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Monitoring of level of mean concentration and toxicity equivalence (TEQ) of polychlorinated biphenyls (PCBs) in selected vegetables, beans and grains in khanewal and multan, Pakistan

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ABSTRACT

Contamination of food chain by Polychlorinated biphenyls through use of pesticides, electric and industrial waste poses human health risk. In previous studies, PCB species were stated as endocrine disrupting pollutants and showed toxic health effects like cancerous and noncancerous in animals. The aim of this study was to investigate the levels of PCBs and its toxicity equivalence in food item from plant source to evaluate the health risk in Khanewal and Multan, Pakistan. Samples were collected and processed for further analysis of PCB species through GC/MS after extraction and clean up. The mean concentrations of PCBs ranged as 2.71–151.67 ng/g in beans and grains and 2.30–97.00 ng/g dry weight in vegetables and were lower than 200–3000 ng/g PCBs recommended by FDA tolerance level for all foods. The mean concentrations of two NDL-PCB species detected in all vegetables, beans and grains except *S.indicum and T.aestivum* were lower than maximum allowable concentration of non-dioxin like PCBs i.e. 40ngg^{-1} reported by European Commission. Mean TEQ of sum of 14 PCB species ranged as 1.52–5.91 ng-WHO-TEQg^{-1} in vegetables and 1.46–10.04 ng-WHO-TEQg^{-1} in beans and grains. The present study concluded that the mean concentrations and mean TEQs of PCB species in most of the vegetables, beans and grains were found safe but due to higher consumption rate of some vegetables and grains, posed the moderate level of risk for human health. This study emphasizes on an implement of the strict rules regarding the use of restricted chemicals to diminish the effluence in food chains. Current research will be useful in up gradation of effective measures to reduce the poisonous contribution of PCB sources and the sustainability of terrestrial ecosystem in the country.

1. Introduction

Contamination of food chain by Polychlorinated biphenyls (PCBs) through pesticides, electric and industrial waste poses human health risk through oral exposure worldwide. They undergo bioaccumulation in human and animal adipose tissues (Ulutaş et al., 2015) and reach into the human body through food from plant and animal sources. (Ohlhoff et al., 2021 & Weber et al., 2018)

PCB species are released into the environment by disposal of PCB-containing products in municipal landfills, improper and illegal dumping of waste that contained PCBs, such as transformer fluids, Leaks from electrical transformers and capacitors containing PCBs and poorly maintained toxic waste sites. Once contaminants are released into the environment, they become bio-accumulated and bio-magnified on transformation from lower to higher trophic level in food chains, degrade relatively slowly and persist within the ecosystem (Safe, 2007).

PCBs entered in a larger amount into water of river Chanab and Ravi in Pakistan when they were used to control pests, termites and insects during last fifty years (Eqani et al., 2011). Polychlori-

Abbreviations: PCB, Polychlorinated Biphenyles; TEQ, Toxicity equivalence Quotients (TEQ).

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nated Biphenyls species have been recorded in several environmental matrices although there is no clear proof of its natural occurrence based on ecosystems (Bordajandi et al., 2008).

PCB congeners have lower water solubility as compare to PCBs with lesser number of chlorine atoms. They show greater power of bioaccumulation and bio-magnification through food web (Vafeiadi et al., 2014; Ghaeni et al., 2015).

. Bioaccumulation of PCBs depends upon body mass index age, weight, sex, food intake and exposure. TEQ values of PCBs gives health risk assessment in animals as well as human beings. (Van den Berg et al., 2006).

ATSDR (2000) determined the toxicity of the contaminants based on the chlorination pattern of Polychlorinated biphenyls. A number of PCB species show dioxin-like toxicity those have no more than one chlorine atom at the *ortho*-position (polychlorinated non-ortho and mono-ortho biphenyls), and adopt a coplanar structure. In non-dioxin-like toxicity, PCB congeners have two or more of the *ortho*-positions for chlorine atoms in the biphenyl molecules and the both phenyl rings are not in the same plane.

The toxicity of PCB species shows variations considerably among congeners. The coplanar PCBs, known as non-ortho PCBs because they are not substituted at the ring positions ortho to (next to) the other ring, e.g., PCBs 77, 126 and 169 have tendency to have dioxin-like properties, and generally are among the most toxic congeners (Brown et al, 2006).

Pesticides like chlorpyrifos, cypermethrin and imidacloprid were identified in the 65–70% of the okra, cucumber, eggplant, Pumpkin, spinach and cabbage vegetables picked from Lahore city (Munawar & Hameed, 2013). 91% vegetables comprises of pesticide residues or their metabolites beyond the maximum permissible limit in Africa (Mutengwe et al., 2016). Park (2018) found 70% of usually grown vegetables contaminated with pesticides. Fatunsin et al., (2020) detected organophosphate and carbamate pesticides in food from plant source grown in Nigeria were below the permissible limit.

Esposito et al., (2017) determined the level of concentration of polychlorinated biphenyl species ranged from 0.011 to 2.26 ng per gram for the six examined non dioxin like PCB species and 0.0009 to 0.096 pg per gram of WHO toxic equivalent (TEQ) for sum of dioxin-like PCB species in food samples of selected vegetables and fruit from agricultural farmhouses sited in the south of Italy.

