the existence of toxic metals and organic pollutants such as polybrominated diphenyl ethers (PBDEs), OCPs, PCBs *etc.* in Pakistani environmental compartments as a result of rapid industrialization and the growing agriculture sector.<sup>7,12</sup> Open burning of e-waste has also been reported to release a huge amount of PCBs and other toxic chemicals.<sup>13</sup> Additional sources of POPs in Pakistan include electronic industries, transformer repairing units, leakage during the transportation and auction of old transformers, abandoned DDT factories and obsolete pesticide stockpiles at different locations throughout Pakistan.<sup>4,9,11,12</sup>

Soil is reported as an environmental sink of POPs and other chemicals, and as a result of climatic/seasonal variations may emit the stored chemicals into the air *via* volatilization.<sup>14,15</sup> It has been widely reported that the monitoring of soil and air samples can be useful to infer the air-soil exchange of POPs and cycling of POPs into different ecological/climatic zones. Additionally, the fugacity of ambient air can also provide quantitative evidential proof of the direction of POP movements and tracking of the source while the mechanisms controlling the air-surface exchange may significantly influence the fate and distribution of contaminants.<sup>14-16</sup> In the current study, for the first time, we measured the levels of POPs in the air and soil of the colder areas of Pakistan and Indus flood plain, which offers insight into the occurrence and dispersion trends, partitioning, long-range transport of POPs and sources of origin. This study focused on the mountainous areas of Pakistan (*i.e.* Himalayan and its surrounding glacial areas) as these cold areas have the potential to receive gaseous POPs *via* the cold trapping process and are also vulnerable to hosting fine dust particles through

long range/short range atmospheric transport *via* the altitudinal fractionation process from the lower reaches of the Indus flood plain and neighboring countries (China and India).<sup>2,17</sup> Furthermore, the measurement of POPs in the lower reaches of the Indus flood plain (the most populated and well known agricultural areas of Punjab and Sindh provinces) would be very interesting for evaluating the current use of POPs, their re-emission from colder areas into the Indus River and historical use signatures. This study can also be an important tool to evaluate the contribution of Pakistan and its neighboring areas towards "global POP emissions" and the effectiveness of control measures taken by regional and international authorities under the Stockholm Convention in developing countries.

## 2. Methods and materials

### 2.1. Air sampling

Polyurethane foam passive air samplers (PUF-PASs) were deployed at fifteen sampling locations along the Indus River, Pakistan. The study area was divided into four main zones: frozen mountain zone (FMZ), wet mountain zone (WMZ), alluvial riverine zone (ARZ), and low-lying zone (LLZ). FMZ areas included various locations *viz.* Hunza, Gilgit, Skardu, Kalam Swat, Gulibagh Swat, and Malamjaba Swat. The WMZ comprises the districts of Islamabad, Muree, Swabi and Nowshera. The ARZ includes agricultural areas of the following districts: Mianwali, Bhakkar, Layyah, and Dera Ghazi Khan. The LLZ comprises districts of Sukkar, Khairpur, and Hyderabad. The PUF-PASs were deployed in open areas and positioned >3 m above the ground. All the PUF-PASs, including those for samples, field blanks, and transportation blanks, were pre-extracted with acetone and dichloromethane (DCM) at the Environmental and Public Health laboratory, COMSATS University Islamabad, Pakistan. The transportation PUF was kept sealed in a jar throughout the sampling, whereas for the field blank, the PUF was kept open at the sampling site for 5 minutes with clean gloves and then sealed in a jar. The passive air samplers (polyurethane foam (PUF)) were fixed at heights >3 m above the ground in inverted stainless-steel bowls in an open area at each sampling station. The bowl protected the PUF from rainfall, direct radiation, and wind speed effects. The PUF-PASs were deployed for 28 days as reported by Shoeib & Harner (2002)<sup>14</sup> between June and July 2014. Each PUF disk was retrieved, resealed, and transferred to the Lohmann lab, University of Rhode Island, USA for further analysis.

### 2.2. Soil sampling

Fifteen surface/top soil samples (each sample is a composite of five sub-samples of soil from each PUF-PAS deployment site) were collected at a 0-5 cm depth at selected sampling sites along the Indus River. One surface soil sub-sample at each sampling station was taken from the exact location where the PUF-PAS was installed, and the other four soil samples were taken at a 500 m distance in different directions.<sup>15</sup> Soil samples were collected using a hand trowel, kept in properly labeled polyethylene bags, and then taken to the Environmental and Public Health lab at COMSATS University Islamabad, Pakistan.

Soil samples were air-dried and sieved using a 2 mm mesh and then transferred to the Lohmann lab, University of Rhode Island, USA for further analysis.

### 2.3. Extraction of soil and passive air samples

About 20 g of soil and PUF disks was Soxhlet extracted with DCM for 24 hours. A mixture of standards (surrogate) of PCB-209 and tetrachloro-*m*-xylene (TCmX) was added to each sample before extraction. Then for soil, activated copper granules were added to the collection flask for removing sulfur (elemental). Concentration of the extract took place and then the solvent was changed to hexane, purified on an 8 mm alumina/silica column packed from the bottom to the top, neutral alumina (3 cm, 3% deactivated), then neutral silica gel (3 cm, 3% deactivated), 50% sulfuric acid silica (3 cm), and anhydrous sodium sulfate (1 cm). The columns were eluted with 50 mL DCM/hexane (1 : 1). Neutral silica gel, neutral alumina and anhydrous sodium sulfate were then Soxhlet-extracted (48 h) with DCM and baked for 12 h at 250 °C, 180 °C, and 450 °C, respectively. All the fractions were concentrated with a gentle high purity nitrogen stream to 0.2 mL after adding dodecane (25 µL) as solvent keeper. The air and soil extracts were then purified using silica/alumina columns. The columns were eluted with 50 mL dichloromethane/hexane (1 : 1). PCB and DDT fractions were solvent exchanged to *n*-hexane and then concentrated to 0.5 mL in gas chromatograph vials under a gentle nitrogen stream and PCB-54 was added as an internal standard before GC-MS analysis. More details about extraction methods can be found in ref. 7.

