INVESTIGATION AND ECOLOGICAL RISK ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBON POLLUTION IN THE RED BEACH WETLAND, PANJIN, CHINA

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Abstract. In order to study the pollution status of polycyclic aromatic hydrocarbons (PAHs) in sediments, seawater, and *Suaeda heteroptera* in the Red Beach Wetland of Panjin City, China, in September and November of 2020, as well as May and July of 2021, sediment, seawater, and *Suaeda heteroptera* samples were collected from both Site A and Site B. The concentrations and risk levels of 16 priority PAHs regulated by the US (Environmental Protection Agency EPA) were analyzed. The results showed that the concentrations of PAHs in the sediments ranged from 0.7 to 98.5 ng·g-1, in seawater ranged from 0 to 41.5 ng·kg-1, and in *Suaeda heteroptera* ranged from 0 to 108 ng·g-1. Temporally, the total PAH concentrations in sediments at Site A showed a decreasing trend from 2020 to 2021, while the total PAH concentrations in seawater exhibited an increasing trend. At Site B, the total PAH concentrations in sediments increased, while the total PAH concentrations in seawater and *Suaeda heteroptera* decreased. Furthermore, ecological risk assessments of sediment PAHs were conducted using the sediment quality guidelines and sediment quality standard methods, while the ecological risk of seawater PAHs was assessed using the quotient approach. The toxic equivalent concentration method was employed to evaluate the ecological risk of PAHs in *Suaeda heteroptera*. The results indicated relatively low ecological risks of PAHs in the sediments and seawater of the Red Beach Wetland in Panjin. China. However, (Bap benzo[a]pyrene) exhibited the highest toxic equivalent concentration in *Suaeda heteroptera*, suggesting a significant potential carcinogenic risk that requires attention.
Keywords: *sediments, seawater, Suaeda heteroptera, sediment quality guidelines, quotient approach, toxic equivalent concentration*

Introduction

The Earth has been naturally exposed to (polycyclic aromatic hydrocarbons PAHs) for billions of years generated through volcanic eruptions, rock formations, forest and grassland fires, certain seaweeds, and microbial synthesis. However, natural sources contribute only a small fraction of the overall PAHs found in the environment. With advancing technology and industrialization across various sectors, the quantity of PAHs has significantly increased. Incomplete combustion of petroleum and coal has further intensified the generation and dispersion of PAHs. Low molecular weight PAHs remain in the atmosphere as gases, polluting the environment through

atmospheric movements. High molecular weight PAHs are adsorbed onto atmospheric particulate matter, subsequently depositing onto land surfaces or water bodies through atmospheric deposition. Through water and vapor evaporation, PAHs can re-enter the atmosphere, perpetuating the pollution cycle (Thorsen et al., 2004). The accumulation of PAHs in the environment is influenced by factors such as topography, wind speed, precipitation, river flow velocity, and temperature. Studies have shown that cities with a higher concentration of petroleum and energy chemical plants, particularly those situated in valley terrain or with significant topographical variations, exhibit higher levels of soil PAHs. Research by Ko and Baker (2004). revealed a positive correlation between PAH concentrations and river flow velocity, with higher suspended particulate matter leading to elevated PAH concentrations. PAHs are resistant to natural degradation in the environment, and their high lipophilicity enables bioaccumulation in organisms, leading to metabolic disturbances and adverse effects on growth and development. Economic development at the expense of natural resources has given rise to numerous environmental challenges, particularly the persistent and hazardous nature of PAHs, which pose serious threats to human health. Consequently, reducing PAH levels and mitigating their toxicity in the environment are urgent issues that need to be addressed.

Located at the estuary of the Liao River in the downstream region, the Red Beach Wetland in Panjin is one of the best-preserved wetlands, playing a crucial role in intercepting and purifying pollutants from the tail end of the Liao River and maintaining a healthy ecosystem balance in the surrounding coastal areas, including the Liaodong Bay. However, rapid economic development has brought convenience to human life while causing extensive mortality of *Suaeda heteroptera* plants in the Red Beach Wetland, leading to the degradation of its ecosystem. Scholars have suggested that the degradation of the Red Beach Wetland may be attributed to human activities such as oil field development, aquaculture expansion, and dam construction (Bai and Wang, 2020). In this study, a comprehensive investigation and monitoring of PAH types and concentrations in surface sediments, seawater, and *Suaeda heteroptera* plants at different sampling sites in the Red Beach Wetland, Panjin, were conducted. Additionally, an ecological risk assessment was performed to provide scientific insights for the ecological management and conservation of the Red Beach Wetland.

Materials and methods

Instruments and reagents

The determination of PAHs was carried out using (high-performance liquid chromatography HPLC) method. The instruments used are listed in *Table 1,* and the experimental reagents are listed in *Table 2*.

