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# Human health risk assessment, congener specific analysis and spatial distribution pattern of organochlorine pesticides (OCPs) through rice crop from selected districts of Punjab Province, Pakistan

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## HIGHLIGHTS

- Pioneer study to report OCPs in rice from Punjab Province, Pakistan
- Risks to human well beings via consumption of rice grains were assessed.
- Potential carcinogenic risks to humans were observed.

## ARTICLE INFO

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## ABSTRACT

To evaluate the screening level risk assessment of OCPs in rice (*Oryza sativa* L.) straw (n = 20) and rice grains (n = 20), samples were collected from different districts of Punjab Province, Pakistan. $\sum$OCPs' levels (ng $g^{-1}$) in rice straw and grains ranged from 3.63 to 39.40, 2.72 to 49.89, respectively. DDTs were found predominant over the other detected OCP isomers followed by HCH and heptachlor. Results of one way ANOVA reflected no significant difference for OCPs' levels among sampling sites, except heptachlor for rice grains. $\sum$OCPs' concentration in rice straw samples was exceeding the minimal residual levels (MRLs) (Australian and Japanese). Results of dietary intake and risk assessment suggested that rice straw is not safe for animals to consume as fodder. Human health was suggested to have some carcinogenic risks by consumption of rice grains, however, no considerable hazardous risk (non-carcinogenic) to human health was found.



## 1. Introduction

The pesticide manual stated that about 881 substances are considered as pesticide (biological and chemical substances or mixture of different substances) worldwide (Sanzidur and Rahman, 2003; Bolognesi and Merlo, 2011; Dors et al., 2011; Lichtenberg, 2013). Organochlorine pesticides (OCPs) are chemically stable/persistent, toxic and bioaccumulative substances and have a tendency to travel across a long distance in the environment (El-Shahawi et al., 2010). DDTs (isomers of DDT) and HCHs (isomers of HCH) are potential pollutants among OCPs (Mishra et al., 2012). To get the maximum yield of food crops use of pesticides is common across the globe, especially in developing countries; rice (*Oryza sativa* L.) being a staple food is also under heavy pesticides pressure in developing countries (Oerke, 2006; Hou et al., 2013).

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In Pakistan use of pesticides was upshifted after 1950, when 250 metric tons (mt) of pesticides were imported. Pesticide usage increased by 2158.6% from 1952 till 2004 (Khan et al., 2010). Rice grains fulfill about 60% of population's food requirement throughout the world while rice straw is a potential source of fodder for animals during winter season (Drake et al., 2002; Mahato and Harrison, 2005; Nguyen et al., 2008). Pathway of OCPs to human and animal body leads from pesticide applications on food crops to consumption of such foodstuffs (Nag and Raikwar, 2011; Mrema et al., 2014; Mahmood et al., 2014a). As of their toxicological effects like carcinogenic, teratogenic, and mutagenic, pesticides are dangerous by exhibiting acute and chronic effects to the health of livelihoods (Dasgupta et al., 2007; Juraske et al., 2009; Tsatsakis et al., 2009; Fantke et al., 2012; Hernández et al., 2013). Chronic effects are neurological disorders (Moretto and Colosio, 2011), neurodegenerative diseases, cancer (Kanavouras et al., 2011; Parrón et al., 2011; Mrema et al., 2014), neuro-behavioral dysfunctioning (Colosio et al., 2009), reproductive errors (Mrema et al., 2013), respiratory problems (Hernández et al., 2011; Mostafalou and Abdollahi, 2013) and severe human ailments as hypertension and liver diseases (Khan et al., 2010). Aside from humans, animals and other environmental integrities have been reported to be affected by this problem (Ecobichon, 2001; Konradsen et al., 2003; Hoai et al., 2011; Walorczyk et al., 2013).

Pakistan has signed a number of multilateral environmental agreements (MEAs) including Stockholm convention on persistent organic pollutants (POPs). Unfortunately, no legal framework for application and proper discarding of banned pesticide exists in Pakistan (Ahad et al., 2010; Malik et al., 2011; Mahmood and Malik, 2014) and stockpiles of outdated pesticides exist in urban areas along with the manufacturing units (Syed and Malik, 2011; Mahmood et al, 2014d). They have been practiced without any awareness of using personal protective equipment, lack of safety standards, and unavailability of washing amenities and pesticide bottles are also not properly labeled (Feola and Binder, 2010; Lesmes-Fabian et al., 2012).

Scientific communities are paying attention on POPs' contaminations in food crops along with their health implications on livelihoods. A number of reports on POPs' contamination in food crops and associated risks assessment are increasing day by day. Briefly, by reviewing the available literature it was found that published reports are available on OCPs' contamination in rice from Korea (Nguyen et al., 2008), India (Suresh Babu et al., 2003; Deka, 2004; Mahdavian and Somashekar, 2013; Nag and Raikwar, 2011), China (Nakata et al., 2002; Liu et al., 2006; Ng and Zhang, 2011; Hou et al., 2013; Wang et al., 2012; Liu et al., 2014; Song et al., 2014), Kazakhstan (Lozowicka et al., 2014), Poland (Walorczyk et al., 2013), Brazil (Dors et al., 2011), and Greece (Tsiplakou et al., 2010). Furthermore, studies have been conducted to estimate the dietary intake of pesticides via foodstuffs and risks to humans' health were determined from Russia (Polder et al., 2010), the USA (Dougherty et al., 2000), China (Chung et al., 2008; Qin et al., 2011; Wang et al., 2011) and Sweden (Darnerud et al., 2006).

