Assessment of polycyclic aromatic hydrocarbons (PAHs) ecological risk in surface seawater from the west Bohai Bay, China

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Abstract. In order to understand the pollution characteristics of polycyclic aromatic hydrocarbons (PAHs) in west Bohai Bay, China, the sixteen PAHs listed by US EPA in surface seawater were investigated in the Qinhuangdao (QHD), Caofeidian (CFD) and Huanghuagang (HHG) areas. Distribution and composition of PAHs in the dissolved phase (DP) and the suspended particulate associated phase (SP) were detected by gas chromatography and mass spectrometry (GC-MS), respectively. An ecological risk assessment was evaluated using risk quotients (RQ). The results showed that the 16 PAHs were prevalent in west Bohai Bay and the 2-3 rings PAHs were the predominant chemicals. The QHD area had the highest concentration of total PAHs (TPAHs), which ranged from 186.3 to 531.3 ng/L in DP and 222.7 to 715.7 ng/L in SPM. In all three areas, the PAHs levels in SPM were higher than those in DP. The risk assessment showed that there was a relatively low potential ecological risk of PAHs in the coastal regions of Bohai Bay.

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs), which have the potential to be toxic, mutagenic and carcinogenic, can enter the marine environment through a variety of ways, such as river runoff, atmospheric precipitation, sewage outfalls and maritime transport [1]. PAHs are hydrophobic organic compounds that are prone to combine with particles in the water column and settle into the bottom sediment. Therefore in aquatic environments, water is considered a pollution transfer media and sediments are regarded as a reservoir for PAHs [2]. Due to their persistence, PAHs can exist in the environment for a long time and accumulate in organisms through the food chain [3]. However, there are only limited data about the level of PAHs in the marine environment and their ecological risk [4,5].

Bohai Bay is a typical semiclosed shallow sea in northeast China surrounded by the industrialized coastal regions including Tianjin and Hebei Province. Therefore, the marine environment in Bohai Bay has become one of the most severely polluted coastal areas in China [6]. PAHs contamination from the petroleum industry, shipping industry and other human activities cannot be ignored in this area. Because of the potential impact of PAHs on organisms in the marine environment, it is necessary to study the ecological risk of PAHs in Bohai Bay. However, there is not enough current research about the state of PAHs pollution in the seawater of Bohai Bay to make a risk assessment [7].
The aim of the present study is to evaluate the ecological risk of PAHs in surface seawater by investigating the pollution status of PAHs. The three typical coastal regions, QHD, CFD and HHG, selected all have a developed industry or port. This research could provide the basic dates for contamination control of PAHs and coastal environment management.

2. Materials and methods

2.1. Study area and sampling
A total of 36 samples were analysed to detect the PAHs concentrations in surface seawater in the west Bohai Bay. The investigation was carried out in three areas: QHD (8 samples), CFD (15 samples) and HHG (13 samples). The sampling sites are shown in figure 1. The samples were collected by a surface water sampler and were stored in pre-cleaned brown glass bottles at -4°C until analysis.

![Figure 1. Location of sampling areas in QHD, CFD and HHG of the west Bohai Bay, China.](image)

2.2. Reagents and materials
US EPA priority control 16 PAHs (purity > 99%) mixed standards and phenanthrene-d10 were purchased from AccuStandard in USA. Methanol and dichloromethane (DCM) (purity ≥ 99.9%) were purchased from Biologic Reagent. Anhydrous sodium sulfate was heated at 600°C for 3 hrs in a muffle furnace and placed in a desiccator. C18 columns were obtained from Simon Aldrich in Germany.

2.3. Sample extraction and analysis
Samples were filtered by glass fiber filters (Whatman GF/F, pore size is 0.7 μm, Φ47 mm). The filtered seawater was used to analyze the dissolved phase (DP) PAHs in seawater. The solid materials in the filter membrane were analyzed for suspended particulate associated phase (SP) PAHs in seawater. The analysis was done with the following procedure. First, each water sample was gathered by solid-phase extraction (SPE) with a C18 column (preconditioned with 10 ml DCM, 10 ml methanol and 10 ml ultrapure water two times) at a flow rate of 5 ml·min⁻¹. Then, PAHs were eluted from the column with 12 ml DCM. The extraction was concentrated to 0.5 ml using Termovap Sample Concentrator in a water bath (45°C) and analyzed with GC-MS. Second, the solid materials separated by GF/F glass fiber filters were freeze-dried and weighed. The dried filters were extracted with 150 ml
of the mixed solvent n-hexane and DCM (1:1, v/v) for 24 hrs using a soxhlet apparatus. Extractions were purified by a self-pack silica-alumina column (from top to bottom: anhydrous sodium sulphate, 1 cm; the mixture of silicone and n-hexane, 10 cm; anhydrous sodium sulphate, 1 cm; a few glass fiber). Finally, the PAHs eluent was concentrated to 0.5 ml for GC-MS analysis.