PCBs have a variety of bad health issues with human beings like cancerous and noncancerous i.e., neurological, reproductive and immunological disorders in living things including human beings (Sharma et al., 2009). Persistent organic pollutants especially PCBs had been reported as endocrine disrupting chemicals due to hormonal disruption of thyroid and sex glands in humans (Green et al, 2021) fish and other animals (Zoeller et al., 2021) and associated with disorders of breast cancer and structures of reproductive organs in women (Tanabe et al., 2002).

Acetylcholinesterase inhibition, oxidative stress and other hazardous concerns on different ecological components including human, directly via bioaccumulation or indirectly through the food chain were reported as a toxicological influence of highly hazardous pesticides especially organochloine pesticides, organophosphorus pesticides, carbamates and triazine pesticides. (Parra-Arroyo, et al, 2021).

The higher level of PCBs in human beings through dietary exposure of vegetables causes non-cancerous effects those may be respiratory and gastrointestinal problems, acute effects on the liver, kidney and brain, decreased conception, prolonged menstruation, reduced birth weight and shortened gestational age of their babies in women, low sperm counts and decreased sperm motility in men (ATSDR, 2014).

Impacts of pesticides on human headaches, asthma, nausea, eye irritation, skin irritation, sore throat, diarrhea, sinusitis, pharyngitis, contact dermatitis, nasal irritation, inflammation and endocrine disruption are short term effects on human (Bourguet & Guillemaud, 2017) whereas infertility, endocrine disruption, depression, birth defects, neurological deficits, diabetes and cancer are caused due to exposure of pesticides for a long period (Mostafalou & Abdollahi, 2013).

In vivo and *in vitro* studies indicated the endocrine-disrupting effects of PCB species those interfere thyroid and reproductive functions in human and other animals (Djordjevic et al., 2020).

Unavoidable practice of pesticides to raise the yield of crops and waste of industry in modern era has called the special responsiveness of the researchers to eliminate the contaminants especially pesticides. The enzymes-mediated bioremediation is a fascinating and significant approach for biodegradation of pesticides into harmless chemical substances. Oxidoreductases hydrolases and transferases and ligninolytic enzymes, particularly laccases, are of special interest of researchers in finding and developing of suitable enzymes-mediated bioremediation (Bilal et al., 2019).

Exceedingly risky pesticides resulted in enzymatic inhibition and the induction of oxidative stress. An intensive care of contaminants especially pesticides and implementation of regulations in developing countries are required by a number of analytical recognition, regulatory, and moderation attentions for competently eliminating hazardous pesticides. (Parra-Arroyo et al, 2021).

MXenes-based materials have been developed as an environmental sensing and remediation applications due to its exceptional features. This tool is important to detect pesticide pollutants from ecosystems (Rizwan et al., 2021). Present study also attracts the attention of the authorities and researchers to develop control measures and remedies against contaminants especially pesticides having dioxins and dioxin like PCBs.

Pakistan being a member of Stockholm convention (2001) follows its recommendations to control POPs across the country. A few studies have been reported on the level of PCBs in food from Pakistan. This study is an important instrument to measure the contribution of Pakistan towards "Global POPs Emissions". It will be important tool to determine the level of toxicity and evaluate the effectiveness of control measures taken by Pakistan. This study will also be helpful to follow the recommendations of Stockholm convention 2001. Therefore, to investigate the levels of PCBs and its toxicity equivalence (TEQ) in vegetables, beans and grains to evaluate the potential human health risks due to PCB species in district Khanewal and Multan, Pakistan.

2. Material and methods

2.1. Sampling area and irrigation system

Multan and Khanewal are two major agricultural districts of in south of Punjab province, Pakistan. The River Ravi and Chenab, and their distributary canals are important to irrigate the area of both districts. Lower Bari doab, Sidhnai and Mailsi link sidhnai are the major distributary canals in both districts. Unchecked use of pesticides, disposal of industrial and municipal waste with electric fluids is main source of contamination in study area.

Akhter and Amjad (2020) described that Sidhnai Canal is an irrigation canal originating from river Ravi at Sidhnai head work Abdul hakim, District Khanewal of province Punjab, Pakistan. Thirteen distributaries originating from the Sidhnai canal irrigate 114,132 acres, the greater portion of Multan and Khanewal.

Each district was considered a main location which was divided into three replications at 5Km radius of distributary channels and triplicated samples were collected from each district. The cash crops i.e. grain crops and vegetables are cultivated and hence con-

sidered main source of income for people there. The selection of sampling sites was based upon anthropogenic activities in study area.

2.2. Sample preparation and analysis

Eighty four samples of some selected vegetables i.e. *Praecitrullus fistulosus , Lagenaria siceraria, Momordica charantia, Luffa acutangula, Solanum melongena, Daucus carota sativus* and *Abelmoschus esculentus* and some selected beans and grains i.e. *Vigna radiate, Cyamopsis tetragonoloba, Vigna unguiculata, Sesamum indicum, Brassica campestri Triticum aestivum, Oryza sativa* weighing of 500 g/sample from each replication freshly grown from agricultural fields of both districts, Khanewal and Multan were picked. The samples were placed in polythene zipped bags and transferred to lab where they were prepared for further process.

