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ECOLOGICAL AND HUMAN HEALTH RISK ASSESSMENT OF OCP CONGENERS IN AGRICULTURAL SOIL ALONG RIVER CHENAB CATCHMENT

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ABSTRACT: Pesticide contamination of agricultural soil is matter of concern owing to associated food safety. Based on the pertinent literature survey no other study has reported the ecological and total carcinogenic risk assessment of OCPs in agricultural soils of the study area. This study aims to assess the occurrence, distribution and source apportionment of OCP congeners along with probable ecological and human health risk evaluation. The agricultural soil samples (n=165) were collected from selected food crops fields along tributaries of Nullah Aik and Nullah Palkhu. After extraction and clean up samples were analyzed using GCMS. The residues of ΣOCPs were detected ranging from 63.45 ng/g – 124.81 ng/g (mean 94.80 ng/g) with highest detection range (11.37 - 19.95 ng/g) of DDT. The findings of spatial distribution revealed the highest pollution load downstream of both Nullahs. SQGQ for all sampling sites were greater than 1 suggesting high risk to ecological integrities to DDTs in Soil. Total Carcinogenic Risk (TCR) was ranging from 6.75E-09 - 1.57E-07 with risk order of dermal > ingestion > inhalation. The assessment of the results revealed that carcinogenic risk is within the acceptable limit (10^{-6}) suggesting no potential carcinogenic risk to human health to selected OCPs through contaminated soils in the study area.

Keywords: Agricultural soil, Total carcinogenic risk, Ecological risk assessment.

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INTRODUCTION

At current global increase in food demand has led to agricultural intensification and widespread use of pesticides (Ohoro *et al.* 2023). Organochlorine insecticide including DDT, hexachlorocyclohexane (HCH), aldrin, and dieldrin belong to among the most widely used pesticides in Asian nations because they are inexpensive and have the ability to combat a variety of pests (Sultan *et al.*, 2023). Organochlorine pesticide, renowned for their organic, chlorinated and hydrophobic nature boast a high absorption coefficient, making them extensively employed in agricultural pest control sector across diverse crops and health sector. Yet they are plagued by their poor water solubility and notable metabolic resistance (Necibi and Mzoughi, 2023). The connection between OC exposure and a higher likelihood of memory loss, Alzheimer's disease (AD), and other neurological disorders including Parkinson's disease has grown. The OCPs and their derivatives have been associated to an array of human health conditions, including cancer; cardiovascular disease, diabetes, and neurological and reproductive anomalies. Children are more vulnerable to the toxic effects of these pollutants than adults. Birth defects, low birth weight, and fetal mortality are among the consequences. Furthermore, these substances may transfer from the placenta into the developing fetus (Mrema *et al* 2012: Ashesh *et al*., 2022).

The organochlorine pesticides accumulate in soils through two main pathways: direct application in farming and sanitory operations, and indirectly accumulation through either dry or wet processes of airborne contaminants emanating from regions where OCPs originally were administered (Bajwa *et al*., 2016). OCPs within soil can undergo transport via mechanisms like leaching, diffusion, volatilization, and mass flow into the air, ground, and water. Various factors, including the properties of the OCPs, soil composition, application concentrations, persistence duration, application methods, rates, frequency, and characteristics of species involved, collectively determine their destiny within soils (Kafei *et al*., 2020)

In Pakistan, local production and usage of OCPs has been banned under Stockholm convention. At current Pakistan has no manufacturing unit except 19 firms producing formulations based upon imported ingredients from India and other countries (Sultan *et al*. 2019). In the country, there are 6030 million tons of outdated organochlorine pesticides, with Punjab holding 917 tons in several storage facilities (Sana *et al*. 2021). Despite the ban, presently low cost, multipurpose industrial usage and week regulatory framework are crucial aspects contributing to occurrence of these toxic contaminants in environmental compartments and different food groups within the region (U. Ali *et al*. 2014; Aamir *et al*. 2018; Baqar *et al*. 2018; Ali *et al*. 2019: Sultan *et al*. 2023). In most recent 11th meeting of Stockholm convention held at Geneva, in May, 2023 the conference of parties concluded that DDTs are only used for vector control (mosquito control) and will eventually be phased out when more cost-effective alternatives become available.

According to a research study about 80-90% of pesticides employed in crop fields pollute environmental matrices including soil, water, air, and non-target plants, whether directly or indirectly, as a result of runoff and drift caused by pesticide accumulation. Approximately 80-90 percent of these chemical residues are further transformed by biodegradation or chemical activities that survive in the natural environment for more than a decade ending into food chain (Baqar *et al*. 2023). Hence, pesticide contamination of agricultural soil is more directly linked with food safety and requires specific consideration. Based on pertinent literature survey no other study has reported the ecological and total carcinogenic risk assessment of OCPs in agricultural soils of the study area. This study aims to assess the occurrence, distribution and source apportionment of OCP congeners along with probable ecological and human health risks.

MATERIALS AND METHODS

Study area: The research area is located across the River Chenab, which originates from the snow-capped Himalaya ranges in Himachal Pradesh, India. It then enters Pakistan in the Sialkot region, upstream to the Marala Barrage. The Nullah Palkhu and Nullah Aik are important tributaries of River Chenab. They originate from Jammu and Kashmir, India, and drain an area of about 1,875 km^2 towards Pakistan, consisting of agricultural land. The catchment area of both streams includes the rural and urban areas (Mahmood *et al*. 2014).