The quantification of PAHs was performed by gas chromatography and mass spectrometry (GC-MS: Agilent 7890A GC-5975 C MS). The GC was equipped with a DB-5 MS capillary column (30 m×0.25 mm×0.25 μm). GC operating conditions were programmed from 70 °C (initial time, 1 min) to 260 °C at a rate of 10 °C·min⁻¹, 120 °C (initial time, 4 min) to 300 °C at a rate of 5 °C·min⁻¹, and held at 300 °C for 4 min. PAHs were then quantified by selected ion monitoring (SIM).

2.4. Quality assurance/quality control
Some quality assurance measures were taken to vouch for the reliability of the results. Phenanthrene-d10 was added as a recovery indicator to each sample before extraction and the method recovery of 16 PAHs in DP and in SP was between 80% and 110%. Pyrene-d10 was applied as the internal standard to calculate the concentration of 16 PAHs.

2.5. Risk assessment
Risk quotients (RQ) were proposed by Kalf [8] to calculate the ecological risk of PAHs and also used to evaluate risk of PAHs on aquatic organisms [4,9]. RQ are commonly determined as follow:

\[
RQ_{NCs} = \frac{C_{PAHs}}{C_{NCs}}
\]

\[
RQ_{MPCs} = \frac{C_{PAHs}}{C_{MPCs}}
\]

Where \(C_{NCs}\) is the negligible concentrations (NCs) of PAHs and \(C_{MPCs}\) is the maximum permissible concentrations (MPCs) of PAHs in water [8]. \(RQ_{NCs}\) and \(RQ_{MPCs}\) are risk quotients of the NCs and MPCs of PAHs in water, respectively. In addition, the above method was further optimized to judge the ecological risk of 16 PAHs [10]. The risk grade of individual PAH and total PAHs (TPAHs) are listed in table 1.

| individual PAHs | TPAHs |
|----------------|-------|
| Risk Grade     | RQNC  | RQMPC |
| Lower risk     | 0     |       |
| Medium risk    | ≥1    | <1    |
| High risk      | ≥1    |       |

| Risk Grade     | RQNC  | RQMPC |
|----------------|-------|-------|
| Lower risk     | =0    |       |
| Low risk       | ≥1 & <800 | =0 |
| Medium risk 1  | ≥800  | =0    |
| Medium risk 2  | <800  | ≥1    |
| High risk      | ≥800  | ≥1    |

3. Results and discussion

3.1. PAHs distribution in surface water
The DP and SP PAHs concentrations in the three investigated areas are listed in table 2. The SP PAHs concentrations were higher than DP PAHs concentrations, which indicate that PAHs are prone to being absorbed by particles in water column. The highest concentration of TPAHs was detected in QHD. This may be due to the rivers nearby the QHD sampling sites such as the Shi and Xinkai Rivers. These rivers bring terrigenous pollution into the coastal area. The concentration of TPAHs in CFD was the lowest among the three survey areas. The variation of PAHs concentrations between the three
areas may be due to differences in industrial development. However, there is no significant difference of the PAHs concentrations between the three areas (p>0.05, one-way anova).

Table 2. PAH concentrations in surface seawater from the three coastal areas of the west Bohai Bay (ng/L).