Sample collection

The study area is located in the Red Beach Wetland in Panjin City, Liaoning Province, China. Monitoring and analysis were conducted through a combination of field sampling and laboratory experiments. Sampling was conducted at different locations near Red Beach in September and November 2020, as well as in May and July 2021. The specific sampling points are shown in *Figure 1*.
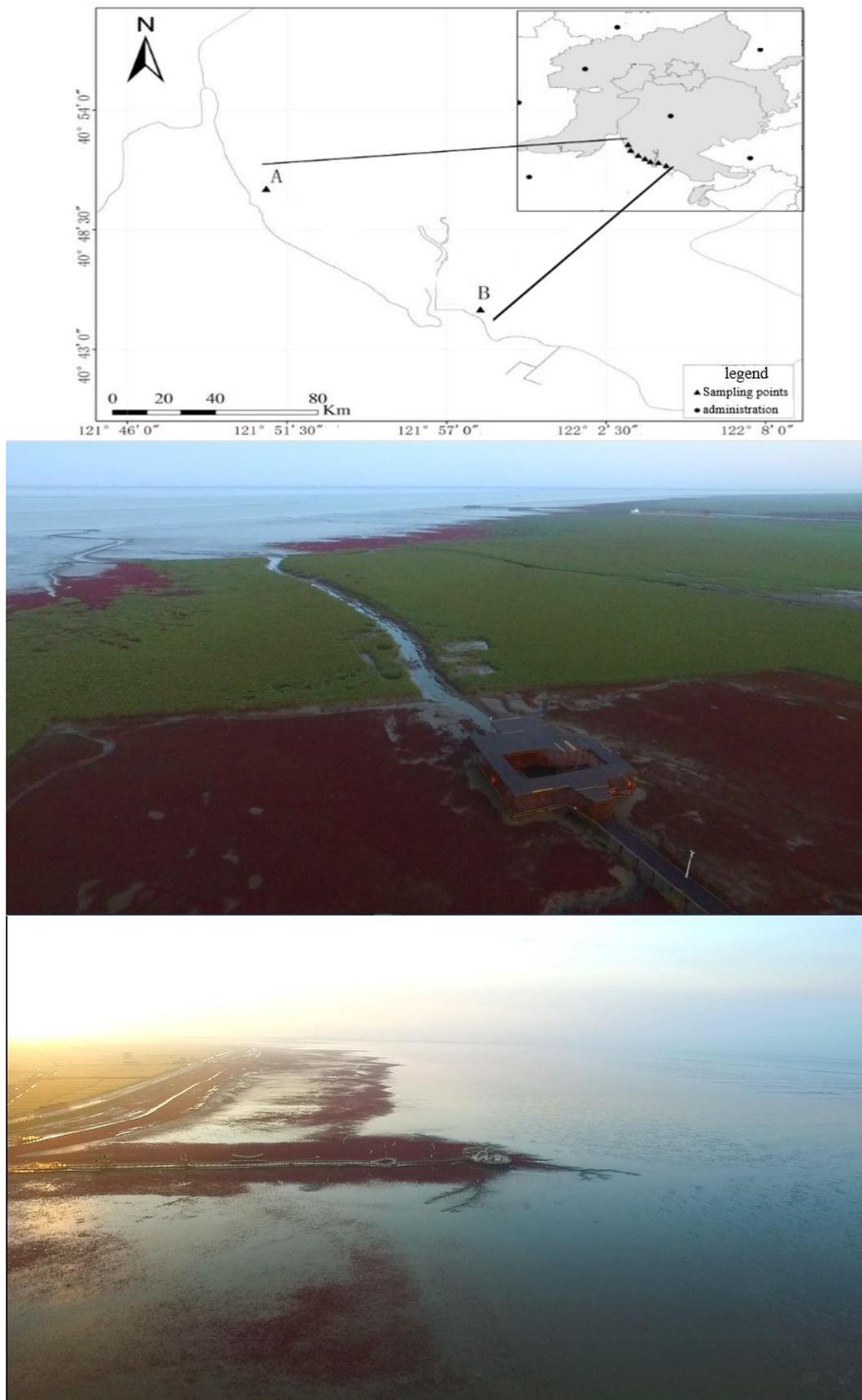
Figure 1. *Schematic diagram of sampling points from 2020 to 2021*

Table 1. *Information on main instruments*

Serial number	Equipment name	Instrument model	Brand/manufacturer
1	Electronic balance	PB 602-N, Sensitivity 0.01 g	Mettler-Toledo, Switzerland
2	Micropipette	Eppendorf Research® plus	Eppendorf, Germany
3	Ultrasonic cleaner	KQ5200E	Kunshan Ultrasonic Instrument Co., Ltd.
4	High performance liquid chromatography	LC-20A	Shimadzu Corporation
5	Accelerated solvent extractor	ASE-350	American Dionex Corporation
6	Chromatographic column	Waters PAH C18	American Waters Company
7	Magnetic stirrer	RETBS25	Aika (Guangzhou) Instrument Equipment Co., Ltd.
8	Blast drying oven	YG101	Wuhan Guoliang Instrument Co., Ltd.
9	High speed refrigerated centrifuge	3K15	German sigma company
10	Ultrapure water machine	Synergy ®	American Millipore Corporation

Table 2. *Information on main reagents*

Serial number	Reagent name	Brand/manufacturer
1	Acetone (analytical pure, chromatographically pure)	Chengdu Kelong Chemical Reagent Factory
2	Dichloromethane (chromatographically pure)	Tianjin Damao Chemical Reagent Factory
3	n-Hexane (chromatographically pure)	Tianjin Damao Chemical Reagent Factory
4	Dichloromethane (analytically pure)	Tianjin Fuyu Fine Chemical Co., Ltd.
5	n-Hexane (analytical grade)	Tianjin Fuyu Fine Chemical Co., Ltd.
6	Concentrated sulfuric acid (concentration 98%)	Lianjiang Ai Lian Chemical Reagent Co., Ltd.
7	Anhydrous Sodium Sulfate	Sinopharm Chemical Reagent Co., Ltd.
8	Floridian Clay Column	Germany SimonAldrich Company
9	Acetonitrile (chromatographically pure)	American ThermoFisher Corporation
10	PAHs mixed standard	American AccuStandard Company
11	Quartz sand	Sinopharm Chemical Reagent Co., Ltd.

At each sampling point, three sets of sediment samples, surface water samples, and *Suaeda heteroptera* plant samples were randomly collected. Sediment samples (0-15 cm) were obtained using a Luoyang shovel. Surface water samples were collected using a water sampler. *Suaeda heteroptera* plant samples were collected, ensuring the integrity of their roots and stems, with 10-15 plants per set. Each soil sample from each sampling point was mixed thoroughly, and each set of *Suaeda heteroptera* samples was properly labeled and stored in sealed bags. All samples were transported to the laboratory and kept frozen. The analysis of PAHs was outsourced to the National Marine Environmental Monitoring Center, and the analysis method was provided by the center. Surface water samples were analyzed within 24 h of collection.

A total of 16 PAHs, listed as priority control pollutants, were analyzed in this study, including (naphthalene Nap), (acenaphthylene Acy), (acenaphthene Ace), (fluorene Flu), (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), (benzo[1,2,3-cd]pyrene Ind), (dibenzo[a,h]anthracene DiB), and (benzo[ghi]perylene BgP).

