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Congener specific analysis, spatial distribution and screening-level risk assessment of polychlorinated naphthalenes in water and sediments from two tributaries of the River Chenab, Pakistan

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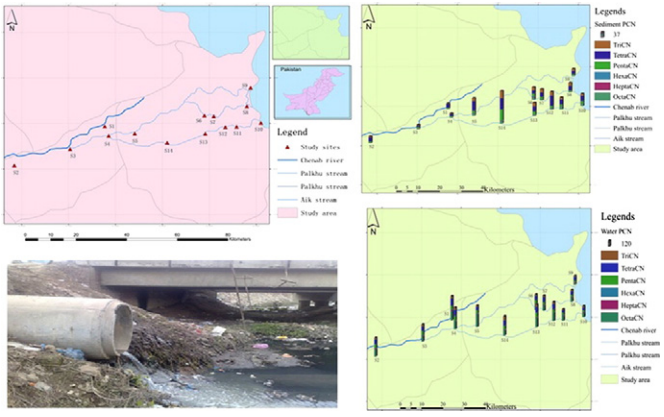
HIGHLIGHTS

- First study to report PCN in environmental compartment from Pakistan
- Urban/industrial sites were classified as potential sources of PCN in the study area.
- TEQ values were considerably higher than previously published data.

GRAPHICAL ABSTRACT



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ABSTRACT

The number of reports regarding PCN screening-levels and ecological risk assessment in environmental compartments is limited. This study presents information on congener specific analysis, distribution pattern of PCN and ecological risk assessment via PCN exposure/contamination through water and sediment from two tributaries of the River Chenab, Pakistan. A total twenty eight samples of water and sediment were collected during Jan, 2013 to June, 2013 to analyze the $\sum_{39}$PCN congeners. $\sum_{39}$PCN concentrations ranged between 8.94 and 414 ng g^{-1} dw and 178–489 ng l^{-1} in sediment and water, respectively. Water exhibited higher TEQ values while in case of sediments TEQ values were at higher than the previously reported data from other parts of the world. This is the first report of PCNs' distribution pattern and screening-level risk assessment from Pakistan. The results of toxicity exposure of PCN warrant auxiliary devotion in future, to this group of contaminant.

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1. Introduction

PCNs (polychlorinated naphthalenes) have been identified about 170 years ago and their commercial production have been started for about 100 years ago (Hayward, 1998), but the understanding about the occurrence, sources, fate, formulation and impact on life and the environment is still partial (Brack et al., 2003). PCNs gained aggressive anxiety in the environmental chemistry, within the last decade as their properties are enough to meet the persistent organic pollutants (POPs) criteria (Paasivirta, 1998; Lerche et al., 2002). The toxic impacts of PCN mixtures are attributed predominantly to penta-, hexa- and hepta-chlorinated naphthalenes (CNs), which exhibit dioxin like special effects on human and animal liver cell lines (Blankenship et al., 2000; Villeneuve et al., 2000). Bioaccumulative and persistent potency of PCNs boost the hazards to animal life (Falandysz, 1998; Noma et al., 2004).

Commercial production of technical PCN mixture is under the title of Halowax (America) and Nibren wax (Germany) (Jarnberg et al., 1999). Various industrial processes are identified for PCN emissions, which are also in favor to PCDD and PCDF formation (Brack et al., 2003). Industrial units, including chloralkali industry, waste incineration plants, magnesium production and copper smelting units are responsible for PCN emission (Kannan et al., 1998; Falandysz, 1998; Hanari et al., 2013). Global production of PCNs has been estimated about 150,000 tons (Falandysz, 1998). Historically, PCNs were being manufactured during the period of 1910–1970 and have been used in various industrial applications due to their best dielectric properties as well as low reactivity (Hanari et al., 2013).

