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

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ABSTRACT

The contamination of surface sediments in Guan River Estuary, China, by polycyclic aromatic hydrocarbons (PAHs) has been fully investigated. Total concentrations of 21 PAHs ranged from 90 to 218 ng/g with an average of 132.7 ng/g, which is relatively low in comparison with other estuaries around the world. PAH concentrations appeared to be positively correlated with clay content and negatively correlated with sediment grain size. Source identification implied that the PAHs originated mainly from pyrolytic sources. However, source patterns may be continuously changed to a petrogenic origin due to the heavy ship traffic and continuous discharge of oily sewage in this area. The PAH levels were also compared with international Sediments Quality Guidelines and Sediments Quality Criteria, and the results indicated low negative effects for most individual PAHs. However, toxic effects related to FLO would occur occasionally in most locations in the estuary.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a typical group of chemicals containing two or more aromatic rings, are prevalent in the environment. Because of their persistence, carcinogenicity, toxicity and mutagenicity (Zedeck, 1980; Marin-Morales et al., 2009), PAHs are of particular concern, and 16 priority PAHs are regulated by the United States Environmental Protection Agency (USEPA). For decades, the distribution and sources of PAHs have been the focus of numerous investigations (Soclo et al., 2000; Doong and Lin, 2004; Men et al., 2009; Chen and Chen, 2011; Barakat et al., 2011; Huang et al., 2012). PAHs can derive from natural sources, but anthropogenic activity is generally considered to be the major source (Baumard et al., 1998). Pyrogenic and petrogenic sources are two major origins of anthropogenic PAHs in the environment. Pyrogenic PAHs are formed as trace contaminants by the incomplete combustion of organic matter, such as wood, fossil fuels, asphalt and industrial waste. Petrogenic PAHs are usually contained in crude and refined petroleum (Liu et al., 2009).

Once produced, PAHs can be transported to the marine environment through wastewater discharge, surface runoff, atmospheric deposition and other means, such as oil leaks (Heemken et al., 2000). In the marine environment, PAHs adhere tightly to sediments because of their high hydrophobicity and weak degradation (Warren et al., 2003). When the environmental conditions change, the adsorbed PAHs can be resuspended into the water via chemical and biological processes, which thus cause secondary pollution to the surroundings (Wang et al., 2010; Lu et al., 2012). Therefore, sediments act both as an important reservoir and as a secondary source for PAH contamination, and the investigation of sedimentary PAHs is needed to provide estimates of PAH inputs into marine areas.

Guan River is the only natural river in northern Jiangsu Province with no water-gates on the main stream, which connects to the Beijing–Hangzhou Grand Canal and the Yangtze River in China (Liu et al., 2006). It flows into the Yellow Sea at the estuary, which facilitates trade with Japan and Korea. In terms of economic development, Guan River plays an important role in Jiangsu, equal to that of the Rhine in Germany and the Thames in England. In recent years, Guan River Estuary (GRE) has experienced a great deal of economic development, leading to an increasing risk of pollution by toxic chemicals. Previous studies have shown that with the increases of local sources, heavy metal pollution of surface sediments has become more and more serious in this area (Yuan and Liu, 2003; Huang and Yin, 2007; Chen et al., 2008). In the case of PAHs, both local sources and long-range atmospheric transport may play

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important roles in their distributions (Lammel et al., 2007; Tamamura et al., 2007). However, there is a scarcity of data on sedimentary PAHs, and this gap must be filled so that an effective environmental policy can be built upon sound scientific knowledge of the emission sources.

The present work aimed to determine the levels and spatial distribution of PAHs in surface sediments in GRE and to identify the major sources of PAHs in this area. Special attention has also been paid to ecological risk assessment of PAHs because of their threats to human health.

2. Materials and methods

2.1. Sample collection

Thirteen surface sediment samples were collected using a stainless steel grab sampler in April 2011. The sample locations are shown in Fig. 1. All samples were placed in dark glass bottles that had been pre-washed with n-hexane and kept in a refrigerator at −20 °C for further analysis.

2.2. Chemicals

A composite standard solution of 21 PAHs (Table 1) at 2000 mg/L was obtained from AccuStandard Chem. Co. (USA). Deuterated PAH internal standard solutions (ACE-d_{10}, PHE-d_{10}, CHR-d_{12} and perylene-d_{12}) at 4000 mg/L and surrogate standard solutions (2-fluorobiphenyl and 4-terphenyl-d_{14}) at 2000 mg/L were also purchased from AccuStandard. A certified reference material (CRM) sample was obtained from National Institute of Standards and Technology (NIST, SRM 1941). All solvents used for sample processing and analysis were HPLC grade from Tedia Co. (USA). Deionized water was produced by a Milli-Q system (Millipore Co., USA). Analytical grade anhydrous sodium sulfate was also used.

