Marine Pollution Bulletin 100 (2015) 507–515

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

# Environmental risk assessments and spatial variations of polycyclic aromatic hydrocarbons in surface sediments in Yangtze River Estuary, China

Wenwen Yu, Ruimin Liu *, Fei Xu, Zhenyao Shen

*State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, No. 19, Xinjiekouwai Street, Beijing 100875, China*

ARTICLE INFO

*Article history:*
Received 15 July 2015
Received in revised form 31 August 2015
Accepted 1 September 2015
Available online 12 September 2015

*Keywords:*
Polycyclic aromatic hydrocarbons
Risk assessment
Potential toxicity
Sediments
Yangtze River Estuary

ABSTRACT

In this study, based on sampling data from 30 sites in August 2010, the environmental risks associated with 16 priority PAHs were estimated in surface sediments from the Yangtze River Estuary (YRE). The results indicated that the toxic equivalent quantities of the benzo[a]pyrene ($TEQ_{Bap}$) from 30 sites were in the range of 1.93–75.88 ng $g^{-1}$, and the low-molecular-weight PAHs were the dominated species with higher potential toxicity. The results of the Incremental Lifetime Cancer Risk (ILCR) model indicated that the ILCR values of dermal contact were higher than $10^{-6}$ in the northeast region, suggesting that there were significant potential carcinogenic health risks for fishermen exposure to sedimentary PAHs via dermal contact in these areas. RQ values of PAHs indicated the various distributions of ecological risk levels in the study area. These variations might be caused by the natural and anthropogenic inputs and currents in the YRE.



Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds consisting of fused aromatic rings without a heteroatom or substituent (Liu et al., 2012; X. Wang et al., 2015; Z. Wang et al., 2015). PAHs are highly persistent, toxic and widely distributed in environment, especially in lakes, rivers, oceans and estuaries (Yang et al., 2013; Bai et al., 2014; Keshavarzifard and Zakaria, 2014). PAHs may accumulate in the organisms due to their low solubility and high octanol-water partition coefficient and undergo long-range transport (Chen et al., 2012; Liu et al., 2013). Additionally, PAHs present potential carcinogenic risks to people (Sun et al., 2012). The United States Environmental Protection Agency (US EPA) selected 16 PAHs as the priority pollutants due to their frequency and risks, and seven of them are classified as carcinogenic PAHs by the International Agency for Research on Cancer (W. Yang et al., 2014; Y. Yang et al., 2014). Four-to-six-ring PAHs are highly mutagenic and carcinogenic, while two-to-three-ring PAHs are less mutagenic but can be highly toxic (Xiao et al., 2014).

Estuary is one of special aquatic ecosystems which have been selected as the primary ecosystem resource category for study by the US EPA (Telesh, 2004). PAHs mainly enter estuary environment by direct discharges, atmospheric deposition and oil spills (Guan et al., 2009; Fathallah et al., 2012; Nilsen et al., 2015). Once PAHs enter the aquatic ecosystem, they are prone to enrichment and retain for a long time in sediments due to the ubiquity and persistence nature (Nozar et al., 2014; Spasojevic et al., 2015). Therefore, sediments play key roles in the estuarine environment to the transformation, migration and accumulation of PAHs, and to demonstrate the degree of industrial pollution of PAHs between land and sea (Hu et al., 2014). Additionally, estuaries regions are always with dense population and developed economy which increase the contaminations (Huguet et al., 2009; Ou et al., 2010). It is necessary to assess the potential adverse environmental risk of sedimentary PAHs in estuaries.