Strategy for sampling: A total number of eleven sampling sites were selected for agricultural soil sampling along Pulkhu and Aik, tributaries. The area under investigation was categorized into three zones depending on the origin of tributaries, level of anthropogenic activities and habitat variation. The upstream zone was located in a rural area consisting of agricultural land. The second midstream zone received urban runoff and discharge from several industries in Sialkot. The third zone was situated downstream of tributaries, including peri-urban and some urban sites of Sialkot. The sampling was carried out during December 2020 to February 2021. Each sampling site was marked for coordinates using the Global Positioning System.

Agricultural soil sampling: The agricultural soil samples (n=165) were collected from selected food crops fields from depth of 0 to 20 cm using stainless steel auger. Collected samples were mixed to make a composite sample of 1 kg and packed in aluminium foil and transported to lab after sealing in bags. All samples were sieved with 2mm mesh size and stored at -20˚C until further analysis (Ali *et al*. 2019).

Chemical analysis

Extraction and cleanup: Soil samples were extracted following the protocol of solid-liquid extraction. Before extraction 2,4,5,6-tetrachloro-m-xylene was added in each sample as surrogate standard (Baqar *et al*. 2018). Soxhlet extraction of about 20g of each sample was done with DCM for 24h. Granules of activated carbon were added to conical flask for removal of elemental sulfur. Extracts were dried through a rotary evaporator after exchange of solvent phase to hexane. For cleanup, fractioned extracts were passed through glass column having an internal diameter of 8 mm containing 3% deactivated neutral alumina, 3% deactivated neutral silica gel, 50% sulfuric acid silica and anhydrous sodium sulfate. Elution of column was done with 1:1 solution (50ml) of hexane and dichloromethane (Mahmood *et al*. 2014). Soxhlet-extraction was carried out for all column-packing reagents with dichloromethane for a period of 48h. After that anhydrous sodium sulfate, neutral alumina and neutral silica were baked at 450°C, 250°C and 180°C respectively for 10h. After adding solvent keeper dodecane (25µl), extract was kept under nitrogen stream to concentrate. All samples were spiked with known concentration of PCB-209 as an Internal standard (Xu *et al*. 2014).

Chromatographic analysis: Isomers of OCPs, including Σendosulfan, dichloro-diphenyldichloroethylene (DDD), dichloro-diphenyltrichloroethane (DDT), dichloro-diphenyldichloroethane (DDE), alpha-hexachlorocyclohexane (α-HCH), beta-hexachlorocyclohexane (β-HCH) and chlorothalonil were determined using GC-ECD containing DB-5 capillary column (30 m × 0.25 mm × 0.25 µm). Nitrogen gas was used as mobile phase. The rate of flow of column was kept at 1.8 ml per min. Split less mode of injector was regulated at 250 °C. At first, the column temperature was adjusted for 3 min at 50 °C, then enhanced for 20 min at 20 °C/min to 280 °C. Levels of investigated isomers were calculated and interpreted by comparing data of obtained peaks with authentic reference data.

Quality control protocol (QA/QC): To obtain quality results, strict quality assurance protocols were practiced. All glassware after washing with distilled water, was sterilized at 400°C for 4h using a muffle furnace to avoid cross contamination. Prevention of column overflow and contamination was ensured by analyzing blanks after every 15 samples. All reagents were of analytical grade (MERCK, Germany) and were analyzed for false peaks. Surrogate and internal standards were obtained from Dr. Ehrenstorfer GmbH, Germany. Recovery ratios and blanks were used to correct the analytical results. Calibration curve were measured using standards of variable concentrations (2, 10, 20, 50, 100 and 200 µg/L) as reported by Baqar *et al*., (2018).

Interpretation of Data and Risk Evaluation

Ecological Risk Assessment: In present study ecological risk of investigated OCPs was evaluated using sediment quality guidelines and sediment quality guideline quotient method (Emoyan *et al*. 2022). The equation is as follows:

$$SQGQ = \frac{\Sigma^{P}ELQ_i}{n} \qquad (1)$$

$$\mathrm{PEL}Q_i = \frac{C_i}{PEL} \qquad (2)$$

Where $PELQ_i$ refers to PEL quotient for pollutant i, n is the number of analysed isomers having SQGs C_i denotes level of OCP, and PEL indicates probable effect level for pollutant. The values for SQGQ less than 0.1 represents no effects and greater than 1 indicates adverse effects to ecological integrities.

Carcinogenic risk assessment: Carcinogenic risk via inhalation, ingestion and dermal exposure route was calculated using equation followed by Kafai *et al*. 2020.

$$CR_{ing} = \frac{Cs \times IR_{ing} \times F \times ED \times CF}{\mathrm{BW} \times \mathrm{AT}} \times SF \qquad (3)$$

$$CR_{der} = \frac{Cs \times A \times AF \times F \times ED \times CF}{\mathrm{BW} \times \mathrm{AT}} \times SF \qquad (4)$$

$$CR_{inh} = \frac{Cs \times IR_{inh} \times F \times ED}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}} \times SF \qquad (5)$$

$$CR_{total} = CR_{ing} + CR_{der} + CR_{inh} \qquad (6)$$

Where Cs is level of OCP determined in soil mg/kg, F refers to exposure frequency, ED indicated duration of exposure, CF indicates conversion factor (10^{-6} Kg/mg), BW represents body weight, AT indicates average lifetime, IR_{ing} show rate of intake of polluted soil, A refers to adhered soil, AF indicate bioavailability factor, IR_{inh} show rate of inhalation, PEF represents particle emission factor and SF indicates slope factor.

