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## Baseline

## Distribution, composition, and ecological risk of surface sedimental polychlorinated naphthalenes in the East China Sea

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## ABSTRACT

To reveal the pollution levels and estimate the ecological risks of polychlorinated naphthalenes (PCNs) in the East China Sea (ECS), seventy-five surface sediment samples were collected and analyzed by high-resolution mass spectrometry. PCN contents ranged from below detection limit to 261.71 ng/g dry weight (d.w.), with an integrally seaward decreasing trend. Mono-, tetra-, and hepta-CN were the dominant homologs, and CN-2, CN-73, and CN-75 were the major individual components in most samples. CN-2 presented an obvious boundary with lower contents ( $16.48 \pm 3.40$  ng/g d.w.) in the center of the study area and higher contents ( $50.88 \pm 10.39$  ng/g d.w.) in the north and south of the boundary. The toxic equivalent (TEQ) contents ranged from 0 to 0.212 ng/g, and CN-2 and CN-73 were the predominant contributors to the TEQ.

Polychlorinated naphthalenes (PCNs) have been of concern in the past decades because of their persistence, dioxin-like effects to mammals, and wide detection in the environment (Die et al., 2017; Harner et al., 2000; Q. Li et al., 2017; Şişman and Geyikoğlu, 2008; Villeneuve et al., 2001; Vinitetskaya et al., 2005). PCNs were first used as industrial materials in the early 1900s, such as cable insulation, wood preservation, engine oil additives, electroplating masking compounds, dye carriers, capacitors, and refractive index testing oils (Falandyz, 1998); then, they were gradually replaced by polychlorinated biphenyls (PCBs) after incidents of worker-related toxicity (Harner et al., 2000). Although the usage of PCNs has declined in the past few decades, these formulations have still been frequently detected in the environment as a result of incomplete prohibition in most countries (Harner et al., 2000; Kannan et al., 1998). Additionally, it has been revealed that PCNs can be unintentionally formed and released through thermal processes, such as municipal waste incineration and nonferrous metallurgy process (Jansson et al., 2008; Oh et al., 2007). A latest study has reported that secondary nonferrous metallurgical facilities in China are a bigger contributor than the waste combustion of PCNs at present (Ba et al., 2010; Pan et al., 2011). Recent studies have also shown that PCN levels are comparable to dioxin-like PCB levels, even higher in some mediums (Kannan et al., 2001; Kannan et al., 1998; Lee et al., 2007; S. Li et al., 2017; Zhao et al., 2011).

Data on PCN recovery from sediment cores, for example, as those collected in Tokyo Bay, Japan (Yamashita et al., 2000), Esthwaite

Water in northwest England (Gevao et al., 2000; Lundgren et al., 2003), and Kempenfelt Bay of Lake Simcoe (Helm et al., 2011), have begun to decrease in the past few decades. However, in China, there are about 52–7300 kg PCNs discharged as byproducts of in the PCB production process per year because of the unintentional production to a large extent (Zhang et al., 2015b). To date, only limited research has indicated that PCN levels in sediments and air of China are at a relatively higher level than those found worldwide (Lee et al., 2007; Lundgren et al., 2003; Pan et al., 2007). Accordingly, it is still necessary to study their pollution levels and corresponding ecological risks in China (Q. Li et al., 2017). Unfortunately, there are only very few data of PCNs in China, especially in the coastal regions, where large cities and industrial parks are concentrated (Pan et al., 2011).

The East China Sea (ECS), one of the largest continental shelves in the world, is a river-dominated shelf sea. The coast of the ECS is one of the most developed regions in China. The ECS serves as the receptor of the pollutants carried through riverine discharges and the Asian continental outflow atmospheric deposition (Chu et al., 2009; Hu et al., 2011; Liu et al., 2007). Owing to the high nutrient inputs, there is high marine primary productivity and thus abundant fishery resources in this region (Fan et al., 2014). Organic pollutants including PCNs ingested through seafood consumption would be the major pathway for the exposure of residents (Fan et al., 2014; Wang et al., 2011). Owing to the bioaccumulation of PCNs from sediments to marine organisms (Wang et al., 2012a), more attention should be paid to the occurrence

