Science of the Total Environment 640–641 (2018) 264–272

Contents lists available at ScienceDirect

Science of the Total Environment

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

Polycyclic aromatic hydrocarbons in sediments and marine organisms: Implications of anthropogenic effects on the coastal environment

Runxia Sun [a,b], Yue Sun [c], Qing X. Li [d], Xiaobo Zheng [e,*], Xiaojun Luo [b], Bixian Mai [b]

[a] School of Marine Sciences, Nanjing University of Information Science and Technology, Nanjing 210044, China
[b] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[c] School of Pharmacy, Fudan University, Shanghai 200433, China
[d] Department of Molecular Biosciences and Bioengineering, University of Hawaii at Manoa, 1955 East-West Road, Honolulu, HI 96822, USA
[e] College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, China

HIGHLIGHTS

- The highest PAH concentration was found in the site near the estuary.
- Fish exhibited lower lipid weight normalized PAH levels than invertebrates.
- Pyrolytic source was increasingly important in the study area.
- Seafood consumption may induce health risks to human.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 3 March 2018
Received in revised form 8 May 2018
Accepted 25 May 2018
Available online xxxx

Editor: Yolanda Picó

Keywords:
PAHs
Sediments
Seafoods
The coastal environment
Anthropogenic activities

ABSTRACT

Intensive human activities aggravate environmental pollution, particularly in the coastal environment. Sixteen priority polycyclic aromatic hydrocarbons (PAHs) were determined in the sediments and marine species from Zhanjiang Harbor, a large harbor in China. The total PAH concentrations ranged from 151 to 453 ng/g dry weight (dw) in sediments and from 86.7 to 256 ng/g wet weight (ww) in organism tissues. High levels of PAHs occurred in the sample sites next to the estuary. A decrease in PAH levels was observed in comparison to the previous survey prior to 2012. Fish exhibited lower lipid weight normalized PAH concentrations than the other species, which may be related to their efficient metabolic transformation. Three ring PAHs dominated both in marine sediments and species, but low molecular weight PAHs exhibited higher proportions in biota than in sediments ($p < 0.05$). Petrogenic and pyrolytic sources both contributed to the occurrence of PAHs, and the latter became increasingly important in the study area. The ecological risk from PAHs in the sediments was relatively low (9% incidence of adverse biological effect) according to the effects-based sediment quality guideline values. Exposure to PAHs via consuming seafoods might pose a health risk to local residents. Overall, these results revealed anthropogenic activities in the coastal area have an impact on the local ecosystem.

1. Introduction

PAHs are a group of lipophilic organic compounds with a fused ring structure of two or more benzene rings. They are produced from

* Corresponding author.
E-mail address: zhengxiaobo@scau.edu.cn (X. Zheng).

https://doi.org/10.1016/j.scitotenv.2018.05.320
0048-9697/

incomplete combustion or pyrolysis of organic materials and natural diagenesis. PAHs are highly mobile in the environment due to their physicochemical properties, which enables them to undergo long-range transport causing global pollution. PAHs are found extensively in both biotic and abiotic matrices worldwide (Dat and Chang, 2017; Kim et al., 2013; Louvado et al., 2015; Sarria-Villa et al., 2016). Exposure to PAHs has been associated with diseases like cancer and reproductive disorders (Kim et al., 2013). The occurrence of PAHs has been getting increased attention in recent years. Due to high toxicity, carcinogenicity, teratogenicity, and mutagenicity, 16 priority pollutant PAHs have been regulated by the United Sates Environmental Protection Agency (US EPA) and European Union (EU).

PAHs can be released into the environment by natural source such as forest fires and diagenesis of organic matter. However, the majority of PAHs are emitted from anthropogenic sources including incomplete combustion of fossil fuels and petroleum leakage (Thompson et al., 2017). Intensive human activity occurs in estuaries and offshore waters, which aggravates environmental pollution by various persistent organic pollutants in those coastal waters (Hao et al., 2015). PAHs spread into the marine environment through wastewater discharge, surface runoff, marine transport, petroleum spills, and atmospheric deposition. Coastal marine sediment acts both as an effective sink and as a source for PAHs. PAHs in the marine ecosystem are inclined to bound to suspended particles and to be subsequently deposited on sediments due to their hydrophobic nature. However, PAHs in sediments can be remobilized and become bioavailable in the water body with changes in water-flow patterns and water temperature. Consequently, these contaminants are accumulated by indigenous organisms and finally have a negative impact on human beings via trophic transfer.

PAHs enter the human body through different exposure pathways. Dietary intake, especially seafood consumption is an important route of exposure to PAHs in the general population (Binelli and Provini, 2003; Martorell et al., 2010). Zhanjiang Harbor is located in Zhanjiang, China's largest seafood producing and exporting center. Zhanjiang Harbor waters are a vital natural aquatic resource in China, which has expanse of waters, large capability and strong force of tides, stable beaches and water troughs. It is famous for prominent aquaculture, abundant fishery resources, prosperous seaport transportation. Remarkably, anthropogenic activities including industrial and urban developments and marine transportation are aggravating environmental pollution and ecological degradation in this region. Higher levels of PAHs were observed in sediments from inner Zhanjiang Harbor than those from outside Zhanjiang Harbor (Huang et al., 2012). These bring concerns on adverse impacts related to bioaccumulation of PAHs and seafood contamination. However, little information is available on the occurrence of PAHs in Zhanjiang Harbor. In particular, the body burden of PAHs in marine organisms has never been reported.

