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RESEARCH ARTICLE

Organochlorine pesticides in the surrounding soils of POPs destruction facility: source fingerprinting, human health, and ecological risks assessment

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Abstract

The elimination of persistent organic pollutants (POPs) obsolete pesticides stockpiles, particularly the organochlorine pesticides (OCPs), is one of the critical environmental issues faced by many developing countries. This pioneering study aimed to investigate the occurrence, source fingerprinting, human health, and ecological risks of OCPs in the surroundings of the lone POPs pesticide destruction facility in Pakistan. The ΣOCPs residual levels in soil ranged from 35.98 to 566.77 ng/g dry weight (dw), with a mean concentration of 174.42 ± 111.62 ng/g (dw). The OCPs contamination levels in the soil followed the pattern as ΣHCHs > Σendrins > Σendosulfans > dieldrin > Σheptachlors > ΣDDTs > Σchlordanes > methoxychlor. The ΣHCHs residual concentrations were comparatively higher than the previous national and global soil studies. The recent accumulation of HCHs, DDTs, and heptachlor was observed in the study area as identified by β-HCH/∑HCHs, (DDE + DDD)/ΣDDTs, heptachlor/Σheptachlor, and heptachlor exo-epoxide/heptachlor ratios. The OCPs' lifetime carcinogenic risk through ingestion, dermal, and inhalation exposure routes ranged from 1.65E-08 to 2.91E-07, whereas the noncarcinogenic hazard quotient (HQ) ranged from 9.12E-05 to 1.61E-03. The risk vulnerability among age groups was in the order: adult > toddler > child > teen > infant. The calculated risk levels were within an acceptable limit of one in a million (1×10^{-6}) for carcinogenic risk and HQ < 1 for noncarcinogenic risk. The current OCPs residual levels, especially dieldrin and endrin, exhibited low to medium ecological risks when compared to various worldwide limits. The upsurge of the OCPs' environmental contamination levels over the years and consideration of the food chain transfer might amplify the human health and ecological risks intensities.

Keywords Organochlorine pesticides contamination · Human health risk · Ecological risk · Pesticide destruction facility

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Introduction

Organochlorine pesticides (OCPs), which are semi-volatile and persistent synthetic compounds, penetrate the environment through multiple matrices (Keithmaleesatti et al. 2007; Wang et al. 2015) and bioaccumulate in food chains while traveling through various ecological trophic levels (Park et al. 2011). The past few decades witnessed the widespread use of OCPs in the agricultural sector to control the pest, mainly due to their cost-effectiveness and broad-spectrum applications (Wang et al. 2009). Additionally, these chemicals were widely employed in tropical countries to prevent vector-borne epidemic diseases. This excessive usage of OCPs ultimately led to contamination, sometimes poisoning, of environmental

matrices (Mansouri et al. 2017; Oliveira et al. 2016). Environmental exposure to OCPs poses severe threats to biota, including the development of tumors, disruption of the endocrinal system (especially estrogenic mechanism), and chronic and acute complications – in immunological, reproductive, neurotoxic, and carcinogenic – in human and wildlife (Dickhut et al. 2009; Letcher et al. 2010; Rachoń 2015). These effects went unnoticed and unaddressed early on; however, in the recent past, different measures were taken to curb these problems. In the same context, multiple regional and global-scale multilateral treaties were negotiated and implemented (Buccini 2003; Zhang et al. 2002). The Stockholm Convention on Persistent Organic Pollutants (POPs), convened in 2001, proved instrumental in restriction and elimination of harmful POPs, including OCPs (Haffner and Schecter 2014; Tsai 2010; Xu et al. 2013). Although many developing nations are signatories to the Stockholm Convention (2001), yet alarming levels of OCPs have been reported in those countries including Pakistan (Chakraborty et al. 2016; Eqani et al. 2012; Zhang et al. 2008).Pakistan, being an agricultural country, has contributed one of the most substantial parts in the consumption of these pesticides – both through indigenous production and import before the ratification of the Stockholm Convention (Baqar et al. 2017). The public health and environment are still being compromised due to a poor associated legislative structure leading to possible ongoing usage of the obsolete OCPs in some parts of the country (Baqar et al. 2018b; Eqani et al. 2011; Syed et al. 2014). In 1950s more than 250 metric tons (MT) of pesticides were imported, and its use is inflated from 1952 to 2004 (2158.6%) (Khan et al. 2010). Besides its abundant applications, a significant fraction of these obsolete pesticides is stored in various areas of Pakistan, making it the country with one of the largest stocks of banned/outdated OCPs globally (Ahad et al. 2010). The improper storage practices result in the leakage of these chemicals into the environment through rotten sacks and corroded drums (Baqar et al. 2017; Eqani et al. 2011). (The document of Pakistan's National Implementation Plan (NIP) for the Stockholm Convention mentions the storage of an estimated 6030 MT of obsolete OCPs across the country (Environment 2004). However, a nationwide survey conducted by the United Nations Development Program (UNDP) in 2012 has documented the even higher volume of stored OCPs. In order to destroy 1200 MT of these obsolete OCPs, only one project, at whole Pakistan, has been launched, involving co-incineration of the OCPs in the rotary kiln of a cement industry at Chakwal District, Pakistan (GEF 2014). Although the co-incineration at extreme temperatures with appropriate turbulence and residence time may destroy the POPs (Lundin and Jansson 2017), however, the main focus of destruction facility is to deal with the devastation of dirty dozen persistent pollutants. The destruction facility is lacking the appropriate environmental and risk management, thus, the possibility of contamination of the nearby environment. Furthermore, the poor transportation services for the disposal of the contaminated soil are another reason to contaminate the nearby soil and the water resources. The available literature further elaborates that the surrounding soil in the vicinity of the pesticide destruction facility could act as a vital deposition media for the OCPs, owing to the existence of abundant organic matter in the soil (Chakraborty et al. 2015). Thus, the present pesticide destruction facility is a significant source of OCPs into the soil either by poor management practices or the accidental release during transportation (Chakraborty et al. 2015; Pokhrel et al. 2018; Alamdar et al. 2014).

Therefore, this study was designed to ascertain the occurrence, source fingerprinting, human health, and ecological risks of OCPs contamination in the surrounding soils of the potential source such as the obsolete pesticides destruction facility. To the best of our knowledge, this is a pioneer study assessing the OCPs contamination from the surrounding of OCPs destruction plant, employing co-incineration in a cement kiln in developing country, thus, providing the baseline information for future research studies in this particular area.

