



Baseline

Distribution, sources and ecological risk assessment of PAHs in surface sediments from the Luan River Estuary, China



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ABSTRACT

The distribution, sources and risk assessment of 16 polycyclic aromatic hydrocarbons (PAHs) of surface sediments in the Luan River Estuary, China, have been investigated in the research. The results indicated that the total concentrations of 16 PAHs in surface sediments of the Luan River Estuary ranged from 5.1 to 545.1 ng g⁻¹ dw with a mean value of 120.8 ng g⁻¹ dw, which is relatively low in comparison with other estuaries around the world. The PAHs in the study area were mainly originated from pyrogenic sources. Besides, PAHs may be contaminated by petrogenic PAHs as indicated by the selected ratios of PAHs, the 2-tailed Pearson correlation analysis and principal components analysis at different sites. The result of the ecological risk assessment shows little negative effect for most individual PAHs in surface sediments of the Luan River Estuary, China.

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Polycyclic aromatic hydrocarbons (PAHs), a group of two or more fused aromatic rings of carbon and hydrogen atom organic pollutants, are bioaccumulative and difficult to be degraded in the environment. (Bouloubassi et al., 2012; Bragato et al., 2012; Callén et al., 2013; Carver et al., 1986; Kaivosoja et al., 2012; Lea-Langton et al., 2013; Readman et al., 2002). Along with rapid development of the industrialization and economy, the PAHs pollution to the environment is accelerating (USEPA; WHO) which is likely to pose a threat to human health. For the reasons above, PAHs' distribution, sources and environmental risk to ecological systems have been extensively studied in the last few decades. The previous studies showed that PAHs exist in water, sediments, plants and other organisms all over the world (Chen and Chen, 2011; Deng, 2013; Guo et al., 2012; Lu et al., 2007; Wu et al., 2003). More recently, there has been an ever-increasing interest in the study of PAHs in the marine sediment, especially in the coast and estuary, which are increasingly affected by human activities. Studies of PAHs in the estuarine sediments have been carried out in several parts of China for the purpose of marine environment protection (Hu et al., 2010; Jiao et al., 2012; Li et al., 2012; Wu et al., 2003; Yuan et al., 2015). These studies, with few exceptions (He et al., 2014; Wang et al., 2015), focused only on the major large Chinese river estuaries, such as the Yangtze River, the Yellow River and the Pearl River. However, the study of sedimentary PAHs in other relatively

small estuaries of China is scarce and necessary to be carried out. That is because only a sound scientific knowledge can support an effective environmental policy.

The Luan River originates in the Mongolia Plateau, snakes through the Yan Mountains and the eastern Hebei plain, and joins the Bohai Sea at Leting County after 888 km. Luan River plays an important role in Hebei and Tianjin in terms of economic development. The environment around the river has been affected by the increasing human activities, accelerated process of industrialization and rapid evolution of the booming economy, exposed to an increasing risk of pollution from toxic chemicals. Researches on one of the important contaminants, PAHs, were mainly carried out in the Luan River or the whole Bohai Sea. (Cao et al., 2010; Hu et al., 2010; Jiao et al., 2012; Li et al., 2010, 2015). To our knowledge, little information is of the PAHs in sediments of the Luan River Estuary, which is more closely related to people. Hence, we aimed to investigate the levels, spatial distribution, and sources of PAHs in surface sediments in the Luan River Estuary. The risk assessment of PAHs was also conducted to provide scientific data for organic pollution control of the coast.

The study is focused on the sediments of the Luan River Estuary, China (Fig. 1). 24 sampling sites were collected along the estuary. Surface sediments (depth 0–5 cm) were collected from these sites using the Smith–Mcintyre grab samplers. All sediment samples analyzed in this study were packed into cleaned solvent-rinsed dark glass flasks and stored at –20 °C until chemical analysis.

(The black dots are the sampling sites that surface sediments collected from.)