PAH detection method

In natural environments, such as sediment, surface seawater, and chrysanthemum plants, the levels of PAHs are generally low. Under the assumption of ensuring the

accuracy of experimental results, appropriate analytical methods should be selected based on the principles of shortening analysis time, reducing analysis costs, and minimizing pharmacological hazards. Through comparing factors such as extraction time, extraction reagent cost, operational difficulty, and (United States Environmental Protection Agency USEPA) recommendations, it has been found that ultrasonic extraction method possesses advantages such as simple operation, minimal reagent usage, and short extraction time. Therefore, in this study, ultrasonic extraction method was employed for the extraction of PAHs from all sediment samples, seawater samples, and plant samples (Long, 2017).

Sample pretreatment

Ultrasonic extraction method: Accurately weigh 2.00-5.00 g of sediment (biomass) and 2 g of anhydrous sodium sulfate. Mix them thoroughly. Completely saturate a circular filter paper cylinder with chromatographically pure n-hexane. Place the weighed sediment (biomass) and anhydrous sodium sulfate inside the cylinder, and store it in a 100 mL colorimetric tube with a stopper. Add 60 mL of dichloromethane and 50 µL of PAHs surrogate standard solution. Allow it to soak for 12 h, followed by 20 min of ultrasonic extraction and 5 min of settling. Transfer the extraction solution to a rotary evaporator flask. Repeat the ultrasonic extraction twice with 20 mL of dichloromethane, and combine the extracted solutions in the rotary evaporator flask. Add 1 mL of iso-octane and evaporate the solvent under rotation until the volume is reduced to 1 mL. Add 1 g of copper powder for purification.

Purification: Add n-hexane to a glass chromatographic column, and then add silica gel, neutral alumina, and anhydrous sodium sulfate in sequence. Rinse the column with 40 mL of n-hexane at a flow rate of 2 mL/min for 20 min, discarding the eluate. Transfer the entire sample extract onto the chromatographic column and rinse the column with 80 mL of dichloromethane at a flow rate of 2 mL/min. Collect the eluate using a rotary evaporator flask and concentrate it to approximately 2 mL. Add 5 mL of n-hexane and continue concentrating until the volume reaches 1.0 mL. Transfer the concentrated solution to a sample vial, add 50 µL of deuterated triphenyl internal standard solution, mix well, and proceed with analysis.

Instrument analysis conditions

Chromatographic conditions: HP-5 capillary column (5% Phenyl Methyl Siloxane) with a rated length of 30.0 m, rated inner diameter of 250.00 µm, and rated film thickness of 0.25 µm. The column oven is initially set at 50°C and held for 34 min, then ramped up to a maximum temperature of 325°C. The samples are introduced through the front inlet (without splitting), with 5 injections and an injection volume of 1 µL. The initial temperature of the inlet is set at 290°C. The initial flow rate is 1.0 mL/min with a pressure of 7.54 psi, corresponding to an average linear velocity of 36 cm/s. The purge flow rate is set at 20.0 mL/min for a duration of 0.75 min. The split flow rate is 23.9 mL/min. The gas-saving device is activated, with a gas-saving flow rate of 20.0 mL/min and a gas-saving time of 2.00 min. The gas used for the gas-saving mode is helium.

Data processing

The analysis of polycyclic aromatic hydrocarbon sampling data for each month was conducted. Data analysis was performed using Excel 2016 for initial examination,

followed by one-way analysis of variance (ANOVA) and Duncan's post hoc multiple comparisons using SPSS 24. Differences were considered statistically insignificant when P > 0.05.

Risk assessment method

Sediment quality criteria method

For the assessment of PAHs in the sediments of Panjin Red Beach, this study employed the (sediment quality guidelines SQGs) proposed by Long et al. (1995) to conduct an ecological risk evaluation. The commonly used indicators in SQGs are the (Effects Range Low ERL) and (Effects Range Median ERM). When the concentration of PAHs is below the ERL, the sediments exhibit negligible toxic effects on organisms, with a probability of harmful biological effects less than 10%. When the concentration of PAHs exceeds the ERM, the sediments pose a certain level of toxicity and a significant threat to the survival of organisms. When the pollutant concentration falls between the ERL and ERM, the probability of harmful effects on organisms ranges from 10% to 50%, occasionally resulting in adverse impacts. Furthermore, compounds such as BbF, BkF, Ind, and BgP do not have specified minimum safety values. However, the mere presence of these PAH components in the environment carries a certain level of ecological risk.

Sediment quality guideline method

Currently, there is no unified standard for the risk assessment of pollutants in sediments. Therefore, this study adopted the sediment quality standards from the province of Quebec (Suman et al., 2016), Canada, to evaluate the concentrations of PAHs in the sediments of Panjin Red Beach. These standards consist of five reference values in descending order, covering 12 PAH compounds. They include the (Frequent Effect Level FEL), (Probable Effect Level PEL), (Occasional Effect Level OEL), (Threshold Effect Level TEL), and (Rare Effect Level REL).

Quotient value method

In this study, the quotient value method, as described by MacDonald et al. (2000), was used for the ecological risk assessment of PAHs in the seawater of Panjin Hong Beach. The calculation method for the (hazard quotient HQ) is as follows:

$$HQ = \text{Exposure}/TRV \tag{Eq.1}$$

In *Equation 1,* Exposure refers to the measured exposure concentration, while TRV refers to the toxicity reference value (ecological benchmark). The comparison of PAHs exposure with the ecological benchmark is used to calculate the HQ. An HQ greater than 1 indicates the presence of ecological risk, with a higher ratio indicating a higher risk. Conversely, an HQ less than 1 indicates a lower ecological risk.

