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Impacts of human activities on the spatial distribution and sources of polychlorinated naphthalenes in the middle and lower reaches of the Yellow River

Qilu Li [a], Xianghui Cheng [a], Yan Wang [b], Zhineng Cheng [c], Liya Guo [a], Kechang Li [c], Xianfa Su [a, *], Jianhui Sun [a, **], Jun Li [c], Gan Zhang [c]

[a] *School of Environment, Henan Normal University, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Xinxiang, Henan 453007, PR China*
[b] *Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China*
[c] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

HIGHLIGHTS

- Study on the behavior of PCNs in the SPM in the middle and lower reaches of the Yellow River were scarce.
- PCNs mainly accumulated on the SPM, in particular in samples near the reservoir.
- High proportion of CN-23 may originate from coal burning.
- Industrial processes and reservoir construction may influence the PCN distribution.

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ABSTRACT

The concentrations and compositions of polychlorinated naphthalenes (PCNs) in sediments and suspended particulate matters (SPM) in the middle and lower reaches of the Yellow River were investigated. The mean concentrations of PCNs were 7.15 ± 19.3 ng/g dw in the sediment and 38.1 ± 58.4 ng/g dw in SPM. Tri- and tetra-CNs were the dominant homologue groups in most samples. CN-23 was the predominant congener at all sites, and its presence may be attributed to coal combustion. Combustion indicators showed that local combustion source was the main contributor to the PCN concentrations. These sources were related to the energy structure of this region, where coal is the most important energy resource. Human activities, including industrial thermal processes and reservoir construction, were major factors affecting PCN levels and hydrological conditions, which strongly influenced the environmental fate of PCNs in the Yellow River.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 compounds with one to eight chlorine substitutions at different positions on their naphthalene rings. They have the potential for toxicity, bioaccumulation, persistence and long-range transport similar to dioxin, furans and co-planar polychlorinated biphenyls (PCBs) (Falandysz, 1998; Mahmood et al., 2014b). Since the 1980s, the production of technical mixtures of PCNs has been banned in most countries (Falandysz, 1998; Hogarh et al., 2012). However, PCNs remain ubiquitous contaminants (Bidleman et al., 2010; Xu et al., 2015). Besides their history of industrial production, past uses of technical mixtures of PCNs were as insulators and coolants for thermal stability, combustion processes (Li et al., 2012) and various PCB-associated applications (Hogarh et al., 2012; Lee et al., 2007). Some PCNs are unintentionally produced from waste

* Corresponding author. No. 1 Jianshe Donglu, Muye District, Xinxiang 453007, China.
** Corresponding author. No. 2 Jianshe Donglu, Muye District, Xinxiang 453007, China.
E-mail addresses: xfsu8008@126.com (X. Su), sunjhhj@163.com (J. Sun).

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incineration and chemical production.

Rivers are not only a key component of the global geochemical cycle (Oelkers et al., 2012; Viers et al., 2009), but also provide resources necessary for human life, such as drinking water, power generation, landscape services and aquatic products. Rivers are also among the aquatic systems most heavily affected by human activities. Studies have indicated that, globally, rivers are the largest sink for human pollution emissions, and they provide great potential for long-range transport (Gaillardet et al., 2003; Jickells et al., 2005; Walling, 2006). Sediment and suspended particulate matter (SPM) play vital roles as secondary pollution sources for subsequent contamination of aquatic ecosystems (Filgueiras et al., 2004; Lin et al., 2013). They can change the environmental behaviour of pollutants through adsorption and desorption, as well as deposition and re-suspension. Thus, they contribute greatly to the overall global distribution of persistent organic pollutants (POPs) (Holoubek et al., 2009).

The Yellow River is an important water source in north China, and carries a high load of silt (Li et al., 2016b; Xu, 2000). Over the last 40 years, the middle and lower reaches of the Yellow River and its tributaries have suffered greatly from water pollution. This pollution was mainly from urban and industrial sources, as well as surface pollution carried by rainfall run-off into the water (Yellow River Conservancy Commission of China (YRCC), 2011). A previous study indicated that 9.23×10^8 m^3 of sewage was discharged into the Yellow River every year, and that organic pollutants were abundant (He et al., 2006). The middle and lower reaches of the Yellow River flow through Sanmenxia, Luoyang, Zhengzhou, Kaifeng, and other urban areas within the central plains urban agglomeration. In recent years, economic development has brought serious pollution to these cities, which has led to an increase in the concentrations of organic pollution. Of course, human activity, including hydroelectric projects, also influences the distribution of pollutants. Two major hydroelectric projects were located in this section of the Yellow River, Sanmenxia Reservoir (SMXR) and Xiaolangdi Reservoir (XLDR), which regulate the balance of water and sediment. These dams increase degradation and deposition of organic pollutants in the sediment due to the long residence time of water (Ammar et al., 2015). Studies have shown that reservoir construction affected the transport of particulate matter in rivers (He et al., 2010) and the composition of SPM. In addition to the construction of dams, various contaminants were continually discharged into the river and its tributaries, which affected the levels and distribution to a certain degree.