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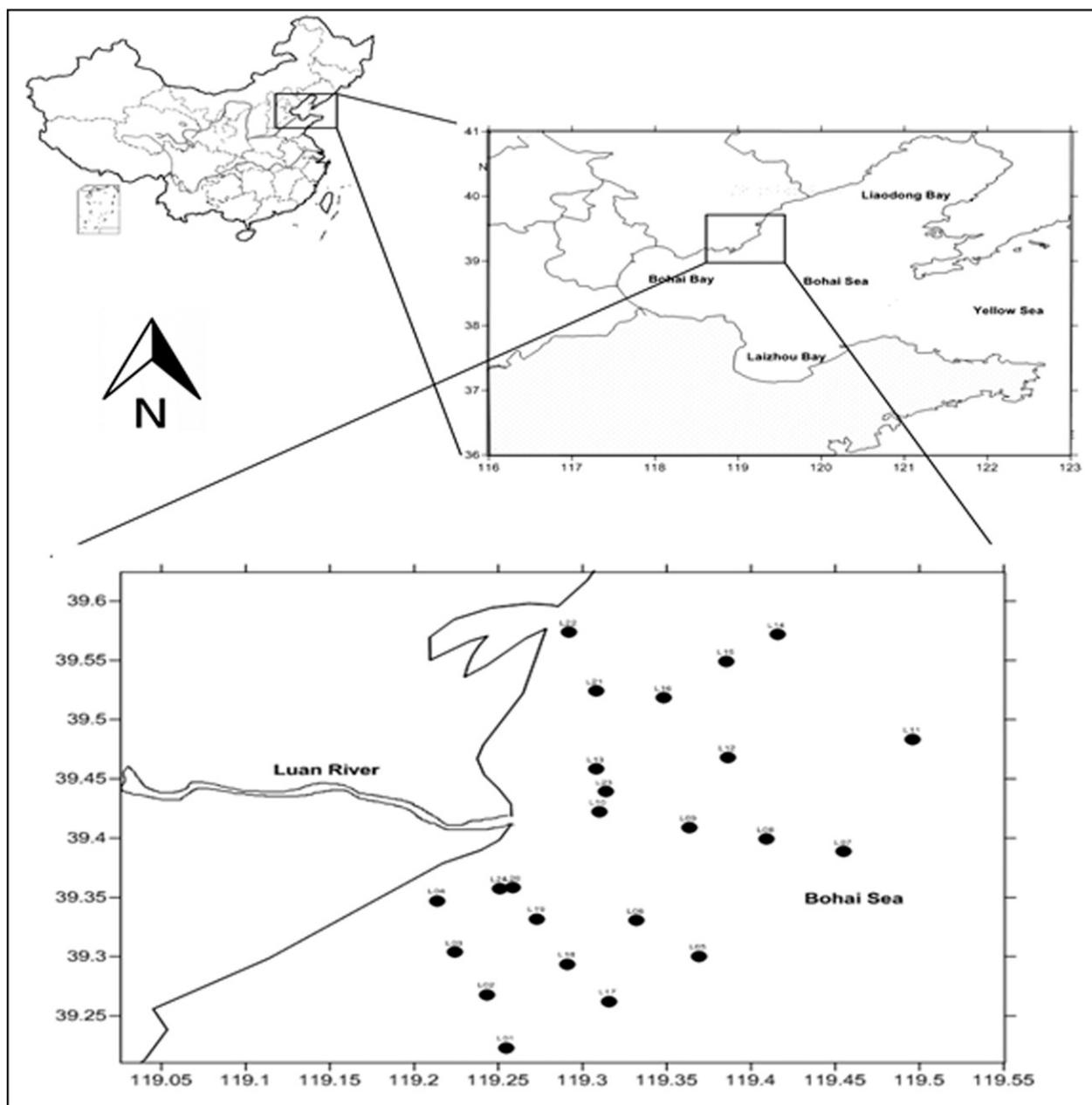


Fig. 1. Location of sampling sites in the Luan River Estuary.

For PAHs analysis, the samples were freeze-dried and ground into fine powder (<0.25 mm). Extraction of PAH samples was carried out according to the method reported by Nicola et al. (2005). 10 g sieved samples were spiked with a mixture of perdeuterated internal standards ([d-10]phenanthrene, [d-10]pyrene, [d-12]chrysene, [d-12]perylene and [d-12]benzo(g, h, i) perylene) and each were mixed with equal quantities of anhydrous sodium sulfate, in 60 mL of a mix dichloromethane: acetone (1:1, v:v) for 20 min by a sonicator, subsequently for 3 times. The extract was concentrated and solvent exchanged to n-hexane, and further reduced to approximately 1 mL under weak nitrogen flow. The achieved extract was charged to a 1:2 alumina/silica gel glass column for fractionation and clean-up. The first fraction, containing aliphatic hydrocarbons, was eluted with 15 mL of n-hexane. The second containing PAHs were collected by eluting 5 mL n-hexane and 70 mL of methylene chloride: n-hexane (30:70). The PAH fractions were concentrated to 0.4 mL under a gentle N_2 stream. Known quantities of internal standard were added to the sample prior to instrumental analysis. Consecutively, the dried residues

were dissolved in 1 mL of n-hexane. Concentrations of PAH were measured by gas chromatography (HP 5890 GC, with HP-5MS capillary column 30 m, 0.25 mm i.d., 0.25 μ m film thickness) coupled to mass spectrometry (HP 5975 mass selective detector). Helium was used as carrier gas at a constant flow rate of 1.0 mL min^{-1} . The oven temperature program started at 70 $^{\circ}C$ and increased, with ramp rate 20 $^{\circ}C$ min^{-1} , to 280 $^{\circ}C$ and held for 24 min. Quantitations were conducted using the primary ions for each compound, and two to three secondary ions were used for qualitative confirmation.

The spatial distribution patterns of PAHs in surface sediments of the Luan River Estuary are depicted in Fig. 2. The total concentration of 16 US EPA priority PAHs ranged from 5.1 to 545.1 $ng\ g^{-1}\ dw$ with a mean value of 120.8 $ng\ g^{-1}\ dw$. The highest concentration was obtained at site L13 (545.1 $ng\ g^{-1}\ dw$) followed by site L17 (392.1 $ng\ g^{-1}\ dw$), and site L3 (389.0 $ng\ g^{-1}\ dw$), while the lowest concentration was at the site L14 (5.1 $ng\ g^{-1}\ dw$) with only 3 PAH compounds. The 16 PAHs were all detected at sites L1, L2, L3, L7, L13, L15, and L17, followed by site L7, where 15 PAH compounds were detected. Lower

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