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Baseline

Distribution characteristics, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in sediments from the Qinhuangdao coastal wetland, China

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ABSTRACT

Sixteen USEPA priority polycyclic aromatic hydrocarbons (PAHs) were analyzed by gas chromatography–mass spectrometry. Twenty-three samples were collected from the surface sediments of Qinhuangdao coastal wetlands in this survey. This research aimed to identify the PAHs contamination level, composition pattern, pollution sources, and assess the ecological risk of PAHs. The results showed that the sum of PAH concentrations ranged from 341.61 ng/g to 4703.80 ng/g (mean: 1367.80 ng/g), which is higher than the reported values for different wetlands worldwide. Five- and four-ring PAHs (34.08% and 32.97% of Σ16PAHs, severally) were predominant in the wetland sediment. The PAH source distribution in the surface sediments was determined using diagnostic ratio and PCA/MLR. Consequently, multiple PAH sources were found. Of the total PAHs, 70.01% was derived from vehicular emission, 25.73% from coke oven, and 4.26% from petroleum-based product spills. The effect range low/effect range median (ERL/ERM) values indicated a low toxicity risk level. However, the DBahA concentrations exceeded the ERL level, and even the ERM level, in some stations. The mean effects range–median quotient (M-ERM-Q) suggests a low ecological risk for the PAHs, but a medium risk for some stations in the coastal wetland sediments.

Polycyclic aromatic hydrocarbons (PAHs) that a class of persistent organic pollutants (POPs) are ubiquitously present in the environment (Arias et al., 2010). They are major derived from human activities and combustion. Given their mutagenicity, carcinogenicity and toxicity, PAHs raise great concerns worldwide (Yang, 2000). The United States Environment Protection Agency (USEPA) and the European Union (EU) listed 16 PAHs as priority control of pollutants (Ma et al., 2009). PAHs are able to accumulate in the air, water, sediments, and plant or animal samples because of their lipophilicity. PAH concentrations are higher in sediments than in other phase levels. Hence, sediments are an important environmental reservoir for PAHs. Sediments can also be remobilized into overlying water through sediment resuspension, which occur frequently in the river system. During this process, the PAHs adsorbed onto sediment particles might be released into the water and cause secondary pollution (Kurunthachalam et al., 2005; Liu et al., 2016). Hence, it is significative to assess the potential risk for protecting human health and ecological environment (Kannan et al., 2005; Houlahan et al., 2006).

Wetlands are highly abundant, biodiverse ecosystems. These places provide habitat, food, and spawning grounds for numerous plants and animals (Wu et al., 2005). Wetlands play the irreplaceable roles in regulating climate, removing harmful substances and protecting biological diversity. With the advancing industrialization in China, the problem of sediment pollution in wetlands is becoming serious and widespread. Due to potential ecological environment risk and negative effect of PAHs pollution, such a concern attracts increasingly attention.

The coastal wetland of Qinhuangdao, Hebei Province is the largest urban wetland park in China and is affected by rapid urbanization. Only few studies were conducted to determine the sources and evaluate the potential risk of PAH pollution for this coastal wetland. Therefore, the contamination levels in the sediments deserves investigation, the results of which may help provide potential strategies for Qinhuangdao coastal wetland protection.

Twenty-three surface sediment samples were collected in November 2016 from the Qinhuangdao coastal wetland. The locations of the sample station were shown in Fig. 1. All samples were collected using a stainless steel grab sampler, placed in polyethylene bags, stored in an icebox and then immediately returned to the laboratory. The sediment samples were freeze-dried for twenty-four hours, passed through 100-mesh sieve and stored at − 20 °C until analysis for PAHs.

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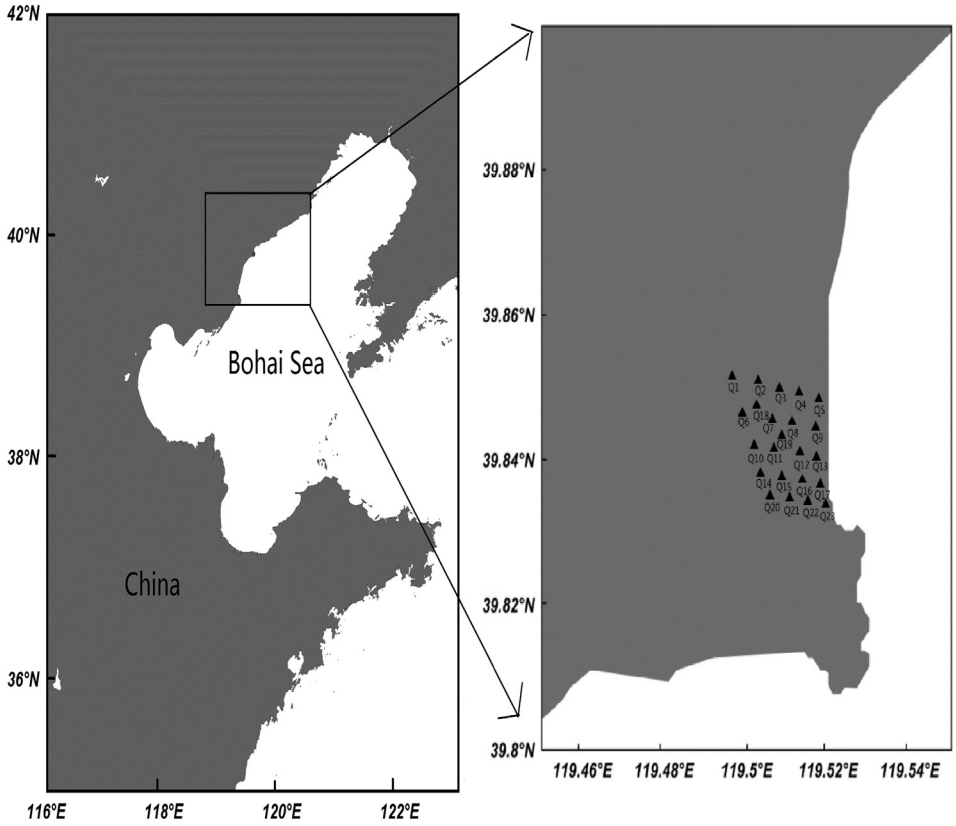