Non Carcinogenic risk assessment: The evaluation for non-carcinogenic risk (HQ) to consumers was done using following equations.

$$HQ = \frac{CDI\ nc}{\mathrm{Rf}} \qquad (7)$$

$$Hazard\ Index\ (HI) = \Sigma\mathrm{HQ}$$
$$= HQ_{ing} + HQ_{inh} + HQ_{der} \ (8)$$

$$CDI_{ing-nc} = \frac{Cs \times IR_{ing} \times F \times ED \times CF}{\mathrm{BW} \times \mathrm{AT}} \qquad (9)$$

$$CDI_{der-nc} = \frac{Cs \times A \times AF \times F \times ED \times CF}{\mathrm{BW} \times \mathrm{AT}} \qquad (10)$$

$$CDI_{inh-nc} = \frac{Cs \times IR_{inh} \times F \times ED}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}} \qquad (11)$$

where, CDI refers to chronic daily intake, Rf indicates reference dose. The USEPA- IRIS Rf values were used to assess non-cancer risk.

RESULTS AND DISCUSSION

General profile of OCPs in Soil: The basic descriptive statistics of levels of detected organochlorine pesticides in agricultural soil samples are summarized in table 1. The residues of ΣOCPs were detected ranging from 63.45 ng/g – 124.81 ng/g with mean concentration of 94.80 ng/g. All studied isomers were detected in soil samples collected from agricultural land along tributaries of River Chenab. The mean detected levels of OCPs were in the following order: DDT> DDE > DDD > β-HCH > α-HCH > Chlorothalonil > β-endosulfan > α- endosulfan (Figure 1). Several previous studies have reported higher levels of pesticides in soils from different countries. In the soil samples of the present study, the concentrations are greater than those observed by the following; in agricultural soils of Tanzania (Nyihirani *et al*., 2022); Korea (Yun *et al*., 2022); Huangpi, China (Gereslassie *et al*., 2019); Dalaki, Iran (Kafaei *et al*., 2020); Azad Jammu and Kashmir, Pakistan (Ali *et al*. 2018); along River Chenab, Nullah Aik and Nullah Palkhu, Pakistan (Mahmood *et al*., 2014b); Punjab Province, Pakistan (Ali *et al*., 2020). However, the findings of this study are lower than the results reported in the previous studies for soils of Chakwal, Pakistan (Ali *et al*., 2019) (Table 2).

OCPs Levels and Source Fingerprinting in Soil

DDT: Among all detected isomers DDT showed the highest detection range (11.37 - 19.95 ng/g) with mean concentration 15.44 ng/g indicating that it is major residual pesticide in the agricultural soil of study area. The average measured levels of DDT were higher than HCH in soil samples. This finding is in accordance with the trend observed in previous studies (Ukalska-Jaruga *et al*., 2020; Yun *et al*., 2022; Nyihirani *et al*., 2022). According to the fact reported in literature it is assumed that persistence of pesticides including DDT is related to soil physicochemical properties such as presence of organic matter, chemical structure and half-life (10 years) of pesticides (Yun *et al*. 2022; Nyihirani *et al* 2022). Considering the fact, longer half life of DDT (10 years) and presence of organic matter may be linked with more adsorption of OCPs in soil by increasing water solubility (Syed & Malik, 2011).

Some isomers of OCPs are degraded in environment and can provide useful information about the source and usage of contaminants (Mungai & Wang, 2019). Microbial degradation of DDT in soil occur in two ways, aerobic and anaerobic decomposition. In aerobic environment, DDT reacts to form DDE, and under anaerobic conditions it forms DDD. Isomer ratio has been used as evaluation method to determine the source of contaminants, extent of degradation and recent or past influx (Kata *et al*., 2015). Ratio (DDE+DDD)/ DDT > 1 indicates past use and complete decomposition. Whereas (DDE+DDD)/ DDT < 1 shows the new inputs (Gao *et al.*

2023; Qu *et al*., 2015). From assessment of results, it was found that the average value of (DDE+DDD)/DDT in agricultural soil along Nullah Aik and Nullah Palkhu was 1.83, revealing that the DDTs were mainly from historical use of technical DDT (Figure 2). Moreover, the ratio of DDE/DDD ranged between 0.5-1.12 indicated the use of technical DDT in the study area (Eqani *et al*., 2012; Mahmood *et al*., 2014). This finding is consistent with the results of (Yao *et al*., 2022; Yun *et al*., 2022; Ali *et al*., 2019 and Kafaei *et al*., 2020). It is well documented in literature that the soil texture, pH, temperature, content of organic matter and quantity of fertilizer affect the degradation of isomers of DDT in soil. As per studied literature lack of microbial degradation in agricultural soils of study area can be the possible source of historical residues (Kafaei *et al*., 2020).