| PAHs                        | QHD  | CFD  | HHG  |
|-----------------------------|------|------|------|
|                             | DP   | SP   | DP   | SP   | DP   | SP   |
| naphthalene (Nap)           | 50.8-321 (194.4) | 24.5-253.6 (163.8) | 8.84-437 (119.3) | 31.62-264.57 (172.61) | 10.2-418 (111.0) | 22.79-519.61 (229.88) |
| acenaphthylene (Acy)        | 0.69-2.1 (1.50) | 0.37-5.08 (2.8) | 0.10-1.91 (1.01) | 1.25-4.70 (3.32) | 0.27-2.15 (1.2) | 1.87-8.63 (4.10) |
| acenaphthene (Ace)          | 1.54-25.0 (7.94) | 1.47-9.90 (6.1) | 0.72-11.9 (5.22) | 2.81-9.43 (6.32) | 1.06-24.3 (8.6) | 3.00-65.02 (10.65) |
| fluorene (Flu)              | 11.9-49.6 (23.21) | 12.59-32.56 (26.1) | 3.49-36.9 (19.90) | 14.74-33.23 (23.45) | 2.7-53.2 (24.31) | 17.75-45.07 (26.12) |
| phenanthrene (Phe)          | 26.1-87.8 (45.24) | 43.87-98.93 (73.8) | 22.6-93.1 (50.97) | 32.68-77.56 (54.67) | 5.2-108 (51.8) | 40.83-98.65 (59.49) |
| anthracene (Ant)            | 3.38-7.09 (5.02) | 8.85-12.45 (9.5) | 2.49-7.90 (5.48) | 4.66-12.61 (8.17) | 0.91-11.5 (5.5) | 5.65-15.49 (9.32) |
| fluoranthene (Flua)         | 6.62-17.8 (11.62) | 18.83-43.78 (34.5) | 5.45-27.6 (15.68) | 13.77-33.64 (23.85) | 2.09-25.0 (14.9) | 18.81-43.51 (29.10) |
| pyrene (Pyr)                | 22.0-35.0 (27.00) | 31.74-93.36 (70.1) | 10.8-35.7 (28.29) | 38.99-99.16 (60.38) | 5.1-45.0 (26.9) | 46.13-114.05 (77.94) |
| benzo[a]-anthracene (BaA)   | 0.31-1.42 (0.83) | 2.13-19.29 (5.6) | 0.26-1.67 (0.96) | 1.09-3.04 (2.03) | 0.11-1.77 (0.92) | 1.60-4.28 (2.56) |
| chrysene (Chr)              | 0.69-2.01 (0.98) | 2.44-18.48 (5.8) | 0.27-2.47 (1.14) | 0.78-3.13 (2.15) | 0.17-4.37 (1.28) | 1.60-5.38 (2.89) |
| benzo[b]-fluoranthene (BbF) | 0.74-2.31 (1.34) | 3.73-32.49 (10.5) | 0.47-2.40 (1.47) | 1.83-6.80 (3.71) | 0.52-2.11 (1.27) | 2.37-8.04 (4.14) |
| benzo[k]-fluoranthene (BkF) | 0-0.91 (0.55) | 0.70-7.39 (2.7) | 0.24-1.06 (0.66) | 0.71-2.33 (1.32) | 0.34-0.94 (0.61) | 0.74-2.31 (1.23) |
| benzo[a]pyrene (BaP)        | 0.43-0.86 (0.65) | 1.67-12.54 (4.3) | 0.18-1.22 (0.71) | 1.91-4.86 (2.27) | 0.36-1.51 (0.94) | 1.44-4.17 (2.11) |
| indeno[1,2,3-cd]pyrene (InP) | 0-0.96 (0.60) | 1.59-15.05 (4.8) | 0.15-1.59 (0.70) | 0.65-2.96 (1.70) | 0.29-1.14 (0.64) | 1.35-3.65 (2.12) |
| dibenzo[a,h]-               | 0-0.81 | 1.06- | 0.03-1.09 | 0.81-1.53 | 0.05- | 0.66-1.71 |
Compared to reports on other coastal areas, the PAHs concentrations in west Bohai Bay are at a medium pollution level. For example, TPAHs concentrations in west Bohai Bay were higher than in Xiamen coastal area [5], Western Taiwan Straits [11] and Northwestern Mediterranean Sea in France [12]. However, the PAHs concentrations in west Bohai Bay were lower than that in the Persian Gulf [13]. The deteriorating PAHs contamination condition in the Persian Gulf may be due to the Gulf War which led to a large amount of oil pollution [13]. According to the criteria distinguishing the PAHs pollution level [4], the three investigated areas in the present research can be classified as a mild or moderate PAHs pollution status.

### 3.2. Composition of PAHs

The composition patterns and relatively abundant DP and SP PAHs individuals in the investigation areas are shown in figure 2. The compositions of DP PAHs were similar as those in SP PAHs except for the QHD area. For the CFD and HHG areas, Nap was the most dominant chemical and comprised almost 50% TPAHs for both DP and SP PAHs. In contrast, Nap comprised more DP PAHs (about 60%) than SP PAHs (about 40%) in the QHD area.

Furthermore, the proportion of 2-ring and 3-ring low molecular weight (LMW) PAHs ranged from 83.4% to 88.9% in DP PAHs and from 69.6% to 78.3% in SP PAHs. This was higher than the proportion of 4-6 rings PAHs in DP, which are defined as high molecular weight (HMW) PAHs. This phenomenon may be because HMW PAHs have low water solubility and are prone to being absorbed by the particles [4] and deposit in sediments [13].

