Marine Pollution Bulletin xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Distribution, potential sources and ecological risks of two persistent organic pollutants in the intertidal sediment at the Shuangtaizi Estuary, Bohai Sea of China

Xiutang Yuan [a,*,1], Xiaolong Yang [b,1], Anguo Zhang [c], Xindong Ma [a], Hui Gao [a], Guangshui Na [a], Humin Zong [a], Guize Liu [a], Yongguang Sun [a]

[a] National Marine Environmental Monitoring Center, State Oceanic Administration, Dalian 116023, PR China
[b] Fisheries College, Ocean University of China, Qingdao 266100, PR China
[c] College of Fisheries and Life Science, Dalian Ocean University, Dalian 116023, PR China

ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form 24 September 2016
Accepted 27 September 2016
Available online xxxx

Keywords:
POPs
PAHs
EDCs
Shuangtaizi estuary
Intertidal sediment
Ecological risk

ABSTRACT

Spatial distribution, source apportionment, and potential ecological risks of sixteen polycyclic aromatic hydrocarbons (PAHs) and seven endocrine disrupting compounds (EDCs) in the intertidal sediment at the Shuangtaizi Estuary, Bohai Sea of China were analyzed. Results showed that the total PAH concentrations ranged from 28.79 ng g^{-1} dw to 281.97 ng g^{-1} dw (mean: 115.92 ng g^{-1} dw) and the total EDC concentrations from 0.52 ng g^{-1} dw to 126.73 ng g^{-1} dw (mean: 37.49 ng g^{-1} dw). The distribution pattern for the PAHs was generally different from that of the EDCs possibly due to their distinct sources and n-octanol-/water partition coefficients (K_{OW}). Qualitative and quantitative analytical results showed that PAH sources were mainly from a mixture of pyrogenic and petrogenic contributions. The higher levels at the southeast of Geligang indicated that the EDC pollutants may have mainly originated from the plastic industry and other chemical plants located along the Liao River. Ecological risk assessment revealed that PAHs exhibited low ecotoxicological effects, whereas EDCs, especially 4-*tert*-octylphenol and bisphenol A, had high ecological hazard to the estuarine biota.

1. Introduction

Persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs) and endocrine disrupting compounds (EDCs), in the aquatic environment have attracted much attention (Pojana et al., 2007; Soclo et al., 2000; Ying and Kookana, 2003; Zhang et al., 2012). PAHs belong to a large group of organic compounds containing two or three aromatic rings with linear, cluster, or angular arrangement (Abdollahi et al., 2013). Sixteen PAHs are listed as priority pollutants by the United States Environmental Protection Agency (US EPA) because of their carcinogenicity. Two well-defined sources of PAHs have been identified from human activities in the marine environment. Those sources are petrogenic sources, which refer to PAHs associated with spills of crude and refined oil, and pyrogenic sources, which are those produced from crude oil combustion, asphalt production, and biomass burning (Baumard et al., 1998; Elias et al., 2007). EDCs, being known as phenolic xenoestrogens, encompass a wide range of chemicals, such as bisphenol (BPA), octylphenol (OP), and nonylphenol (NP). These compounds have attracted much interest because of their significant estrogenic activity. This characteristic can cause a series of reproductive abnormalities, such as feminization and decreased fertility, and alter immune function by interfering with the normal function of exposed animals (Arditsoglou and Voutsa, 2012). NP and OP are biodegradation products of their corresponding ethoxylates, which are used as nonionic surfactants. BPA is released from polycarbonate plastics, epoxy resins, and phenoxy resins, which are utilized in food storage containers and dental sealants (Khim et al., 1999).The alkylphenols, mainly NP, OP, 4-*tert*-butylphenol (4-*t*-BP), 4-*tert*-octylphenol (4-*t*-OP), as well as BPA and 2,4-DCP, have been considered as the main EDC pollutants in the marine environment (David et al., 2009). Besides, these xenoestrogens have been detected in marine habitats around the world at considerable concentrations (Pedersen and Lindholst, 1999). PAHs and EDCs have been extensively investigated because of their delayed effects, including carcinogenicity, teratogenesis, mutagenicity, and environmental estrogenic effects (Jenssen, 2006; Fossi et al., 2007; Isobe et al., 2007; Yan et al., 2009; Zhang et al., 2012).