HCH: Commercially, two types of OCPs are used Industrial/technical HCH and lindane. Technical HCH comprised of 60 – 70% α-HCH, 5 – 12 %, β-HCH, 10-15% γ-HCH and 6-10% δ-HCH. In present study the mean levels of ΣHCHs for all the sampling sites ranged 10.58 - 20.14 ng/g with mean concentration of 15.58ng/g. The obtained levels were lower than DDTs. This finding is in accordance with the finding reported in previous research studies Yun *et al*., 2022. In present study mean concentrations of β-HCH were higher than α-HCH. This finding is in line with the finding of Gereslessai *et al*., 2019; Jaruga *et al*., 2020; Yun *et al*. 2022. The probable microbial conversion of γ-HCH to β-HCH may be the cause for high concentrations of β-HCH in soil samples. Moreover, microbial degradation of β-HCH in soil does not occur easily due its more stable nature, greater bioaccumulation potential, lower vapor pressure and high boiling and melting point. In addition, β-HCH can be adsorbed onto organic matter in the soil and more resistant to evaporation (Yun *et al*. 2022).

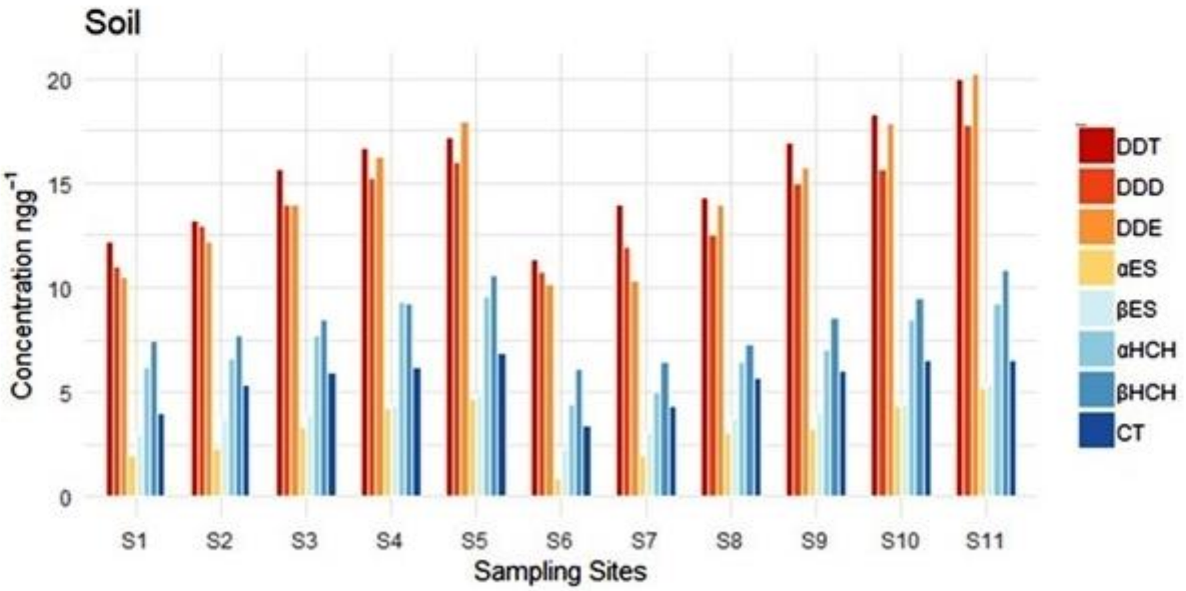

Figure 1: Concentrations of OCPs isomers in agricultural soils of Nullah Aik and Nullah Palkhu

Table 1: Descriptive statistics of OCPs in agricultural Soil (ng/g) along tributaries of River Chenab

OCPs	Mean	Std. dev.	Min.	Max.	Median
DDT	15.44	2.65	11.37	19.95	15.68
DDD	13.89	2.23	10.78	17.78	13.99
DDE	14.48	3.44	10.21	20.22	14.01
α-ES	3.21	1.32	0.92	5.18	3.24
β-ES	3.88	0.87	2.33	5.34	3.88
ΣES	7.1	2.18	3.25	10.52	7.21
α-HCH	7.28	1.73	4.46	9.56	7.03
β-HCH	8.39	1.57	6.12	10.89	8.48
ΣHCH	15.59	3.14	10.58	20.14	15.61
CT	5.54	1.15	3.43	6.89	5.97
ΣOCPs	94.8	0.86	0.92	20.22	7.85

Table 2: Comparison of average levels (ng/g) of OCPs in soils from study area with previous studies

Study area	Soil type	ΣDDTs	ΣHCH	ΣEndosulfan	Reference
Along Nullah Aik and Nullah Palkhu, Pakistan	Agricultural	46.81	15.58	7.09	Present study
Peshawar, KPK	Waste dumping site	6.46	3.50	2.65	Sulatan *et al*. 2019
Azad Jammu and Kashmir, Pakistan	Residential and Agricultural	1.54	0.07	0.10	Ali *et al*. 2018
Chakwal, Pakistan	Industrial and residential	10.38	46.37	28.86	Ali *et al*. 2019
Along River Chenab, Nullah Aik and Nullah Palkhu, Pakistan	Agricultural and Rural	103	8.83	0.44	Mahmood *et al*. 2014
Punjab Province, Pakistan	Industrial, Agricultural and Urban	40	7.8	-	Syed *et al*. 2013
India	Urban, suburban and rural	4	2.2	5.8	Chakraborty *et al*. 2015
Huangpi, China	Agricultural	1.63	2.52	-	Gereslassie *et al*, 2019
Korea	Agricultural	1.07	0.08	15.38	Yun *et al*. 2022
Dalaki, Iran	Agricultural	0.728	0.301	-	Kafaei *et al* 2020
Daye lake, China	Urban	2.09	2.26	0.17	Bhutto *et al* 2021