In South Asia, published reports on PCN levels and distribution are limited. A recent report monitored the atmospheric level of PCN from India and Pakistan (Xu, et al., 2014). However, there is no published report available from Pakistan on distribution, screening level risk assessment and bioaccumulation of PCN. With many questions regarding PCN in South Asia, the current study is the first aimed to sketch the distribution pattern, congener specific analysis, screening-level risk assessment and potential sources of PCN from Pakistan. To the best of our knowledge, there is no published report available on PCN levels in rivulets and river water from South Asia. This study was conducted along two upstream tributaries of the River Chenab namely Nullah Aik and Nullah Palkhu, Punjab Province, Pakistan. The study area is situated on an area of 600 km^2 with population density of 903 people/km^2. A total of 3229 industrial units have been reported from this area and its vicinity (Anonymous, 2006). These include 264 tanneries and 220 factories producing surgical instruments, chemical and electroplating units, transformer repairing units, and rubber industries. A total of 52 million l per day of municipal and industrial wastewater — along with 1.1 million l of tannery wastes, electroplating and transformer repairing workshop generated waste is discharged into Aik and Palkhu tributaries (Anonymous, 2006). This study area has also been investigated by Qadir et al. (2008) to assess the heavy metals levels, and was found highly contaminated with screened metals in fish and water samples.

2. Material and methods

2.1. Sampling strategy

The study area (32°63 N–74°99 E and 32°45 N–74°69 E) was divided into three major zones; up-stream zone, including sites S8, S9, S10 and S11, mid-stream zone (S6, S7, S12 and S13) and down-stream zone (S1, S2, S3, S4, S5 and S14). This zonation was done on the basis of origin of these streams (locally called as Nullahs). Up-stream zone was characterized as purely rural and agricultural areas, mid-stream zone consisted of urban/industrial areas receiving urban and industrial wastewater of Sialkot city and down-stream zone is the down-stream of these Nullahs which are passed from urban and peri-urban areas of Sialkot and Gujranwala districts. A total of fourteen sampling locations were marked for water and sediment samples within 170 km stretch along the two tributaries of River Chenab i.e., Nullah Aik and Nullah Palkhu. Samples were collected during Jan, 2013 to June, 2013. Among fourteen sampling sites, twelve sites were located along Aik and Palkhu Nullahs and two sites were on River Chenab (Fig. 1).

2.2. Water sampling

Water samples (n = 28) were collected from 14 selected sites at Nullah Aik and Palkhu, in January–March 2013. Each sample was the composite of five sub-samples, collected from a depth of 2–3 m below the top surface of water in 5 l pre-cleaned (washed with organic solvent) sampling jars. After collection samples were placed in ice containing cooler and transferred immediately to the Environmental Biology and Ecotoxicology Laboratory, Quaid-I-Azam University, Islamabad, Pakistan. In laboratory water samples was filtered with glass wool to remove debris and other small particles and finally stored in −8 °C until further analysis.

2.3. Sediment sampling

Composite sediment samples (n = 28) were collected by combining 4–5 subsamples from the bottom of Nullahs. From each site, stretch of 500 m across both banks of Nullahs was marked for sample collection. Samples were stored in polythene bags, labeled and transported to the Environmental Biology and Ecotoxicology Laboratory, Quaid-I-Azam University, Islamabad, Pakistan. Samples were freeze dried, sieved with 2 mm sieve and transported to the State Key Laboratories of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China where stored in freezer until further analysis.

2.4. Extraction of sediment samples

About 20 g of sediment was Soxhlet-extracted for 24 h with DCM (dichloro methane). A mixture of decachlorobiphenyl (PCB 209) and 2,4,5,6-tetrachloro-m-xylene (TCmX) was added as surrogate standard in each sample prior to extraction. For the removal of elemental sulfur, activated copper granules were added in the collection flasks. The extract was concentrated and the solvent phase was changed from DCM to hexane through rotary evaporator.

2.5. Extraction of water samples

Water samples were extracted through liquid–liquid extraction in separating funnel. 1 l of filtered water was mixed with the 25–35 ml of DCM and shaked vigorously for 2–4 min and allowed to settle down for 10 min to get two layers. Lower transparent layer of organic solvent containing pollutants was collected on anhydrous Na_2SO_4 and a mixture of decachlorobiphenyl (PCB 209) and 2,4,5,6-tetrachloro-m-xylene (TCmX) was added as surrogate standard in each sample. The extract was concentrated via rotary evaporator and the solvent phase was changed from DCM to hexane.

2.6. Clean-up procedure

Extracts of sediment samples were washed with H_2SO_4 prior to column clean up. For column clean-up silica alumina column was used. Silica gel, anhydrous Na_2SO_4 and alumina were soxhlet extracted with DCM for 48 h and finally backed at 450 °C for 6 h before using. The volume of samples fraction was reduced to 0.2 ml under the gentle nitrogen (high purified) stream after adding 30 μl of iso-octane as solvent keeper. PCB-54 was added as internal standard in each sample prior to GC–MS analysis.