Toxicity equivalence method

Given that BaP is highly carcinogenic and the existing ecotoxicological studies on it are more detailed than other PAHs monomers (Cao et al., 2008), researchers in the field of ecotoxicology both domestically and internationally often use the (toxicity

equivalence concentration TEC) with BaP as a reference for ecological risk assessment. In the late 20th century, Nisbet and Lagoy (1992) conducted toxicity experiments and demonstrated that BaP and Dib were the most carcinogenic among the 16 monomeric PAHs controlled by the USEPA, while low molecular weight PAHs had lower carcinogenicity. They further obtained the (toxic equivalence factors TEFs) for various monomeric PAHs relative to BaP through experimental analysis. According to the USEPA's "Provisional Guidance for Quantitative Risk Assessment," the TEF values for each monomeric PAH are determined as follows: TEF = 1.0 when TEF is between 0.51 and 5.0; TEF = 0.1 when TEF is between 0.051 and 0.50; and TEF = 0.01 when TEF is between 0.0051 and 0.050 (Tsai et al., 2004). TEF reflects the "estimated order of potential potency," where a higher TEF indicates greater carcinogenic and toxic potential of the PAHs.

Currently, the toxic equivalence factor method has been widely adopted by researchers both domestically and internationally (De Nicola et al., 2011; Orecchio, 2007). It involves calculating the TEC with BaP as a reference based on the measured concentrations of individual PAHs and their corresponding TEF values. The (total toxicity equivalence concentration TTEC) of the detected PAHs is then obtained by summing up the TEFs of each individual PAH. This approach is used to evaluate the potential ecological and human health risks posed by PAHs based on the TTEC of the target compounds. The calculation formula for TTEC is as follows:

$$TTEC = \sum_{i=1}^{n} TECi = \sum_{i=1}^{n} MSCi \times TEFi \qquad \text{(Eq.2)}$$

In *Equation 2,* TTEC represents the total toxicity equivalence concentration, TEC_i represents the toxicity equivalence concentration of the i-th substance, MSC_i represents the measured concentration of the i-th substance, and TEF_i represents the toxic equivalence factor of the i-th substance (Duan et al., 2009).

Results and discussion

PAHs content in sediment samples from different sampling points in Red Beach Wetland

As depicted in *Figure 2,* a total of 16 priority-controlled PAHs were detected in sediment samples from site A for the years 2020-2021, with PAH concentrations ranging from 0.661 to 56.252 μg/kg. Among these, the highest concentration was observed for BgP at 56.252 μg/kg, which was approximately 85 times higher than the lowest detected compound, DiB. Additionally, aside from BgP, relatively high concentrations of Fla and Phe were also detected at site A, with concentrations of 16.326 and 13.909 μg/kg, respectively. When comparing these results to the sediment PAH monitoring data from 2020 at site A, it can be observed that in 2021, BgP, Fla, and Phe still exhibited relatively high concentrations. However, BgP showed a substantial decrease of 49.522 μg/kg, while Fla and Phe concentrations exhibited smaller variations.

Figure 3 presents the PAHs content in sediment samples from site B at the Red Beach for the years 2020-2021. The number of priority-controlled PAHs detected in sediment samples from this site is the same as that at site A for the same year, with concentrations ranging from 0.896 to 98.465 μg/kg. Notably, Ace exhibited the lowest

concentration at 0.896 µg/kg, while BgP displayed the highest concentration at 98.465 µg/kg, approximately 110 times higher than naphthalene. Five PAHs, namely Phe, Fla, Chr, Bbf, and Ind, exhibited relatively high concentrations at 20.865, 33.858, 19.859, 18.14, and 21.156 µg/kg, respectively.
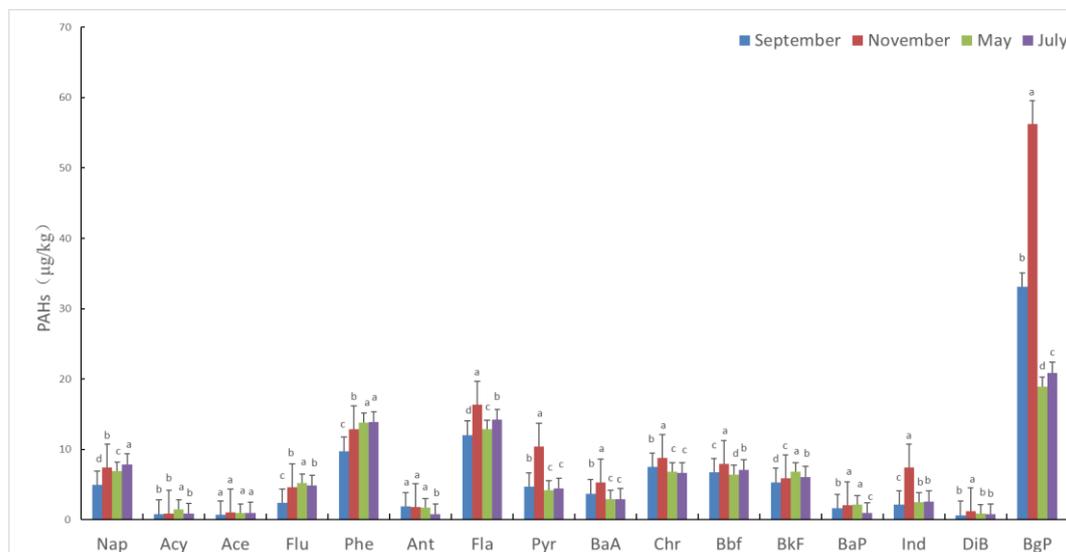