The present study determined the presence of 16 priority pollutant PAHs in sediments and marine edible species (i.e., fish, crustacean, bivalve mollusc and cephalopod) from Zhanjiang Harbor. We aimed to investigate the contamination status of PAHs in sediments and marine organisms, and to identify potential source in the coastal environment under drastically increased anthropogenic activities. We evaluated the bioaccumulation in marine organisms and the potential ecological and human health risks caused by PAHs in this region.

2. Materials and methods

2.1. Sample collection

Marine sediments and organisms were collected from Zhanjiang Harbor in April 2013. Sediment samples (above 5-cm depth) were obtained with a stainless-steel grab sampler at 15 sampling sites (S1–S15) (Fig. 1). Marine organisms were sampled at six sites (S4, S5, S9, S10, S14, and S15) by using bottom trawling. All samples were stored in the insulated cooler with sufficient ice and transported to the laboratory immediately. The sediment samples were freeze-dried, and ground to pass through an 80-mesh sieve. Marine species were identified by professionals in fishery resources. The target species were selected on the basis of most common species consumed by local residents, abundance, and wide geographic distribution. The species included 12 fish (i.e., *Ilisha indica*, *Trachurus japonicus*, *Trichiurus lepturus*, *Platycephalus indicus*, *Aetoplatea zonura*, *Polynemus sextarius*, *Muraenesox cinereus*, *Saurida elongata*, *Nematalosa nasus*, *Johnius belengeri*, *Leiognathus brevirostris*, *Thryssa hamiltonii*,), 12 crustaceans (*Metapenaeopsis palmensis*, *Parapenaeopsis hardwickii*, *Penaeus penicillatus*, *Penaeus merguiensis*, *Metapenaeus affinis*, *Parapenaeopsis hungerfordi*, *Oratosquilla interrupta*, *Charybdis feriatus*, *Charybdis natator*, *Charybdis japonica*, *Scylla serrata*, *Portunus pelagicus*), 2 bivalve molluscs (*Pinctada martensi*, *Atrina pectinata*), and 2 cephalopods (*Sepia latimanus*, *Loligo duvaucelii*). Each composite biota sample was composed of 10–30 individuals of the same species from a given sampling site, irrespective of the gender. The edible parts were freeze-dried, and homogenized by a stainless-steel blender. In total, there were 15 sediments samples and 46 composite biota samples (totaling 1305 specimens for pool). Details of the samples were given in Table 1. All samples were kept at −20 °C before analysis.

2.2. Sample preparation and instrumental analysis

PAH mixed standards and internal standards were purchased from AccuStandard Company (USA). PAH analytical procedures followed those previously established (Sun et al., 2016). Briefly, sediment samples were spiked with internal standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12), and then extracted three times by sonication with 20 mL of hexane-dichloromethane (1:1, v/v) for 30 min at room temperature. Meanwhile, copper granules were added to remove elemental sulfur in the sediments. The extracts were concentrated, and purified by open column chromatography (4 cm florisil, 3 cm neutral aluminium oxide and 2 cm anhydrous sodium sulfate). The target PAHs were eluted with 50 mL hexane-dichloromethane (7:3, v/v), and finally concentrated to 300 μL. A known quantity of recovery standard (hexamethylbenzene) was added to all samples prior to the gas chromatography–mass spectrometry (GC–MS) analysis.

Biological tissue samples were ultrasonic extracted twice with 20 mL of hexane-dichloromethane (2:1, v/v) for 30 min. The internal standards similar to sediment samples were added prior to extraction. The extracts were purified with 9 M sulfuric acid, and column chromatography (3 cm florisil, 3 cm neutral aluminium oxide and a 3 cm anhydrous sodium sulfate). The clean extracts finally concentrated and fortified with recovery standard for GC–MS analysis.

Sixteen priority PAHs, i.e., naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene(Pyr), benzo[*a*]anthracene(BaA), chrysene(Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (InP), dibenzo[*a*,*h*]anthracene (DBahA), benzo[*g*,*h*,*i*]perylene (BghiP), were identified and quantified with an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass spectrometer. Gas chromatographic separation was achieved on a HP-5MS (30 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. The oven temperature program was as follows: initially isothermal 100 °C for 2 min, then increased to 210 °C at 10 °C/min, keeping for 1 min, and finally 290 °C at 5 °C/min, holding the final temperature for 5 min. Helium was used as the carrier gas with a constant flow rate of 1.3 mL/min. Extract injection (1 μL) was performed in the splitless mode, and the temperature of injector was set at 290 °C. The mass spectrometer was operated in electron impact ionization, and three ions were monitored for all PAHs. The temperature of ion source and electron ionization energy was set at 280 °C and 70 eV, respectively.

PAH analytical procedures were implemented under strict quality assurance and quality control protocols (QA/QC). Procedural blanks