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Baseline

Polycyclic aromatic hydrocarbons in surface sediments from the Coast of Weihai, China: Spatial distribution, sources and ecotoxicological risks

Daolai Zhang [a,b,c], Jinqing Liu [a,b,c], Ping Yin [b,c], Xuehui Lin [b,c], Na Liu [b,c], Xianwei Meng [d,*]

[a] Qingdao Institute of Marine Geology, Qingdao, China
[b] Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources, Qingdao, China
[c] College of Marine Geosciences, Ocean University of China, Qingdao, China
[d] First Institute Oceanography of SOA, Qingdao 266100, China

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ABSTRACT

This study was conducted to measure the polycyclic aromatic hydrocarbon (PAH) concentrations and evaluate the distribution, sources in surface sediments from various coastal sites in Weihai, which create good conditions for rapid development because of their excellent geographical location and abundant marine resources. The results indicated that the total PAHs contents in the sediments of Weihai ranged from 2.69 to 166.50 ng g^{-1}, with an average of 67.44 ng g^{-1}. Phenanthrene, Fluoranthene, Benzo(*b*)fluoranthene, Chrysene, and Pyrene were dominant in sediments, primarily as a result of high temperature combustion and biomass. Molecular ratios suggested that these PAHs in the sediments of Weihai were predominantly from pyrogenic sources such as grass, wood and charcoal combustion, as well as engine exhaust which is similar to the result of the study of the Yellow River Delta, China. The result of probability risk assessment additionally elucidated low PAH ecological risk in the surface sediments of Weihai, China.

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants formed by two or more fused aromatic rings of carbon and hydrogen atoms that are ubiquitous in the environment and known to be toxic, carcinogenic and mutagenic (Callén et al., 2013; Cébron et al., 2013). Because of their high toxicological risk, 16 selected PAHs are listed as priority pollutants by the United States Environmental Protection Agency (USEPA), seven of which are potentially carcinogenic to humans according to the International Agency for Research on Cancer. Because of their low aqueous solubility and high octanol/water partition coefficient, PAHs entering the ocean tend to associate with particulate material and accumulate in the sediments (Lindgren et al., 2014; Naes et al., 1995). PAHs in the sediments will remobilize in the water column, then pose a threat to native aquatic organisms and finally accumulate in higher trophic levels because their half-life can range from years to decades (Cachot et al., 2006; Lindgren et al., 2014; Siddall et al., 1994; Tobiszewski and Namieśnik, 2012; Vane et al., 2013). Most PAHs persist in sediments until they are degraded (Tobiszewski and Namieśnik, 2012; Valentín et al., 2006), therefore, sediment studies can be effective approaches to PAHs contamination research, and PAHs are good indicators of historical anthropogenic impacts on the sedimentary environment.

PAHs in marine sediments have been receiving increased attention because of their negative effects on marine aquatic systems and humans around the world (Aoki et al., 2014; Commendatore et al., 2012; Culotta et al., 2006; Guzzella et al., 2005; Li et al., 2014; Soliman et al., 2014; Yuan et al., 2014). Large amounts of PAHs have been discharged into the ocean, predominantly through human activities associated with combustion and petroleum production (Bouloubassi et al., 2012; Bragato et al., 2012; Callén et al., 2014; Carver et al., 1986; Kaivosoja et al., 2012; Lea-Langton et al., 2013; Readman et al., 2002). Previous studies have shown that PAHs are widely distributed in marine aquatic environments, such as estuaries, coastal areas, wetlands, off-shore areas and the deep sea due to anthropogenic processes and their comparatively long half-life (Counihan et al., 2014; Jörundsdóttir et al., 2014; Oros et al., 2007; Porte and Escartín, 2000; Yancheshmeh et al., 2014). Many studies have shown that there were also PAH contaminants in sediments from marine systems around China, including the Bohai, Yellow, East China and South seas (Deng et al., 2013; Hung et al., 2014; Ma et al., 2001; Men et al., 2009; Yang, 2000; Zong et al., 2014). While many studies have investigated the specific spatial distribution and sources of PAHs in the above seas and many important bays, little is known about PAHs contaminants in marine sediments around the city on the beach of the Yellow Sea (Weihai Beach), which has been designated a major region of the Shandong Peninsula Blue Economic Zone by the government of China (Bouloubassi et al., 2001; He et al., 2014; Li et al., 2012; Maskaoui et al., 2002; Yuan et al., 2001; Zhang et al., 2009). Similar to

* Corresponding author.
E-mail address: mxw@fio.org.cn (X. Meng).

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other coastal regions worldwide, Weihai is facing increasing anthropic pressure through population growth, economic development and industrialization. The City of Weihai has developed rapidly in past decades because of exploitation of the ocean (Ning and Hoon, 2011). In addition, rapid economic growth in the coast around Weihai has raised concern of significant pollution of aquatic environments, especially of sediments that act as a natural repository of organic pollutants. The state and quality of the marine environment around Weihai has been the source of some concern during the past few years. However, only a few studies of the characteristics of inorganic geochemistry and the distribution and amount of heavy metal contaminants present in sediments in the coast around Weihai have been conducted (Jiang et al., 2014; Huang et al., 2013). Accordingly, there is a lack of data describing sediment PAHs concentrations for the Weihai coast.

Therefore, this study was conducted to investigate the present level of PAHs pollution and their spatial distribution in surface sediments collected from the Weihai coast. Isomeric PAHs ratios were analyzed to estimate their potential sources in the target area, and the toxicological effects of PAHs to marine organisms were evaluated by comparing PAHs concentrations in sediments with the Sediment Quality Guidelines (SQGs) and threshold levels proposed by Long et al. (1995) and Maliszewska-Kordybach (1996), respectively. The results of this study will serve as a baseline to assess future anthropogenic effects and will be valuable to local governments.