### 2.4. Chromatographic analysis

Selected POPs such as DDTs (*o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT) and PCBs ( $\sum_{31}$ PCBs) (3CBs: PCB-11 and PCB-28; 4CBs: PCB-58, PCB-74, PCB-70, PCB-44, PCB-49, PCB-37, PCB-60, PCB-66, and PCB-77; 5CBs: PCB-82, PCB-87, PCB-101, PCB-123, PCB-118, and PCB-114; 6CBs: PCB-126, PCB-105, and PCB-153; 7CBs: PCB-187, PCB-169, PCB-156, PCB-128, PCB-166, PCB-158, PCB-170, and PCB-183; 8CBs: PCB-198, PCB-195, and PCB-189; 9CBs: PCB-206, PCB-208, and PCB-209) were analyzed by GC-MS applying a 50 m capillary column (Varian, CP-Sil 8 CB, 50 m, 0.25 mm, 0.25 µm). The injector temperatures were set to 250 °C. The initial temperature of the oven was set at 150 °C for 3 min, and then raised to 290 °C at a rate of 4 °C min<sup>-1</sup> and held for 10 min. POPs were then measured in selected ion mode (SIM). MSD source and quadrupole temperatures were 230 °C and 150 °C. The MS used in this case was in SIM mode having two ions monitored for each of the target compounds grouped in a specific window. DDT inlet degradation was also checked daily and controlled within 15%. All the studied OCPs and PCBs were quantified using HP-Chemstation to confirm the peaks. More details are given in our previously published report.<sup>17</sup>

### 2.5. Quality control/quality assurance (QC/QA)

All the analytical methods were regularly monitored using strict quality assurance and control measures. The instruments were calibrated daily with a calibration standard. The field blank,

laboratory blank, and transportation blank were analyzed the same way as actual samples. The internal standard was then injected into the GC during each batch before the sample injection. For TCmX and PCB-209, the average surrogate recoveries were 77 ± 4% and 97 ± 9% for air samples and 67 ± 7% and 93 ± 11% for soil samples, respectively. The lowest standards were used to calculate the instrument detection limit (IDL) by extrapolating the analyte amount that generates a signal-to-noise ratio of 3 : 1. The IDL value ranged from 0.01 to 0.5 ng for the studied POPs and values of the compounds below this range were not considered. All chemicals used in the study were of analytical grade and obtained from Merck, Germany. All solvents used in the study were redistilled to purify solvents to reduce any interference effects. OCP and PCB standards were obtained from Dr. Ehrenstorfer GmbH, Germany.

### 2.6. Fugacity calculations

The air–soil exchange gradients were calculated using the soil/air fugacity approach, an excellent indicator of the soil–air exchange potential of OCPs. The fugacity fractions (ff) represent a compound's chemical potential to transfer into diverse environmental compartments.<sup>16</sup> The fugacity of OCPs in air (fa) and soil (fs) was calculated by Harner *et al.* (2001).<sup>18</sup>

$$f_s = C_s RT / 0.41 \phi_{om} K_{OA} \quad (1)$$

and

$$f_a = C_a RT, \quad (2)$$

where  $C_s$  and  $C_a$  indicate the concentration in the medium (mol m<sup>-3</sup>),  $R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ,  $T$  is the absolute temperature in Kelvin (K),  $\phi_{om}$  is the organic matter fraction in the soil (1.7 times that of the organic carbon fraction), and  $K_{OA}$  denotes the octanol–air partition coefficient.

The 0.41 factor improves the soil–air partition coefficient and  $K_{OA}$ .<sup>16,19</sup>  $K_{OA}$  can be obtained from the following equations:

$$K_{OA} = K_{OW} / K_{AW}, \quad (3)$$

$$K_{AW} = H / 100 RT, \quad (4)$$

and

$$R = R' \times 100, \quad (5)$$

where  $K_{OW}$  denotes the octanol–water partition coefficient,  $K_{AW}$  is the air–water partition coefficient,  $H$  is the Henry's law constant (Pa m<sup>3</sup> mol<sup>-1</sup>), and  $R'$  is the gas constant (0.08205 L atm K<sup>-1</sup> mol<sup>-1</sup>).

$H$  correlation for temperature was done by using the integrated Van't Hoff equation:

$$\ln(H_1/H_2) = -\Delta H_{AW}(1/T_1 - 1/T_2)/R, \quad (6)$$

where  $H_1$  and  $H_2$  denote Henry's law constants at two temperatures,  $\Delta H_{AW}$  is the enthalpy of vaporization (J mol<sup>-1</sup>), and  $T_1$  and  $T_2$  are the temperatures (K).

The fugacity fraction ( $ff$ ) is obtained as fugacity in the soil divided by the sum of the fugacity in the soil and the air which gives an indication of the net direction of the air–soil exchange.<sup>18</sup>

Results are shown as  $ff$  which is calculated from eqn (7)

$$ff = fs / (fs + fa) \quad (7)$$

Fugacity fractions ( $ff$ ) are a good and helpful tool in determining air–soil equilibrium ( $ff = 0.5$ ), net deposition ( $ff < 0.5$ ) and net volatilization ( $ff > 0.5$ ). Due to uncertainties in fugacity fraction calculations, values between 0.3 and 0.7 were not significantly different from equilibrium.<sup>16,18</sup>

### 3. Results and discussion

#### 3.1. Gaseous DDTs and PCBs

The concentrations of the studied POPs were adjusted over the sampling period (28 days) and considering the standard value of air level of  $\sim 3.5 \text{ m}^3$  per day derived from the previous calibration study.<sup>14</sup> The levels ( $\text{pg m}^{-3}$ ) of DDTs in the air ranged from

50 to 560 and the sum of polychlorinated biphenyls ( $\sum_{31} \text{PCBs}$ ) from 10 to 1100 (Fig. 1a). Among the DDTs ( $\text{pg m}^{-3}$ ), the most frequently detected compound was  $p,p'$ -DDE (74–228) followed by  $p,p'$ -DDT (25–126),  $o,p'$ -DDE (9–31.7),  $o,p'$ -DDT (7–27.9) and  $o,p'$ -DDD (1–9.34) as presented in Table 1 and Fig. 1b.