For analysis purpose, Sample of all selected food items from plant source were collected, removed undesired parts, washed in distilled deionized water, dried in day light, ground and kept in polythene zipped bags for pretreatment and stored in a refrigerator at 5 °C for extraction and further analysis. Anhydrous sodium sulfate was added to digest the tissues. Extraction of 10 g of each dried sample was done in n-hexane by using Soxhlet apparatus at 70 °C and extracts were placed in eppendorf tubes at 4 °C at lab. Rotary evaporator was used to recover n-hexane at 70 °C. (USEPA, 1996).

Rotatory Vacuum evaporator was used to concentrate the extracts up to 2 mL. By performing the multilayered glass column chromatography with modified silica, the extracts were clean up. Multilayered silica column (300 × 30 mm) was packed from bottom to up with 2.5 g silica gel, 5.0 g anhydrous sodium sulfate, 4.0 g silver nitrate silica gel, 4.0 g basic silica gel and 12.0 g acid silica. 100 mL n-hexane was used for pre-rinsing of column before loading of samples.

The elution of PCBs was subsequently carried out using 170 mL n-hexane and concentrated to 1.5 mL. The eluted extracts were concentrated under gentle stream of pure nitrogen using Rotatory Vacuum evaporator to 1.0 mL and transferred to auto sampler vial for fourteen PCBs analysis by gas chromatograph/mass spectrometer. Known quantity of internal standard solution was also prepared and added prior to chromatographic analysis. PCB-77, PCB-81,PCB-105,PCB-114,PCB-118,PCB-123,PCB-126,PCB-156,PCB-157, PCB-167,PCB-169,PCB-170,PCB-180 and PCB-189 were the congeners analyzed. Twelve congeners, DL-PCBs and two NDL- PCBs were separated and quantified to study health risk.

2.3. Quality control measurements

Blank samples were prepared in the same manner as vegetable samples procedure. Spiking approach was applied to test the accuracy, in term of recovery, of analytical results. Known volumes of standard solutions were added to samples of selected vegetables, which were treated as vegetable samples.

2.4. Toxicity equivalence factors and toxicity equivalence quotient

TEQ values are the sum of values those were calculated by multiplying concentration of examined individual PCB congeners with TEF values given by WHO (2003). TEQ values were calculated for different food samples from plant source. TEQ values gave risk characterization and its management (Van den Berg et al., 2006). The TEF is the ratio of the toxicity of one of the compounds in this category to the toxicity of the two most toxic compounds in the category, which are each assigned a TEF of 2,3,7,8-tetrachlorodi benzo-p-dioxin and 1,2,3,7,8-pentachlorodibenzo-p-dioxin. (USEPA, 2010).

2.5. Results

The mean concentration of PCB-189 among all other PCB species was found the lowest i.e. 1.63 ± 0.60 ng/g in *P. fistulosus* in Khanewal

Table 1
Mean Concentrations (ngg^{-1}) ± S.D of examined PCB species in selected vegetables in Khanewal and Multan.