Materials and methods

Study area description and sampling scheme

Chakwal District (32.93 N; 72.86 E) is situated in the north of Punjab Province, Pakistan, with a total area of 6524 km^2 and population of 1.3 million. The climatic condition of the district falls under the BSh category of the Köppen-Geiger climate classification; with maximum temperatures of 8 °C during winter and 42 °C during summers. The district is a home to about 27 large, medium, and small industrial units, with cement industries emerging as mega-industries of the country. Currently, the district caters four large-scale cement industries with a total production capacity of 7700, 000 MT (DOI 2012). A preliminary survey was conducted to design a sampling program and to obtain information about land use. However, it was identified that the study area lacks any intensive agricultural cultivation and recent vector-borne epidemic disease outbreak, leaving atmospheric settling and accidental releases as a key potential source of OCPs contamination in the vicinity. For soil sampling, a total of 30 sampling sites (Fig. 1) were randomly selected from the surroundings of the OCPs destruction facility, predominantly on the basis of the accessibility. The spatial descriptions of the sampling sites are provided in Table S1.

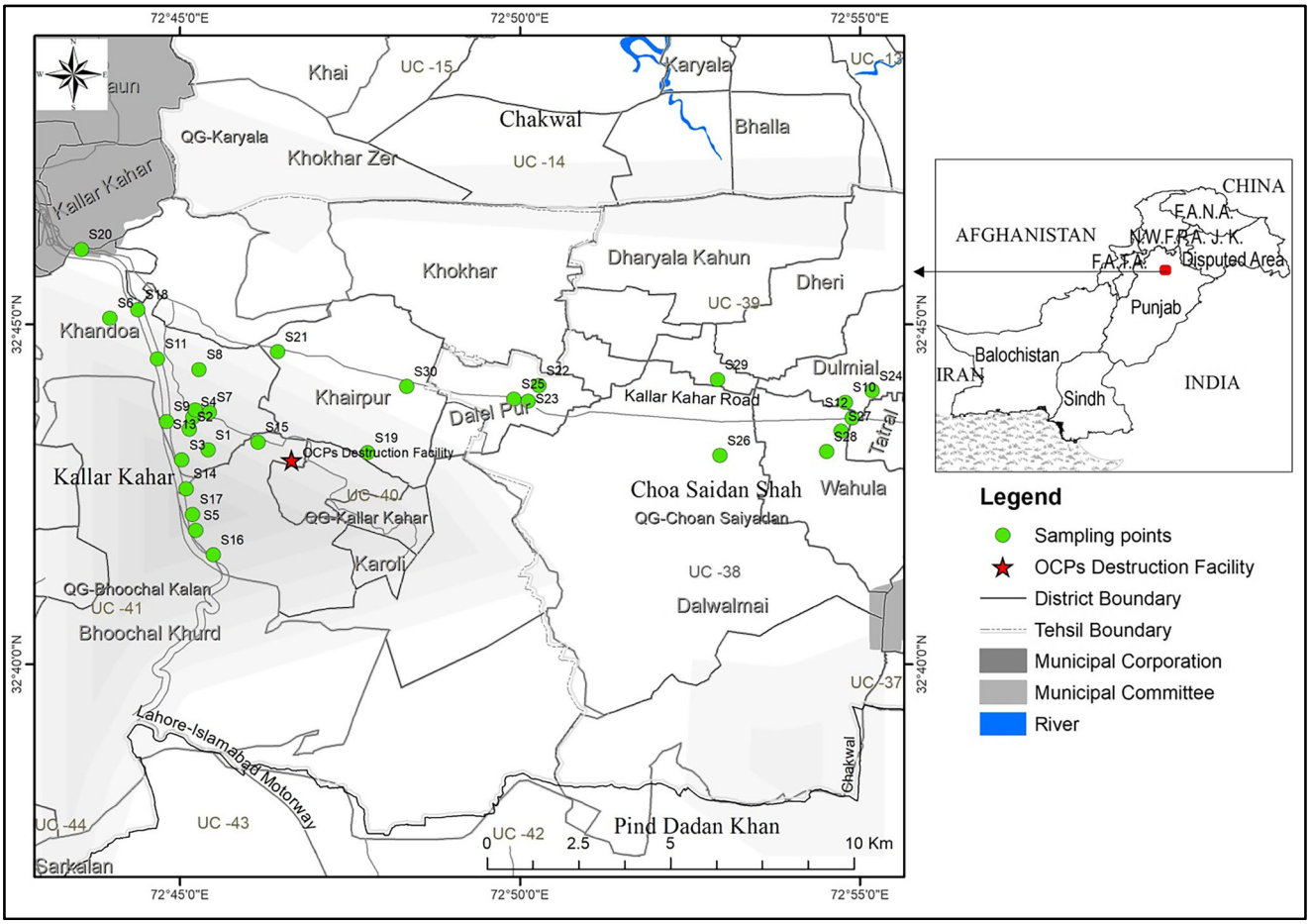

Fig. 1 Map of the study area, indicating the sampling points and OCPs destruction facility from Pakistan

Sample collection and preparation

The surface soil samples were collected at a depth of 0–10 cm using stainless steel shovel in January 2018. Each soil sample was a composite of four subsamples aggregating up to 400–500 g, wrapped in aluminum foil, and packed in polyethylene bags, following by labeling and preservation in the icebox. The samples were transported to the ecotoxicology laboratory at the Sustainable Development Study Center, Lahore, on the same day. The soil samples were then air-dried, sieved through a 2-mm sieve, and stored at −4 °C until further analysis. The soil samples were prepared in acetone, *n*-hexane (1:1, v/v) solution using a solid/liquid extraction method via Soxhlet extractors. Briefly, about 20-g soil sample was packed from top and bottom with 5 g of sodium sulfate in a cellulose thimble (30 x 100mm) and pre-eluted with dichloromethane. Prior to extraction, 50 μL (100 ppb) of 2,4,5,6-tetrachloro-m-xylene (TCMX), as a surrogate standard, was added to each flask containing extraction solution. After extraction, the extracts were concentrated up to 5 ml using rotary evaporator (DIAHAN Scientific WEV-1001 L), and the solvent phase was exchanged to *n*-hexane. The sample extracts were cleaned using 6-ml florisil and 1-g cartridges (pre-activated with 5 ml *n*-hexane: acetone (95:5, v/v) solution). The purified extracts were then concentrated up to 0.5 ml, and pentachloronitrobenzene (50 μL of 100 ppb) was added as an internal standard.