Fig. 1. Location of sampling sites in the coastal wetland sediments of Qinhuangdao.

Approximately 5 g of sample that passed through 100-mesh sieve was ultrasonically extracted twice times in the mixed solution of hexane/dichloromethane (1:1, v/v). The two extracts were combined and concentrated to 2–4 ml by a rotary vacuum at 40 °C. The concentrated extracts were purified by using an silica/alumina (5:7, w/w) chromatography column. The column consisted of two grams of anhydrous sodium sulfate on the top and one gram of activated Cu powder layers. The elution was successively performed with hexane and hexane/dichloromethane (7:3, v/v) mixed solution. The fraction, containing PAHs, was reduced to 1 ml by purified and gentle N_2 flow.

The concentrations of PAHs were quantified by using a GC–MS (Agilent 6890 N GC/5973 N MSD) under selected ion monitoring (SIM) mode. The temperature of injection port was set at 280 °C. 1 μL of sample was conducted in a splitless mode. Highly pure helium was carrier gas and maintained flow rate of 1 ml/min. The column was an Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm) silica-fused capillary column. The GC oven temperature was programmed to increase from 80 °C to 150 °C at a rate of 4 °C/min, increase to 290 °C at 15 °C/min and held for 12 min.

16 priority PAHs were analyzed based on GC retention time and ion *m/z* of individual PAH, which including naphthalene (NaP), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IND), dibenzo(a,h)anthracene (DBahA) and benzo(g,h,i)-perylene (BghiP). PAHs were quantified using external calibration method.

Quality control procedures were successively performed for all samples, including method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spike duplicates and sample duplicates. Target PAHs were not found under method blank. The surrogate recoveries of the phenanthrene-d10 and chrysene were 74.61% ± 21.15% and 80.36% ± 19.81% in the sediment and QC/QA samples. The mean recoveries for 16 PAH standards were 70%–117%. The detection limits of 16 PAHs were 0.30–2.20 ng/g in sediment samples. PAH concentrations of all stations were analyzed on a sediment dry-weight basis and the average relative standard deviation of triplicate was all below 10%.

The sum concentrations and average concentrations of sixteen PAHs in the coastal wetland sediments were 341.6–4703.8 ng/g, 1367.81 ng/g (Table 1). The concentrations of the dominant PAHs DBahA and BghiP were 36.28–810.29 and 34.10–807.95 ng/g, respectively. The PAH pollution levels were divided into four groups: low (0–100 ng/g), moderate (100–1000 ng/g), high (1000–5000 ng/g), and extremely high (greater than 5000 ng/g) (Baumard et al., 1998). Given this classification, the contamination levels of PAHs at most of the coastal wetland sample sites were higher than those in the Zhalong wetland, BaiYangDian wetland, LaLu wetland, Liaohe estuarine wetland,

Table 1
Concentrations of selected and total PAHs in the coastal wetland sediments of Qinhuangdao.

Compound	Ring	Min(ng/g)	Max(ng/g)	Mean(ng/g)
Nap	2	10.21	93.74	37.40
Acy	3	0.11	4.46	2.02
Ace	3	1.17	19.48	7.62
Fle	3	6.10	41.51	18.07
Phe	3	14.38	240.63	73.48
Ant	3	7.37	55.56	19.57
Fla	3	17.58	259.34	82.62
Pyr	4	21.44	214.99	76.68
BaA	4	16.19	215.39	69.94
Chr	4	23.91	476.76	138.08
BbF	5	28.93	672.87	166.31
BkF	5	21.06	282.55	81.74
BaP	5	16.95	359.59	85.50
IND	6	26.73	502.79	115.82
DBahA	5	36.28	810.29	183.15
BghiP	6	34.10	807.95	209.80
ΣPAHs		341.6	4703.80	1367.81