An estuary, which is the transitional area of interaction between land and sea, is one of the most important ecosystems (Barbier et al., 2011). This ecosystem provides numerous ecosystem services because of its high productivity. Meanwhile, it plays an important role in the retention, storage, and purification of pollutants into the sea (Gaston et al., 1998). With the rapid economic development and sea-area overexploitation, however, estuaries have been seriously threatened by intensive

* Corresponding author at: National Marine Environmental Monitoring Center, State Oceanic Administration, 42 Linghe Street, Dalian 116023, PR China.
E-mail address: xtyuan@nmemc.org.cn (X. Yuan).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.marpolbul.2016.09.058
0025-326X/

human activities, such as terrestrial urban, agricultural runoff, industrial effluents, and aquatic chemical spills. Excessive anthropogenic interference activities disturb the estuarine systems and can be widely recognized as major threats to the ecosystem health (Neto et al., 2010), thereby seriously harming the ecosystem services provided by the estuaries. PAHs and EDCs originate from various anthropogenic activities (i.e., sewage discharge from industry, petroleum spill, or combustion of fossil fuels), which also generate different characteristic patterns, leading to distinct magnitudes and distributions in the sediment (Baumard et al., 1998).

Sediments in estuarine regions provide key habitat for many macrobenthos. In addition, sediments are considered good indicators because of their sensitive characteristics to variations in anthropogenic and natural sources (Calmano et al., 1996). POPs are absorbed onto particulate matter and accumulated in the sediment based on their high hydrophobicity and molecular mass (Medeiros et al., 2005). Thus, sediments act as a main pollution reservoir (Xiao et al., 2014). Contaminated sediments would have direct or indirect harmful effects on aquatic organisms in estuarine environment (Lyman et al., 1987). Therefore, surface sediment is ideal for observing and assessing the pollutants at coastal environments (Sprovieri et al., 2007).

Shuangtaizi River, which is one of the most polluted rivers in China, has a basin area of 13, 292 km^2. This river receives a volume of pollutants, such as POPs and heavy metals, from domestic sewage inputs, industrial activities, and agricultural discharges (Liu et al., 2010). Shuangtaizi Estuary (121°30′–122°00′ E and 40°50′–41°20′ N) possesses one of the few remaining intertidal zone with mud flat, mixed flat, and sand flat, and is considered as a significant habitat for various marine organisms, especially for clams and lugworms (Zhang et al., 2013). The Shuangtaizi River divides this intertidal zone into two parts. The first zone is the Panshan Shore (PS), and the other with a fusiform shape is named Geligang (GL, meaning habitats for clam) (Fig. 1). The Shuangtaizi Estuary faces numerous pollution hazards, such as effluents from nearby oilfields (e.g., Liaohe oilfield), agriculture activity (e.g., rice planting), and aquaculture activity (e.g., crab and sea cucumber cultivation). In addition, a large-scale plastic industry and some chemical plants located in the upstream of the Shuangtaizi River emitted a considerable amount of alkylphenolpolyethoxylates including their degradation products, the alkylphenols, and BPA, to the Shuangtaizi Estuary (Qiu et al., 2015). Therefore, the estuarine biodiversity, ecosystem health, and ecosystem services (such as habitat, spawning grounds and seafood supply) have been threatened.