Chromatographic analysis

A total of 21 OCPs including α-hexachlorocyclohexanes (HCHs), β-HCHs, γ-HCHs, δ-HCHs, heptachlor, heptachlor exo-epoxide, trans-nonachlor, cis-nonachlor, trans-chlordane, cis-chlordane, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, dieldrin, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and methoxychlor were detected using GC-MS-QP 2010 (SHIMADZU, Japan), equipped with DB-5MS column (30 m × 0.25 mm i.d × 0.25-μm film thickness) at the School of Environment, Tsinghua University, Beijing, China. The split-less sampling was employed at the injection volume and temperature of 1 μL and 280 °C, respectively. The oven's initial temperature was adjusted at 80 °C (for 1 min) that was increased to 150 °C (at the rate of 20 °C/min) and then finally to 300 °C (at 5 °C/min). The source and transfer line temperatures of GC/MS were set at 270 and 230 °C, respectively. Helium (> 99.999% pure) was

used as a carrier gas at 1 ml/min flow rate, and electron energy was set at 70 eV.

Human health risk assessment

The human health risk assessment, covering the total lifetime carcinogenic risk (TCLR) and total noncarcinogenic hazard quotient (THQ), was calculated using Eqs. (1) and (2), respectively. Humans can be exposed to OCPs in the soil through the exposure route of inadvertent soil ingestion, dermal contact, and inhalation of soil particulates. So, the lifetime human health risks, both carcinogenic and noncarcinogenic, were assessed as a sum of health risks for dermal contact, ingestion, and inhalation exposure using Eqs. 3 to 8 (Sailaukhanuly et al. 2016; Sun et al. 2016; Yadav et al. 2016).

$$TCLR = LCR_{ingestion} + LCR_{dermal} + LCR_{inhalation} \quad (1)$$

$$THQ = HQ_{ingestion} + HQ_{dermal} + HQ_{inhalation} \quad (2)$$

$$LCR_{ingestion} = \frac{C_s \times IR_s \times EF \times ED \times RAF_{oral}}{AT \times BW} \times CF \times CSF \quad (3)$$

$$LCR_{dermal} = \frac{C_s \times SA \times EF \times ED \times AF \times ABS_d}{AT \times BW \times GIABS} \times CF \times CSF \quad (4)$$

$$LCR_{inhalation} = \frac{C_s \times InhR_s \times EF \times ED \times RAF_{inh}}{AT \times BW \times PEF} \times IUR \quad (5)$$

$$HQ_{ingestion} = \frac{C_s \times IR_s \times EF \times ED \times RAF_{oral}}{AT \times BW \times RfD} \times CF \quad (6)$$

$$HQ_{dermal} = \frac{C_s \times SA \times EF \times ED \times AF \times ABS_d}{AT \times BW \times GIABS \times RfD} \times CF \quad (7)$$

$$HQ_{inhalation} = \frac{C_s \times InhR_s \times EF \times ED \times RAF_{inh}}{AT \times BW \times PEF \times RfC} \quad (8)$$

where C_s is the concentration in the soil (ng/g), SA is the skin surface area (cm^2), EF is the exposure frequency (days/year), ED is the exposure duration (years), AF is the skin adherence factor for soil (mg/cm^2), AT is the average lifetime (days), CSF is the cancer slope factor $(mg/kg/day)^{-1}$, BW is the human body weight (kg), IR_s is the soil ingestion rate (mg/day), $InhR_s$ is the inhalation rate of soil (m^3/day), ABS_d is the dermal absorption factor (unitless), GIABS is the gastrointestinal absorption factor (unitless), RAF_{oral} is the relative oral absorption factor (unitless), RAF_{inh} is the relative inhalation absorption factor (unitless), CF is the conversion factor (10^{-9}), IUR is the inhalation unit risk $((\mu g/m^3)^{-1})$, PEF is the particulate emission factor (1.36×10^9 m^3/kg), RfD is the reference dose for oral exposure (mg/kg/day), and RfC is the reference concentration for inhalation exposure (mg/m^3). The values of input parameter used in human health risk evaluation are provided in Tables S2 and S3 of the supplementary data.

Data analysis and quality assurance/quality control (QA/QC)

The QA/QC was positively assured at each stage of the experimentation. Prior to use, all the glassware were twice washed with deionized water, rinsed with DCM/acetone solution (1:1, v/v), and baked at 450 °C for 7–8 h. HPLC grade solvents and pentachloronitrobenzene (internal standard) were provided by from Merck KGaA (Germany) and Dr. Ehrenstorpher GmbH (Germany), respectively. While the TCmX (surrogate standard) and calibration standards were purchased from AccuStandard® (USA), the field blanks were collected during the sampling program, and procedural blanks were prepared to avoid the cross contamination. The blanks were analyzed after each batch (of ten samples) by similar methodology adopted for the samples. All the corresponding blanks were below the detection limits. The six-point standard calibration curve of (10, 50, 100, 200, 500, and 800 μg/ L) was used daily for the quantification purpose. For peaks integration and data acquisition, the Shimadzu GCMS Solution (v. 4.42) postrun analysis was used. The recovery of the surrogate standard (i.e., TCmX) was ranged from 75.9 to 126.1% (mean 91.3%). The descriptive statistics, box plots, and Pearson's correlation tests were evaluated using OriginPro 2018.

Results and discussion

OCPs profile in soil

The OCPs concentrations in the soil samples collected from the surroundings of a OCPs destruction facility are summarized in Table S4. The ΣOCPs levels ranged from 35.98 to 566.77 ng/g dry weight (dw), with a mean concentration of 74.42 ± 111.62 ng/g (dw). Among the studied OCPs compounds, the highest mean levels of contamination in soil was detected for dieldrin (mean: 23.93 ± 33.91 ng/g) (Fig. 2). All the studied OCPs compounds were detected in soil samples from the study area that followed the pattern as ΣHCHs > Σendrins > Σendosulfans > dieldrin > Σheptachlors > ΣDDTs > Σchlordanes > methoxychlor. The relatively higher HCHs levels than DDTs in soil from the study area were inconsistent with the previous findings from soils in other parts of the country (Ahad et al. 2010; Syed and Malik 2011; Syed et al. 2013; Zehra et al. 2015). However, all of these studies were conducted in agricultural activity-affected soils where continuous agricultural use of DDTs has been reported. The current study area is a predominant hub of cement industries with four mega-cement plants, surrounded by barren lands in the Chakwal District (DOI 2012). Previously, HCHs were found to be higher than

