ORGANOCHLORINE RESIDUES IN THE RIVERINE ECOSYSTEM OF PAKISTAN: DISTRIBUTION AND RISK ASSESSMENT

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Introduction:

Organochlorines (OCs) contamination in different environmental compartments has been of great concern at a local, national and international scale.[1] Owing to their persistence, high lipid solubility, and carcinogenic properties [2-5] chlorinated contaminants might pose several health risks to humans and other aquatic organisms. Although the use of organochlorine pesticides is banned/restricted in many countries, they are still being used in developing countries in agriculture and industrial sectors. Being signatory of the Stockholm convention, the use of most of the OCPs and PCBs is banned in Pakistan (May, 2001). However, these toxic chemicals are still in use in Pakistan due to their effectiveness, existing stocks and limited awareness of people of their undesired effects.[6] This recent study designed to investigate on the occurrence of organochlorine contaminants in the River Chenab, Pakistan, during the period 2007-09. The River Chenab is one of the most important water bodies in central Asia, associated with regions inhabited by more than 100 million people. Notwithstanding its importance for the region, the River Chenab has never been in detail studied for the occurrence of important compounds like PCBs and OCPs. Therefore, this study presents for the first time levels of the aforementioned compounds and offers insight on sources, seasonality, accumulation, long-range transport and risk assessment.

Research Plans

Residues of selected OCPs (hexachlorobenzene (HCB), α–HCH, β–HCH, γ–HCH, chlordane (trans), chlordane (cis), oxychlordane, p, p′–DDT, o, p′–DDT, p, p′–DDD and p, p′–DDE) and $\sum_{31}$ PCB (Sum of 31 congeners) were studied in the water, and sediment collected from 25 sampling sites (19 sampling sites were located on the Chenab's mainstream and 6 on the adjoining tributaries i.e. 2 sites on River Ravi, 2 sites on River Jhelum, 1 site on River Sutlej and 1 site is located on the industrial drain dumped into the River Chenab near district Jhang). All the collected samples were analyzed by gas chromatography tandem quadruple mass spectrometry (GC-MS/MS) and detailed methods are described elsewhere [4, 6, 7].

Result and Discussions:

OCP and PCB in the surface water and sediment

Surface water (including particulate phase) and sediment were monitored at 25 sites for OCPs and PCBs and results are showed as Figure 1. The River Chenab is moderately to severely polluted in terms OCP and PCB contaminants, when compared with other water bodies worldwide. DDTs were found predominately in most of water and sediment samples followed by HCHs, Chlordanes, and PCBs (Figure 1). High concentration(s) of DDTs in the water (0.55-545 ng/L), and sediment (5.6-470 ng/g) during both campaigns can be linked to its chronological excessive use [5-7]. In our study, dominance of p, p′-DDE and p, p′-DDD (breakdown product of DDTs) showed the long term

weathering of DDTs, while presence p, p$^{/}$-DDT in most of samples also reflected the recent use of DDTs. On the other hand, trends of HCHs in the water samples in descending order as γ-HCH, α-HCH, β-HCH and δ-HCH. In sediment β-HCH and γ-HCH were contributed mainly in total composition of HCHs. The dominance of β-HCH in sediment may reveal the fact that this isomer, due to relatively more lipophilic nature and low water solubility (high log K_{ow}), may be fractionated towards sediment fraction. Indicative ratio(s) of HCHs indicated both excessive recent and historical use of this pesticide mainly for the crop protection and sanitation purpose. As for PCB, the dominance of lighter chlorinated biphenyl (tri and tetra congener) occupied more than 50% of total PCB in waters, while tetra-CB, penta-CB and hepta-CB were dominant in sediments. PCB compositional trends in water and sediment is consistent with previous studies[10-11], which also suggested the dominance of heavier chlorinated congeners in sedimentary fraction. In contrary to this, dominance of lighter chlorinated congener(s) in water happened due to their high solubility [12-13]. Given that this process is governed by the lipophilic character (K_{ow}) of the compounds, the heavier CBs are expected to deposit to the sediments in favor of the lighter ones. If we take all the aforementioned information in consideration, it can be concluded that the main Aroclor mixtures used in the area should be mainly 1248 and the heavier 1254, 1260 and 1262, however in lower extents. The dl- PCB-TEQ levels ranged from 0.11-29.59 pg $TEQ_{\Sigma 7dl\text{-}PCBs}$ L^{-1} (for water) and 0.01-0.28 pg$TEQ_{\Sigma 3dl\text{-}PCBs}$ g^{-1} (dw) (for sediment) , with PCB-126 and118 accounting for more than 70 % to total dioxin-like PCB-TEQs. All the sites with elevated TEQ values are located in the industrial and urban areas of Pakistan, suggesting that these chemicals occurred due to local usage and not because of long range transport.