		Vegetables						
PCB species	**District**	***P. fistulosus***	***L. siceraria***	***M. charantia***	***L. acutangula***	***A. esculentus***	***D.carota sativus***	***S. melongena***
PCB-77	Khanewal	10.92 ± 1.26	14.84 ± 1.77	13.43 ± 2.03	7.90 ± 0.85	4.66 ± 0.98	4.47 ± 1.14	5.40 ± 2.59
	Multan	18.83 ± 5.20	14.50 ± 1.00	14.18 ± 0.75	19.00 ± 6.08	6.27 ± 1.66	6.87 ± 0.81	22.67 ± 9.02
PCB-81	Khanewal	11.93 ± 1.40	14.63 ± 2.03	25.85 ± 0.27	9.04 ± 1.03	10.09 ± 2.32	7.25 ± 1.22	15.65 ± 11.58
	Multan	15.47 ± 1.29	16.43 ± 0.74	28.00 ± 1.00	22.33 ± 7.65	11.80 ± 1.31	13.37 ± 2.54	28.00 ± 6.08
PCB-105	Khanewal	33.57 ± 1.20	34.71 ± 3.69	29.85 ± 6.06	32.87 ± 1.86	12.55 ± 2.03	11.19 ± 1.73	15.44 ± 6.56
	Multan	35.10 ± 0.85	36.53 ± 1.29	35.00 ± 1.00	35.83 ± 1.26	14.81 ± 1.56	20.70 ± 5.37	34.00 ± 10.00
PCB-114	Khanewal	22.23 ± 0.84	14.13 ± 1.54	41.52 ± 3.92	24.65 ± 1.25	31.11 ± 3.01	13.59 ± 1.10	17.21 ± 6.56
	Multan	24.00 ± 1.00	19.00 ± 3.61	47.67 ± 3.06	28.00 ± 1.00	33.65 ± 1.07	29.00 ± 11.36	32.00 ± 4.36
PCB-118	Khanewal	54.40 ± 4.03	39.85 ± 4.17	76.70 ± 17.93	97.00 ± 1.18	28.47 ± 4.08	22.00 ± 3.94	20.67 ± 7.77
	Multan	57.28 ± 1.15	43.50 ± 0.87	91.57 ± 5.73	96.37 ± 0.71	31.50 ± 2.29	31.93 ± 6.02	29.67 ± 4.54
PCB-123	Khanewal	23.11 ± 1.02	20.54 ± 3.25	62.30 ± 6.80	43.13 ± 0.81	25.26 ± 0.86	21.58 ± 8.37	32.00 ± 10.58
	Multan	24.17 ± 0.76	26.53 ± 1.29	70.00 ± 5.22	43.83 ± 0.76	30.45 ± 3.15	28.23 ± 4.02	36.05 ± 0.82
PCB-126	Khanewal	21.62 ± 1.20	22.98 ± 2.85	26.60 ± 2.25	36.17 ± 5.20	13.83 ± 1.61	11.28 ± 2.75	24.13 ± 2.73
	Multan	25.67 ± 1.60	26.83 ± 0.76	27.65 ± 4.30	47.67 ± 3.79	19.67 ± 3.51	14.50 ± 2.50	28.00 ± 1.00
PCB-156	Khanewal	12.51 ± 1.41	19.63 ± 4.35	14.80 ± 1.59	28.03 ± 1.34	25.37 ± 3.48	20.96 ± 1.83	16.53 ± 4.80
	Multan	16.67 ± 1.53	25.33 ± 1.53	17.67 ± 0.58	33.00 ± 1.00	26.87 ± 1.21	19.11 ± 2.84	35.40 ± 15.47
PCB-157	Khanewal	11.08 ± 1.01	12.76 ± 3.75	16.37 ± 2.49	16.37 ± 1.70	16.03 ± 3.51	13.30 ± 2.78	12.85 ± 3.01
	Multan	17.63 ± 1.00	16.82 ± 2.06	19.85 ± 2.83	18.22 ± 0.70	25.67 ± 2.52	20.88 ± 4.56	32.00 ± 13.11
PCB-167	Khanewal	11.93 ± 1.42	14.09 ± 3.31	23.33 ± 2.08	24.67 ± 1.53	16.91 ± 1.01	11.59 ± 2.45	17.20 ± 7.27
	Multan	16.07 ± 1.37	17.33 ± 0.76	26.85 ± 0.79	27.92 ± 0.88	22.51 ± 3.13	16.64 ± 4.21	37.11 ± 7.90
PCB-169	Khanewal	11.44 ± 2.14	13.82 ± 1.54	35.33 ± 2.47	34.10 ± 2.01	16.20 ± 1.59	12.62 ± 1.80	21.78 ± 8.93
	Multan	13.80 ± 0.35	15.13 ± 1.03	43.33 ± 2.52	37.50 ± 0.50	18.20 ± 1.06	23.13 ± 6.22	24.00 ± 7.21
PCB-170	Khanewal	11.66 ± 1.19	13.38 ± 2.31	33.50 ± 2.18	32.82 ± 2.03	20.74 ± 2.05	21.58 ± 1.67	19.80 ± 6.49
	Multan	14.17 ± 0.76	17.03 ± 1.34	37.50 ± 3.04	39.33 ± 4.73	25.83 ± 1.89	21.12 ± 2.52	27.00 ± 1.00
PCB-180	Khanewal	14.08 ± 2.00	19.41 ± 4.07	22.80 ± 1.59	23.33 ± 1.53	19.22 ± 4.30	16.67 ± 0.29	18.75 ± 3.81
	Multan	17.33 ± 1.53	24.17 ± 1.26	24.45 ± 0.51	27.13 ± 0.75	27.00 ± 1.00	15.67 ± 2.08	22.58 ± 3.36
PCB-189	Khanewal	1.63 ± 0.60	6.49 ± 7.00	8.61 ± 2.87	3.35 ± 0.74	2.30 ± 0.27	5.61 ± 3.33	10.33 ± 11.85
	Multan	4.70 ± 0.82	13.35 ± 1.02	11.35 ± 0.77	9.08 ± 3.02	8.95 ± 3.94	9.85 ± 1.88	14.06 ± 1.87

Data or means of triplicates, ±S.D represent the standard deviation.

and that of PCB-118 was found the highest i.e. 97.00 ± 1.18 ng/g in *L. acutangula* in Multan. Different examined PCBs were found in the range of 1.63–57.28 ng/g, 6.49–43.50 ng/g, 91.57–8.61 ng/g, 3.35–97.00 ng/g, 2.30–33.65 ng/g, 4.47–31.93 ng/g and 5.40–37.11 ng/g in *P. fistulosus, L. siceraria, M. charantia, L. acutangula, A. esculentus*, *D. carota sativus* and *A. esculentus* respectively. *L. acutangula* among all other selected vegetables contributed the highest level of PCBs.