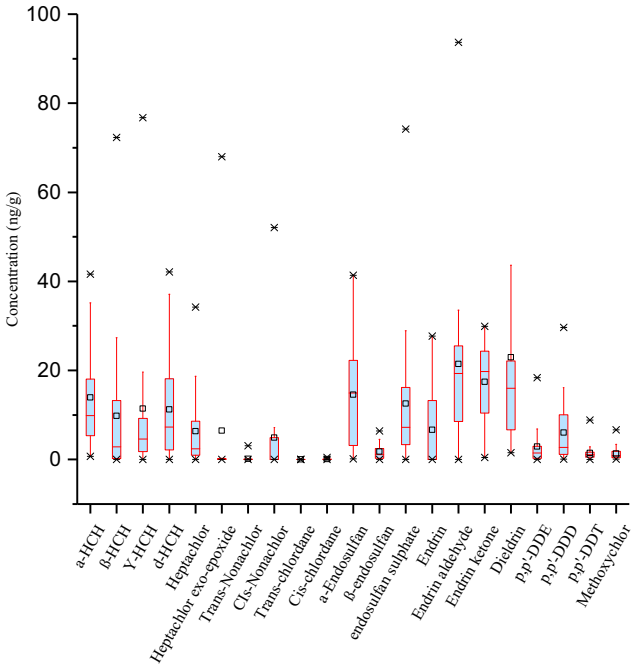

Fig. 2 Box and whisker plots of studied OCPs compounds from Chakwal District, Pakistan

DDTs in soils from Chinese industrial areas in Tianjin Binhai New Area (Wang et al. 2009), Tanggu Chemical Industrial District (Hou et al. 2013), and Beijing (Shi et al. 2009). Therefore, the relative higher levels of HCHs are consistent with previous findings.

Among the HCHs, α-HCH was found to be the most dominant isomer, followed by γ-HCH, δ-HCH, and β-HCH with 30, 24.7, 24.2, and 21.1% contribution to the ΣHCHs concentrations, respectively. The predominance of α-HCH and γ-HCH is of great public health concern as α-HCH can be neurological, endocrinal, renal, and liver disorders, along with abnormalities to gastrointestinal and immune systems (Kong et al. 2014), whereas, the γ-HCH has been reported to cause endocrinal alterations in prostate cells and promote tumors (Dich et al. 1997; Kalantzi et al. 2004). In the soil samples from Chakwal District, endrins were found to be the second most prevalent OCPs class. In the past, convulsions due to endrin poisoning were observed in the village of the adjacent district (i.e., Attock, Pakistan) (Rowley et al. 1987). Among the Σendrins concentration, the constituents were in the order as follow: endrin aldehyde (47.11%) > endrin ketone (38.31%) > endrin (14.58%). The endrin metabolites, i.e., endrin aldehyde and endrin ketone, are present as impurities or as degradation products of endrin when exposed to sunlight or high temperature (up to 230 °C) (ATSDR 1996). However, little is known about the toxicological profile of endrin metabolites.

Among the endosulfans and heptachlor, the high levels of endosulfan sulfate and heptachlor exo-epoxide are of great apprehension. Because this metabolite of technical endosulfan formed via microbial oxidation process is more toxic than parent endosulfan isomers and is hard to decompose further (Camacho-Morales and Sánchez 2016; Qiao et al. 2010; Singh and Singh 2011), similarly, the heptachlor exo-epoxide is more toxic than the parent heptachlor (Berntssen et al. 2012; Pohanish 2014). The univariate correlation matrix by Pearson's correlation coefficient revealed the association among studied OCPs compounds (Table S5); where strong positive correlations were observed between ∑HCHs and heptachlor (r = 0.74), ∑HCHs and dieldrin (r = 0.72), ∑DDTs and methoxychlor (r = 0.82), ∑DDTs and chlordanes (r = 0.75), and ∑heptachlor and dieldrin (r = 0.84), thus, indicating common possible sources of contamination for these OCPs compounds.

The OCPs distribution pattern analysis – within the study area – highlighted that the highest levels of ∑OCPs contamination were observed at the nearest sampling sites to the OCPs destruction facility (Fig. 3), with the highest level of contamination observed at sampling sites S1 and S3. The sampling sites located in the west and northwest of the facility were found to be the most contaminated. This might be attributed to the fact that the prevailing winds direction in the study area is from east to west or southeast to the northwest (Chaudhry et al. 2009). Furthermore, the HCHs were a relatively larger contributor to total OCPs contamination at these sampling sites, whose ongoing recent addition has been identified (later in Section 3.3.1).

Comparative analysis

National comparison

The OCPs levels in soil samples from the study area as compared to the previously published data nationwide are summarized in Table 1. The ΣHCHs concentrations in soil from present study area were found to be considerably higher than those reported from Lesser Himalayan Region of the Azad Jammu and Kashmir, Nowshera District, Chenab River and its tributaries (Nullah Aik and Nullah Palkhu), and Punjab Province (Ali et al. 2018; Mahmood et al. 2014; Syed et al. 2013; Zehra et al. 2015). However, relatively comparative levels of the ΣHCHs were reported by the studies conducted in the surrounding of obsolete pesticides dumping sites in Hyderabad and Kalashah Kaku areas (Alamdar et al. 2014; Syed and Malik 2011). Thus, the HCHs contamination in the study area is relatively higher than the residential, agricultural, and urban settings from the country, whereas, the ΣChlordane, ΣEndosulfans, and ΣHeptachlor concentrations in the soil have shown noticeably higher contamination levels than other parts of the country (Table 1).

The concentrations of ΣDDTs in soil from the present study were observed to be only higher than the levels reported from the Lesser Himalayan Region of the Azad Jammu and Kashmir (Ali et al. 2018) and comparative to those reported from agricultural, residential, and industrial soils from Nowshera area and in the vicinity of the obsolete pesticides