Potential carcinogenic toxicity and the ecological risk were two major assessments about PAHs. With known quantitative concentration–response relationships, toxic equivalent quantity (TEQ) for each individual PAH compound can be derived, then the sum of the equivalent concentrations of all PAHs can be used to assess the overall potential toxicity effect (Zeng et al., 2013). This method has been widely used to calculate the toxicities especially the carcinogenicities of PAHs based on the toxic equivalency factors of the benzo[a]pyrene (Bap) (Bosveld et al., 2002; Fisher et al., 2011; Yu et al., 2014; Mehdinia et al., 2015). The Incremental Lifetime Cancer Risk (ILCR) model was used to calculate the risk of residents exposed to PAH according to the Exposure Factors Handbooks, which was the further application of the TEQ (US EPA, 2002; Yu et al., 2014). To evaluate the ecological risk levels of sedimentary PAHs, various assessment methods of sedimentary PAHs have been proposed (Pongpiachan et al., 2013; Cesar et al., 2014; Maranho et al., 2015). Long et al. suggested that the parameters called the "effects range low" (ERL) and the "effects range median" (ERM) could be used to evaluate risks associated with the presence of organic pollutants (Long et al., 1995). The US National Oceanic and Atmospheric Administration provided a scientifically justifiable basis called Sediment Quality Guidelines for evaluating the potential

* Corresponding author.
*E-mail address:* liurm@bnu.edu.cn (R. Liu).

http://dx.doi.org/10.1016/j.marpolbul.2015.09.004

biological effects (Long and MacDonald, 1998). Kalf et al. proposed the risk quotient (RQ) for assessing ecological risks from organic pollutants (Kalf et al., 1997).

PAHs were not homogeneity in the sediment. The distribution of PAHs in the sediment is influenced by complex factors, such as properties of sediment (composition and structure, grain-size, etc.) and the external water environment condition (temperature, hydrodynamic conditions, etc.) (Liu et al., 2015; Zhao et al., 2015; Zhu et al., 2015). According to these factors, the concentrations and the associated risks of PAHs in sediment change spatially and temporally (El Nemr et al., 2014; Tang et al., 2015). The spatial distribution of PAHs in sediments is very important when clarifying the pollution process of aquatic systems and identifying the sources of pollutants input (Bai et al., 2014). In recent decades, many researchers have analyzed the spatial distribution of PAHs in sediments (Moreno-Gonzalez et al., 2013; Nozar et al., 2014; Li et al., 2015). However, most previous studies only focused on the assessment of the PAHs in a whole region and ignored the distribution of the risk levels, especially the risk from the individual PAH.

Based on 30 sample data in surface sediments of Yangtze River Estuary in August 2010, environmental risk assessments and spatial variations of PAHs were carried out in this study. The key objectives included the following: 1) assessed the ecological and toxicological risk levels of the sedimentary PAHs; 2) discovered the spatial variation of the risk levels with the ordinary Kriging interpolation; and 3) analyzed the factors influencing the spatial distributions.

The Yangtze River Estuary (YRE) is an important part of the Yangtze River, located in one of the most urbanized and industrialized regions in China. It deposits more than 240 Mt year$^{-1}$ fine sediments and about 26 Mt–210 Mt month$^{-1}$ kinds of pollutants carried by the Yangtze River (Wang et al., 2013; Meng et al., 2015). The Yangtze Estuary is a multi-channeled estuary with a three-level bifurcation, it is ramified into the South Branch and the North Branch by Chongming Island, and the South Branch is further divided into North Bay and South Bay by the Changxing Island (Fig. 1). At present, about 95% of the runoff water and sediment discharge is through the outlets in the South Branch (Qi et al., 2014).

The fast economic development, heavy population density, and construction of great dam on the upstream Yangtze River make the YRE a representative area affected by anthropogenic activity in Asia and even in the world (Wang et al., 2012). The concentrations of PAHs in the YRE sediments increased with serious pollutions and the environmental risks by the sedimentary PAHs also enhanced (Gu et al., 2011; Zhang and Yang, 2014; Nicolaus et al., 2015).