Furthermore, atmospheric depositions also contribute to HCH levels in soils as warmer temperature promote evaporation of OCPs (Jaruga *et al*. 2020). The ratios of β-HCH/ΣHCHs above 0.5 (mean: 0.54) in most sampling sites demonstrated that β-HCH was the dominant HCH isomer and have originated from historical deposition (Jaruga *et al*. 2020; Amir *et al*. 2018; Ali *et al*. 2019). Additionally, the ratio of β-HCH/(α-HCH + β-HCH) ratio was evaluated to consider the impact of α-HCHs accumulation due to atmospheric transport. The ratio value falling between 0 to 0.1 represent an α -HCH pollution possibly due to atmospheric deposition. However, in this study this ratio ranged from 0.52 to 0.56 (mean: 0.54), indicating limited influence of long range atmospheric transport in high mean levels of α-HCH in the soil. Hence, the HCHs in the soil is attributed to the recent influx of technical HCHs with the least possible impact of long range atmospheric deposition (Ali *et al*. 2019).

Endosulfan: The technical mixture of endosulfan contain 70 % α-endosulfan (Half life 27.5 days) and 30 % β-endosulfan (Halflife 157 days) (Baqar *et al*., 2018b; Ali *et al*. 2019). In present study compositional percentage of β-endosulfan (5%) was greater than α-endosulfan (4%). According to research reports the dominance of β-endosulfan is attributed to its stable chemical structure, low vapor pressure and low solubility (Nyihirani *et al*. 2019; Syed *et al*. 2011). The ratio of α-endosulfan/β-endosulfan ratio is used to assess the history of application of technical mixture (Figure 2). The ratio value greater than 2.33 indicates the recent input and vice versa. In present study, α-endosulfan/β-endosulfan proportions ranged from 0.55 to 0.97 (mean: 0.76), signifying historic input in the study area. This finding is in line with the reports of Ali *et al*. 2019; Gong *et al*., 2020; Syed *et al*. 2011.

Spatial Distribution of OCPs in Soil: It is well documented fact that occurrence of OCPs has anthropogenic origin therefore fate and distribution is affected by regional emission sources, degradation and deposition of contaminants (Taufeeq *et al*., 2021). Soil deposition of the OCPs is regulated by physicochemical characteristics of the soil and pollutant, in addition spatial and temporal variation in source contribution (Nyihirani *et al*. 2022). Patterns of spatial distribution of ∑OCPs in soil along agricultural fields of Nullah Aik and Palkhu is shown in Figure 3. Findings of the results indicated the highest pollution load downstream of both Nullahs with highest levels at site 11 along Nullah Palkhu near Wazirabad city. Other sites also exhibited considerable contamination levels at downstream of Nullah Aik (S4, S5) and Palkhu (S10). At midstream zone, the highest contamination load was observed at S9 near Bhopalwala. Other sampling sites including S2, S3 along Nullah Aik, S7, S8 along Nullah Palkhu also showed significant contamination load (Figure 4). This finding is in accordance with reports of previous studies (Mahmood *et al* .2014; Gong *et al* 2020).

Mid-stream zone constitutes urban area, also include chemical, paint and pigment industries. Additionally abandoned pesticides dumping stores are present near Simbrial and Wazirabad city. This finding has been associated with high contamination load in the mid and downstream zones (Mahmood *et al*. 2014). Among three sampling zones lowest contamination was observed at upstream zone along both streams. The upstream zone is agricultural and rural area. Irrigation from wastewater of streams was observed as primary method in the agricultural fields of studied zones. Wastewater irrigation and ongoing usage as indicated by source fingerprinting of banned pesticides may be attributed to occurrence of contamination in the said zone of study area (Bhutto *et al*. 2021).

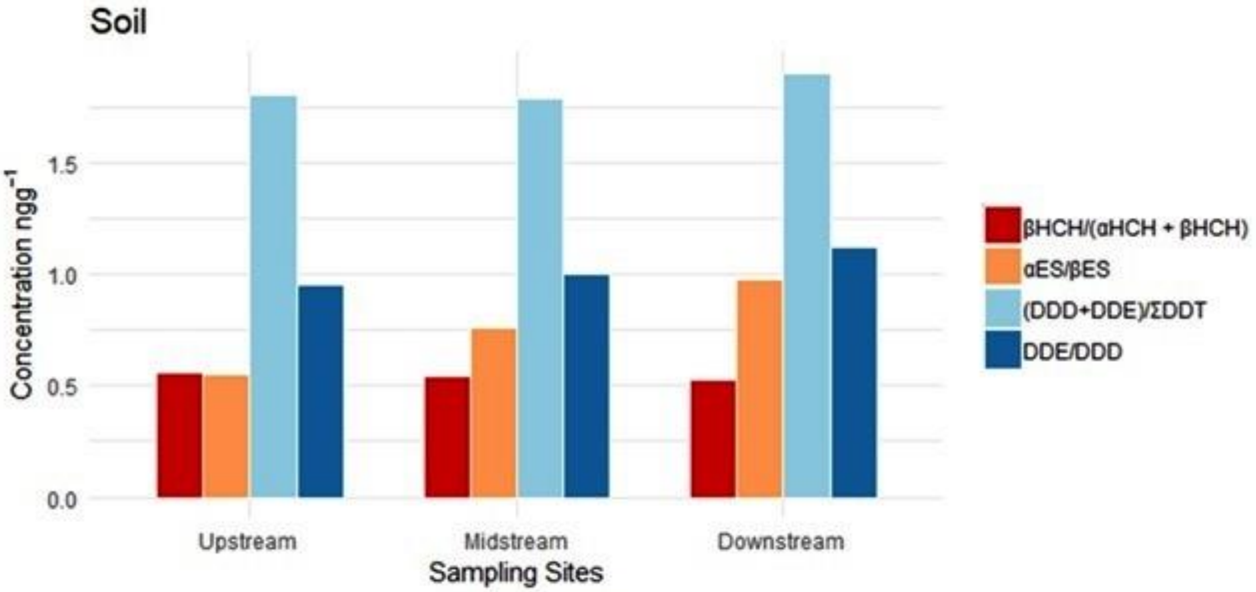

Figure 2: Isomeric ratios for source apportionment of OCPs in agricultural soil along Nullah Aik and Nullah Palkhu.