In Pakistan interests toward the POPs' contamination are increasing and few reports have been published previously on OCP levels for different environmental matrices (soil, sediment, water, and air) (Tariq et al., 2004; Ahmad et al., 2008; Khan et al., 2010; Malik et al., 2011; Syed and Malik, 2011; Eqani et al., 2013; Syed et al., 2013a,b; Alamdar et al., 2014; Mahmood et al., 2014e,f). However, a very few reports on screening level risk assessment of PCBs (polychlorinated biphenyls), PCNs (polychlorinated napthalenes), PBDEs (polybrominated diphenyl ethers), DPs (dechloran plus) and OCPs in food crops have been published in recent past, which reflected a dare need of detailed and comprehensive screening of POPs in food stuffs across the Pakistan especially Punjab Province (Mahmood et al., 2014a, b, c; Mahmood et al., 2015). As far as our information is concerned no published data is available on OCPs' contaminations in rice crops and grains from Punjab. This pioneer study was designed to assess the levels of OCPs in rice crop, spatial distribution pattern across the study area, and associated health risks by estimating the dietary intake of OCPs through rice grains.

## 2. Materials and methods

### *2.1. Sampling strategy and sampling*

A total of four districts (Sahiwal, Okara, Lahore and Sheikhpura) were selected from Punjab Province, Pakistan for rice straws and rice grain sampling (Fig. 1). Five locations were selected from each district and samples were collected from distance of 15 km of each site following according to stratified random sampling.

Super rice variety was collected in October–November 2013 during harvesting season. Whole plant was harvested, roots were removed while the remaining parts i.e. stem and kernel were separated and stored in sampling bags after proper labeling. Samples were shifted to ice box and transported to the Environmental Toxicology Laboratory, College of Earth and Environmental Sciences, University of the Punjab, Pakistan and placed in a freezer at −20 °C until further analysis was performed (Mahmood et al., 2014c; Sojinu et al., 2012).

### *2.2. Extraction and clean-up*

Rice straw ($n = 20$) and rice grains ($n = 20$) were ground to fine powder and 10 g of each sample was Soxhelt extracted for 24 h (Barriada-Pereira et al., 2003; Ahmad et al., 2008). Samples were cleaned by silica–alumina column after evaporating through rotary evaporator. Cleaned fraction of sample was concentrated under gentle high purity nitrogen stream to 0.2 ml (Syed et al., 2013a; Mahmood et al., 2014g). All the chemicals used during the experimentation were of analytical grade and purchased from Merck (Germany). Standards for OCPs were purchased from Dr. Ehrenstorpher GmbH, Germany.

### *2.3. Chromatographic analysis*

Samples were analyzed on an Agilent 7890A GC–ECNI–MS (gas chromatography electron capture negative ion mass spectrometry). OCPs (α-HCH, β-HCH, -HCH, δ-HCH, ϒ-HCH, Hexachlorobenzene (HCB), cis-chlordane (CC), trans-chlordane (TC), o,p′-DDD, p,p′-DDD, o,p′-DDT, p,p′-DDT, o,p′-DDE, p,p′-DDE, β-endosulphan, heptachlor, mirex) were analyzed in selected ion monitoring (SIM) mood. Column used for sample analysis on GC–ECNI–MS was CP-Sil 8CB, 50 m, 0.25 mm, and 0.25 μm (Varian). The injector port temperature throughout the analysis was kept at 250 °C. The overall analysis was performed according to following scheme; for first 3 min the temperature was 150 °C, 4 °C/min to 290 °C, and isothermal process was kept for 10 min. The source temperature of MSD (mass spectrometric detector) was 230 °C and 150 °C was the quadruple temperature (Mahmood et al., 2014g).

### *2.4. Quality control and quality assurance (QC/QA)*

Quality control procedure was strictly followed for all the samples to ensure the quality of results. Calibration standards were used daily for instrument calibration. Field, procedural and solvent blanks were analyzed by similar methodology, adopted for original samples. Glassware was double washed with distilled water and baked at 450 °C for more than 6 h. Agilent MSD Productivity Chemstation software was used for data processing and acquirement. MDLs (method detection limits) was calculated within the region where signal to noise ratio is >5, along with the mean concentration of target compound (field blanks) plus three times standard deviation and MDL ranged from 0.1 to 0.2 pg $g^{-1}$. The surrogate recovery for TCmX (2,4,5,6-tetrachloro-*m*-xylene) and PCB-209 (decachlorobiphenyl) ranged between 75 and 84% for all the samples. A standard of 5, 10, 20, 50, 100 and 200 μg $L^{-1}$ was used to quantify the calibration curves.