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Concentrations and trophic magnification of polychlorinated naphthalenes (PCNs) in marine fish from the Bohai coastal area, China☆

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ABSTRACT

Polychlorinated naphthalenes (PCNs) have been found widely in the aquatic environment and can be transferred through food chains, which can magnify or dilute their toxic effects on humans. In this study, PCNs were analyzed in samples of 17 species of fish with different dietary habits collected in the Bohai coastal area in China. Dichloronaphthalenes, which have rarely been quantified in previous studies, were determined. The total PCN concentrations were from 7.3 to 214 pg/g wet weight, and the highest concentration was found in ditrema. The trichloronaphthalenes were the most abundant PCNs, followed by the dichloronaphthalenes and pentachloronaphthalenes. The relatively high contributions of the less-chlorinated homologs to the total PCN concentrations indicated that the main PCN sources around the Bohai were industrial thermal process emissions rather than technical PCN formulations. The trophic magnification factors of the PCN homologs were from 3.1 to 9.9, indicating that PCNs were biomagnified by fish. The trophic magnification factor of dichloronaphthalene and trichloronaphthalenes was 5.8 and 6.4, respectively, indicating for the first time that dichloronaphthalene and trichloronaphthalenes can undergo trophic magnification by fish. The two highest trophic magnification factors were for the pentachloronaphthalenes and hexachloronaphthalenes, probably because these PCNs having fewer vicinal carbon atoms without chlorine atoms attached are less easily biotransformed than the other homologs. The dioxin-like toxicities of the PCNs in the samples, expressed as potential toxic equivalences (TEQs), were assessed. The highest total TEQ was 0.0090 pg/g ww, in Pacific herring, and the hexachloronaphthalenes were the dominant contributors to the total TEQs in the fish samples. The PCN TEQs were much lower than the polychlorinated dibenzo-*p*-dioxin and dibenzofuran and dioxin-like polychlorinated biphenyl TEQs found in fish from the Bohai in previous studies, and made marginal contributions to overall human exposure to dioxin-like TEQs, suggesting that PCNs pose no toxicological concerns.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of compounds containing between one and eight chlorine atoms per naphthalene molecule. There are 75 PCN congeners. PCNs have been found to be toxic, bioaccumulative, and environmentally persistent (Fernandes et al., 2010). PCNs were mostly produced from the 1930s to the 1980s (Falandysz, 2003), and it has been roughly estimated that a total of 150,000 t were produced globally so far (Falandysz, 1998). There are data available from the member countries of the United Nations Economic Commission for Europe, but data on the production and use of PCNs in other countries are very scarce (Falandysz and Szymczyk, 2001; UNEP, 2012). China has never produced technical PCNs formulations, except for some small-scale

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production of octachloronaphthalene for research purposes (Hogarh et al., 2012). It is generally accepted that intentional production of PCNs has ceased except for some illicit manufacture. For example, some stockpiled PCN formulations and raw rubber contaminated with PCNs were illegally imported from the United Kingdom and Canada and used in Japan around the year 2000 (Falandysz et al., 2008; Yamashita et al., 2003). Some PCNs have planar structures and physicochemical properties similar to dioxins and dioxin-like polychlorinated biphenyls (PCBs), and can cause "dioxin-like" toxic effects (Falandysz et al., 2001; Hayward, 1998). They cause a range of toxic responses, including mortality, embryotoxicity, hepatotoxicity, immunotoxicity, dermal lesions, teratogenicity, and carcinogenicity, through mechanisms mediated by the aryl hydrocarbon receptor (Blankenship et al., 2000; Engwall et al., 1994; Hanberg et al., 1990; Villeneuve et al., 2000). However, compared with the toxicities of most dioxins and dioxin-like PCBs, the relative potencies (REPs) of PCNs are much lower (Falandysz et al., 2014; Van den Berg et al., 2006). PCNs were widely used as dielectrics, but they were also used as engine oil additives, in cable insulation, and in wood preservatives, as were PCBs. However, PCNs were not included in the Stockholm Convention Annexes A and C until 2015, 41 y after PCBs (Fernandes et al., 2017). Unintentional PCN emissions during the incineration of waste and industrial thermal processes are currently considered to be the main sources of PCNs to the environment (Lee et al., 2007; Liu and Zheng, 2013; Van der Gon et al., 2007).