Figure 2. The contents of 16 PAHs in the sediments at station A from 2020 to 2021. Note: Those marked with different lowercase letters indicate significant difference (P < 0.05), otherwise there is no significant difference (P > 0.05). The error line in the figure is expressed by standard deviation, which is the mean of the distance of each data from the mean, the same below
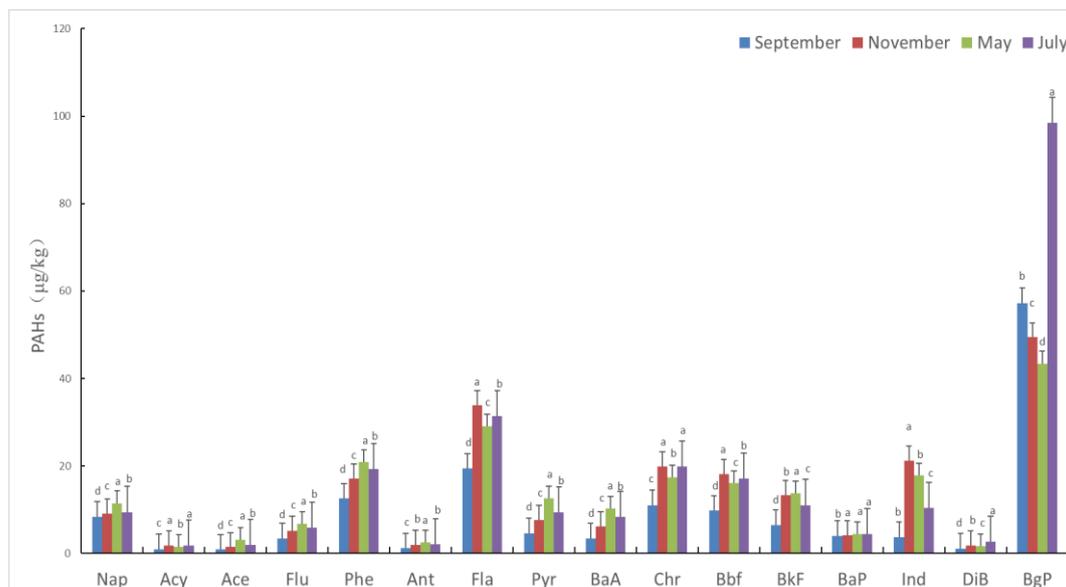

Figure 3. The contents of 16 PAHs in the sediments at station B from 2020 to 2021

From *Figures 2* and *3,* it can be observed that the total PAHs content in sediment at the Red Beach Wetland for the years 2020-2021 follows a cumulative pattern from site

A to site B. The total PAHs content at site A is approximately 0.53 times that at site B, with BgP showing the largest increase in detected content, rising by 119.318 μg/kg from site A to site B.

PAHs concentrations in water samples from different sampling points in Red Beach Wetland

Water samples were collected from Station A in Red Beach Wetland in September and November 2020, and May and July 2021 for PAHs monitoring, its PAHs content is shown in *Figure 4*. The concentrations of PAHs in the water samples ranged from 0.09 to 18.98 ng/L, 0.23 to 23.60 ng/L, 0.05 to 28.65 ng/L, and 0.16 to 28.71 ng/L, respectively. During the monitoring period from 2020 to 2021, all 16 priority PAHs were detected in the water samples at Station A. The concentrations of low molecular weight PAHs, such as Nap and Phe, were consistently higher than those of other PAH species in each month. Over time, the concentration of Nap showed an increasing trend, with a significant increase from September 2020 to July 2021 ($P < 0.05$). The concentration of Phe was also relatively high and exhibited a similar trend as Nap. The concentrations of other detected low molecular weight PAHs were generally higher than those of high molecular weight PAHs, which could be attributed to the higher solubility of low molecular weight PAHs in water.
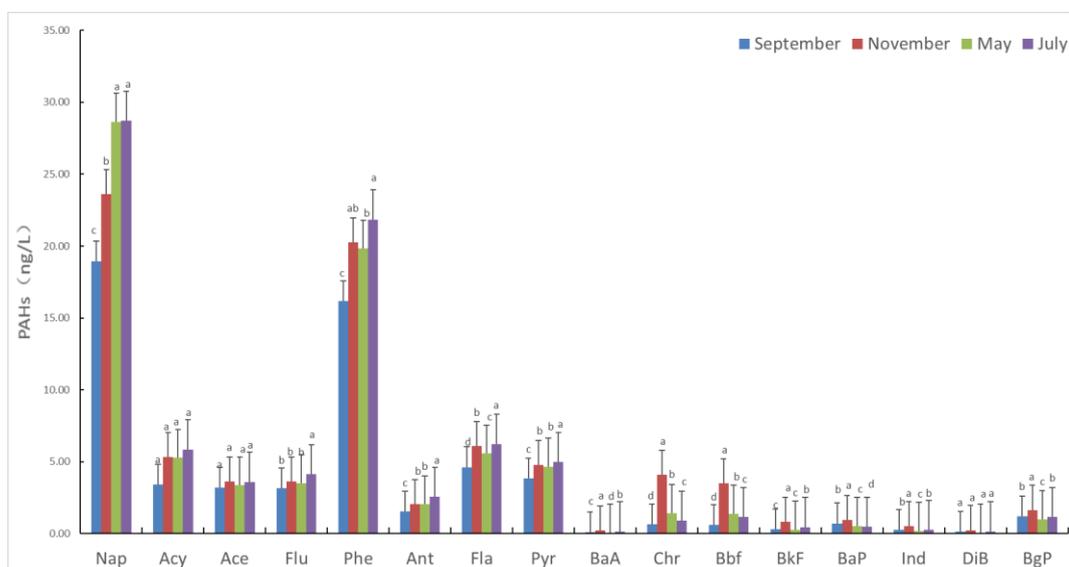

Figure 4. *Contents of 16 PAHs in seawater at station A from 2020 to 2021. Note: For the same PAH, those marked with different lowercase letters indicate significant differences between groups ($P < 0.05$), otherwise there are no significant difference between groups ($P > 0.05$). The error line in the figure is expressed by standard deviation, which is the mean of the distance of each data from the mean, the same below*