![Figure 2](image.png)

**Figure 2.** The composition profile of different ring numbers in surface seawater from QHD, CFD and HHG in DP (a) and SP (b) PAHs.
3.3. Ecological risk assessment

The mean values of RQ_NCs and RQ_MPCs of the PAHs of QHD, CFD and HHG in the west Bohai Bay are listed in Table 3. For the three investigated areas, the RQ_MPCs of individual PAHs ranged from 0 to 0.50 and the RQ_NCs of almost all of the 16 PAHs except for Chr and DahA were higher than 1.0, demonstrating a medium risk level of all individual PAHs. For 2-4 rings PAHs, e.g. Nap, Flu, Phe and Pyr, the RQ_NCs values were high especially for Flu and Pyr. This suggests that there is a higher ecological risk for these PAHs individuals. In particular, the RQ_NCs values of Nap and Acy in QHD were higher than those in CFD and HHG. This suggests that the ecological risk for these chemicals is higher in QHD. However for some PAHs individuals, including Ace, Flu, Phe, Ant, Chr, BaP and DahA, the RQ_NCs values in CFD and QHD were higher than those in HHG, indicating a higher ecological risk in the two areas. Generally, the ecological risk for TPAHs in the surface waters of the three investigated areas was low. The RQ_{TPAHs(NCs)} value was between 1.0-800 and the RQ_{TPAHs(MPCs)} value was <1.0. The values of RQ_{TPAHs(NCs)} and RQ_{TPAHs(MPCs)} for the three areas were similar. Thus, the ecological risk for TPAHs for the three areas is similar as well. The results indicate that TPAHs in the surface water of west Bohai Bay have mild potential risk on the aquatic biota. The management for PAHs pollutions in west Bohai Bay should be considered, especially for Flu and Pyr.

| PAHs | TEFs | Water (ng/L) | QHD | CFD | HHG |
|------|------|--------------|-----|-----|-----|
|      |      | NCs | MPCs | RQ_NC | RQ_MPC | RQ_NC | RQ_MPC | RQ_NC | RQ_MPC |
| Nap  | 0.001| 12.0| 1200 | 16.20 | 0.16 | 9.94 | 0.10 | 9.25 | 0.09 |
| Acy  | 0.001| 0.7 | 70   | 2.14  | 0.02 | 1.45 | 0.01 | 1.77 | 0.02 |
| Ace  | 0.001| 0.7 | 70   | 11.34 | 0.11 | 7.45 | 0.07 | 12.35 | 0.12 |
| Flu  | 0.001| 0.7 | 70   | 33.16 | 0.33 | 28.43 | 0.28 | 34.73 | 0.35 |
| Phe  | 0.001| 3.0 | 300  | 15.08 | 0.15 | 16.99 | 0.17 | 17.25 | 0.17 |
| Ant  | 0.001| 0.7 | 70   | 7.17  | 0.07 | 7.82 | 0.08 | 7.92 | 0.08 |
| FluA | 0.01 | 3.0 | 300  | 3.87  | 0.04 | 5.23 | 0.05 | 4.96 | 0.05 |
| Pyr  | 0.001| 0.7 | 70   | 38.57 | 0.39 | 40.42 | 0.40 | 38.44 | 0.38 |
| BaA  | 0.1  | 0.1 | 10   | 8.30  | 0.08 | 9.62 | 0.10 | 9.23 | 0.09 |
| Chr  | 0.01 | 3.4 | 340  | 0.29  | 0.00 | 0.34 | 0.00 | 0.38 | 0.00 |
| BbF  | 0.1  | 0.1 | 10   | 13.40 | 0.13 | 14.70 | 0.15 | 12.72 | 0.13 |
| BkF  | 0.1  | 0.4 | 40   | 1.38  | 0.01 | 1.64 | 0.02 | 1.53 | 0.02 |
| BaP  | 1.0  | 0.5 | 50   | 1.30  | 0.01 | 1.42 | 0.01 | 1.87 | 0.02 |
| InP  | 0.1  | 0.4 | 40   | 1.50  | 0.02 | 1.76 | 0.02 | 1.60 | 0.02 |
| DahA | 1.0  | 0.5 | 50   | 0.70  | 0.01 | 0.87 | 0.01 | 0.89 | 0.01 |
| BghiP| 0.01 | 0.3 | 30   | 1.83  | 0.02 | 2.23 | 0.02 | 2.07 | 0.02 |
| TPAHs| 27.2 | 2720| 11.83 | 0.12 | 9.29 | 0.09 | 9.23 | 0.09 |  

*a* The values of toxic equivalency factors (TEFs) were from references [4,14].

**b** The values were from reference [10].

4. Conclusions

The concentrations of DP TPAHs were lower than those of SPPAHs for the three investigated areas. The TPAHs in QHD were higher than those in CFD and HHG. For all three areas, the PAHs contamination was mild to moderate.

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