ABSTRACT

Organophosphate esters (OPEs) are widely applied as the substitutes for brominated-flame retardants and characterized as emerging contaminants. Due to their toxicity and persistent nature, OPEs are becoming a matter of greater concern worldwide. The present study was conducted to examine the occurrence, spatial distribution patterns, bioaccumulation potential, human health and ecological risks of organophosphate esters (OPEs) across river Ravi and its four tributaries (Degh Nullah, Basantar Nullah, Baen Nullah and Hudiara nullah). Furthermore, the current study also evaluated the efficacy of three AOPs, including photo-ozone peroxide, photo-fenton and sono-fenton, for the removal of OPEs in synthetic and river water samples. The current research work is the pioneer study from Pakistan that provides the fundamental baseline data about the contamination status of OPEs in aquatic ecosystem. The samples of surface water (n=24), sediments (n=24) and seven fish species of two distinct feeding habits i.e., carnivores and herbivores (n=84) were collected from twenty-four sampling sites located on Ravi River and its four tributaries. The concentrations of $\sum_{10}$OPEs were in the range of 19.2 - 105ng/L, with the dominance of chlorinated-OPEs (51%) in surface water, whereas in case of sediments, the $\sum_{10}$OPEs concentrations ranged from 20.7 to 149ng/g dw, with high abundance of non - chlorinated alkyl-OPEs, which contributed about 56% to total OPE concentration. In case of fish species, $\sum_{10}$OPE concentration ranged from 42.8 - 288 ng/g ww (mean: 145 ± 105 ng/g ww). The concentration of OPEs varied significantly between both fish groups, with higher concentrations observed in carnivorous species (256 ± 28.1 ng/g ww); principal component and agglomerative hierarchical cluster analysis further confirmed the dominance of OPE concentrations in carnivorous species. Among studied OPEs, alkyl-OPEs were most dominant contributing 62% to total OPE levels, followed by chlor-OPEs (20%). The correlation analysis signified a strong positive relation of OPEs with TOC ($p < 0.05, R = 0.76$) in sediments; and with lipid content ($p < 0.05, R = 0.80$) in fish species, implying that hydrophobicity and lipophilicity play significant roles in OPE distribution in different environmental matrices. Furthermore, the assessment of bioaccumulation potential revealed that both BAF and BSAF were exceeding the permissible threshold limits (log BAF ≥ 3.7; log BSAF >1), suggesting that studied OPEs are highly bio-accumulative by fish species. The global comparison revealed that contamination status of OPEs in the current study was comparatively lower than the other regional findings. Spatial distribution analysis identified midstream and upstream sites

along Degh Nullah and the main river Ravi as significant contributors to OPE contamination, and the riverine flux of ∑10OPEs was estimated to be 0.68 tons/yr. Furthermore, principal component analysis suggested vehicular emissions, industrial discharges, household supplies and atmospheric deposition as main sources of OPEs occurrence in current study region. The ecological risk assessment indicated that all OPEs, except EHDPP and TCrP, showed negligible or insignificant ecological risks for aquatic organisms, while the human health risk assessment indicated that exposure to OPEs via fish consumption in the current study region is likely to pose very limited risks (Hazard quotient < 1) to human health, at both medium (50th) and high (95th) exposure scenarios. Regarding OPE treatment, the study found that the degradation of aryl-OPEs and alkyl-OPEs occurred more rapidly as compared to the chlor-OPEs in all treatment methods. Moreover, the degradation rates and removal efficiencies of OPEs in river water samples were comparatively lower than those observed in synthetic water. Among evaluated methods, the photo – fenton process was identified as most efficient, achieving a removal efficiency of 93% in synthetic water and 71% in river water, with a corresponding EE/O of 22 kWh/m^3 and 55 kWh/m^3, respectively. The findings of this study offer critical insights into the current pollution status of

OPEs, laying a foundation for future research and management strategies aimed at mitigating their environmental and health impacts.