Understanding the environmental impacts of xenobiotics on estuaries is crucial to maintain habitat quality and ecosystem health (Barbier et al., 2011). Investigations on PAHs and EDCs in estuarine environments have been conducted worldwide (e.g., Hwang et al., 2006; Ribeiro et al., 2009; Vane et al., 2007; Wang et al., 2009). Monitoring and assessment of several pollutants (heavy metals, polychlorinated biphenyls and organochlorine pesticides) for the intertidal sediment in Shuangtaizi Estuary have been reported (Yang et al., 2015; Yuan et al., 2015). However, no studies have focused on the PAHs and EDCs, which is surprising considering that the estuary is a pollution hotspot and has the aforementioned ecological significances. The present study was performed to (i) determine the occurrence levels, composition, and sources of PAHs and EDCs in the surface sediments, (ii) explore the relationships affecting the distribution of PAHs and EDCs with sediment geochemical factors, and (iii) assess potential ecotoxicological effect of sediment-borne POPs on marine organisms. Such data and

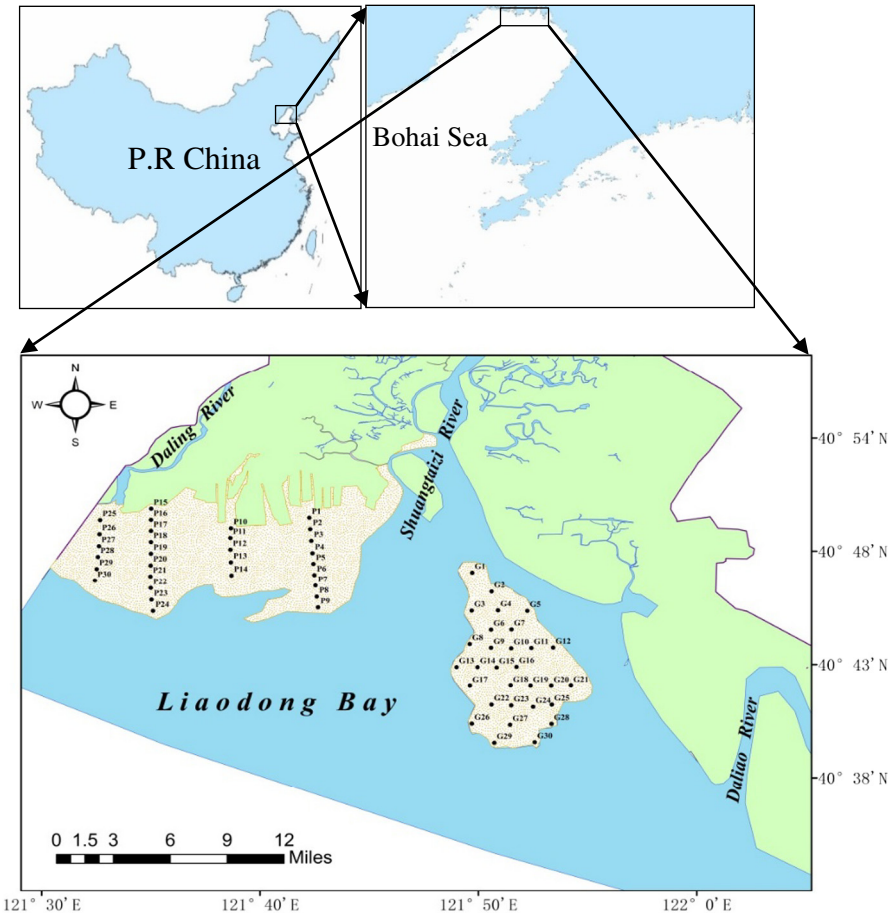

Fig. 1. Sediment sampling sites in the intertidal zone of Shuangtaizi Estuary. Area shaded in yellow are Panshan Shore (PS) and Geligang (GL, in fusiform shape). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article as: Yuan, X., et al., Distribution, potential sources and ecological risks of two persistent organic pollutants in the intertidal sediment at the Shuang..., Marine Pollution Bulletin (2016), http://dx.doi.org/10.1016/j.marpolbul.2016.09.058