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# Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area, China

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## HIGHLIGHTS

- PAHs in three compartments from estuary were investigated simultaneously.
- SPM is the most polluted compartment in estuary, even though PAH is hydrophobic.
- Ecological risk in SPM was more serious than that in water or sediment.
- ECOTOX data on freshwater and marine species could be used together for estuarine risk assessment.

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) contamination was investigated in concurrently sampled surface water, suspended particulate matter (SPM) and sediment of Daliao River estuary and the adjacent area, China. The total concentrations of PAHs ranged from 71.12 to 4255.43 ng/L in water, from 1969.95 to 11612.21 ng/L in SPM, and from 374.84 to 11588.85 ng/g dry weight (dw) in sediment. Although the 2–3 ring PAHs were main PAH congeners in water and SPM, the 4–6 ring PAHs were also detected and their distribution was site-specific, indicating a very recent PAHs input around the area since they were hydrophobic. The PAHs pollution was identified as mixed combustion and petroleum sources. Based on species sensitivity distribution (SSD), the ecological risk in SPM from 82% stations was found to be higher obviously than that in water. The risk in water was basically ranked as medium, while the risk in SPM was ranked as high. Analysis with sediment quality guidelines (SQGs) indicated that negative eco-risk occasionally occurred in about 50% stations, while negative eco-risk frequently occurred in about 3% stations only caused by Phenanthrene(Phe) and Dibenzo(a,h)anthracene(DBA). Here freshwater acute effects data together with saltwater data were used for SSD model. And this method could quickly give the rational risk information, and achieved our objective that compared the spatial difference of risk levels among three compartments. The results confirmed that the use of freshwater acute effects data from the ECOTOX database together with saltwater effects data is acceptable for risk assessment purposes in estuary.



## 1. Introduction

PAHs are a group of persistent organic pollutants that are ubiquitous in the environment. They are generally formed by natural processes and anthropogenic activities and introduced into the environments via various routes (Durand et al., 2004; Xu et al., 2006). Due to the toxic, mutagenic and carcinogenic characteristics of aromatic compounds, 16 PAHs have been identified as the priority pollutants by the United States Environmental Protection Agency (EPA, Manoli et al., 2000). Furthermore, seven of them which include benz[a]anthrance, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indo[1,2,2-cd]pyrene, and

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dibenzo[a,h]anthracene are potentially carcinogenic to humans, according to the International Agency for Research on Cancer. Furthermore, recently four PAHs (benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene and chrysene) were determined as the most appropriate indicators for the presence of carcinogenic and genotoxic PAHs in foodstuff (Commission, 2011). Therefore, PAHs have always been of great concern, and it is very important to routinely monitor their pollution levels and to evaluate their potential toxicity in the environment.

Liaodong Bay is located in the northeast of the Bohai Sea, China, that is a nearly closed interior sea. Daliao River is one of the main rivers flowing into the Liaodong Bay. Its upper reaches included Hun, Taizi and Sancha Rivers which flowed through a lot of main industrial cities in Northeast China (e.g. Shenyang city, Benxi city, Tieling city, Liaoyang city, Anshan city). With recent rapid economic development in the past five decades, Daliao River has received the discharged water from upstream and the surrounding regions. It was estimated that about 2074 million tons of industrial and domestic wastewater had been discharged into the Daliao River catchments each year (Tan et al., 2009), and the level had been increasing. Thus Daliao River watershed, estuary and the adjacent coastal area is now experiencing serious pollution stress. In the past, many pollution investigations have been performed in the Daliao River. For example, Guo et al. (2007) investigated the spatial distribution of PAHs in Daliao River watershed; Men et al. (2009) investigated the distributions of PAHs in the Daliao River estuary; Zhao et al. (2011) investigated the pollution levels and distribution of polybrominated diphenyl ethers (PBDEs) in sediment of Daliao River estuary. The previous research in the study area only concentrated in the river watershed or the estuary, while almost no studies have been performed concurrently in the Daliao River watershed, estuary and the adjacent coastal area. Furthermore, PAHs in sediment have long been concerned because of their low water-soluble. However, in the field, the pollution in the surrounding region occurred at any moment, while the fresh water with various contaminants continually discharged into the estuary and its adjacent coastal area. The contaminants created a new redistribution at any time in the different water area, and among the different compartment (i.e. water, suspended particulate matter and sediment).