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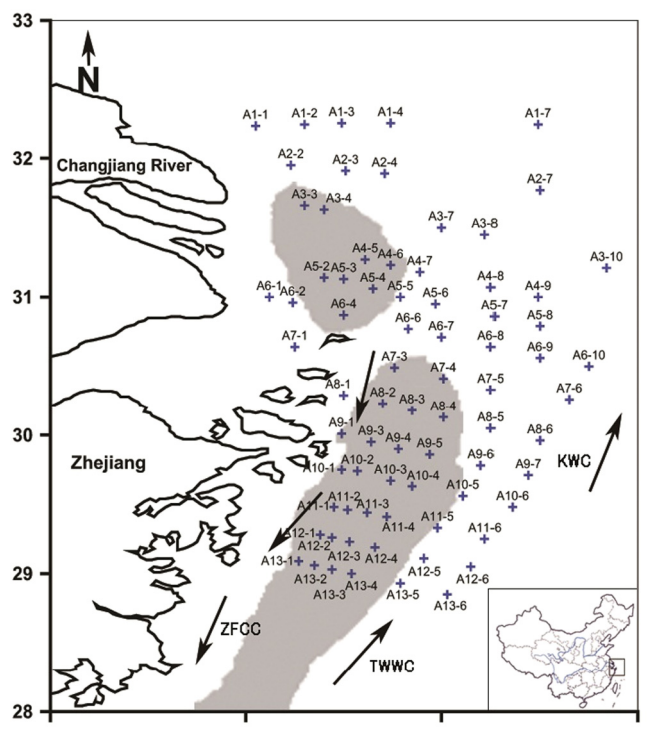


Fig. 1. Map of the sampling sites for the surface sediments in the ECS.

and distribution of PCNs in the ECS. However, only very few data of PCNs in the ECS have been reported till now.

In this study, seventy-five surface sediment samples from the ECS were collected and analyzed by high-resolution mass spectrometry (HRMS). The purpose was to reveal the pollution levels and spatial distribution of PCNs, to clarify the PCN analogs in this sea region, evaluate the ecological risks, and then provide information for regulating PCN discharge.

Seventy-five surface sediment samples (depth: 0–3 cm) were collected from the coast to the out shelf of the ECS during the cruise in March 2014 using a stainless steel box-corer (40 cm × 60 cm × 50 cm) from the R/V Runjiang 1. The location of sampling sites is shown in Fig. 1. All the samples were freeze-dried, homogenized, and sieved through a stainless steel 75-mesh (0.5 mm) sieve and stored at  $-20^{\circ}\text{C}$  until analysis.

ZFCC: Zhejiang-Fujian Coastal Current; TWWC: Taiwan Warm Current; KWC: Kuroshio Warm Current. Mud areas are marked in gray.

Approximately 10 g aliquot of a sediment sample was mixed with 10 g of diatomaceous earth and 5 g of activated copper powder (to remove elemental sulfur). Before extraction, two internal standard solutions, ECN-5102 (containing 10 ng each of  $^{13}\text{C}_{10}$ -labeled CN-27, CN-42, CN-52, CN-67, CN-73, and CN-75) and DLM-2005-S (containing 10 ng of hepta-deuterated CN-2), supplied by Cambridge Isotope Laboratories (Andover, MA, USA) were added to the samples. The mixture was extracted using an accelerated solvent extraction system (ASE 300; Dionex, Sunnyvale, CA, USA). The extract was concentrated with a rotary evaporator and then cleaned using a combination silica column filled with  $\text{Na}_2\text{SO}_4$  (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 with hexane as eluent. Finally, the extract was concentrated to approximately 200  $\mu\text{L}$ . After that, an injection standard (ECN-5260, containing 20 ng of  $^{13}\text{C}_{10}$ -labeled CN-64; Cambridge Isotope Laboratories) was added to the concentrated solution for further analysis.