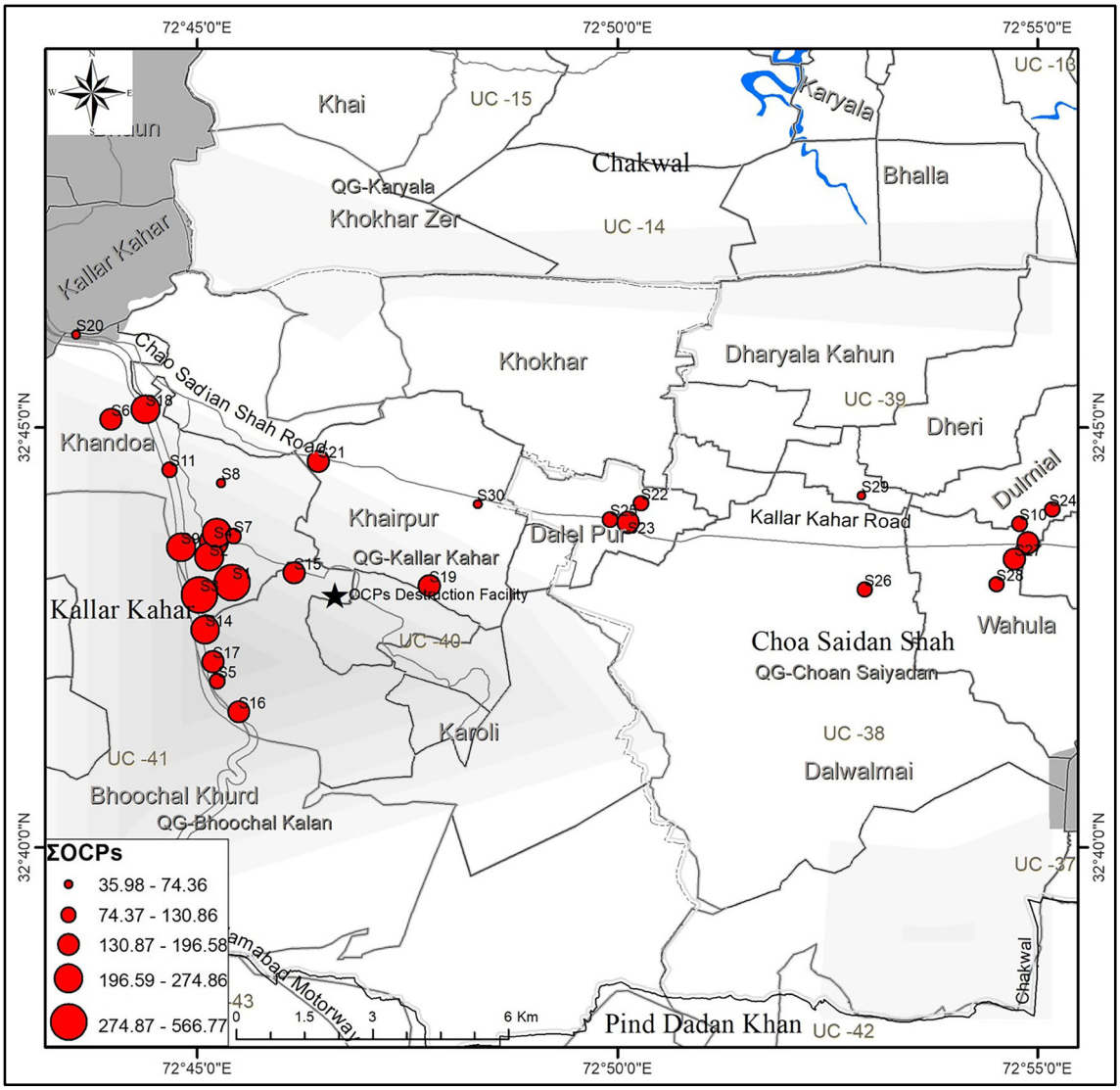

Fig. 3 Spatial distribution of ΣOCPs levels (ng/g(dw)) in soils in the surrounding OCPs destruction facility

dumping ground in Hyderabad District of Pakistan. Other national studies from Chenab River and its tributaries (i.e., Nullah Aik and Nullah Palkhu), Punjab Province, Kalashah Kaku, and obsolete pesticides stores of Pakistan reported much higher levels of ΣDDTs than those reported in the present study (Ahad et al. 2010; Alamdar et al. 2014; Mahmood et al. 2014; Syed and Malik 2011; Syed et al. 2013; Zehra et al. 2015). This might attribute to the possible ongoing usage and accidental release of DDTs as acclaimed by these studies, conducted in Pakistan's most intensive agricultural region or around obsolete pesticides stores.

Global comparison

The OCPs concentrations comparison with previous global studies were also carried out (Table 2). The ΣHCHs concentrations in soil from present study were found to be relatively higher than those reported from Kathmandu and Pokhara (Nepal), Campanian Plain and Central-Southern Regions of Italy, Kenya, Central Europe, and Indian Himalayan Region (IHR) (Degrendele et al. 2016; Devi et al. 2015; Pokhrel et al. 2018; Qu et al. 2016; Sailaukhanuly et al. 2016; Sun et al. 2016; Thiombane et al. 2018) and lesser than those reported from Kyzyl Kairat village, Kazakhstan, and Shenzhen, China (Ni et al. 2011; Sailaukhanuly et al. 2016). Similarly, the Σendosulfans concentrations in soil from the study area were found to be higher than previous findings from Nepal, China, and IHR (Devi et al. 2015; Ni et al. 2011; Niu et al. 2016; Pokhrel et al. 2018) and much lower than those reported from Southern Italy (Thiombane et al. 2018). The Σheptachlors and Σchlordanes concentrations in the soil were found to be higher than those reported in agricultural soils of China (Niu et al. 2016). In terms of ΣDDTs residual levels in soil, the current levels were comparable to those reported from Kenya and Central Europe (Degrendele et al. 2016; Sun et al. 2016), higher than a Nepalese study (Pokhrel et al. 2018), and much

Table 1 Comparison of OCPs concentrations (ng/g (dw)) in soil from study area with previous nationwide studies

Study Area	Soil characteristics	ΣHCHs Range (mean)	ΣHepta-chlors Range (mean)	ΣChlordane Range (mean)	ΣEndo-sulfans Range (mean)	ΣDDTs Range (mean)	Reference
Chakwal Pakistan	Industrial & residential	3.40–165.07 (46.37)	ND-102.20 (12.84)	ND-55.62 (5.15)	2.82–89.67 (28.86)	0.53–56.87 (10.38)	Present study
Azad Jammu & Kashmir	Residential & agricultural	0.01–0.28 (0.07)	0.0003–0.03 (0.01)	0.004–0.08 (0.03)	0.03–0.78 (0.10)	0.63–4.63 (1.54)	(Ali et al. 2018)
Nowshera	Agricultural, industrial, & rural	1.67–32.66 (4.7)	–	–	–	1.04–60.39 (20)	(Zehra et al. 2015)
Hyderabad	Surrounding of obsolete pesticides dumping site	43–1100	–	–	–	28–41	(Alamdar et al. 2014)
Along River Chenab, Nullah Aik &Nullah Palkhu	Agricultural & rural	4.54–18.9 (8.83)	0.33–1.01 (0.64)	–	0.06–0.94 (0.44)	23.3–309 (103)	(Mahmood et al. 2014)
Punjab Province	Industrial, agricultural, & urban	1.7–20.0 (7.8)	–	0.95–6.7 (3.8)	–	8.6–210 (40.0)	(Syed et al. 2013)
Kalashah Kaku	Industrial, Agricultural & Rural	6.38–121.71 (28.72)	ND-31.52 (3.2)	–	–	759.65–1811.98 (205.82)	(Syed and Malik 2011)
Across Pakistan	Obsolete pesticides stores	–	–	–	–	86–10,892	(Ahad et al. 2010)

lower than those reported from Italy, Kazakhstan, China, and India (Devi et al. 2015; Ni et al. 2011; Qu et al. 2016; Sailaukhanuly et al. 2016; Sun et al. 2016; Thiombane et al. 2018).

