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Organochlorine pesticides across the tributaries of River Ravi, Pakistan: Human health risk assessment through dermal exposure, ecological risks, source fingerprints and spatio-temporal distribution

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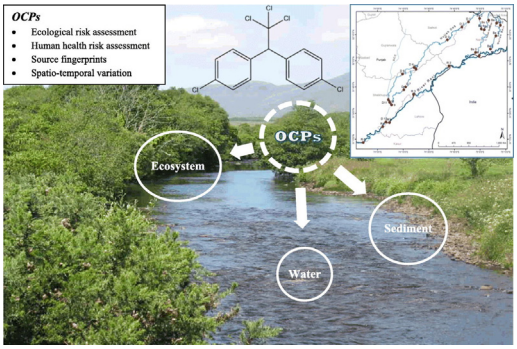
HIGHLIGHTS

- Pioneer OCPs study from northern tributaries of the River Ravi, Lahore, Pakistan.
- Ongoing OCPs usage was identified.
- Ecological risks were exceeding RQ value 1 at all studied streams.
- Higher carcinogenic risks associated to aldrin, dieldrin, *p,p'*-DDT and β-endosulfan.

GRAPHICAL ABSTRACT



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ABSTRACT

This study monitored the human health risks through dermal exposure, hazardous risks to ecological integrity, contamination levels, spatio-temporal distribution, and congener specific analysis of organochlorine pesticides (OCPs) across River Ravi and its three northern tributaries (Nullah Bein, Nullah Basanter and Nullah Deg). The residual levels of OCPs isomers were screened for water (n = 54) and surface sediment (n = 54) samples from twenty seven sampling sites in two alternate seasons (pre-monsoon and post-monsoon). The ∑OCPs concentrations ranged from 13.61 to 1992.18 ng/g dry weight and 12.89 to 128.16 ng/L with predominance of β-endosulfan and *p,p'*-DDT in sediment and water matrixes, respectively. Distribution pattern revealed significantly higher concentrations in upstream and midstream, suggesting considerable transboundary OCPs pollution. Calculated ratios of α-HCH/γ-HCH, *o,p'*-DDT/*p,p'*-DDT, (DDE + DDD) / ∑DDTs and *cis*/*trans*-chlordane for water and sediments identified the fresh addition of lindane, technical DDTs and chlordane in the study area. Risk quotient (RQ) based ecological risk was found to be >1 at all studied streams during both seasons and elucidates higher risks for endosulfan (α-endosulfan) and endrin. Human health risk assessment indicated absence of hazardous (non-carcinogenic) risk through bathing in studied streams; as the hazard index values ranged from 1.09E − 05 to 2.48E − 02 (acceptable limit; <1). However, the calculated carcinogenic risk possessed by OCPs through dermal exposure ranged from 1.39E − 10 to 1.98E − 05 that highlighted the considerable carcinogenic

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risk associated to aldrin, dieldrin, *p,p′*-DDT and β-endosulfan at certain studied sites. Therefore, the high levels of ecological risk and carcinogenic human health risk had emphasized an immediate elimination of ongoing OCPs addition in the studied area.

1. Introduction

The organochlorine pesticides (OCPs) are synthetic chemicals that are of great global concern due to their persistence, toxicity, bioaccumulation, and adverse ecological effects (Dan et al., 2012; Parween et al., 2014). They have been extensively used all around the world, predominantly during 1950–1980s in agricultural countries to intensify the agricultural productivity (Maurya and Kumar, 2013). However, often <0.1% of the applied pesticides target their pests, while >99.9% fraction escapes into environment through surface runoff, spray carry-over, infiltration or residue retention on food crops (Pimentel, 1995; Miller, 2004; Zhang et al., 2011) and have a tendency of long distance travel in the environment (El-Shahawi et al., 2010).

Pakistan is an agro-based country; where 70% of its population is agriculture dependent that makes it self-sufficient in terms of the food production (Hussain and Routary, 2012). The consumption of pesticides in this agricultural country has been increased significantly from 1954 through 2003 from 254 metric tons/year to 78,132 metric tons/year, respectively (Tariq et al., 2004; Syed and Malik, 2011; Sultana et al., 2014). Currently, the pesticides consumption rate is increasing with an annual rate of 6% (WWF, 2007) that would further increase manifold as several vector-borne epidemics hit the country (Jahan, 2011; Nieto et al., 2012). Another principal source of OCPs in environmental matrixes of Pakistan is uncontrolled disposal of thousands of kilograms of obsolete or/and banned OCPs, within or in the neighborhood of abandoned OCPs factories in various parts of the country (Eqani et al., 2012a; Tariq et al., 2007). The prohibition in the production or usage of DDTs and other OCPs after Stockholm Convention on the Persistent Organic Pollutant in 2001, to which Pakistan is also a party, left behind the largest stock of obsolete pesticides, demolished factories, chemical storages and dump grounds in/around the populated cities of the country (Jan et al., 2009; Syed and Malik, 2011; Eqani et al., 2012a). Moreover, the inland use of banned OCPs is still reported in many parts of Pakistan owing to their low cost, effectiveness and inappropriate national regulatory mechanism (Syed and Malik, 2011; Eqani et al., 2011; Tariq et al., 2007). Consequently, a substantial fraction of the applied OCPs contaminates various environmental compartments of the country (Ahad et al., 2010; Syed and Malik, 2011; Malik et al., 2011; Alamdar et al., 2014; Sultana et al., 2014; Mahmood et al., 2014a; Syed et al., 2014a; Zehra et al., 2015; Ali et al., 2016a). However, to date no policy has been developed to prevent the illegal practice and unsafe storage of the banned POPs (Ahad et al., 2010).