PCNs are increasingly recognized as important pollutants in aquatic ecosystems, and many studies (Ishaq et al., 2009; Li et al., 2016a; Lundgren et al., 2003; Marvin et al., 2002) have indicated that rivers serve as one of the major sinks for PCNs. The Yellow River carries the most sand and clay (as transported sediment and SPM) among all rivers in the world and provides an ideal site for studying the release and migration behaviour of PCNs. There are many combustion based, industrial and thermal sources of PCNs, including iron-steel production, metal reefing and coal combustion. Coal currently plays a dominant role in the energy economy of Henan province, providing up to 77.7% of total energy consumption (Henan Statistics Yearbook 2015). Most PCN related studies of water body were focused on the sediment and water phases, but very few studies have been conducted on PCN in the SPM phase. Moreover, very few reported any information about the SPM phase in the Yellow River. Therefore, we have described the environmental behaviour of PCNs in the middle and lower reaches of the Yellow River, including the sediment and SPM phases. This study could provide useful experimental data for elucidating seasonal variation, spatial trends and environmental behaviour of PCNs in the study area.

2. Materials and methods

2.1. Sample collection

Sampling was conducted in the Henan section of the Yellow River in 2014 during the normal season (May), wet season (August) and dry season (December). The location of 20 sampling sites is shown in Fig. S1, including 13 sampling sites in the main stream (M1 to M13) and 7 sampling sites in tributaries (T1 to T7).

A total of 60 surface sediment samples and 60 SPM samples were collected. Sediment samples were collected using a stainless-steel grab sampler, and SPM samples were collected in clean brown glass jars, and immediately transported to the laboratory on ice. Sediment samples were subsequently freeze-dried for 72 h, mixed and sieved through a stainless-steel 70-mesh sieve. All samples were stored at −20 °C until further analysis.

2.2. Extraction and analysis

2.2.1. Sediment

Prepared sediment samples (20 g each) were spiked with ^{13}C-trans-chlordane (10 ng) as surrogate standards and then Soxhlet-extracted with dichloromethane (DCM) for 48 h. Activated copper was added to remove elemental sulphur. The extract of each sample was concentrated in a rotary evaporator (RV 05 basic; IKA, Staufen, Germany) and solvent-exchanged to hexane. The extract was first cleaned using a column containing 50% (w/w) sulphuric acid silica gel, and then purified through a multi-layer column filled with anhydrous Na_2SO_4 (1 g), florisil (2 g, 2% deactivated), neutral silica gel (3 g, 3% deactivated) and neutral alumina (3 g, 3% deactivated) from top to bottom. 6 mL hexane was used to activate the column and then the eluent collected about 25 mL. Finally, the extract volume was reduced to approximately 25 μL by a gentle nitrogen stream. A known quantity of ^{13}C-PCB141 was added as an internal standard for instrumental analysis.

2.2.2. SPM samples

Water samples containing SPM were collected at each site into a 50 L pre-cleaned stainless-steel bucket. NaN_3 was added at 100 mg/L to each container to inhibit bacterial growth during transportation and temporary storage. After transportation to the laboratory, SPM was isolated by filtering the water sample through a 0.7 μm glass fibre filter (GF/F, 150 mm diameter; Whatman, Maidstone, UK), which had been combusted at 450 °C and weighed prior to use. After filtration, glass fibre filters were sealed in aluminium foil. The filters loaded with SPM were freeze-dried, weighed, and Soxhlet-extracted. Analysis of the extract followed the method described above.

2.2.3. Sample analysis

All samples were analysed for PCNs using an Agilent 7890A gas chromatography electron capture negative-ion mass spectrometer (GC-ECNI-MS) in selected ion monitoring (SIM) mode. Retention Time (RT) and target compound can be found in the Supplementary Material (Table S1). A DB-5MS column (30 m length × 0.25 mm i.d., 0.25 μm film thickness) was used for separation. The retention time of the peaks from the individual standards and ion ratios was compared, and the elution order of the PCN congeners was also considered. The following PCN congeners were analysed in all samples: Tri-CNs: CN-19, -24, −14, −15, −16, −17/25, −23; tetra-CNs: CN-42, -33/34/37, −47, −36/45, −28/43, −27/30, −39, −32, −35, −38/40, −46; penta-CNs: CN-52/60, −58, −61, −50, −51, −54, −57, −62, −53, −59, −49, −56; hexa-CNs: CN-66/67, −64/68, −69, −71/72, −63, −65; hepta-CNs: CN-73, -74; and octa-CN: CN-75.