Figure 5 presents the monitoring results of PAHs concentrations in water samples collected from Station B in Red Beach Wetland during 2020-2021. As shown in *Figure 5*, the concentrations of PAHs in the water samples varied between 0-20.197 ng/L, 0-41.533 ng/L, 0-39.724 ng/L, and 0-15.412 ng/L for each month, respectively. In September 2020, 14 priority PAHs were detected, followed by 15

priority PAHs in November 2020. In May and July 2021, 13 priority PAHs were detected, with the absence of BaP in all months at Station B. Nap and Phe exhibited relatively high concentrations in all months, with the highest values observed in November 2020 and May 2021, reaching 30.722 ng/L and 39.724 ng/L, respectively. Overall, BgP also showed relatively high detection levels, with the maximum concentration of 41.533 ng/L observed in November 2020.
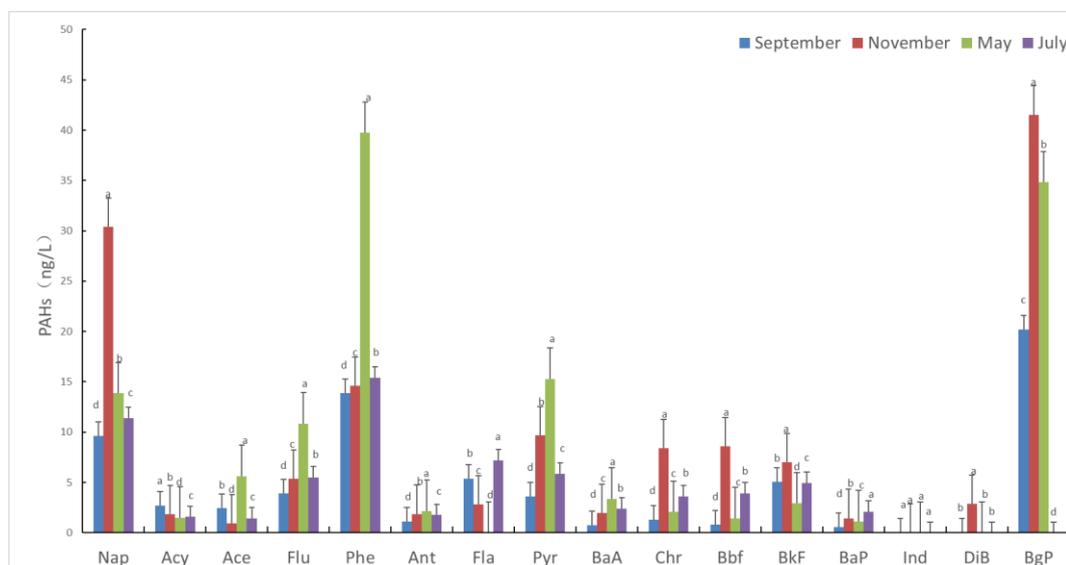

Figure 5. Contents of 16 PAHs in seawater at station B from 2020 to 2021

PAHs content in Suaeda heteroptera samples from various sampling points in Red Beach Wetland

Based on the detection results presented in *Table 3,* it was observed that a total of 16 PAHs were detected in *Suaeda heteroptera* plants from Station B in Red Beach Wetland in 2020. The detected concentrations of each PAH ranged from 0 to 76.299 μg/kg. Among the detected PAHs, Phe, Ant, and BgP exhibited higher levels of accumulation in the roots, stems, and leaves compared to other PAHs. Phe and Ant showed elevated concentrations in all plant tissues, while BgP exhibited lower levels in roots but higher levels in stems and leaves. In September, the total PAHs content in *Suaeda heteroptera* plants was highest in leaves, followed by stems and roots. In November, the total PAHs content was highest in stems, followed by leaves and roots. The differences in total PAHs content among roots, stems, and leaves were statistically significant for each month ($P < 0.05$), and the total PAHs content in roots was consistently lower than that in stems and leaves (*Fig. 6a*).

Based on the monitoring results of PAHs types and content in *Suaeda heteroptera* plants from Station B in Red Beach Wetland in 2021 (*Table 4*), the detected concentrations of PAHs in *Suaeda heteroptera* plants ranged from 0 to 108.03 μg/kg. A total of 14 target PAHs were detected in 2021. Based on the monitoring results in May, Nap exhibited higher concentrations in the roots, stems, and leaves of *Suaeda heteroptera* plants, ranging from 36.654 to 43.622 μg/kg, with the highest content found in leaves. Phe showed the highest concentration in the stems, reaching 108.03 μg/kg, approximately 13 times higher than that in the roots. In the monitoring results of July,

Nap showed the highest concentration in the roots of *Suaeda heteroptera* plants, reaching 67.155 µg/kg, while the lowest concentration was observed in the stems (10.311 µg/kg). Phe exhibited the highest concentration in the roots, reaching 36.793 µg/kg, approximately 5 times higher than that in the stems.