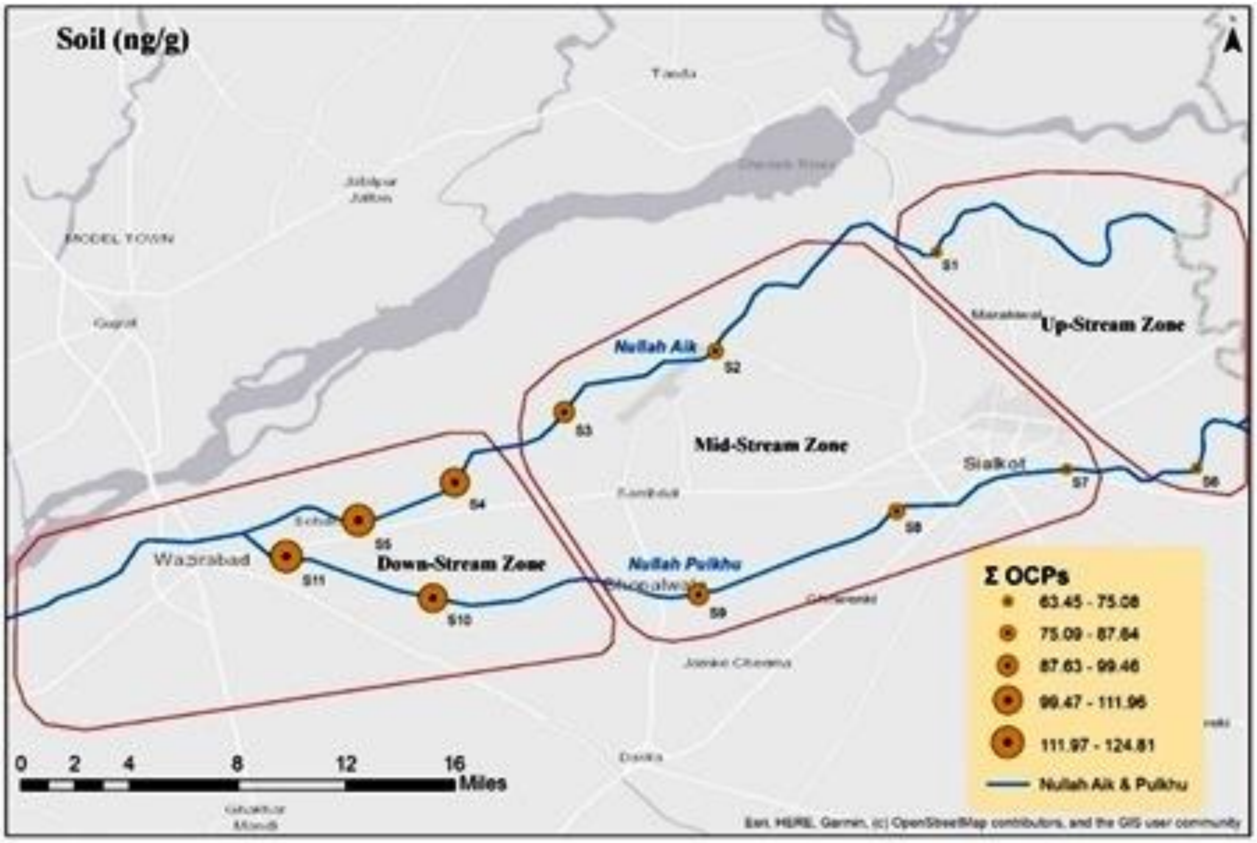

Figure: 3 Spatial distribution of Sum OCPs in Soil along agricultural fields of Nullah Aik and Nullah Palkhu