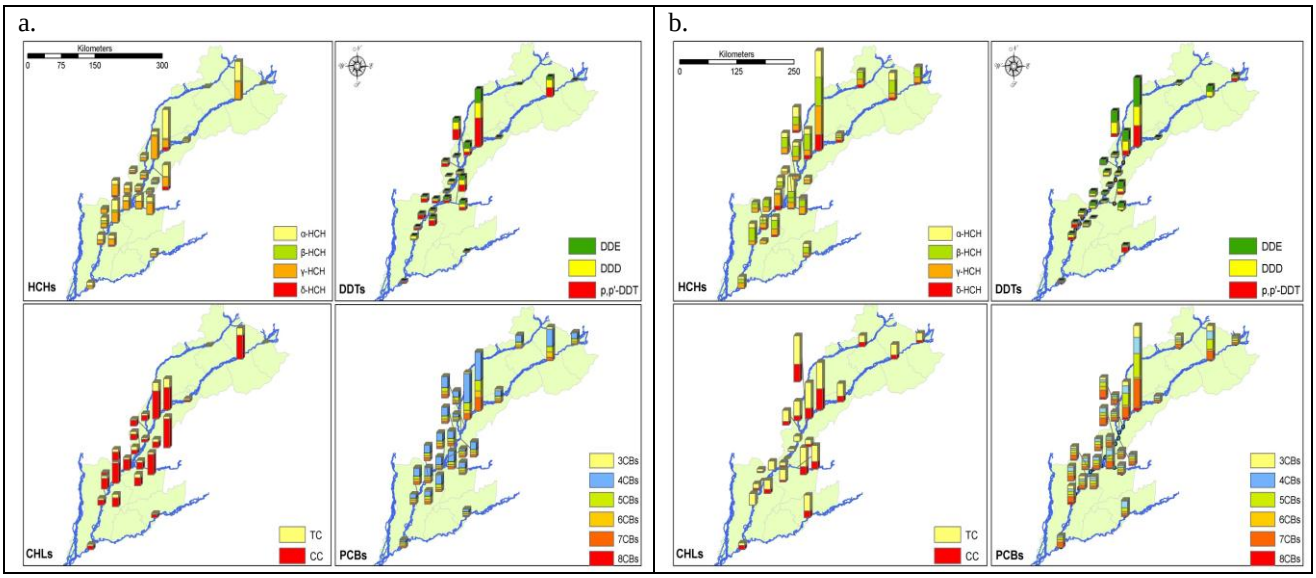

Figure 1. showing the distributional patterns of the OCPs and PCBs in both a. water and b. sediment samples collected from River Chenab, Pakistan.

Ecotoxicological concern of OCP and PCB:

Evaluating the risk of OCPs and PCBs in the surface water of River Chenab by comparing our dataset with current USEPA national recommended water quality criteria (USEPA, 2006). PCBs and DDTs were exceeded the limits for human health risk standards in 80 % of total water samples during both seasons. These exceedances suggested that

high concentrations of OCPs and PCBs, especially at industrial and urban sites, might cause several potential health risks to the human and aquatic organism. As for sediment the comparison of HCHs with available quality guidelines, suggesting that risk from HCHs is moderate, while severe contamination of DDTs and its metabolites indicating the adverse biological effects in this studied area especially in industrial sites samples and urban sample. As for PCBs, the concentration exceeded the TEL and ERL values in more than 35% of total sediment samples. Generally, the sediment collected from the industrial sites and urban sites indicated that serious potential risks posed to the aquatic life of River Chenab.

Conclusions

In general, the present study provided the first systematic data on the distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyl (PCBs) in the water, and sediment, collected from River Chenab, Pakistan. This study showed that DDTs were relatively more prevalent in the aquatic ecosystem of Pakistan, followed by PCBs, HCHs, Chlordanes and ∑other OCPs in descending order. Extensive industrial activities, illegal use of banned chemicals, and existence of biggest stockpiles of obsolete pesticides in the Punjab province of Pakistan, are sources of these toxic chemicals in different environmental matrices of River Chenab, Pakistan. This study played a significant role to evaluate the contribution of Pakistan towards POPs emission in global environment and effectiveness of control measures taken by regional and international authorities under Stockholm convention in developing countries. However, this study provides the comprehensive and appropriate reflection of the scenario and stresses to conduct more detailed studies to evaluate the ecotoxicological effects of these contaminants in the aquatic ecosystem of River Chenab Pakistan. Still, there are many limitations in this initial screening study, therefore continual monitoring of OCPs and PCBs and other contaminants such as polychlorinated dibenzo-p-dioxins/ dibenzofurans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs) are needed to mitigate the impacts of these contaminants on human health and ecological environment.

Recommendations

1. To conduct more detailed studies in future (in present study area and some others), to form the baseline data of organochlorine residues in different environmental matrices i.e. air, soils, sediments, biota etc. which is of great concern at both national and international level.
2. Proper management of toxic chemicals stored at different location in stores and demolished factory units of OCPs, threatened human health, our natural water resources (including River Chenab and its adjoining tributaries) and other environmental compartments.

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