The PCNs were identified and quantified using a gas chromatograph coupled with an HRMS, Agilent 7200 GC-Q-TOF-MS (Agilent

Technologies, Santa Clara, USA) equipped with an electron impact (EI) ion source. A DB-5MS column (30-m length, 0.25-mm i.d., 0.25- $\mu\text{m}$  film thickness; Agilent Technologies) was used for separation. Helium was used as carrier gas at a constant flow rate of 1.0 mL/min. The injection volume was 1.0  $\mu\text{L}$ . The GC oven temperature program began with 1 min, and the initial temperature was held at  $60^{\circ}\text{C}$  followed by increasing it to  $120^{\circ}\text{C}$  at  $40^{\circ}\text{C}/\text{min}$  and then to  $310^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$ . The following PCN congeners were analyzed in all the samples: Mono-CN: CN-2; Di-CN: CN-5, CN-6, CN-3, CN-9; Tri-CN: CN-13; tetra-CN: CN-42, CN-36/28, CN-27, CN-48, CN-46, CN-31; penta-CN: CN-52, CN-50, CN-53/54; hexa-CN: CN-66/67, CN-68/72, CN-69/70; hepta-CN: CN-73; and octa-CN: CN-75.

To achieve high standards of quality control and quality assurance, the entire analysis process was monitored. A laboratory blank (anhydrous sodium sulfate) and a surrogate spiking blank sample were treated with each batch (10 samples) of samples to avoid cross-contamination. The method detection limits ranged from 0.0002 to 0.002 ng/g d.w. Mean recoveries of the  $^{13}\text{C}_{10}$ -labeled PCNs in the real sediment samples ranged from 60% to 105%.

PCNs were detected in all the surface sediment samples, and the PCN contents ranged from below detection limit to 261.71 ng/g d.w., with a mean value of  $77.63 \pm 59.14$  ng/g d.w. Comparison of PCN contents in surface sediments was made between the ECS and other regions from China and other developed countries (Table 1). The results indicated that monitoring environmental PCN levels and controlling its discharge in the ECS remains an urgent issue.

PCNs presented a seaward decreasing trend (Fig. 2), with the highest values in the Changjiang Estuary and Subei Shoal (site A2-3, 261.71 ng/g d.w.; site A5-2, 258.34 ng/g d.w., and site A5-3, 213.67 ng/g d.w.), and the second highest values were found in the Zhejiang-Fujian mud area (inner shelf of the ECS) (site A12-2 and A13-3, 209.48 ng/g d.w. and 209.97 ng/g d.w., respectively). The characteristic of spatial distribution of PCN is consistent with those of many other pollutants that enter the sea, such as PCBs, DDTs, and HCH (Hu et al., 2011; Liu et al., 2017); this suggests that sedimental PCNs in the Changjiang Estuary were mainly from the riverine input of Changjiang River, and sedimental PCNs in the inner shelf of the ECS were from the coastal direct discharge to a large extent (Zhang et al., 2015b). Similar to other organic pollutants, PCNs are prone to be bound onto fine particles, then transport, and deposit onto surface sediments (Cailleaud et al., 2009; Zhao et al., 2011). It has been revealed that these sites with high contents of PCNs are rich in fine particles and organic matters (Liu et al., 2017). Therein, PCNs showed a seaward decreasing trend with high values in the estuary and coastal region, regardless of whether they resulted from riverine input or atmospheric deposition. However, it should be noted that PCN contents ( $34.85 \pm 29.75$  ng/g d.w.) near Zhoushan Islands were at a relatively low level compared with those at other coastal sites. The abnormal data may be attributed to the natural barrier of islands and the large difference in the distance between samples and these islands. Additionally, this area is far from the

Table 1

PCN contents in the surface sediments from China and other developed countries.

Locations	PCN contents (ng/g d.w.)	References
The ECS	Below detection limit - 261.7	Our study
Daliao River Estuary	0.03–0.3	Zhao et al., 2011
Qingdao coastal sea	0.2–1.2	Pan et al., 2007
Baltic Sea	0.6–7.6	Falandysz et al., 1996; Järnberg et al., 1999
Swedish west coast (Kattegat)	0.6	Järnberg et al., 1999
Venice and Orbetello lagoons in Italy	0.03–1.5	Eljarrat et al., 1999; Lundgren et al., 2003

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