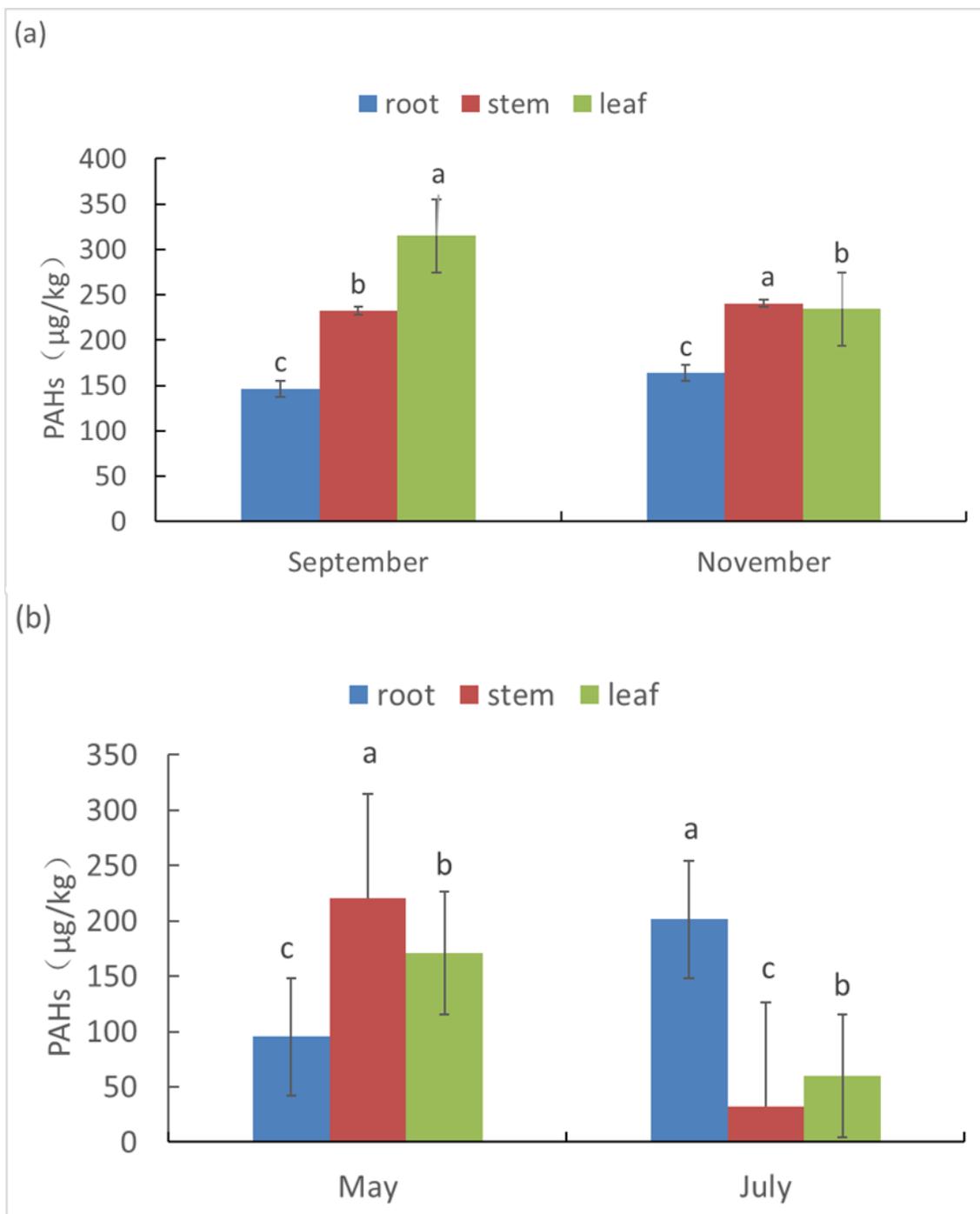***Figure 6.*** *The total amount of various PAHs in Suaeda heteroptera at station B in 2020 and 2021. Note: At the same time, those marked with different lowercase letters indicate significant differences between groups (P < 0.05), otherwise there is no significant difference between groups (P > 0.05). The error line in the figure is expressed by standard deviation, which is the mean of the distance of each data from the mean*

***Table 3.** Types and contents of Suaeda heteroptera PAHs at station B in 2020*

PAHs content (µg/kg)	September 2020			November 2020		
	Root	Stem	Leaf	Root	Stem	Leaf
Nap	8.759	10.569	16.609	31.614	12.840	15.544
Acy	0.432	0.511	0.950	1.822	0.642	0.780
Ace	2.212	2.305	4.212	4.942	4.970	3.992
Flu	6.277	7.220	11.654	13.334	12.347	16.393
Phe	35.100	47.641	76.299	42.074	61.687	55.827
Ant	1.933	2.316	2.745	1.862	1.576	1.743
Fla	26.600	41.343	48.318	23.763	39.164	34.299
Pyr	17.230	21.410	29.750	12.282	17.779	20.733
BaA	1.107	0.684	0.634	3.229	0.638	0.626
Chr	3.537	6.488	8.322	5.752	7.045	9.894
Bbf	1.813	0.896	3.918	4.380	1.345	2.966
BkF	35.391	18.737	8.539	5.448	11.820	11.458
BaP	1.293	1.732	33.513	2.762	1.610	11.157
Ind	0.482	ND	ND	1.922	0.470	ND
DiB	ND	ND	ND	1.258	ND	ND
BgP	4.116	70.261	69.330	7.096	66.525	48.756
PAHs	146.282	232.113	314.793	163.54	240.458	234.168

ND means not detected

***Table 4.** Types and contents of Suaeda heteroptera PAHs at station B in 2021*

PAHs content (µg/kg)	May 2021			July 2021		
	Root	Stem	Leaf	Root	Stem	Leaf
Nap	37.113	36.654	43.622	67.155	10.311	15.518
Acy	ND	ND	ND	ND	ND	ND
Ace	1.901	4.270	6.180	4.764	0.333	1.704
Flu	5.706	38.134	19.928	14.515	2.032	1.805
Phe	8.543	108.030	49.615	36.793	6.953	12.079
Ant	1.359	4.524	1.911	2.608	ND	ND
Fla	8.802	10.042	17.295	12.989	3.836	19.538
Pyr	8.684	6.270	5.127	21.979	ND	ND
BaA	3.506	0.409	1.683	4.063	0.145	0.813
Chr	5.449	2.501	6.983	7.323	1.821	8.282
Bbf	5.528	0.649	2.368	6.440	0.793	ND
BkF	6.274	3.019	11.171	11.978	ND	ND
BaP	0.534	ND	ND	3.436	ND	ND
Ind	ND	ND	ND	ND	ND	ND
DiB	ND	ND	ND	0.864	ND	ND
BgP	2.038	5.712	4.867	6.343	5.698	ND
PAHs	95.437	220.214	170.75	201.25	31.922	59.739

ND means not detected

According to *Figure 6b*, in May, the total PAHs content in *Suaeda heteroptera* plants was highest in the stems, followed by leaves and roots. In July, the total PAHs content was highest in the roots, followed by leaves and stems, contrary to the results observed in May. The differences in total PAHs content among the roots, stems, and leaves of *Suaeda heteroptera* plants were statistically significant for each month ($P < 0.05$). When compared with the monitoring results of total PAHs content in *Suaeda heteroptera* plants from Station B in Red Beach Wetland in 2020 (*Figs. 2–6*), it can be observed that the total PAHs content in 2021 decreased, and the total PAHs content in stems and leaves of *Suaeda heteroptera* plants showed a significant decrease.

Ecological risk assessment of PAHs in Red Beach Wetland sediments

The corresponding toxicity criteria for PAHs in sediments of the Red Beach Wetland in 2020-2021 are presented in *Table 5*. It can be observed that the concentrations of PAHs in the sediments of the Red Beach Wetland are much lower than the ERL values, indicating that the PAH concentrations at sites A and B are below the ERL values. This suggests that the study area is classified as a low ecological risk area, with minimal potential risks to the ecological environment. Additionally, the ecological risks of BbF, BkF, Ind, and Bgp, which do not have specified safety values, cannot be assessed at present.