Source fingerprint of OCPs

Previously, several studies devised specific isomer ratios as a tool to understand the source and origin of OCPs contaminant, either fresh addition or historical application (Baqar et al. 2018a, b; Pan et al. 2019; Syed et al. 2014). So, the OCPs isomer/s ratios were employed in this study for OCPs source fingerprinting (Table 3).

HCHs

The technical-grade HCH products comprise of α-HCH (60–70%), β-HCH (5–12%), γ-HCH (10–12%), and δ-HCH (6–10%) (Lal et al. 2010). However, γ-HCH only possesses insecticidal characteristics, so they were extracted and purified from HCHs technical mixture to produce lindane, a broad-spectrum pesticide containing 99.9% (Lal et al. 2010; Yu et al. 2014). Among the four environmentally significant HCHs isomers, the γ-HCH is the most toxic (Usman et al. 2014). Nonetheless, the β-HCH and δ-HCH are more stable isomers to degradation than γ-HCH attributing to its relatively lower vapor pressure (Syed et al. 2013; Vega et al. 2007). The α-HCH/γ-HCH ratio was employed in this study to assess the contamination source of HCHs in the study area, i.e., technical HCHs or lindane. The α-HCH/γ-HCH values < 3 specifies lindane source for environmental contamination of HCHs (Baqar et al. 2018b; Pan et al. 2019; Saadati et al. 2012). The mean α-HCH/γ-HCH ranged from 0.02 to 20.36, with a mean value of 4.02 that indicates HCHs contamination associated with both technical mixture and lindane. The β-HCH/∑HCHs ratio indicates the origin of HCHs in the environment, with ratio value < 0.5 which identifies the recent addition of HCHs in an area (Aamir et al. 2018). In the present study, the β-HCH/∑HCHs ratios ranged from 0.01 to 0.7, with 97% of the sampling sites signifying a fresh addition of HCHs. Concurrently, the β-HCH/(α-HCH + β-HCH) ratio was also determined to consider the influence of α-HCHs deposition due to a long-range atmospheric transport (LRAT). The ratio value of 0 to 0.1 indicates an α -HCH contamination possibly due to LRAT (Pan et al. 2019). However, the ratio of β-HCH/(α-HCH + β-HCH) ranged from 0.1 to 0.93 (mean: 0.31), exhibiting limited impact of LRAT in high levels of α-HCH in the soil. Thus, the HCHs contamination in the soil of the study area is attributed to the fresh addition of technical HCHs with the least possible influence of LRAT.

DDTs

The technical DDTs mixture contains 75% p,p'-DDT, 5% p,p′-DDE, and 15% o,p′-DDT, and other 5% is a composite of o,p′-DDE, p,p′-DDD, and o,p′-DDD (Yu et al. 2014). The parent

Table 2 Comparison of OCPs concentrations (ng/g (dw)) in soil from study area with previous global studies

Study area	Soil characteristics	ΣHCHs Range (mean)	ΣHepta-chlors Range (mean)	ΣChlordane Range (mean)	ΣEndo-sulfans Range (mean)	ΣDDTs Range (mean)	Reference
Chakwal Pakistan	Industrial & residential	3.40–165.07 (46.37)	ND-102.20 (12.84)	ND-55.62 (5.15)	2.82–89.67 (28.86)	0.53–56.87 (10.38)	Present study
Kathmandu & Pokhara, Nepal	Urban	ND-1.28	–	–	0.01–16.46	0.01–6.48	(Pokhrel et al. 2018)
Central-Southern Regions of Italy	Urban & agricultural	ND-47.27	–	–	ND-904.2	ND-632.95	(Thiombane et al. 2018)
Campanian Plain, Italy	–	0.03–17.3 (1.38)	–	–	–	0.08–1231 (107)	(Qu et al. 2016)
Kyzyl Kairat village, Kazakhstan	Rural/agricultural	0.1–438	–	–	–	1.38–11,100	(Sailaukhanuly et al. 2016)
Kenya	Rural & suburban	ND-7.38	–	–	–	ND-30.04	(Sun et al. 2016)
Central Europe	–	ND-0.76	–	–	–	0.73–25.4	(Degrendele et al. 2016)
China	Agricultural	–	0–1.90 (0.122)	0–3.16 (0.122)	0–6.27 (0.623)	–	(Niu et al. 2016)
Shenzhen, China	–	0.35–281	–	–	0.51–47.2	1.93–199	(Ni et al. 2011)
Himalayan Region, India	–	0–2.79 (1.12)	–	–	0–2.83 (0.62)	0.28–2127 (217)	(Devi et al. 2015)

*ND not detected

DDTs isomers (p,p'-DDT and o,p'-DDT) transform into DDD via reductive-dechlorination or/and DDE via oxidative-dechlorination pathways under anaerobic and aerobic settings, respectively (Syed et al. 2014). So, the ratio of DDTs metabolites to their parent isomers, i.e., (DDE + DDD)/ΣDDTs ratio, is widely recognized to identify the history of DDTs usage (Aamir et al. 2018; Baqar et al. 2018b; El-Osmani et al. 2014; Mumtaz et al. 2015; Syed et al. 2014). The (DDE + DDD)/ΣDDTs ratio > 0.5 is an indicator of an old/historic usage of DDTs in an area and vice versa (Syed et al. 2014). The (DDE + DDD)/ΣDDTs values in the soil of the study area ranged from 0.05 to 0.68 (mean: 0.33), indicating the recent DDTs contamination in the Chakwal District, Pakistan. The evaluated outcomes of the possible recent addition of DDTs are inconsistent with the previous studies from Pakistan, specifying the fresh addition of DDTs (Ali et al. 2018; Baqar et al. 2018b; Mumtaz et al. 2015; Syed et al. 2014). However, all these studies were conducted in agricultural influenced environments. Additionally, the DDE/DDD ratio specifies the environmental conditions under which the parent DDTs isomers degradation occurs; ratio value < 1 indicates anaerobic decomposition (reductive-dechlorination) of parent DDTs, either microbially or chemically (Baqar et al. 2018b; Saadati et al. 2012; Syed et al. 2014). In the present study, the aerobic metabolic degradation of parent DDTs was observed (Table 3), because of the abundant oxygen availability in surface soils. Previously, Alamdar et al. (2014) and Zehra et al. (2015) also clearly indicated the dominance of the aerobic degradation process in non-/limited agricultural soil (Alamdar et al. 2014; Zehra et al. 2015). Therefore, the current study area being the insignificant agricultural region with recent DDTs contamination is the marker to possible recent DDTs exposure from other DDTs commodities.