Spatial distribution patterns showed that gaseous DDT concentrations ( $\text{pg m}^{-3}$ ) were in the ranges WMZ 120–340 (mean: 230) and ARZ 32–410 (150), followed by FMZ 1–83 (34) and LLZ 2–48 (24) in descending order throughout the stretch along the Indus River flood plain areas. The lower levels of DDTs in LLZ agricultural areas are noticeable and may reflect the influence of flooding in these areas, which may wash away the contaminated soil surface in the monsoon season.<sup>7</sup> These concentrations ( $\text{pg m}^{-3}$ ) measured in the current study were much higher than those levels detected at higher mountain areas in Asia ( $0.3\text{--}75 \text{ pg m}^{-3}$ ),<sup>20,21</sup> Europe ( $0.2\text{--}12$ ),<sup>22</sup> and North America ( $1.6\text{--}55$ )<sup>23</sup> while results in South America ( $1.0\text{--}120$ )<sup>24,25</sup> were consistent with our median concentrations. The concentrations of DDTs in the current study were slightly lower than those measured in Punjab province, Pakistan ( $45\text{--}890 \text{ pg m}^{-3}$ )<sup>15</sup>

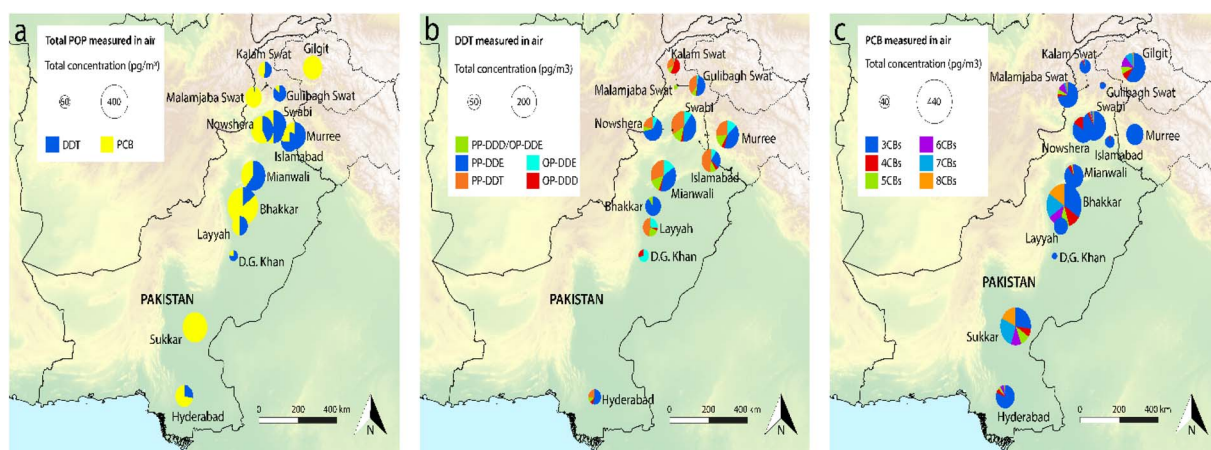


Fig. 1 Proportion of overall DDTs and PCBs (a) and compositional profiles of DDTs (b) and PCBs (c) in air along the Indus River flood-plain, Pakistan.

Table 1 Concentrations ( $\text{pg m}^{-3}$ ) of DDTs in air and outdoor soil ( $\text{ng g}^{-1}$ ) collected from the four different studied zones along the Indus River, Pakistan

OCPs		DDTs in air ( $\text{pg m}^{-3}$ )				DDTs in soil ( $\text{ng g}^{-1}$ )			
		FMZ	WMZ	ARZ	LLZ	FMZ	WMZ	ARZ	LLZ
OP-DDE	Mean $\pm$ std	1.1 $\pm$ 1.3	15 $\pm$ 8.2	18 $\pm$ 13	BDL	0.54 $\pm$ 0.95	0.07 $\pm$ 0.00	0.00	0.06 $\pm$ 0.10
	Min–max	0–2.5	9.5–21	0–32	BDL	0–2.43	0.07–0.07	0.00	0–0.17
PP-DDE	Mean $\pm$ std	17 $\pm$ 20	151 $\pm$ 109	73 $\pm$ 105	13 $\pm$ 19	22 $\pm$ 45	0.87 $\pm$ 0.00	0.60 $\pm$ 0.30	0.97 $\pm$ 0.8
	Min–max	0–40	74–228	0–222	0–27	0–112	0.87–0.87	0.32–0.96	0–1.50
OP-DDD	Mean $\pm$ std	0.5 $\pm$ 0.6	2.6 $\pm$ 4	4.5 $\pm$ 3.9	2 $\pm$ 2.8	1.8 $\pm$ 3.1	0.14 $\pm$ 0.00	0.08 $\pm$ 0.07	0.30 $\pm$ 0.4
	Min–max	0–1.06	0–5.12	0–9.34	0–3.95	0.1–8.2	0.14–0.14	0–0.17	0–0.8
PP-DDD/OP-DDT	Mean $\pm$ std	4.1 $\pm$ 3.1	16 $\pm$ 12	12 $\pm$ 12	2.4 $\pm$ 3	3.9 $\pm$ 7.7	0.21 $\pm$ 0.00	0.08 $\pm$ 0.06	0.14 $\pm$ 0.14
	Min–max	0–7.2	7.7 $\pm$ 24	0–28	0–5	0.08–19	0.21–0.21	0–0.14	0–0.28
PP-DDT	Mean $\pm$ std	12 $\pm$ 15	46 $\pm$ 29	40 $\pm$ 60	8.5 $\pm$ 9.2	35 $\pm$ 81	1.70 $\pm$ 0.00	0.38 $\pm$ 0.26	0.25 $\pm$ 0.43
	Min–max	0–32	25–66	0–126	0–13	0–202	1.70–1.70	0–0.61	0–0.74
DDTs	Mean $\pm$ std	34 $\pm$ 40	230 $\pm$ 162	148 $\pm$ 177	24 $\pm$ 34	64 $\pm$ 137	2.98 $\pm$ 0.00	1.13 $\pm$ 0.35	1.7 $\pm$ 1.5
	Min–max	0–82	115–345	33–413	0–48	0.2–344	2.98–2.98	0.94–1.67	0–2.6

while being higher than those detected from Lahore and Karachi ( $52 \text{ pg m}^{-3}$ ).<sup>4</sup>