PCNs have been detected in many environmental compartments, including air, soil, water, and sediments. They have also been found in aquatic organisms. However, limited studies have investigated their effects. Fish play important roles in aquatic systems and occupy a wide range of trophic levels in food chains. PCNs accumulated in fish indicate not only environmental pollution but also pollutant transfer through the food chain (Cui et al., 2015). Trophic magnification has been investigated less for PCNs than for other POPs like PCBs, and limited information on the trophic magnification of PCNs is available. Previous studies have investigated the biomagnification factors (BMFs) of tetra-CNs to hepta-CNs between predator and prey, and the trophic magnification factors (TMFs) of tetra-CNs to hepta-CNs in marine food chains (Evenset et al., 2005; Falandysz and Rappe, 1996; Falandysz et al., 1996a, 1997a, 1997b; Hanari et al., 2004; Helm et al., 2008; Lundgren et al., 2002; Nfon et al., 2008). The biomagnification potentials of some congeners, in most cases including the hexa-CNs, have been determined. However, monitoring data for di-CNs and biomagnification data for di-CNs, tri-CNs, and octa-CN in organisms are not readily available, even though these compounds are persistent and bioaccumulative pollutants that are included in the Stockholm Convention (Environment Canada, 2011). There is a clear lack of information on trophic magnification of di-CNs, tri-CNs, and octa-CN in fish, and our understanding of the biomagnification of other PCN homologs needs to be improved. Additionally, as mentioned in a review published by Fernandes et al., fish are important sources of protein and omega-3 polyunsaturated fatty acids to humans but have been found to contain PCNs at concentrations orders of magnitude higher than the concentrations found in other foods (Fernandes et al., 2017; Hu et al., 2003). It is clear that fish make important contributions to PCN intakes by humans, particularly those living in coastal regions.

In this study, we systematically analyzed PCNs in marine fish of different trophic levels from a coastal area in the Bohai Rim Region, a typical industrial zone in China. The objectives were (1) to acquire data on PCN concentrations in fish to provide reference data for environmental monitoring studies, (2) to investigate the trophic magnification of PCNs in fish to improve our understanding of the trophodynamics of PCNs, and (3) to estimate the toxic potentials of PCNs to allow effective health risk assessments to be performed and effective environmental management decisions to be made.

2. Methods and materials

2.1. Study area and sample collection

The Bohai, in China, is a semi-enclosed shallow marginal sea with an area of about 77,284 km^2 and a coastline of nearly 3800 km (Zhang et al., 2009). It is surrounded by several metropolises, including Beijing, Tianjin, Dalian, and Qingdao, which together form one of the three most densely populated and industrialized areas in China (Yang et al., 2012). The area around the Bohai has undergone rapid industrialization and urbanization, and the population has increased dramatically, and these changes have led to various land-based pollutants being discharged into the sea and posing great threats to the marine environment (Liu et al., 2007). Pollutants tend to remain in the Bohai for a relatively long time and for even longer in fish. The Bohai is one of the most polluted sea areas in China (Meng et al., 2017).

A total of 122 fish belonging to 17 different species were collected from the Dalian coastal area in May 2014. The fish species were Pacific cod (*Gadus macrocephalus*), bluefin leatherjacket (*Thamnaconus septentrionalis*), big head croaker (*Collichthys lucidus*), blackmouth angler (*Lophiomus setigerus*), southern flounder (*Paralichthys lethostigma*), bastard halibut (*Paralichthys olivaceus*), ditrema (*Ditrema temminckii*), shishamo (*Spirinchus lanceolatus*), largehead hairtail (*Trichiurus lepturus*), small yellow croaker (*Larimichthys polyactis*), large yellow croaker (*Larimichthys crocea*), Pacific saury (*Cololabis saira*), Japanese halfbeak (*Hyporhamphus sajori*), South American pilchard (*Sardinops sagax*), Pacific herring (*Clupea pallasii*), Japanese Spanish mackerel (*Scomberomorus niphonius*), and Japanese seabass (*Lateolabrax japonicus*). The biometric and biological characteristics of the fish are shown in Table S1. The fish species are all commonly eaten by local residents. The different fish species have different dietary habits, making the range of species suitable for investigating the trophic magnification of pollutants (Zhou et al., 2016). After being collected, the samples were stored in an ice chest and transported to the laboratory. In the laboratory, the skin was removed from each fish, and the dorsal muscle tissue was removed for analysis. The muscle tissue was freeze-dried, pulverized, and stored in an amber glass bottle at −20 °C until it was extracted. The water content of the muscle tissue was determined by measuring weight loss during the freeze-drying process.

2.2. Determination of PCNs and lipids

The solvents used, including dichloromethane and *n*-hexane, were of HPLC grade (Fisher Scientific, Fair Lawn, NJ, USA). Native standards of 20 PCN congeners (CN-2, CN-6, CN-13, CN-27, CN-28, CN-36, CN-42, CN-46, CN-48, CN-50, CN-52, CN-53, CN-54, CN-66, CN-67, CN-69, CN-70, CN-72, CN-73, and CN-75) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and Wellington Laboratories (Guelph, Canada). $^{13}C_{10}$ isotope-labeled PCN standards (ECN-5102, containing CN-27, CN-42, CN-52, CN-67, CN-73, and CN-75, used as internal standards, and ECN-5260, containing CN-64, used as an injection standard) were acquired from Cambridge Isotope Laboratories.

A 10 g aliquot of a sample was spiked with 1 ng internal standard (ECN-5102) and the sample was allowed to equilibrate for at least 2 h. The sample was then extracted with a 1:1 mixture of dichloromethane and *n*-hexane in an ASE 350 extraction unit (Dionex, Sunnyvale, CA, USA) using the parameters described previously (Xia et al., 2016). The extract was rotary evaporated to a