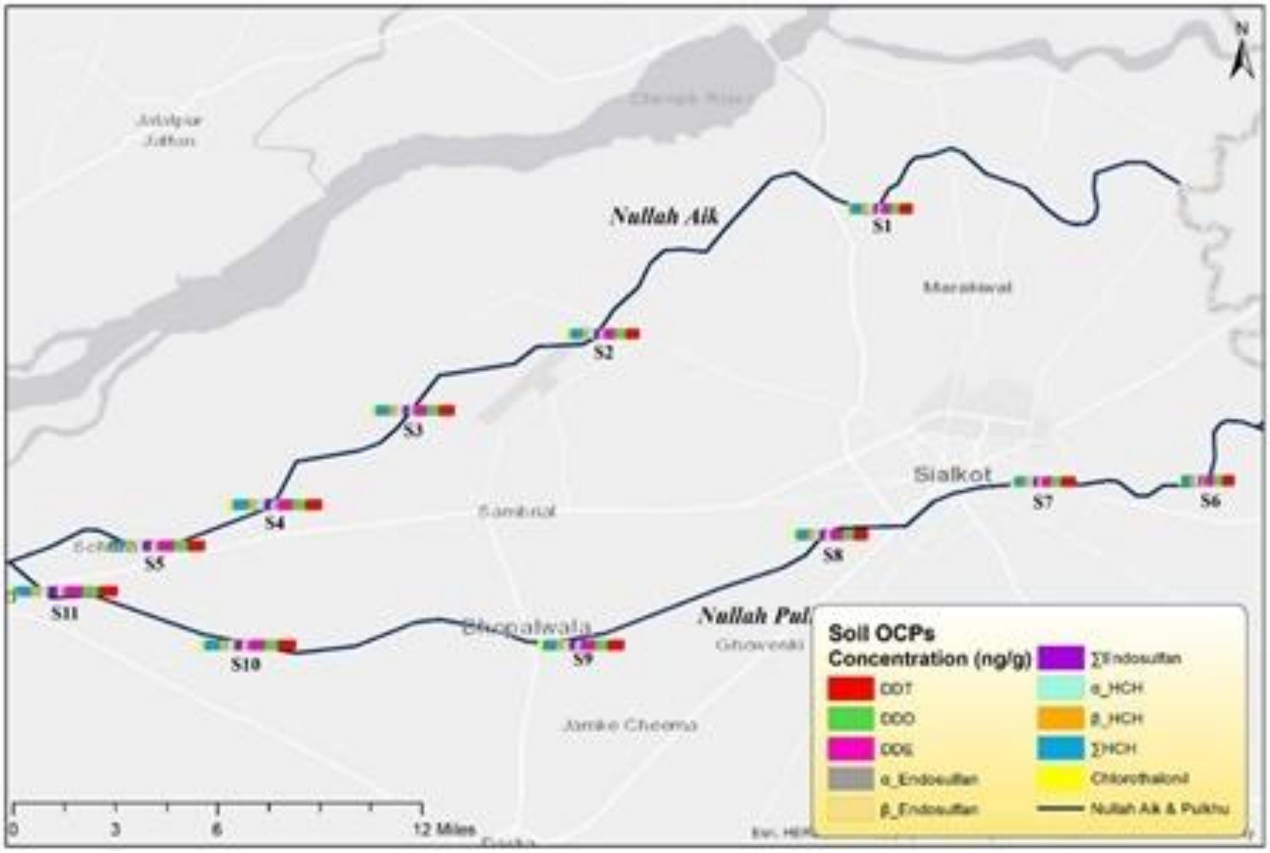

Figure 4: Spatial distribution of detected isomers in soil of agricultural fields along Nullah Aik and Nullah Palkhu

Risk Evaluation

Assessment of risk to ecological integrities: Ecological risk to OCPs in soil was evaluated by comparing concentrations of investigated OCPs with sediment quality guidelines (Emoyan *et al*., 2022). Assessment of the results indicated that mean residual concentrations at all sampling sites for DDT, DDE, DDD and ∑DDTS were exceeding ERL, ERM, TEL and PEL values posing adverse effects to biota of soil along agricultural fields of Nullah Aik and Palkhu (Figure 5). As, yet no standards have been developed in Pakistan, therefore, mean levels of selected OCPs were also compared with Canadian soil Quality guidelines available for agricultural soils. It was shown that average residual levels for ∑DDTS were below the permissible limits (700ng/g) (CCME 1999; Ali *et al*., 2020).

Furthermore, Sediment Quality Guideline Quotient was calculated to assess the risk of investigated OCPs to ecological integrities (Baqar *et al*. 2018; Bai *et al*., 2018;.Wang *et al*., 2017; Gong *et al*., 2020). According to previous reports from national and international studies SQGQ less than 0.1 indicates no effects; biological effects are moderate if SQGQ is less than 1.0 and values above 1.0 indicate severe biological effects (Wang *et al*. 2017). PELQi and SQGQ for DDT, DDD, DDE and ∑DDTs are presented in table 3. Assessment of the findings revealed that SQGQ for all sampling sites were greater than 1 with highest SQGQ at site 11 suggesting high risk to ecological integrities to DDTs in Soil.

Assessment of risk to human health: The Carcinogenic risk to human health to DDT, DDD, DDE, α-HCH and β-HCH through non dietary exposure pathways including dermal, ingestion and inhalation was evaluated for adults (Table 4). Total Carcinogenic Risk (TCR) was ranging from 6.75E-09 - 1.57E-07 with risk order of dermal > ingestion > inhalation. This finding was in line with the results of Ali *et al*. 2019; Yao *et al*. 2022; reporting the dermal route as most contributory factor to carcinogenic risk. The assessment of the results revealed that carcinogenic risk is within the acceptable limit (10^{-6}) suggesting no potential carcinogenic risk to Human health to selected OCPs through contaminated soils in the study area (Jorfi *et al*., 2019; Nigatu & Hussen, 2022; Mungai *et al*. 2019). While results of non carcinogenic risk calculated for DDT, DDE and ∑endosulfan are presented in table 5.4. The findings revealed that ∑HQ was ranging from 1.70E-06 - 5.94E-04. The noncarcinogenic health risks were less than1, lower than the permissible risk level (HQ < 1), inferring the obtained levels of OCPs in soils of study area are not supposed to cause adverse health impacts (Gereslassie *et al*. 2019).

