Science of the Total Environment 539 (2016) 460–469

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Characteristics of the alkylphenol and bisphenol A distributions in marine organisms and implications for human health: A case study of the East China Sea

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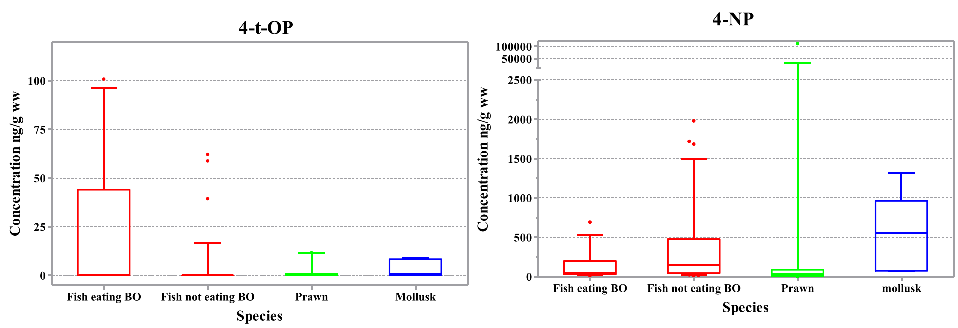
HIGHLIGHTS

- 183 wild samples of marine fish, prawns and molluscs were analysed;
- Significant pollution was observed in cities of Taizhou, Shanghai and Ningbo;
- Species-specific distribution was related to living patterns and trophic transfer;
- Linear alkylphenols showed trophic magnification whereas not for branched ones;
- 4-nonylphenol showed strikingly high values of hazard quotients (0.079 to 0.23).

GRAPHICAL ABSTRACT



Concentrations of 4-tert-octylphenol (4-t-OP) and 4-nonylphenol (4-NP) in biota samples. Biota species include fish species eating and not eating benthic organism (BO), prawns and mollusks. Each box represents 10th and 90th percentile ranges of concentration.

ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 1 September 2015
Accepted 3 September 2015
Available online xxxx

Editor: Adrian Covaci

Keywords:
Endocrine disrupting chemical
Species-specific distribution
Marine organisms
Yangtze River Delta
Human health

ABSTRACT

The distributions of alkylphenol (AP) and bisphenol A (BPA) in marine organisms, including fish, prawns and molluscs, could reflect the exposure of AP and BPA directly and effectively. This paper provides the first report on the species-dependent distribution and the human health risks of four APs (4-t-octylphenol, 4-t-OP; 4-octylphenol, 4-OP;4-nonylphenol, 4-NP; 4-n-nonylphenol, 4-n-NP) and BPA in 95 wild and 88 processed marine biota samples from the East China Sea of the Yangtze River Delta area. 4-NP was the predominant compound with the highest detected concentration of 19,890.50 ng/g ww. Significant pollution was observed in Taizhou, Shanghai and Ningbo. The species-dependent distribution was related to food habits, living patterns and trophic transfer. Higher residual concentrations of 4-t-OP, 4-OP, 4-n-NP and BPA were observed in fish species that consumed benthic organisms or demersal fish species, whereas 4-NP showed different results due to trophic dilution. The trophic magnification factors (TMFs) of the linear APs (4-OP and 4-n-NP) (1.22–2.93) were higher than those of the branched ones (4-t-OP and 4-NP) (0.72–0.90), indicating the relative metabolism stability of linear APs. 4-NP has the lowest TMF value of 0.72, and its trophic dilution might be observed because the branched carbon chain exhibits the lowest dispersion force compared to

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http://dx.doi.org/10.1016/j.scitotenv.2015.09.011

that of the other APs. As for the health risk, 7-year old children may be exposed to the highest health risk of 4-NP with 95th percentile values of the hazard quotient of 0.22 to 0.23; however, the risks of the other chemicals were relatively low.

1. Introduction

Alkylphenolethoxylates (APEs) are used widely as detergents, emulsifiers, solubilizers, wetting agents and dispersants, of which nonylphenolpolyethoxylates (NPEs) and octylphenolpolyethoxylates (OPEs) account for approximately 80% and 20%, respectively. Nonylphenol (NP) and octylphenol (OP) are the primary metabolites of APEs in sewage treatment plants or in the environment (Ying et al., 2002; David et al., 2009). Bisphenol A (BPA) has been widely used as an additive in a variety of products, including plastics (as a polymer, i.e., polycarbonate plastic), PVC, food packaging, dental sealants and thermal receipts (Rochester, 2013; Ehrlich et al., 2014; Peretz et al., 2014). Research indicated that alkylphenols (APs, e.g., NP, OP) and BPA cannot be completely removed in waste water treatment plants (WWTPs) (Zhang et al., 2011) and thus are reported to be ubiquitous in aquatic environments, with detected concentrations at the ng/L to μg/L level being observed. However, these chemicals are endocrine disrupting chemicals (EDCs), which may cause reproductive, teratogenic and developmental toxicities, even at low concentrations (Soares et al., 2008; Peretz et al., 2014).