The environmental contamination of OCPs is of serious concern particularly for aquatic ecosystems as they receive uncontrolled wastewater and agricultural runoffs in Pakistan (Jamil et al., 2015). Moreover, the water is a primary medium for the transportation of OCPs from an application area to elsewhere (Yadav et al., 2015). In aquatic environment, hydrophobic nature of OCPs leads to their subsequent accumulation in surface sediments with in the water bodies; this makes them bioavailable even decades after their prohibition (Oliveira et al., 2016). They accumulate in upper trophic level in the food chain and possess high risk of pesticides poisoning, particularly in developing countries where it is reported to be 13 folds higher than developed countries (Yadav et al., 2015).

Among the surface water bodies of Pakistan, the River Ravi, a transboundary river has a strategic importance for being surrounded by most-intensive agricultural region of the country, i.e. Rachna Doab and Bari Doab, and simultaneously being the most polluted river of Pakistan (Syed et al., 2013, 2014a). Among the five tributaries of the River (four exists in Pakistan), the Nullah Deg, Nullah Basanter and Nullah Bein were focused in present study. All of these tributaries are transboundary streams and are part of Rechna Doab, receiving the surface runoff and sub-surface flow from the surrounding agricultural areas. The water of the Nullahs is used for domestic, livestock and irrigation purposes through unregulated irrigation pumps, and based upon the temperature and rainfall patterns, the cultivation in the catchment area is of cereal crops, i.e. rice grown during the summer monsoon (kharif) season whereas wheat is cultivated during the drier winter (rabi) season. Likewise, the ongoing inland use of banned OCPs is reported from Rachna Doab (Syed and Malik, 2011; Eqani et al., 2011, 2012b). Consequently, a substantial fraction of the applied OCPs contaminates environment of the region.

Therefore, the present study was aimed to reveal the occurrence, human health risk through dermal exposure, ecological risks, source fingerprints and spatial-temporal variation of OCPs in water and surface sediments across the northern tributaries of River Ravi in Pakistan. To the best of our knowledge, present study provides the baseline data for the level of OCPs from the study area that could be significantly valuable in global freshwater ecological and human health risk studies.

2. Materials and methods

2.1. Sampling strategy

The study was conducted along the Nullah Deg, Nullah Bein and Nullah Basantar, located in Upper Rachna Doab in Narowal, Sialkot and Sheikhupura districts of Pakistan. The sampling was also conducted along the River Ravi, upstream and downstream to the confluence points of these three tributaries up to the Balloki headworks on the River. A preliminary survey was conducted in June 2015, prior to research sampling design to obtain background knowledge about the sources of pollutants, nature of the tributaries and to finalize the sampling points based on their accessibility. In order to record the sampling sites, they were marked on field using GARMIN *eTrax* 20 GPS device. The water and sediments samples were collected from twenty seven sampling sites (Fig. 1) in two distinct phases (i.e. post-monsoon and pre-monsoon period) during September 2015 to May 2016. The details of the sampling sites along with their spatial and selection criteria description are provided as Table S.1.

2.2. Sample collection and preservation

2.2.1. Water sampling

The water samples (n = 54) were collected from the selected sampling sites during post-monsoon season (October–November 2015) and pre-monsoon season (March–April 2016). The samples were collected through time-proportional composite sampling in a dichloromethane pre-rinsed amber glass bottles and zero headspace was assured. The collected samples were then sealed and labeled on-site using adhesive tape and self-administered labeling stickers, respectively (APHA, 2005). To ensure the preservation at ≤4 °C, samples were transferred immediately to ice box containing wet ice and later to the Water Quality Laboratory at the College of Earth and Environmental Sciences, University of the Punjab, Lahore (Pakistan). In the laboratory, water samples were filtered via Whatman® ashless, Grade 42 filter paper to remove the suspended matter and/or grit particles, and stored at −20 °C until analysis.