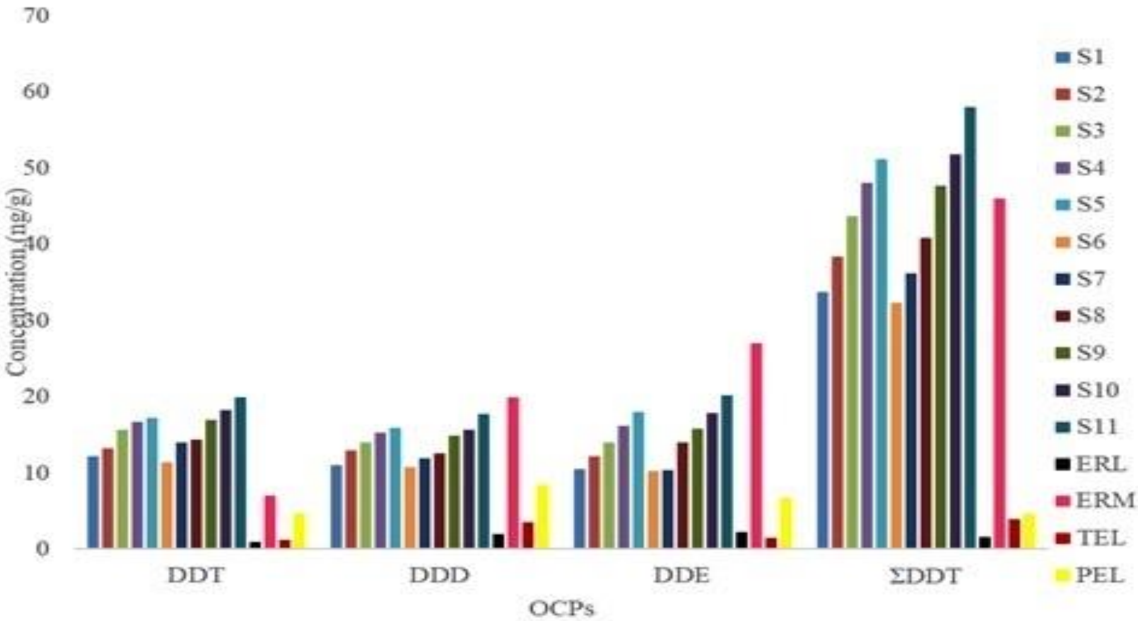

Figure 5: Comparison of levels investigated with sediment quality guidelines to assess ecological risk

Table 3: The PEL quotients (PELQs) and sediment quality guideline quotients (SQGQs) of OCPs in soil.

	PELQ$_i$				
Sampling sites	DDT	DDD	DDE	∑DDTs	**SQGQs**
S1	2.56	1.30	1.56	0.65	1.52
S2	2.78	1.52	1.81	0.74	1.71
S3	3.29	1.64	2.08	0.84	1.96
S4	3.49	1.79	2.40	0.93	2.15
S5	3.61	1.88	2.66	0.99	2.28
S6	2.38	1.27	1.51	0.63	1.45
S7	2.92	1.41	1.53	0.70	1.64
S8	3.01	1.47	2.07	0.79	1.83
S9	3.56	1.76	2.34	0.92	2.14
S10	3.83	1.84	2.65	1.00	2.33
S11	4.18	2.09	3.00	1.12	2.60

Table 4: Mean Values obtained from Total Carcinogenic and non carcinogenic risk assessment of OCPs in Soil along agricultural fields of Nullah Aik and Nullah Palkhu

	Cancer risk				**HI=Sum HQ**	
	OSF	**Rf**	**Mean**	**Range**	**Mean**	**Range**
DDT	0.34	0.0005	1.37E-08	1.01E-08 - 1.77E-08	8.05E-05	5.93E-05 - 1.04E-04
DDD	0.24		8.70E-09	6.75E-09 - 1.11E-08		
DDE	0.34	0.0007	1.28E-08	9.05E-09 - 1.79E-08	3.03E-04	3.80E-05 - 5.94E -04
a-endosulfan	0.34					
b-endosulfan						
∑endosulfan		0.005			3.7E-06	1.70E-06 - 5.49E- 06
a-hch			1.20E-07	7.33E-08 - 1.57E-07		
b-hch	6.3		3.94E-08	4.87E-08 - 5.11E-08		
∑ hch	1.8					
Chlorothalonil	0.02	0.02	2.42E-05	1.79E-10 - 1.34E-04	7.22E-07	4.47E-07 - 8.99E-07

Conclusion: In present research work occurrence, distribution, source fingerprinting along with ecological and human health risks were studied. All studied isomers were detected in soil samples collected from agricultural land along tributaries of River Chenab. The mean detected levels of OCPs were in the following order: DDT> DDE > DDD > β-HCH > α-HCH > Chlorothalonil > β-endosulfan > α- endosulfan. From assessment of results of isomeric ration, it was found that the average value of (DDE+DDD)/DDT in agricultural soil along Nullah Aik and Nullah Palkhu was 1.83, revealing that the DDTs were mainly from historical use of technical DDT. The detection of OCPs may be associated with irrigation of fields from wastewater of tributaries and as well as direct application for pest control. Findings suggested the high risk to ecological integrities. The total carcinogenic risk was within the acceptable limit (10^{-6}) however the contamination of soils with investigated OCP congeners acquires the regular monitoring and elimination of sources of banned toxins to prevent the irreversible damages to ecosystem and human health.

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