Table 3 Ratios of studied OCPs isomers

Specific Ratio	Mean	Range
α-HCH/γ-HCH	4.02	0.02–20.36
β-HCH/∑HCHs	0.11	0.01–0.7
β-HCH/(α-HCH + β-HCH)	0.31	0.01–0.93
(DDE + DDD)/ΣDDTs	0.33	0.05–0.68
DDE/DDD	2.1	0.05–24.72
α-endosulfan/β-endosulfan	0.81	0.11–1
Cis-chlordane/trans-chlordane	2.54	1.01–6.42
Heptachlor/Σheptachlor	0.87	0.26–1
Heptachlor exo-epoxide/heptachlor	0.35	0.01–2.92

Chlordane and heptachlor

The heptachlor and chlordane are homologous cyclopentadiene pesticides, containing 10–20% of each other in their respective technical mixtures (IARC 2001). The cis-chlordane and trans-chlordane are two key chlordane isomers that constitute 65–75% of the technical

chlordane, at cis-chlordane to the trans-chlordane ratio of 0.79 (Devi et al. 2015; Yamada et al. 2008). However, as trans-chlordane degrades slightly quicker than cis-chlordane in the environment, so, the cis-chlordane/trans-chlordane ratio > 1 specifies the older usage of technical chlordane (Baqar et al. 2018b; Devi et al. 2015; Yu et al. 2014). In our study, the ratio values (range: 1.01–6.42) specify the past historic addition of chlordane (Table 3). In soil, the applied heptachlor residue metabolically degrades into much stable heptachlor epoxide via heptachlor epoxidation (Pan et al. 2017; Xiao et al. 2011). Thus, the relative levels of heptachlor or heptachlor exo-epoxide residue in the soil help to determine the history of heptachlor application. The heptachlor exo-epoxide/heptachlor ratio < 1 indicates the recent introduction of heptachlor in the environment (Yu et al. 2014). Similarly, the heptachlor/Σheptachlor ratio near 1 specifies the recent application of heptachlor in an area (Pan et al. 2019). The heptachlor/Σheptachlor and heptachlor exo-epoxide/heptachlor ratios at 83% and 87% of the sampling sites specify the recent/new input of heptachlor in the soil of Chakwal District.

Endosulfan

The technical mixture of endosulfan comprised of α-endosulfan (70%) and β-endosulfan (30%), with a half-life of 27.5 and 157 days, respectively (Baqar et al. 2018b; USEPA 2007c). Therefore, the α-endosulfan/β-endosulfan ratio was widely used to investigate the history of technical endosulfan application in an area; the ratio value ≥ 2.33 indicates the recent environmental contamination and vice versa (Devi et al. 2015; Yadav et al. 2016). In our study, α-endosulfan/β-endosulfan ratios were ranged from 0.11 to 1 (i.e., less than 2.33), specifying older/historic endosulfan addition in the study area. Thus, this contamination was not associated with incineration facility.

Relationship of OCPs with TOC

The total organic carbon (TOC) in the soil plays a vital role in determining the fate of OCPs in the environment. The OCPs, being hydrophobic, have a higher affinity to adsorb organic matter in the soil (Devi et al. 2015). Consequently, the soil acts as a sink to these contaminants reducing their bioavailability to ecological systems (Zehra et al. 2015). At the same time, the high organic matter in the soil, including TOC, facilitates the OCPs' microbial decomposition process (Nam et al. 2008; Yadav et al. 2016). In this study, the TOC levels of the soil ranged from 0.45 to 5.8%. In order to investigate the influence of TOC content to OCPs contamination level, Pearson's correlation test was applied (Table S5). However, weak positive correlation of TOC content was found with DDTs ($r = 0.27$) and chlordane ($r = 0.28$), whereas the very weak positive correlation of TOC content was established with HCHs ($r = 0.04$), heptachlor ($r = 0.01$), dieldrin ($r = 0.08$), and methoxychlor ($r = 0.11$) and very weak negative correlation with endosulfans ($r = -0.03$) and endrins ($r = -0.08$). This very weak correlation between TOCs and OCPs, except DDTs and HCHs, implies that the OCPs might be recently or continuously being added into the study area that has hindered the establishment of equilibrium partition between OCPs and soil (Nam et al. 2008; Sun et al. 2016). Moreover, the current contamination on the OCPs in the study area might be associated to the secondary distribution pattern, involving chemical's transportation away from the point of use and subsequent deposition and accumulation (Qu et al. 2016). The correlation further suggests that land use, soil texture, and chemistry might play a vital role in OCPs absorption in soil from the study area (Zhang et al. 2013). This weak linear correlation between TOC contents and OCPs was consistent with the previous findings from Kenya (Sun et al. 2016), Italy (Qu et al. 2016), and Nepal (Yadav et al. 2016).

Human health risk assessment

The human health risk evaluated through possible human exposure from all three exposure routes were evaluated as aforementioned in Section 2.6. In order to assess the risk of different age groups, the risk was calculated for five age groups, i.e., infants, toddlers, children, teens, and adults (Table S6). The ∑TLCR of all OCPs compounds was ranged from 1.65E-08 to 2.91E-07, with the risk of vulnerability among age groups in the order adult > toddler > child > teen > infant (Fig. 4a). For all the age groups, the highest and lowest risk levels were exhibited by dieldrin (2.92E-08-5.14E-07) and *p,p'*-DDT (3.76E-11 to 6.64E-10), respectively. Among the routes of exposure, the dermal contact and ingestion contribute utmost to the carcinogenic risks from the soil. Likewise, studies have asserted a minor contribution of inhalation of OCPs-contaminated soil/dust to the lifetime carcinogenic risks (Mostafalou and Abdollahi 2013; Sailaukhanuly et al. 2016). However, the carcinogenic risks posed to all age groups were found to be within the acceptable lifetime risk limit of one in a million (10^{-6}), suggested by ATSDR (ASTDR 2004). In respect to noncarcinogenic risk, the ∑THQ of OCPs were ranged from 9.12E-05 (in infants) to 1.61E-03 (in adults) (Fig. 4b). Similar to the carcinogenic risks, the *p,p'*-DDT (2.21E-07 to 3.90E-06) and dieldrin (3.65E-05 to 6.43E-04) exhibit lowest and highest levels of noncarcinogenic lifetime risk in all studied age groups (Table S6). The noncarcinogenic human health risks were assessed to be lower than the acceptable risk level of less than one (HQ < 1) (Baqar et al. 2018b; Sruthi et al. 2017).