The main objective of this study was to investigate the concentration and distribution of PAHs in water, suspended particulate matter (SPM) and sediment of Daliao River estuary and the adjacent area (i.e. the upstream watershed and the coastal area), and to provide useful information on the source and potential risk of PAHs to the local ecosystem.

## 2. Materials and methods

### 2.1. Sample collections

27 stations were selected including 14 in the river zones (L1-L14) and 13 in the river mouth and the adjacent coastal areas (E1-E13) (Fig. 1). These sampling sites have covered the adjacent upstream region flowing into the estuary and the receiving coastal area, and best represented possible pollution sources so that an overall evaluation of PAHs pollution in the Daliao River estuary and the adjacent area could be performed effectively. The field sampling was carried out on Aug. 20–26, 2013. A global positioning system (GPS) was used to identify the precise location of each sampling site. At the time of sampling, the water temperature varied between 23.5 and 24.9 °C, and pH ranged from 7.2 to 8.3. The salinity in estuary and the adjacent coastal area (E1-E13) ranged from 0.2 to 23.5 psu. Surface water (0–20 cm) was collected in a clean acetone rinsed amber glass bottle with Teflon-lined cap. While another surface water was collected for SPM and a known volume was filtered using 0.7 μm glass filter membranes (GF/F 47 mm, Whatman, UK), and the filters with SPM were kept in aluminum foil. The sediments were sampled by Box-type sampler, and then the subsamples at 0–10 cm depth were collected and kept in aluminum foil. All water, SPM and sediment samples were sent back to the laboratory in an icebox and stored at 4 °C (water) and −20 °C (SPM and sediment) until the time for extraction.

### 2.2. Extraction and analysis

Detailed procedures of treatment and extraction were described in a previous study (Guo et al., 2007). All solvents used were of pesticide grade purity (J.T. Baker, USA). PAHs mixed standards (16 US EPA priority control PAHs compounds) were purchased from AccuStandard Company (USA), including Naphthalene(Nap), Acenaphthylene(Acy), Acenaphthene(Ace), Fluorene(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), Dibenzo(a,h)anthracene(DBA), Benzo(g,hi)perylene(BgP) and Indeno(1,2,3-cd)pyrene(InP). PAHs concentrations were analyzed using an Agilent GC7890A-MSD5975C (Agilent Technologies, USA), model of MS column were DB-5 (30 m × 250 μm × 0.25 μm). The GC/MS conditions were: injection port temperature was 250 °C; the column temperature was programmed at 60 °C (hold for 2 min), then increasing at 10 °C/min to 120 °C, and increasing at 4 °C/min to 290 °C (hold for 10 min). The Ionization mode was tuned in electron impact (EI). Scan method was selected ion and carrier gas was $N_2$. The column flow rate was 1 ml/min. The injected sample volume was 1 μl. All analytical procedures were strictly monitored through quality assurance and quality control. 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. The relative standard deviation (RSD) for parallel samples ($n = 3$) was less than 8%. Recoveries for the different PAHs ranged from 69.32% to 117.61% in water samples, from 66.51% to 134.71% in SPM samples and from 79.36% to 127.18% in sediment samples. Based on the method blank, no PAH was observed from the reagents and procedures. The method detection limit was determined as the concentrations that used the present method with a peak that was thrice the signal-to-noise ratio and that ranged from 0.02 to 1.2 ng/L in water and SPM, while it was 0.02–2.0 ng/g dw in sediment.

### 2.3. Species sensitivity distribution (SSD)

The species sensitivity distribution (SSD) method has been proven as a useful site-to-site estimate both for the eco-risk of individual chemicals and for the joint eco-risk of multiple substances (Solomon et al., 1996; Steen et al., 1999). A SSD model is a statistical distribution describing, among a set of species, the variation in toxicity of a certain compound or mixture (van Straalen, 2002). Here SSD was used to assess the ecological risk of PAHs in water and SPM.

#### 2.3.1. Collection of ecotoxicity data

Since BaP is routinely found in environment, more studies about its harmful effects on various organisms have been performed. In order to assess the ecological risk of $\sum$PAH, the toxic equivalency factors (TEFs) approach proposed by Nisbet and LaGoy (1992) was used. Thus we estimated the ecological risk of individual PAHs compared to the potency of BaP by multiplying their concentration in medium with the appropriate TEF. The concentrations of individual PAHs were expressed as equivalents of BaP($BaP_{eq}$), and these