Minimum-maximum of the mean concentrations of individual PCB species were found as PCB-77 (4.47–14.84 ng/g), PCB-81 (7.25–25.85 ng/g), PCB-105 (11.19–34.71 ng/g), PCB-114 (13.59–41.52 ng/g), PCB-118 (20.67–97.00 ng/g), PCB-123 (20.54–62.30 ng/g), PCB-126 (11.28–36.17 ng/g), PCB-156 (12.51–28.03 ng/g), PCB-157 (11.08–16.37 ng/g), PCB-167 (11.59–24.67 ng/g), PCB-169 (11.44–35.33 ng/g), PCB-170 (11.66–33.50 ng/g), PCB-180 (14.08–23.33 ng/g) and PCB-189 (1.63–10.33 ng/g) in vegetables in Khanewal. The mean concentration (ng/g) of PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-170, PCB-180 and PCB-189 were found with minimum–maximum as 6.27–22.67, 11.80–28.00, 14.81–36.53, 19.00–47, 29.67–96.37, 24.17–70.00, 14.50–47.67, 16.67–35.40, 16.82–32.00, 16.07–37.11, 13.80–43.33, 14.17–39.33, 15.67–27.13 and 4.70–14.06 in selected vegetables in Multan respectively. District Multan showed higher toxicity level than district Khanewal due to difference of level of contamination and anthropogenic activities in study area in this research. The mean concentration of PCB species in current study was ranged from 2.30 ± 0.27 to 97.00 ± 1.18 ng/g dry weight in vegetables in both districts (Table 1).

Mean concentration (ng/g) of examined PCB species ranged from 9.82, 2.71, 3.28, 12.51, 7.37, 7.72 and 2.82 to 132.5, 36.85, 28.48, 79.6, 151.67, 78.88 and 39 in *V.radiata, C.tetragonoloba, V.unguiculata, S.indicum, B.campestris, T. aestivum* and *O. sativa* respectively. PCB-118 was found the highest i.e. 151.67 ± 3.21 ng/g in *B.campestris* in Multan and that of PCB-189 was found the lowest i.e. 2.71 ± 1.18 ng/g in *C.tetragonoloba* in Khanewal. In the current study, beans and grains showed higher toxicity in Multan as compare to Khanewal. The mean concentration of PCB species in current study was ranged from 2.71 ± 1.18 to 151.67 ± 3.21 ng/g dry weight in beans and grains in both districts (Table 2).

Mean TEQ value of all examined PCB species 1.52 ± 0.33 ng/g was found the lowest in *D. carota sativus* in Khanewal and 5.91 ± 0.37 ng/g was the highest in *L. acutangula* in Multan among all vegetables in both districts. Mean TEQ values of all examined PCB species were ranged from 1.52 ± 0.33 ng/g in *D. carota sativus to* 4.65 ± 0.58 ng/g in *L. acutangula* in Khanewal respectively. Mean TEQ values of all examined PCBs were ranged from 2.16 ± 0.11 ng/g in *D. carota sativus to* 5.91 ± 0.37 ng/g in *L. acutangula* in Multan respectively as shown in Fig. 1.

Mean TEQ value for ∑14PCBs ranged from 1.46 ± 0.17 ng/g to 9.77 ± 0.09 ng/g in *O.sativa* and *S.indicum* in Khanewal and Multan respectively. Mean TEQ values for ∑14PCBs were found as 2.99 ± 0.45, 3.32 ± 0.40, 1.60 ± 0.18, 8.20 ± 1.03, 8.70 ± 0.63, 3.44 ± 0.39 and 1.46 ± 0.17 in *V.radiata, C. tetragonoloba V.unguiculata, S.indicum, B.campestris, T. aestivum and O.sativa* in Khanewal respectively while Mean TEQ values for ∑14PCBs were found as 6.02 ± 1.79, 4.44 ± 0.32, 2.05 ± 0.16, 9.77 ± 0.09, 10.04 ± 0.10, 4.33 ± 0.30 and 2.01 ± 0.27 in *V.radiata, C. tetragonoloba V.unguiculata, S.indicum, B.campestris, T. aestivum and O.sativa* in Multan respectively as given in Fig. 2. Mean TEQ of sum of 14 PCB species ranged as 1.52 ± 0.33–5.91 ± 0.37ngg^{-1} in vegetables and 1.46 ± 0.17–10.04 ± 0.10ngg^{-1} in beans and grains as given in Fig. 1 and Fig. 2.

3. Discussion

In present study, the mean concentration (ng/g) of PCB- 189 was determined the lowest i.e. 1.63 ng/g in *P. fistulosus* in Khanewal and that of PCB-118 was determined the highest i.e.

Table 2
Mean Concentrations (ngg^{-1}) ± S.D of examined PCB species in selected beans and grains in Khanewal and Multan.