This study focused on sediments (121°21′00″–122°43′00″E, 36°37′00″–37°35′00″N) collected from the coast of Weihai, Shandong, China (Fig. 1). Weihai has a length of 29 km along the west coast of the North Yellow Sea. The mean annual temperature of this area is 24.6 °C, the annual precipitation is 1579.70 mm, and the average salinity of the open water ranges from 23‰ to 26‰. Nearshore development includes aquaculture, container and bulk cargo ship terminals, as well as food production. Nearly 2.8 million people live in urban centers on the shores of this coast. Nineteen sampling sites were selected along the Weihai coast and grouped into three transects divided into three groups based on their coordinates from south to north in a 3949.98 km^2 area.

Surface sediments (depth 0–5 cm) were collected from 19 locations in April 2013 using Smith-Mcintyre grab samplers (Fig. 1). Each sediment sample analyzed in this study was packed into cleaned solvent-rinsed glass flasks and stored at −20 °C until chemical analysis.

Extraction from sediments was carried out according to the method described by Nicola et al. (2005). A total of 10–15 g of freeze dried sediments were dissolved in 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 then mixed with equal quantities of anhydrous sodium sulfate three times in 60 mL of a dichloromethane:acetone (1:1, v:v) mix for 20 min while sonicating. The extract was then concentrated and solvent exchanged with hexane, after which it was further reduced to approximately 1 mL under weak nitrogen flow. The extract was subsequently applied to a 1:2 alumina/silica gel glass column for clean-up and fractionation. The first fraction, which contained aliphatic hydrocarbons, was eluted with 15 mL of hexane. The second fraction, which contained PAHs, was collected by eluting 5 mL hexane and 70 mL of methylene chloride: hexane (30:70). The PAHs 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 hexane.

Concentrations of PAHs were measured by gas chromatography (HP 5890 GC with a HP-5MS capillary column 30 m, 0.25 mm i.d., 0.25 μm film thickness) coupled to a mass spectrometer (HP 5975 mass selective detector). Helium was applied as the carrier gas at a constant flow rate of 1.0 mL min^{-1}. The oven temperature program started at 70 °C, then increased at 20 °C min^{-1} to 280 °C, where it was held for 24 min. Quantitations were conducted using the primary ions for each compound, after which two to three secondary ions were used for qualitative confirmation.

Glassware and sodium sulfate were solvent-rinsed and heated for 4 h at 450 °C prior to use. For each batch of 10 samples, a spiked blank, a procedural blank, matrix spikes and a duplicate sample were processed in the same way as the sample for quality assurance and control. No quantifiable targets were detected in these blanks. Analysis of a reagent blank demonstrated that the analytical system and glassware were free of contamination. The recovery was 75.0%–120.0% for spiked blanks. The results reported in this study were not corrected for recoveries. The relative standard deviation for parallel samples ($n = 3$) was <15%.

A total of 16 PAHs compounds listed as priority pollutants by the USEPA were identified and quantified. The concentrations of individual PAHs compounds and total PAHs from 19 sampling sites on the Weihai coast are shown in Table 1. Total PAHs occurred in variable amounts at the 19 sites. The $\sum$PAHs in the 19 sediments from the research area ranged from 2.69 ng g^{-1} to 166.50 ng g^{-1} of dry matrix with a mean of 67.44 ng g^{-1} of dry matrix. The highest and lowest sediment total PAHs concentrations were found for sites WHB20 and WHB16, respectively. The highest concentrations of $\sum$PAHs were found at site WHB20, which also contained all 16 compounds, followed by station

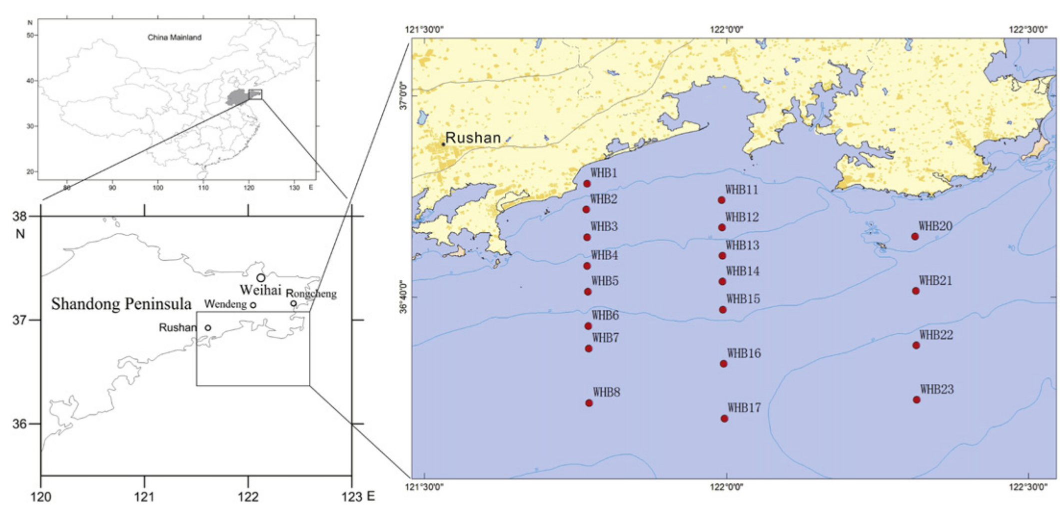

Fig. 1. Location on the coast of Weihai, Shandong, China.