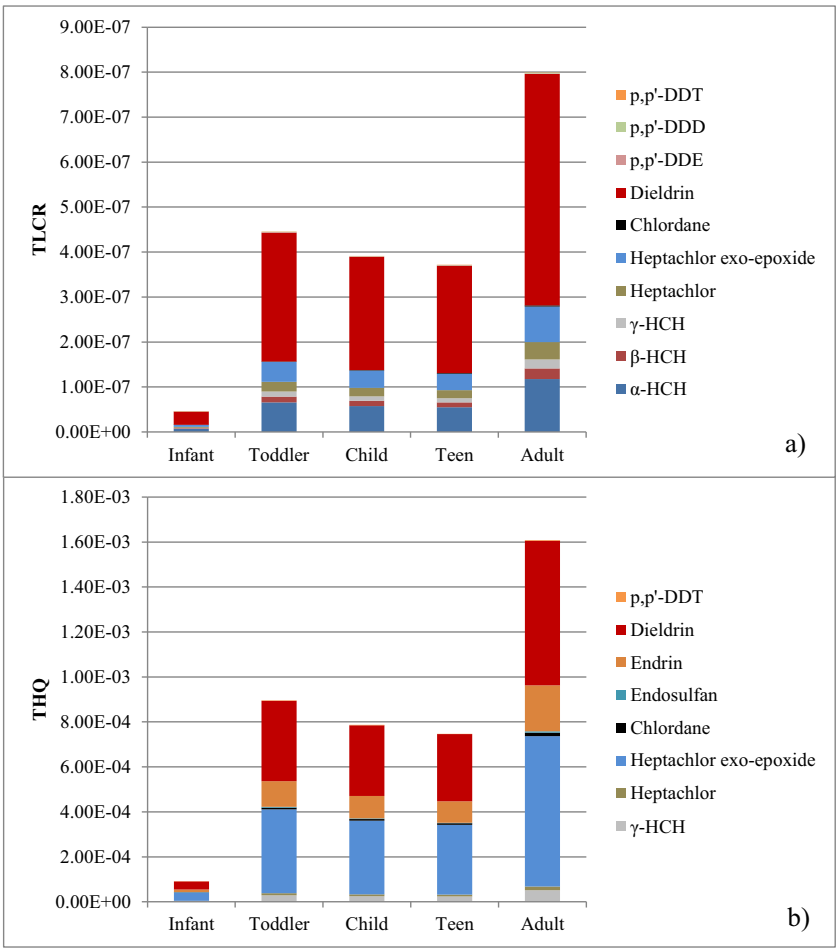

Fig. 4 **(a)** Total lifetime carcinogenic and **(b)** noncarcinogenic (hazard quotient) risks of OCPs among studied age groups

Nevertheless, the concentration of OCPs in the Chakwal District and unsafe handling of OCPs during transportation and co-incineration practices may further upsurge the OCPs contamination levels in the environment, thus amplifying the human health risks intensities over the years.

Ecological risk assessment

The potential risks to ecological integrities associated with OCPs residual levels in soils from the study area were assessed by comparing the contamination levels with guidelines values or standards. As Pakistan has not established any standards for OCPs levels in soil, so the permissible limits established by US, Canadian, Dutch, and Australian authorities were used to evaluate the levels of ecological risks. The Canadian soil quality guidelines for the protection of environmental and human health proposed the standard value of 10 ng/g for lindane (i.e., γ-HCH) and 700 ng/g for ∑DDTs in residential/agricultural soils and 1200 ng/g for ∑DDTs in commercial/agricultural soils (CCME 1999). The γ-HCH residual levels were found to be higher than the standard value (10 ng/g) at 27.6% of the sampling sites, whereas the DDTs were widely within the established limits. Correspondingly, the comparison with Dutch ecological risk limits revealed that current residual levels of ∑endrins and ∑DDTs in soil were exceeding the maximum permissible concentration (MPC) of 9.5 ng/g and10 ng/g at 94% and 52% of the sampling sites, respectively. However, the OCPs concentrations were within the Dutch's serious risk concentration (SRC) of 200, 1000, and 95 ng/g for dieldrin, ∑DDTs, and ∑endrins, respectively (Smit and Verbruggen 2015).

The ecological soil screening levels (ECO-SSLs) established for dieldrin (avian, 22 ng/g; mammalian, 4.9 ng/g) and DDTs (avian, 93 ng/g; mammalian, 21 ng/g) by USEPA were also taken into consideration for screening ecological risks to avian and mammalian ecological receptors (USEPA 2007a, b). The current levels of dieldrin (mean: 23.93 ng/g) were found to be higher than the ECO-SSLs value for terrestrial receptors, indicating the presence of ecological risks. The Australian Department of Environment and Conservation recommends ecological investigation levels (EILs) values of 200 ng/g for dieldrin, 200 ng/g for chlordane, 1000 ng/g for ∑DDTs, and 500 ng/g for ∑heptachlor were not exceeded at any of the sampling sites indicating the absence of any significant ecological risk (DEC 2010). Therefore, the low to medium ecological risks are possessed by the dieldrin and

endrins residual levels in the soil from the surrounding of the OCPs destruction facility.

Conclusions

This preliminary study revealed high levels of OCPs contamination in surrounding soils of the OCPs destruction facility situated at Chakwal District, Pakistan. The ΣHCHs signify as the most dominantly prevailing OCPs – with concentrations comparatively higher than most of the previous national and global soil studies. The recent addition of HCHs, DDTs, and heptachlor were identified in the study area through OCPs isomer ratios. The limited agricultural practices in adjacent areas suggested the contamination from other OCPs sources, possibly the POPs destruction facilities in the vicinity. Considerable levels of carcinogenic and noncarcinogenic human health risks were evaluated on the basis of current OCPs residual concentration and were found to be within the acceptable risk levels. In regard to ecological risk, low to medium levels of risks to ecological integrities were possessed by OCPs' residual levels in the soil as compared to the Canadian, Dutch, Australian, and US standards/limits. However, considering the food chain transfer and an increase in OCPs' residual levels might amplify these estimated human health and ecological risks levels. Therefore, this pioneer screening study would provide baseline data that would contribute significantly to regional as well as global ecological studies. This highlights the dire need to align the OCPs destruction techniques to the best environmental practices.

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