APs and BPA have been detected widely in marine and fresh water, sediment and foodstuffs around the world (Ying et al., 2002; Soares et al., 2008; Niu et al., 2015). Many studies have indicated that APs and BPA might accumulate in an environment matrix (e.g., sediment and biota), even at low water concentrations (Ying et al., 2002; Soares et al., 2008; Mortazavi et al., 2013; Staniszewska et al., 2014). Ying et al. (2002) reviewed that high levels of NP (<0.1–13,700 μg/kg) and OP (<LOD–670 μg/kg) were observed in sediment. Sediment may allow for the transport and deposition of many EDCs at long distances from many inland sources (Writer et al., 2011), thereby exposing aquatic organisms to contamination and toxic effects. Many studies showed that the residues in marine biota (e.g., fish, prawn and mollusc) were higher than those in sediment samples. Diehl et al. (2012) found that levels of 4-NP in marine biota samples were an order of magnitude higher than in the sediment. Casatta et al. (2015) demonstrated that the concentrations of NP, OP and BPA in clams were also higher than those in sediment. However, the occurrence of APs and BPA in marine organisms (fish, prawn and mollusc) has been reported in only a limited number of studies (David et al., 2009; Diehl et al., 2012; Staniszewska et al., 2014; Casatta et al., 2015; Lee et al., 2015). Additionally, the mechanisms of the species-specific distributions have not been thoroughly elucidated.

The oral intake of APs and BPA by humans might be significant, e.g., via seafood, water supply, and food contaminated through leaching packaging. Niu et al. (2015) concluded the mean exposure to BPA and NP with estimated daily intakes (EDIs) of 43 ng/kg bw/day and 520 ng/kg bw/day for Chinese adults, respectively, from the 2007 Chinese total diet study (TDS). Wei et al. (2011) assessed the risks with the estimated BPA intakes of 110 $ng \cdot d^{-1}$ for marine fish and 220 $ng \cdot d^{-1}$ for freshwater fish in the Pearl River Delta, China. The Yangtze River Delta, bounded on the East China Sea, is one of the most important areas of China with a dense population and active industry, which might result in serious AP and BPA pollution and pose potential health risks to residents in this area due to seafood consumption. However, to date, no studies have addressed the issue of AP and BPA exposure in this area.

This study aimed to investigate the AP and BPA distributions in wild marine biota (fish, prawn and mollusc) from the Yangtze River Delta Area, as bounded by the East China Sea. The mechanisms of the species-specific distribution was determined by investigating food habits, living patterns and trophic transfer. Next, the human health risk of these chemicals via seafood consumption to different age groups was assessed.

2. Materials and methods

2.1. Study area and sampling sites

As shown in Fig. 1, the East China Sea, which is part of the Pacific Ocean, covers an area of approximately 1,249,000 km^2. This sea opens in the north to the Yellow Sea, is bounded on the south by the South China Sea, and connects with the Sea of Japan. The Yangtze River is the largest river flowing into the East China Sea. The Yangtze River Delta of China, comprising the triangle-shaped territory of Shanghai, Jiangsu province and Zhejiang province, is one of the most important coastal regions of the East China Sea. This area lies at the heart of the eastern coastal regions of China and is regarded as the most important business centre by the Chinese government. The Yangtze River Delta may have the largest concentration of adjacent metropolitan areas in the world, as it covers an area of 99,600 km^2 and has a population over 140 million people (Rapoza, 2014). In addition, Shanghai was named the largest port in the world according to the report of the Forbes Chinese network (Rapoza, 2014). There might be pollution in this marine area resulting from the frequent human activities. Research in this area has gained prominence in recent years.

The marine biota samples in this study were collected during June 2013 to December 2013 from eight coastal cities (Yangtze River Delta area) of the East China Sea (Fig. 1). The wild samples, including 64 fish samples (18 species), 23 prawn samples (2 species) and 8 mollusc samples (3 species), were randomly caught in the East China Sea. Details of the wild marine samples, including common names, scientific names, mean length, trophic levels, living patterns, and feeding habits, are shown in Table S1 in the Supplementary material. The processed samples, including 12 fish fillet samples, 9 minced fillet samples, 12 canned fish samples, 3 processed squid samples, and 52 shelled fresh shrimp samples, were obtained from local factories. These processed samples were all wild processed seafood. All samples were wrapped in solvent-rinsed aluminium foil. The samples were placed on ice in the field and frozen at −80 °C in the lab prior to analysis. The edible tissues of the seafood samples were measured in this study. Each fish was considered as one sample, whereas prawn and mollusc samples were pooled to obtain samples of 5–10 g.

2.2. Sample preparation and analysis

The five compounds investigated in the present study were 4-tert-octylphenol (4-t-OP) (CAS: 140-66-9, branched compound), 4-octylphenol (4-OP) (CAS: 1806-26-4, liner compound), 4-nonylphenol (4-NP) (CAS: 84,852-15-3, branched mixed isomers), 4-n-nonylphenol (4-n-NP) (CAS: 104-40-5, liner compound), and bisphenol A (BPA) (CAS: 80–05–7). The structures and loK_{OW} of the compounds are shown in Table S2. The target compounds in the biota samples were analysed following our previous method (Gu et al., 2014). Briefly, fish muscle, shrimp and shellfish tissues were ultrasonically extracted with acetonitrile and were purified with a primary secondary amine SPE cartridge. APs and BPA were analysed by liquid chromatography coupled with a triple-stage quadrupole mass spectrometer (LC–MS/MS). The recoveries were in the range