Previous studies have used the diagnostic ratio for parent DDTs and their metabolites to determine recent and historical emissions into the environment.<sup>5,10,12</sup> The DDT/(DDE + DDD) ratio has been widely used for assessing the parent compound decomposition and fresh DDT input. DDT/(DDE + DDD) values were used to determine the microbial DDT degradation, and a value  $>1$  indicated current application.<sup>5,15</sup> In ambient air, the  $p,p'$ -DDT/ $p,p'$ -DDE +  $p,p'$ -DDD ratio was generally  $<1$  suggesting high DDT transformation rates into its metabolites in the soil and which might be emitted into the atmosphere because of high temperature coupled with high wind speeds in the study region (Fig. S1†). However, dicofol application might introduce the DDT into the surrounding environment, as it has been reported to contain  $o,p'$ -DDT traces as an intermediate product during its manufacturing.<sup>8,15</sup> The ratio between  $o,p'$ -DDT and  $p,p'$ -DDT can be used to distinguish the technical DDT application and/or dicofol type usage.<sup>5</sup> In the study area, the gaseous  $o,p'$ -DDT/ $p,p'$ -DDT ratio is  $<1$ , which reflected the predominant usage of technical DDT.

The gaseous  $\sum_{31}$ PCB concentrations ( $\text{pg m}^{-3}$ ) ranged from 10.4 to 1108 (mean: 259) along the Indus River, Pakistan. Generally, compositional profiles of PCB congeners in the air samples (Table 2 and Fig. 1c) were dominated by tri-CBs ( $\sim 12$ –58%) followed by hepta-CBs ( $\sim 5$ –13%), octa-CBs ( $\sim 4$ –12%), hexa-CBs ( $\sim 2$ –7%), tetra-CBs ( $\sim 2$ –5%), and penta-CBs ( $\sim 1$ –3%). The abundance of lighter PCB congeners in the atmosphere can be explained by their chemical tendency to volatilize from painted surfaces and contaminated water.<sup>4,8,26</sup> Additionally, the current compositional profiles complement the commercial PCB formulation of Aroclor-1242, -1248, -1260, and -1262 (Fig. 4A).

Gaseous PCB levels throughout the studied stretch also showed zone-wise trends as higher concentrations of  $\sum_{31}$ PCBs ( $\text{pg m}^{-3}$ ) were measured at the LLZ (279–702, mean: 490) followed by at the ARZ (10.4–1108, 330), at the WMZ (158–225, 191), and at the FMZ (13.5–209, 107) in descending order, respectively. These concentrations ( $\text{pg m}^{-3}$ ) were higher than

the concentrations measured at Lake Erie (19.0–421) and Lake Ontario (7.70–634  $\text{pg m}^{-3}$ ).<sup>27</sup> The atmospheric concentration of PCBs was not significantly different among the four zones ( $p = 0.60$ ). Nevertheless, a few exceptions from the urban settings of LLZ and ARZ areas showed relatively higher proportions of heavier PCBs (*i.e.* hepta-CBs and octa-CBs), pointing to their emission *via* industrial activities as well as long and short range atmospheric transportation of contaminated particulate material.<sup>4,26</sup> The homologous pattern obtained for the PCBs in the current study showed that tri-CBs are the most abundant homologs in the air, in agreement with those already reported along the Ravi River flood plain, Punjab, Pakistan<sup>26</sup> but different from China and India, where tetra-CB homologs were also dominant.<sup>3,28,29</sup> The possible sources of PCBs include solid waste dumps, electronic industries, open burning sites, and the discharge of industrial wastewater into the riverine ecosystem.<sup>5</sup> Low molecular weight CBs volatilize more easily into the gaseous phase and have a longer residence and transport potential, which may explain the higher concentration of tri-CBs and tetra-CBs in air samples.<sup>7,26</sup>

$\sum_7$  dioxin-like PCBs (DL-PCBs) in the air samples ranged from 2.7 to 48.38  $\text{pg m}^{-3}$ . The higher values for ARZ areas indicated the widespread industrial activities in these areas (Table S2†). Previous studies also investigated dioxin-like PCBs, which are of prime importance because of their tetrachlorodibenzo-*p*-dioxin (TCDD)-like carcinogenic properties.<sup>4,26,30,31</sup> These DL-PCBs can also be emitted unintentionally from cooking activities and thermal processes in industrial areas.<sup>4,31</sup> The WHO<sub>05</sub>-TEQ values for mono-*ortho*-dioxin-like PCBs (-105, -114, -118, and -156) and non-*ortho*-dioxin-like PCBs (-77, -126, and -169) were also calculated and found to range from  $1 \times 10^{-4}$  to  $6 \times 10^{-4}$  and  $1 \times 10^{-4}$  to  $2.9 \text{ pg m}^{-3}$ , respectively. Individual mono-*ortho*-DL-PCBs and non-*ortho*-DL-PCBs, PCB-105, -126, and -169, contributed significantly towards the calculated TEQs for the studied air samples. Similarly, PCB-126 and PCB-169 showed higher TEQ values ( $\text{pg m}^{-3}$ ) at the ARZ (0.73 and 0.33) followed by the LLZ (0.67 and 0.07), FMZ (0.211 and 0.079) and WMZ ( $1 \times 10^{-4}$  and  $2.7 \times 10^{-3}$ ), respectively. Higher TEQs for both mono-*ortho*-DL-PCBs and

**Table 2** Concentrations ( $\text{pg m}^{-3}$ ) of PCBs in air and outdoor soil ( $\text{ng g}^{-1}$ ) collected from the four different studied zones along the Indus River, Pakistan