		Beans and Grains						
PCB Species	**District**	***V.radiata***	***C.tetragonoloba***	***V.unguiculata***	***S.indicum***	***B.campestris***	***T. aestivum***	***O. sativa***
PCB-77	Khanewal	36.81 ± 30.42	9.47 ± 5.28	4.97 ± 0.84	12.51 ± 10.51	8.17 ± 4.25	27.67 ± 11.85	10.31 ± 1.70
	Multan	68.00 ± 12.17	16.50 ± 3.46	10.12 ± 4.34	24.83 ± 1.76	13.50 ± 1.00	39.20 ± 5.89	13.13 ± 1.80
PCB-81	Khanewal	9.82 ± 2.56	6.89 ± 0.45	7.50 ± 0.87	25.47 ± 7.43	29.80 ± 12.32	23.33 ± 2.08	19.91 ± 2.98
	Multan	23.17 ± 16.31	31.27 ± 20.68	12.08 ± 1.89	28.33 ± 8.96	43.00 ± 1.00	28.67 ± 3.06	24.67 ± 1.53
PCB-105	Khanewal	11.73 ± 2.58	7.29 ± 5.78	12.48 ± 0.50	35.58 ± 5.15	42.67 ± 0.58	33.83 ± 1.61	2.82 ± 1.38
	Multan	20.67 ± 11.64	12.33 ± 0.58	12.96 ± 2.20	41.83 ± 0.29	35.20 ± 1.06	34.43 ± 1.20	39.00 ± 29.10
PCB-114	Khanewal	18.77 ± 5.69	11.67 ± 1.53	12.82 ± 1.57	60.80 ± 13.60	80.25 ± 5.72	55.13 ± 2.73	3.35 ± 1.10
	Multan	27.02 ± 6.52	14.63 ± 0.32	12.45 ± 0.51	54.80 ± 1.31	77.23 ± 0.68	57.17 ± 0.72	9.93 ± 5.16
PCB-118	Khanewal	132.50 ± 17.97	23.48 ± 2.01	23.87 ± 0.23	49.43 ± 16.03	140.00 ± 7.21	74.93 ± 3.41	15.22 ± 2.79
	Multan	125.09 ± 3.41	24.98 ± 1.36	28.48 ± 3.30	61.33 ± 2.89	151.67 ± 3.21	78.88 ± 1.84	16.57 ± 1.20
PCB-123	Khanewal	66.33 ± 18.50	30.43 ± 2.21	22.37 ± 3.17	76.69 ± 10.25	111.80 ± 12.70	73.91 ± 3.12	20.31 ± 4.09
	Multan	79.33 ± 16.26	34.83 ± 1.44	26.02 ± 1.33	65.70 ± 1.21	144.33 ± 11.06	77.50 ± 1.32	26.80 ± 6.29
PCB-126	Khanewal	22.33 ± 4.35	28.30 ± 3.39	12.67 ± 1.53	69.13 ± 13.99	75.20 ± 5.38	24.14 ± 3.43	10.89 ± 1.31
	Multan	48.17 ± 14.00	36.85 ± 1.23	15.88 ± 1.18	73.48 ± 0.89	86.67 ± 0.58	31.99 ± 2.81	15.83 ± 2.25
PCB-156	Khanewal	21.68 ± 3.19	21.15 ± 1.62	20.00 ± 2.65	54.93 ± 2.56	56.11 ± 1.02	12.60 ± 1.74	12.38 ± 0.54
	Multan	48.50 ± 17.02	26.05 ± 2.27	27.01 ± 2.19	57.00 ± 1.00	14.67 ± 3.06	16.98 ± 5.65	13.19 ± 1.29
PCB-157	Khanewal	22.33 ± 2.08	23.47 ± 0.50	15.09 ± 0.54	44.30 ± 27.16	25.47 ± 1.50	15.00 ± 1.32	12.67 ± 0.80
	Multan	28.73 ± 5.22	31.00 ± 3.00	17.93 ± 0.12	73.67 ± 1.53	27.23 ± 0.68	18.31 ± 1.00	14.50 ± 0.50
PCB-167	Khanewal	12.99 ± 0.58	11.63 ± 0.74	15.77 ± 3.28	39.08 ± 12.93	34.30 ± 1.75	25.87 ± 3.10	10.79 ± 0.55
	Multan	20.65 ± 5.29	14.08 ± 1.01	20.25 ± 2.39	46.87 ± 1.21	35.47 ± 1.50	30.67 ± 1.53	12.58 ± 0.52
PCB-169	Khanewal	24.70 ± 0.75	16.00 ± 2.00	11.00 ± 2.00	42.00 ± 12.17	38.33 ± 3.51	33.50 ± 1.80	11.92 ± 1.41
	Multan	39.10 ± 12.87	23.33 ± 4.51	14.95 ± 1.33	79.60 ± 1.51	44.67 ± 1.53	36.67 ± 0.58	13.82 ± 1.28
PCB-170	Khanewal	16.68 ± 2.89	15.34 ± 1.23	14.93 ± 1.36	42.17 ± 5.20	31.83 ± 7.97	36.70 ± 1.84	10.97 ± 1.00
	Multan	20.24 ± 0.42	17.40 ± 0.91	18.74 ± 0.98	57.53 ± 0.50	36.27 ± 1.42	42.11 ± 0.84	12.00 ± 1.00
PCB-180	Khanewal	18.00 ± 0.66	22.45 ± 2.66	14.39 ± 3.10	27.87 ± 4.50	25.87 ± 0.23	42.83 ± 1.61	12.55 ± 0.62
	Multan	16.69 ± 3.79	24.67 ± 1.15	14.56 ± 1.39	34.51 ± 3.12	23.13 ± 0.81	44.00 ± 1.00	10.93 ± 1.10
PCB-189	Khanewal	13.00 ± 4.58	2.71 ± 1.18	3.28 ± 1.04	13.50 ± 10.76	7.37 ± 4.05	7.72 ± 1.80	7.17 ± 1.27
	Multan	16.92 ± 2.56	6.29 ± 4.94	10.10 ± 1.69	19.00 ± 6.08	14.00 ± 2.00	11.65 ± 1.24	9.27 ± 2.05

Data or means of triplicates, ±S.D represent the standard deviation.