Table 1
PAHs analyzed in this study.

PAHs compounds	Abbreviation
Naphthalene	NAP
Acenaphthylene	ACY
Acenaphthene	ACE
Fluorene	FLO
Anthracene	ANT
Phenanthrene	PHE
Benzo(a)anthracene	BaA
Chrysene	CHR
Fluoranthene	FLA
Pyrene	PYR
Benzo(a)pyrene	BaP
Dibenzo(a,h)anthracene	DBahA
Benzo(b)fluoranthene	BbF
Benzo(k)fluoranthene	BkF
Benzo(g,h,i)perylene	BghiP
Indeno(1,2,3-cd)pyrene	IcdP
Benzo(c)phenanthrene	BcP
Benzo(e)pyrene	BeP
Benzo(j)fluoranthene	BjF
7,12-Dimethylbenz(a)anthracene	7,12-DMBA
3-Methylcholanthrene	3-MECA

2.3. Sample preparation and analysis

For PAH analysis, sediments were freeze-dried, crushed into fine powders, and passed through an 80-mesh sieve. Sieved samples of 10 g each were mixed with anhydrous sodium sulfate and Soxhlet-extracted with 80 ml hexane/acetone (1:1 v/v) for 24 h. Prior to analysis, internal standard solutions were added to each extract, which was then cleaned-up by Gel Permeation Chromatography (LC-Tech, ultra 10836). GPC was carried out with a column of 500 mm × 25 mm i.d. filled with 20 g of biobeads. As the mobile phase, chloroform was used at a flow rate of 5 mL min^{-1}. The extract was rinsed out under 180 mbar and collected between 1600 and 2200 s. The extract volume was further reduced to 1.0 ml using a purified nitrogen stream and sealed in an amber vial for analysis.

The concentrated extract was analyzed by gas chromatography-mass spectrometry (GC–MS) using an Agilent 7890 GC and an Agilent 5975C MS with a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25-μm film thickness). An aliquot of 1.0 μL sample extract was injected into the GC–MS with split stream sampling (split ratio: 10:1). The oven programme maintained the temperature at 50 °C for 1 min, then increased it from 50 to 180 °C at 4 °C/min and from 180 to 280 °C at 15 °C/min, and finally held it constant for 5 min. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The injector temperature was maintained at 250 °C. An electron impact ion source (EI) with electron energy of 70 eV was used for the MS, and the mass range scanned was from 50

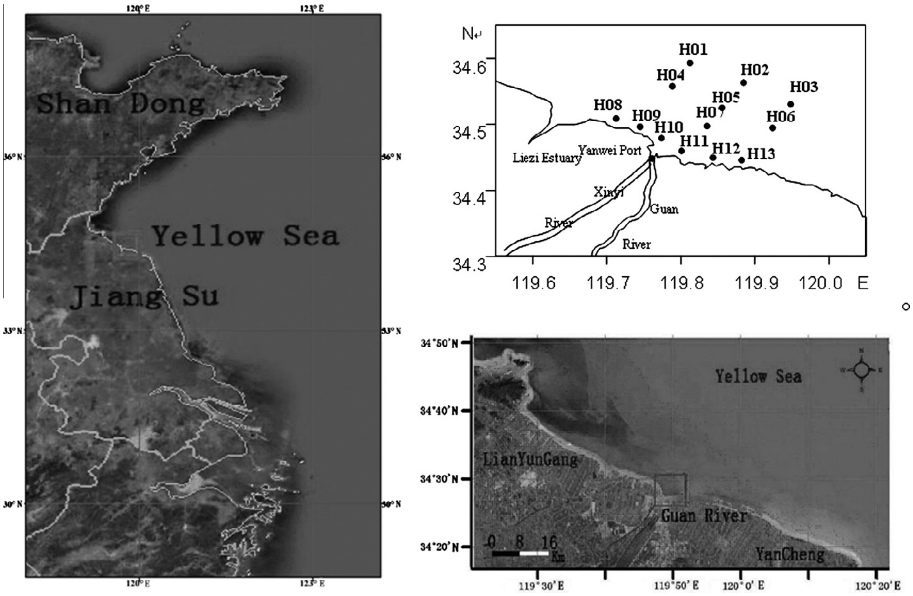

Fig. 1. Map of sampling sites in GRE.