PCBs	PCBs in air ( $\text{pg m}^{-3}$ )				PCBs in soil ( $\text{ng g}^{-1}$ )				
	FMZ	WMZ	ARZ	LLZ	FMZ	WMZ	ARZ	LLZ	
3CBs	Mean $\pm$ std	17 $\pm$ 16	114 $\pm$ 11	168 $\pm$ 54	186 $\pm$ 29	1.5 $\pm$ 0.24	0.5 $\pm$ 0.0	0.7 $\pm$ 0.07	0.9 $\pm$ 0.07
	Min–max	0.92–74	5–152	0.10–337	10–170	0.01–1.4	0.06–0.12	0.02–0.19	0.02–0.95
4CBs	Mean $\pm$ std	6.1 $\pm$ 0.8	8 $\pm$ 5.3	14 $\pm$ 3.7	16.1 $\pm$ 0.8	0.2 $\pm$ 0.05	0.1 $\pm$ 0.0	0.10 $\pm$ 0.01	0.1 $\pm$ 0.02
	Min–max	0.16–5.2	1.5–26	0–22	1.6–6.5	0–0.24	0.01–0.10	0.01–0.11	0–0.07
5CBs	Mean $\pm$ std	6.6 $\pm$ 1.7	0.6 $\pm$ 0.3	11 $\pm$ 3.8	19 $\pm$ 3.9	0.6 $\pm$ 0.10	0.2 $\pm$ 0.0	0.3 $\pm$ 0.03	0.4 $\pm$ 0.08
	Min–max	0–4.57	0–3.8	0.9.3	0–11	0.01–0.53	0.03–0.22	0–0.13	0.01–0.35
6CBs	Mean $\pm$ std	10.4 $\pm$ 1.6	0.9 $\pm$ 0.4	30 $\pm$ 7.6	22 $\pm$ 2.2	1.4 $\pm$ 0.19	0.2 $\pm$ 0.0	0.5 $\pm$ 0.05	0.8 $\pm$ 0.10
	Min–max	0–6.7	0–1.2	0–28.7	0–13.4	0.07–1.39	0.01–0.31	0.02–0.38	0.03–0.28
7CBs	Mean $\pm$ std	6.8 $\pm$ 3.7	1.2 $\pm$ 1.1	46 $\pm$ 31	77 $\pm$ 35	1 $\pm$ 0.40	0.1 $\pm$ 0.0	0.2 $\pm$ 0.03	1.2 $\pm$ 0.29
	Min–max	0–10.5	0–3.4	0–103	0–123	0.01–0.80	0.04–0.15	0–0.17	0.01–1.11
8CBs	Mean $\pm$ std	1.9 $\pm$ 1.3	0.5 $\pm$ 0.8	39 $\pm$ 38.5	81 $\pm$ 56	0.7 $\pm$ 0.5	0.04 $\pm$ 0.0	0.1 $\pm$ 0.1	0.1 $\pm$ 0.1
	Min–max	0–3.7	0–2.6	0–82	0.8–66	0.03–0.86	0.01–0.01	0–0.21	0.01–0.15

non-ortho-DL-PCBs were observed from the ARZ and LLZ (urban zones) due to the industrial activities in these areas. The WHO-TEQs of PCBs from the study area were lower as compared to those reported from Punjab province ( $3 \text{ pg m}^{-3}$ )<sup>26</sup> and other developing nations.<sup>3,30,31</sup>

### 3.2. DDTs and PCBs in the surface soil

The levels of  $\sum \text{DDT}$  ( $\text{ng g}^{-1}$ , dry weight) ranged from 0.19 to 346 in the surface soil samples collected throughout the studied stretch of the Indus flood plain (Table 1 and Fig. 2b). DDTs (*o,p'*-DDD, *o,p'*-DDE, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT) were detected in >90% of surface soil samples, indicating widespread DDT contamination throughout the country. Compositional trends of DDTs showed that *p,p'*-DDE, and *p,p'*-DDT contributed significantly ( $p < 0.05$ ) towards the total DDTs. In general, the DDT levels in surface soil samples were similar to those reported from Chinese cities, and different areas of Pakistan.<sup>6,15,32</sup> In surface soil, ~50% cases showed the value of *p,p'*-DDE/*p,p'*-DDT <1, which indicated the recent input of the DDT into the environment (Fig. S2†) and suggested the weak implementation of environmental legislation in the country.<sup>5,12,32,33</sup> On the other hand, different studied soil samples from Indus agricultural areas and remote mountainous areas showed *p,p'*-DDE/*p,p'*-DDT values >1, which reflects the past usage of these chemicals as an insecticide and possible LRAT of contaminated particulate material to these areas.<sup>4,32</sup> The current dataset highlighted that urban mountainous areas should be investigated on priority for checking the sources and recent emissions of banned toxic chemicals, such as DDTs. Considering the general declining trend of the *p,p'*-DDTs in the European Union and USA, it seems that the DDT emission patterns in Pakistan were similar to those reported in developed countries before the actions of the Stockholm Convention.<sup>32,34,35</sup>

In general, higher DDT concentrations ( $\text{ng g}^{-1}$ ) were measured in the soil samples ( $p < 0.05$ ) collected from the WMZ (28.05) followed by the LLZ (6.81), ARZ (1.86) and FMZ (1.73), respectively. The Gulibagh Swat and Gilgit sites in the FMZ

exhibited the highest concentration of DDTs ( $50\text{--}343 \text{ ng g}^{-1}$ ), which highlighted the current illegal application of these banned pesticides for crop protection (*i.e.*, fruits and vegetables).<sup>14,17</sup> Another reason for the high DDT concentrations in the FMZ could be LRAT from the low altitude areas to these high altitude valleys. A possible justification of POP build-up levels in the soils of these colder areas is the very high temperature and low organic matter content in the low altitude arid/semi-arid areas, which emitted most of the OCPs through volatilization and short and long term dust transportation to colder areas where they deposited into organic matter rich soils for longer times.<sup>4,17,34</sup> It is also worth mentioning that the high levels of various DDT metabolites, which indicated high transformation rates of DDT isomers into their metabolites, are due to the subtropical climatic conditions of Pakistan. Higher particulate OCP and PCB levels in urban areas might be due to rapid urbanization, and the existence of demolished DDT manufacturing units and pesticide stockpiles in the cities of Lahore, Nowshera and Islamabad, respectively.<sup>8,12,32,33</sup>