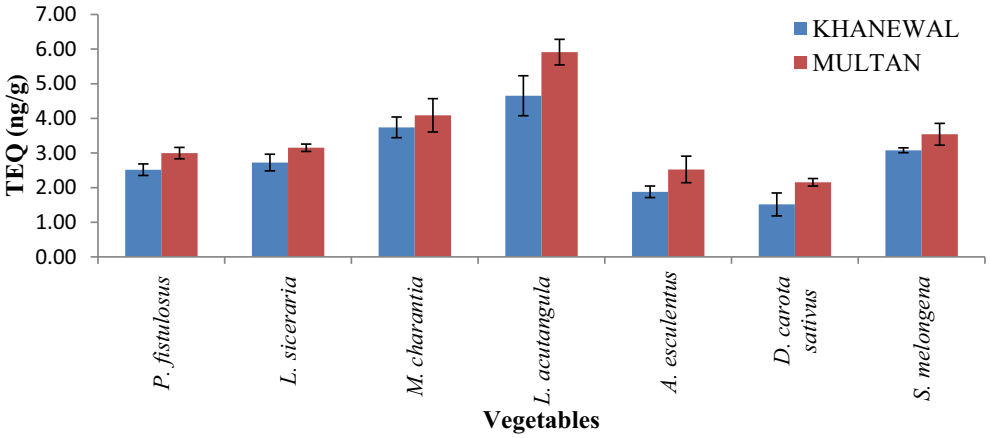

Fig. 1. Mean TEQ (ng/g) ± S.D values of all examined PCB species in different vegetables in study area.

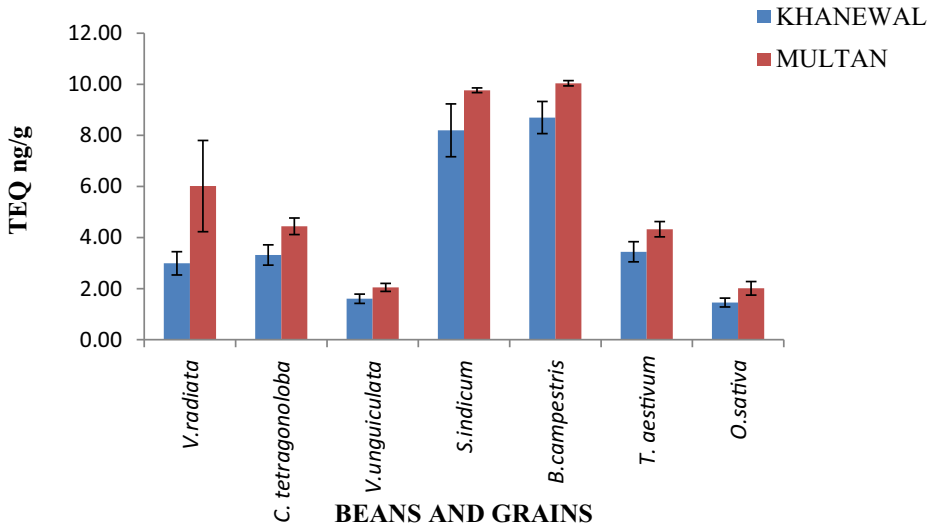

Fig. 2. Mean TEQ (ng/g) ± S.D of all examined PCB species in different beans and grains in study area.

97.00 ng/g in *L. acutangula* in Multan which is lower than that of Asiri et al. 2020 determined in KSA. He reported the mean levels of PCBs in all fruit and vegetable samples in the range of < LOD to 399 ng/g.

In current study, Mean concentration (ng/g) of PCB-180 ranged from 14.08 to 23.33 ng/g and 15.67–27.13 ng/g in vegetables in Khanewal and Multan respectively that was found higher to that of Asiri et al 2020 detected PCB-180 in apple, mint, lettuce and mulukhiyah with the levels (ng/g) of 0.004, 6.43, 9.27 and 7.13 respectively. In present study, the values of mean concentration in 82% vegetables, 79% beans and grains were found higher than those of Grassi et al 2010 determined in vegetables in the range 0.03339–10.130ngg^{-1} fresh weight (fw) for the sum of the 26 PCBs analyzed, while mean $TEQ_{-14PCBs}$ in vegetables, beans and grains was found than higher than 4.0x10^{-7}–1.398x10^{-3}ng toxic equivalent (TEQ) g^{-1} fw for PCBs determined in foodstuffs from plant source by Grassi et al 2010.

Esposito et al., (2017) determined the concentrations of polychlorinated biphenyls (PCBs) in fruit and vegetables ranged as 0.011–2.26ngg – 1 for the six "indicator" non-dioxin-like PCBs and 9.0x10^{-7}–9.6x10^{-5}ng toxic equivalent (TEQ) g – 1 for the sum of dioxin-like PCBs those were found lower than those observed in current study.