Thirty surface sediment samples were collected with grab sampler in August 2010. Then PAHs were extracted from the freeze-dried sediments samples. Sixteen US EPA priority PAHs were analyzed by HPLC (Dionex UltiMate 3000) with a UV and fluorescence detector for all sediment samples: naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ane), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (Baa), chrysene (Chr), benzo[b]fluoracene (Bbf), benzo[k]fluoracene (Bkf), benzo[a]pyrene (Bap), dibenzo[a,h]anthracene (Daa), benzo[g,h,i]perylene (Bgp), and indeno[1,2,3-cd]pyrene (Inp). Detail chemical analytical procedure was reported previously (Niu et al., 2003; Li et al., 2012). Strict quality control was operated in the experiment. Quantification was performed by the external standard method using a 16 PAH reference material mixture, with correlation coefficients for calibration curves all higher than 0.999. Recoveries of 16 PAHs were in the range of 75–120%, whereas the respective relative standard deviations were in the range of 5–17%. Method blanks operation showed no detectable amounts of PAHs. The low molecular weight PAHs with two-to-three ring are denoted as LWM and the high molecular weight PAHs with four-to-six ring are denoted as HWM.

In order to estimate the potential toxicity of PAHs, toxic equivalent quantity of the Bap ($TEQ_{Bap}$) was calculated based on the Bap toxic equivalency factors (TEFs). The TEFs were assigned to various individual PAHs by assuming a relative value of 1 for Bap which is considered to be one of the most potent carcinogens in the PAH

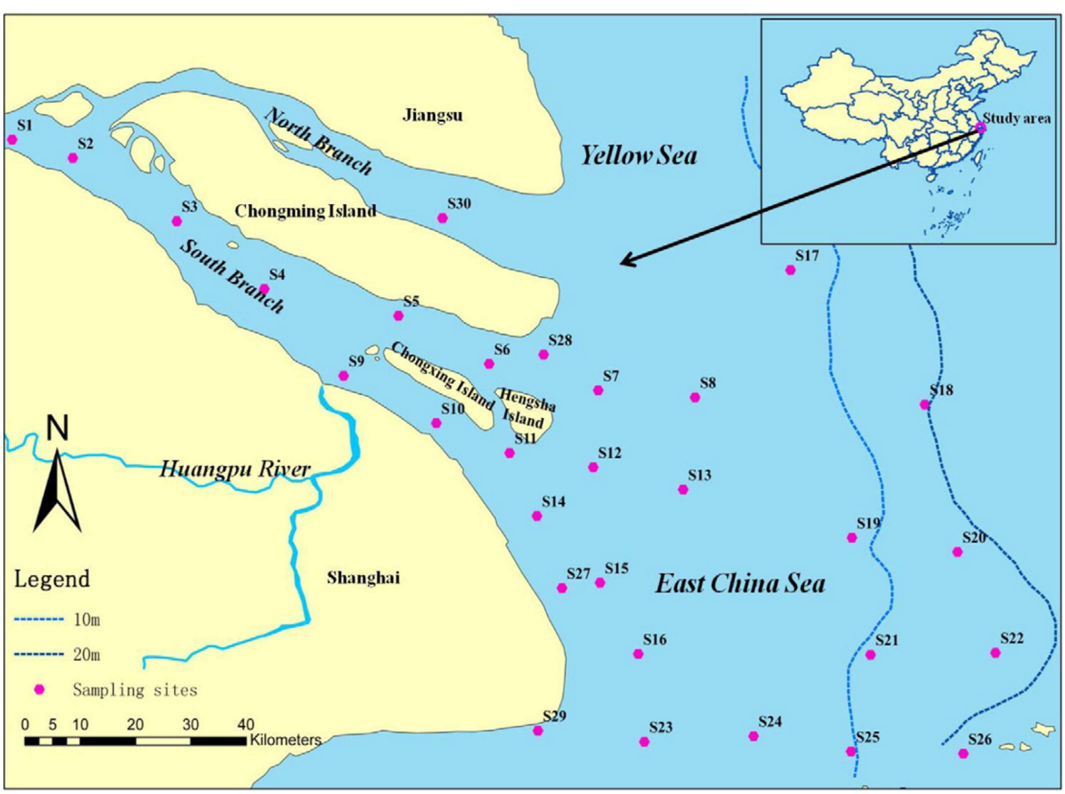


**Fig. 1.** Location of the study area and the 30 sampling sites of sediment.