The  $\sum_{31} \text{PCBs}$  ( $\text{ng g}^{-1}$ , dry weight) in surface soil samples ranged from 1.4 to 20 (mean: 5.3) throughout Pakistan (Table 2 and Fig. 2c). Nevertheless, PCB concentrations were found to be significantly higher ( $p > 0.05$ ) in the low elevation LLZ (2.06–20.18) and high altitude FMZ areas (2.62–14.22), which is a consequence of rapid urbanization and/or industrial activities.<sup>7</sup> The values measured for the WMZ (2.09–2.09) and ARZ samples ranged from 1.40 to 2.75  $\text{ng g}^{-1}$ . Generally, compositional profiles of PCB congeners in the surface soils were dominated by tri-CBs (~35–42%) followed by hexa-CBs (~15–24%), hepta-CBs (~9–27%), penta-CBs (~3–8%) and tetra-CBs (~1–3%). The abundance of lighter PCB congeners in the atmosphere can be justified by their chemical tendency to volatilize from painted surfaces and contaminated water.<sup>36</sup> The PCB homolog distribution in the soil samples from the present study were similar to China's urban and rural soil.<sup>37,38</sup> The compositional profiles in soil derived here were similar to the commercial PCB formulation of Aroclor-1248 and -1254 (Fig. 4B) for surface soil and for sediment samples from

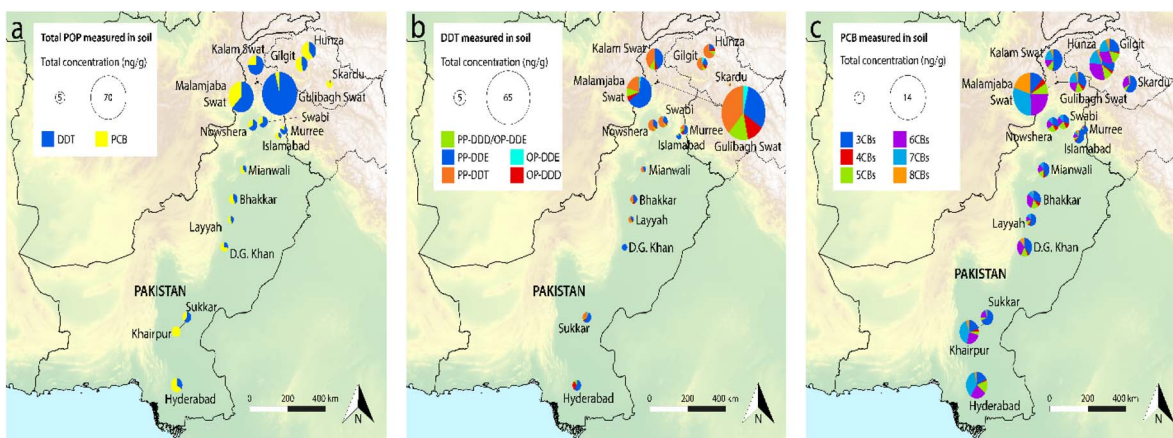


Fig. 2 Proportion of overall DDTs and PCBs (a), compositional profile of DDTs (b) and PCBs (c) in the collected surface soil samples along different study zones of the Indus River flood-plain, Pakistan.

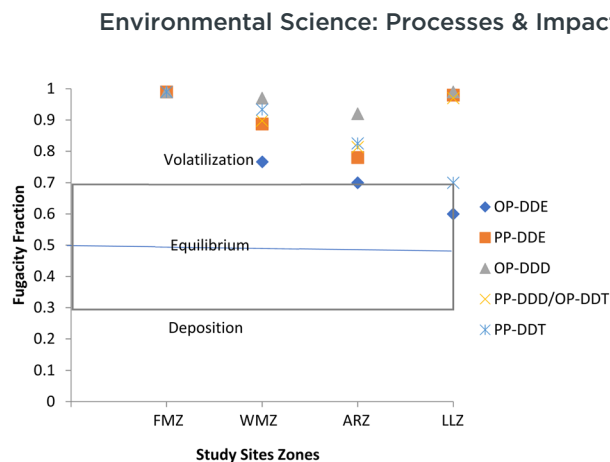
Pakistan.<sup>10,17</sup> Nevertheless, a few exceptions from urban settings in the cities of Islamabad and Lahore show up to 65% proportion of heavier PCBs (*i.e.*, hepta-CBs and octa-CBs), pointing to the high usage of Aroclor-1260 and -1262 for industrial applications as well as accidental spillage in these areas.<sup>26,32</sup> Furthermore, higher molecular weight PCBs in urban samples reflected unintentional PCB leakage from industrial thermal processes. The PCB homolog patterns for surface soil samples were similar to those measured in China, due to the presence of higher quantities of the low chlorinated PCB congeners in Chinese PCB products (tri-CBs: 40%) as compared to those found in the global PCB derivative products (tri-CBs: 25%).<sup>38</sup> In contrast to the patterns of PCB homologs in the studied soil samples, the trends differ from the previously reported data of PCBs in urban and rural India.<sup>3</sup>

$\sum_7$  dioxin-like PCBs in surface soil samples ranged from 1.1 to 153 ng g<sup>-1</sup>. The WHO<sub>05</sub>-TEQ values for mono-*ortho*-dioxin-like PCBs (-105, -114, -118, and -156) and non-*ortho*-dioxin-like PCBs (-77, -126, and -169) were also calculated, which ranged from 0.001 to 0.019 and 1.1 to 153 pg TEQ per g dw, respectively. Among DL-PCBs, PCB-126 and PCB-169 showed higher TEQ values for the frozen mountain zone soil with the mean values of 33.42 and 4.97 pg TEQs per g followed by the LLZ (13 and 3.0 pg TEQs per g), ARZ (6.05 and 0.06 pg TEQs per g) and WMZ (0.97 and 0.15 pg TEQ per g) respectively. Higher TEQs for both mono-*ortho*-DL-PCBs and non-*ortho*-DL-PCBs were calculated from urban samples (Table S4†), presumably due to industrial activities in these areas. Moreover, a few exceptions from remote highland areas (*i.e.*, Sarkdu and Gilgit) also exhibited higher TEQ values, pointing to the LRT of these super-lipophilic chemicals to these remote areas. The current TEQ values are much lower than those reported at informal e-waste recycling sites in Chennai,<sup>39</sup> and a major e-waste recycling area in Taizhou, China. The TEQs calculated are in good agreement with the values reported and from soil and sediment samples collected from various areas of Pakistan.<sup>2,4,26</sup> The TEQ values for DL-PCBs in the surface soil of the Indus flood-plain, Pakistan were much higher than those calculated for Dalian (1.372 ng kg<sup>-1</sup>), Taiyuan (0.006 ng kg<sup>-1</sup>), and Harbin (0.009 ng kg<sup>-1</sup>), China.<sup>21,40,41</sup>