The highest mean concentration (ng/g dry weight.) of individual PCB species in current study was found 151.67 ng/g in beans and grains and 97.00 ng/g in vegetables are lower than that of FDA (1996c) recommended tolerances of 200–3000 ng/g PCBs for all foods. Shen et al., (2013) reported 1260ngg^{-1} for seven PCBs in seventeen varieties of vegetables was found much higher than those of current study. Toms et al., (2016) observed PCBs concentrations ranged up to 0.095 ng/g fresh weights in infant's food like fruit purees, meat and vegetables, dairy desserts, cereals and jelly foods and Zhang et al., (2008) determined concentrations of DL-PCBs as 0.00121 ng/g in vegetables those were lower than that of current study. In current study, Non dioxin like PCB-170 and PCB-180 ranged from 11.66 to 33.50 ng/g and 14.08 to 23.33 ng/g in Khanewal and 14.17 to 39.33 ng/g and 15.67 to 27.13 ng/g in Multan in vegetables whereas the highest mean concentration of Non dioxin like PCB-170 and PCB-180 were found as 42.17 ng/g d.w. and 57.53 ng/g d.w. in beans and grains in Khanewal and Multan respectively.

The mean concentration (ng/g d.w.)of non-dioxin like PCBs (PCB-170 and PCB-180) in all vegetables, beans and grains except *S.indicum and T.aestivum* in Khanewal and Multan respectively in present study was found significantly lower than maximum allowable concentration of non-dioxin like PCBs is 40 ng g^{-1} reported by

European Commission, 2011. The mean of TEQng/g of all examined PCBs in all vegetables, beans and grains of present study were found higher than cereals, $1.7x10^{-5}$ng/g > vegetables, $1.3x10^{-5}$ng/g determined by Lee et al., (2013).

The mean concentration of all examined PCB species i.e. 485.217 ng/g gave 5.91 ng/g mean TEQ value in *L. acutangula* in Multan which was observed the highest among all vegetables in present study. It showed that 485.217 ng/g of mean concentration of all examined PCB species can develop toxicity equal to 5.91 ng/g of either of the two most toxic compounds 2,3,7,8-tetrachlorodi benzo-p-dioxin and 1,2,3,7,8-pentachlorodibenzo-p-dioxin in the world. However, 718.50 ng/g of mean concentration of examined 14 PCB species in *S.indicum* with mean TEQ value 9.77 ng/g among all beans and grains can develop toxicity equal to 9.77 ng/g of either of the two most toxic compounds 2,3,7,8-tetrachlorodi benzo-p-dioxin and 1,2,3,7,8-pentachlorodibenzo-p-dioxin which was found the highest among all beans and grains in current study.

Sun et al, (2021) analyzed food from plant source comprised of cereals, beans, potatoes, leafy, root and stem vegetables, melon, legume vegetables, palatable fungi and oil extracted from different seeds to examine the level of PCB species. The concentrations of toxic equivalency (WHO-TEQ) ranged of $9x10^{-7}$–$1.45x10^{-5}$ng/g in upper bound scenario and $2x10^{-9}$–$7.37.3x10^{-6}$ng/g in lower bound scenario on a fresh weight of plant foodies were lower than those of current study.

Most congeners of PCBs can be metabolized by introducing the oxygen via cytochrome P450 enzyme system in living things especially in human beings. Mono-oxygenase reaction is carried out by the particular CYP isozyme that depends upon pattern of substitution of chlorines in those congeners hence current study proved lower rate of bio-accumulation and decreased concentration of PCB species with lesser number of chlorines on ring in selected food items in the body of plants and animals. Sevindik et al. (2018) supported this argument by investigations on antioxidant and anti-microbial potential of *Leucoagaricus leucothites* exposed the presence of natural borne anti-oxidant and anti-microbial potential in selected mushroom species enriched with diverse bioactive compounds possessing human health promoting effects. Talas et al. (2009) investigated the protective effects of synthetic organoselenium compounds in rats. Current study also emphasized over the use of *Leucoagaricus leucothites* and other synthetic compounds for remedy to remove PCB species through metabolism in living things after cautious studies to avoid any type of health issue due to PCBs.

4. Conclusion

The present study concluded that the level of mean concentration and mean TEQ of total examined PCB species in the most of the vegetables, beans and grains was found safe but can pose a moderate level of risk for human health after higher ingestion rate of some vegetables and beans with higher lipid contents and long duration of oral exposure. Due to higher contribution of local contamination along with biotransformation of PCBs through water, District Multan received more contaminants as compare to district Khanewal, Pakistan. The mean concentration of PCB species in current study was ranged from 2.71 ± 1.18 to 151.67 ± 3.21 ng/g dry weight in beans and grains and 2.30 ± 0.27 to 97.00 ± 1.18 ng/g dry weight in vegetables in both districts. Mean TEQ of sum of 14 PCB species ranged as 1.52 ± 0.33–5.91 ± 0.37ngg^{-1} in vegetables and 1.46 ± 0.17–10.04 ± 0.10ngg $^{-1}$ in beans and grains in study area. This study emphasizes on an implement of the strict rules regarding the use of restricted chemicals in both agricultural and industrial sector to diminish the effluence in terrestrial and aquatic food chains. Effective measures may be upgraded to reduce the poisonous contribution of PCB sources for the improvement of irrigating water and soil quality. Current research work will be useful for the sustainability of terrestrial ecosystem in the country.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Contribution of author

MA, A, and MSA have contributed in the research idea and design, data finding and data analysis and interpretation of results. While, KSA and NH contributed in the sampling and statistical analysis of data.

Ethical approval

There is no ethical conflict of interest.

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