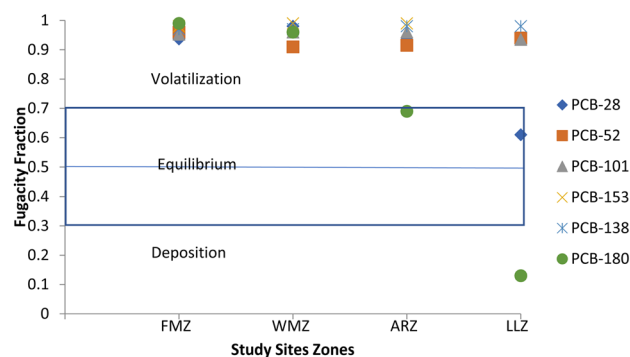
### 3.3. Air–soil exchange of OCPs and PCBs

The calculated fugacity fraction (ff) values for DDTs (Fig. 3A) depicted the general trend of net volatilization and deposition of DDTs in the study area. The fugacity fraction indicated a wide variation of individual DDTs ranging from 0 to 1.0. Similar trends of fugacity fraction were recorded in other studies from Punjab, *viz.* values for ff of DDTs (*o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) ranged from 0.1 to 0.9 and 0.1 to 0.6 in agricultural and industrial areas,<sup>15</sup> Hyderabad city, Sindh, Pakistan, *i.e.* (ff = 0.9–1.0) > industrial (ff = 0–0.9) > background (ff = 0.0–0.6) > residential areas (ff = 0–0.3),<sup>33</sup> Mexico, Europe, and the USA.<sup>42,43</sup>

In the colder areas of the frozen mountain zone (FMZ), *viz.* Kalam, Gulibagh and Malamjaba (Swat region), air–soil exchange gradients for the studied POPs implied net



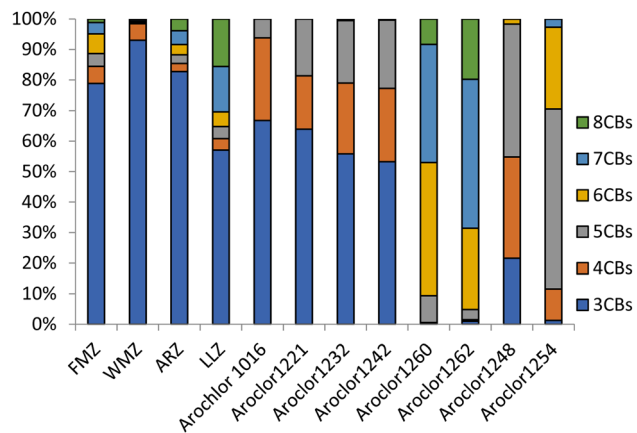
A.



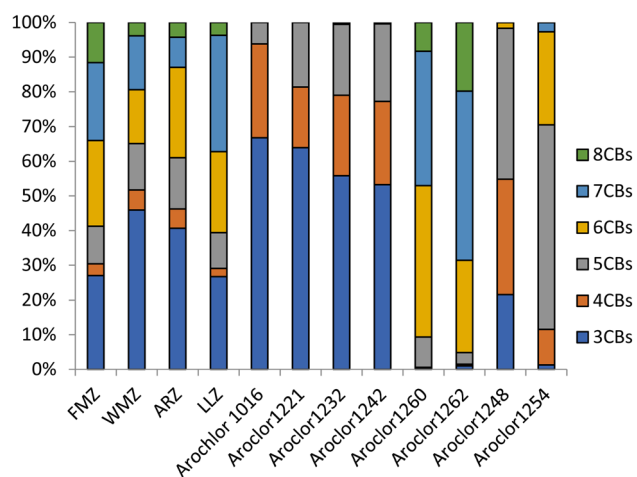
B.

Fig. 3 Air–soil gradients of DDTs (A) and PCBs (B) from the four study zones, along the Indus River, Pakistan.

volatilization of DDTs, which is suggestive of extensive pesticide use on fruit trees and crops and may act as primary sources of DDT volatilization into ambient air along with seasonal temperature fluctuations, particularly in summers.<sup>4</sup> Our background information also points to the smuggling of DDT and other banned chemicals into these areas from Afghanistan and farmers prefer to use DDTs for effective crop protection.<sup>4,32</sup> Moreover, the ff ratios showed that *o,p'*-DDE and *p,p'*-DDE at the Swabi site, *o,p'*-DDE at the Murree site, and *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT at the Mianwali site are at or near equilibrium. Meanwhile, *o,p'*-DDE, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT at the Nowshera site crossed the value of 0.9, which indicated net volatilization and suggested extensive DDT contamination at Nowshera. The Nowshera area is a widely reported POP hotspot due to there being a demolished DDT factory with tons of obsolete pesticide heaps, which is one of the major sources of DDTs in the surrounding areas.<sup>32</sup> Conversely, at the Mansehra site, ff ratios were <0.5, indicating net deposition of DDTs and this scenario suggested that current pesticide usage in agricultural/orchard fields is responsible for high DDT concentrations.<sup>44</sup> These areas are also characterized by mid altitude forest land and canopy interception which may play an important role in capturing the suspended particulate material from the surrounding areas and finally raising POP levels in the



A.



B.

Fig. 4 (A) Composition (%) of PCBs in air and comparison with Aroclor mixtures. (B) Chemical patterns of PCB homologues in the studied surface soil for each studied zone and their matching with Aroclor commercial mixtures.

vegetation and soil of these areas.<sup>1,4</sup> Nevertheless, Bhakkar and Layyah showed net volatilization of DDTs due to historical agricultural activities. Although Abbottabad, Islamabad and Hyderabad showed  $ff$  ratios  $>0.5$ , suggesting net volatilization due to rapid urbanization and land use change (deforestation), this may be a result of emission of accumulated POP residues *via* soil volatilization processes in the context of micro-climatic change.<sup>45</sup> DDT usage for malarial control may also act as an additional source. High DDT levels in the ambient air of Islamabad and Hyderabad sites are already reported and linked to the existence of pesticide burial grounds in these areas, which may be further facilitated by high temperature coupled with abrupt land-use change.<sup>33</sup> The current results of different studied zones showed overall net volatilization of DDT metabolites as shown in Fig. 3A, which highlighted the current usage of DDT in different areas of Pakistan and also the impact of local climate change, *i.e.* high seasonal temperature fluctuations in the summer season aid in DDT volatilization.<sup>1,4</sup>

The fugacity fraction ( $ff$ ) values of six PCB congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180) were calculated for studied sampling sites along the Indus River floodplain areas, Pakistan (Fig. 3B). The PCB congener's fugacity fractions showed a wide variation ranging from 0.1 to  $<1$ , indicating net deposition and volatilization of these compounds. The fugacity fraction ( $ff$ ) values for most of the sites in various zones such as FMZ, WMZ, ARZ, and LLZ crossed the benchmark of 0.5, which showed overall net volatilization of PCB congeners from the soil surface into the air. Meanwhile, the  $ff$  values of PCB-28, PCB-52, PCB-101, PCB 153, and PCB 138 were  $>0.7$ , indicating their secondary emission from soil into the air, which strongly suggests soil as the source of PCB emission. The current findings are consistent for heavier PCB congeners (PCB-101, -138, and -153) as reported<sup>26</sup> and also lighter congeners (PCB-28 and PCB-52) in Indian cities.<sup>39</sup>

The overall results of  $ff$  values from different zones, *i.e.*, FMZ, WMZ, ARZ, and LLZ, showed the volatilization of PCBs, indicating in general that soil acts as a significant source of PCB emissions and high temperature during summers further facilitates the emission process.<sup>46</sup> Moreover, at the Hyderabad site in the Low-Lying Zone (LLZ),  $ff$  values for PCB-28 were  $<0.5$ , indicating net deposition because of industrial and urban activities.<sup>7,47</sup> Thus, these findings are in line with the study of the air–soil exchange of OCPs and PCBs in Punjab province, Pakistan.<sup>26,33</sup>

### 3.4. Air circulation patterns and POP occurrence trends along the Indus River, Pakistan

Several studies have used backward trajectory analysis for source tracking and transport of different pollutants *via* air circulation movement among different regions.<sup>4,26,31</sup> The backward trajectory for site-wise air circulation is presented as Fig. S3 and Table S5.† Backward trajectory analysis revealed that the air masses arriving in high altitude colder areas [Hunza (S-1), Gilgit (S-2), and Skardu (S-3)] were mainly travelling in the northwestern direction from central Asia regions ( $\sim 50\%$  of the total air mass) and China (15%) as compared to local sources which made up to 30–40% contribution. A similar pattern was also observed at the Swat (S-4) site, where the primary air circulation occurred dominantly in the northwest and western directions across the border ( $\sim 70\%$ ) of the studied site location, and around 20% of the air mass was contributed by local sources. These trends indicated that in the colder regions (FMZ), the POP burden was dominated by trans-boundary movement *via* the LRAT process, which may act as a secondary source of POPs in these areas and re-emit through melting snow during the summer season.<sup>1,4,17</sup>

Nevertheless, local sources also contributed towards the recent emission of these toxic chemicals and transportation into the Indus River ecosystem by wet/dry deposition processes.<sup>7,17</sup> In addition, lesser Himalayan areas were experiencing a significant influence from local land-use change in the Indus River floodplain and Indian Punjab and receiving several atmosphere mediated chemical impurities from these areas.<sup>4,8</sup> In recent years, due to rapid urbanization and deforestation, these areas are potentially re-emitting POPs and other



chemicals *via* short/long term dust transport and through abrupt climate change episodes.<sup>2,4</sup> Interestingly, relatively low OCP and PCB levels have been reported from low-lying coastal zones and south Punjab sites compared to other Punjab areas and lesser Himalayan areas.<sup>4</sup> This may be due to POPs and other contaminants being flushed away due to strong air currents and these areas also experienced floods in previous years, which resulted in high fluxes of POPs into the Arabian Sea.<sup>1,4,17</sup>

## 4. Conclusion

This study reports for the first time the presence of POPs in the soil and air in selected zones (alluvial riverine, wet mountain, low-lying mountain, and frozen mountain) along the Indus plain, Pakistan. The study provides an estimation of the presence of POPs in the area, air–soil exchange of POPs to evaluate emission–distribution patterns, and contribution of local and regional sources. Results of this study revealed DDTs as the most predominant OCPs present in the atmosphere and surface soil of the Indus River floodplain areas. Compositional trends of DDTs show that *p,p'*-DDE and *p,p'*-DDT contributed significantly towards the total DDTs. PCBs were found to be more predominant in all studied zones along the Indus plain. Furthermore, results suggested that urban mountain areas and the Indus plain should be given high priority for source emission tracking and recent emissions of banned toxic chemicals, such as DDTs and PCBs. Industrial activities, illegal usage of these banned chemicals in the agriculture/health sector, and the existence of large stockpiles of obsolete pesticides are the likely sources of these toxic chemicals in various environmental matrices of Pakistan. Air–soil exchange of DDTs and PCBs shows their volatilization from low-lying areas because of high temperatures and agricultural and industrial activities, and deposition in frozen mountain areas due to low temperatures. This was confirmed by backward trajectory analysis that revealed the overall wind direction from southern areas northward, which showed LRAT of DDTs and PCBs from the low-lying areas towards mountainous areas and further, their deposition in colder areas. It also revealed that air masses arrived in high altitude colder areas from central Asia regions and local sources are also possible sources of these chemicals in this area. The buildup of DDT and PCB levels in the colder areas might be attributable to melting snow during the summer season and contamination of the Indus River environment and may pose several ecological health risks. The findings of this study may help policymakers to understand the emissions and spatial distribution trends of POPs with climate variations and further focus on POP abatement and control strategies in the area based upon scientific evidence.

## Conflicts of interest

There are no conflicts to declare.

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