Table 5. Toxicity assessment of PAHs in Red Beach Wetland sediments

Compound	ERL	ERM	Concentration of PAHs in sediment (µg/kg)		
			Min	Max	Average
Nap	160	2100	4.94	11.47	8.2
Acy	16	500	0.83	1.79	1.26
Ace	44	640	0.72	3.06	1.37
Flu	19	540	2.41	6.76	4.79
Phe	240	1500	9.74	20.87	15.02
Ant	85.3	1100	0.82	2.49	1.74
Fla	600	5100	12.05	33.86	21.15
Pyr	665	2600	4.23	12.61	7.25
BaA	261	1600	2.93	10.27	5.38
Chr	384	2800	6.68	19.86	12.23
Bbf			6.43	18.14	11.16
BkF			5.33	13.72	8.59
BaP	430	1600	0.93	4.46	2.96
Ind			2.12	21.16	8.47
DiB	63.4	260	0.66	2.64	1.35
BgP			18.93	98.46	47.20

Table 6 presents the reference values for PAHs in sediments of the Red Beach Wetland. It can be observed from the *Table 6* that the concentrations of PAHs in the sediments of Red Beach are below the REL. This indicates that the ecological risk in the Red Beach area of Panjin is low, which is consistent with the assessment results based on SQGs.

Table 6. *Quality evaluation criteria for PAHs in Red Beach Wetland sediments*

Compound	REL	TEL	OEL	PEL	FEL	Concentration of PAHs in sediment (µg/kg)		
						Min	Max	Average
Nap	17	35	120	390	1200	4.94	11.47	8.2
Acy	3.3	5.9	30	130	340	0.83	1.79	1.26
Ace	3.7	6.7	21	89	940	0.72	3.06	1.37
Flu	10	21	61	140	1200	2.41	6.76	4.79
Phe	25	42	130	520	1100	9.74	20.87	15.02
Ant	16	47	110	240	1100	0.82	2.49	1.74
Fla	47	110	450	2400	4900	12.05	33.86	21.15
Pyr	29	53	230	880	1500	4.23	12.61	7.25
BaA	14	32	120	390	760	2.93	10.27	5.38
Chr	26	57	240	860	1600	6.68	19.86	12.23
Bbf						6.43	18.14	11.16
BkF						5.33	13.72	8.59
BaP	11	32	150	780	3200	0.93	4.46	2.96
Ind						2.12	21.16	8.47
DiB	3.3	6.2	43	140	200	0.66	2.64	1.35
BgP						18.93	98.46	47.20

Ecological risk assessment of PAHs in seawater of Red Beach Wetland

The HQ results of PAHs in the study area are presented in *Table 7*. It can be observed from the results that the HQ values in the Red Beach Wetland of Panjin are significantly lower than 1, indicating a very low ecological risk.

Table 7. *TRV and HQ of each PAHs*

Compound (ng/L)	TRV ($\times 10^3$)	HQ ($\times 10^{-3}$)
Nap	490	0.04
Acy		
Ace	23	0.13
Flu	11	0.45
Phe	30	0.67
Ant	3	0.63
Fla	6.16	0.77
Pyr	7	0.94
BaA	34.6	0.04
Chr	7	0.4
Bbf		
BkF		
BaP	0.014	70
Ind		
DiB	5	0.09
BgP		

Ecological risk assessment of PAHs in Suaeda heteroptera in Red Beach Wetland

The toxic equivalent concentrations of PAHs in the *Suaeda heteroptera* plants in Panjin Red Beach Wetland were calculated using the TEF method. The total toxic equivalent concentration of the 16 PAHs and the BaP toxic equivalence factor are shown in *Table 8*. From *Table 8*, it can be observed that BaP contributes the highest percentage to the total toxic equivalent concentration (with an average value of 69.08%), followed by BkF (15.27%), Bbf (3.84%), BgP (3.59%), and DiB (2.62%). This contribution is closely related to the relative toxicities of the PAHs as determined by their TEF values. BaP and BkF, as the major contributors, pose the highest potential carcinogenic risks and should be given special attention.

Table 8. *Toxic equivalent concentration of polycyclic aromatic hydrocarbons in Suaeda heteroptera in Red Beach Wetland*

Compound (µg/kg)	TEF	TEC	TTEC
Nap	0.001	0.31	
Acy	0.001	0.005	
Ace	0.001	0.04	
Flu	0.001	0.15	
Phe	0.001	0.54	
Ant	0.01	0.23	
Fla	0.001	0.29	
Pyr	0.001	0.16	
BaA	0.1	1.8	81.065
Chr	0.01	0.73	
Bbf	0.1	3.11	
BkF	0.1	12.38	
BaP	1	56	
Ind	0.1	0.29	
DiB	1	2.12	
BgP	0.01	2.91	

Source analysis of PAHs in Red Beach Wetland

PAHs, one of the earliest identified chemical carcinogens, are not metabolites of the human body, but are associated with incomplete combustion of fuels such as petroleum and coal, leaks from petroleum products, and production processes in various organic chemical industries. PAHs can settle at low temperatures and volatilize at high temperatures. Influenced by atmospheric transport, they can be distributed across multiple latitudes worldwide, affecting the endocrine and reproductive systems of organisms and disrupting the stability of ecosystems, ultimately posing a risk to human health (Dudhagara et al., 2016). In a study by Li et al. (2020) on sediment samples from the summer of 2016 in the Zhoushan Sea area, the sources and distribution of PAHs in the sediments were investigated. The results showed that the PAHs content in coastal sediments of the Zhoushan Sea area was generally high, with petroleum leakage being a primary source, and their distribution was influenced by factors such as vessel navigation and tidal currents (Gao et al., 2021). conducted an investigation on the

distribution and sources of PAHs in sediments of the northern South China Sea. The results indicated that 12 priority PAHs were detected in the sediment samples, with low molecular weight Ind and high molecular weight BgP being the most abundant. The PAHs in the sediments of the northern South China Sea were mainly derived from charcoal residues of land-based fires, which is consistent with the findings of Ke et al. (2014). The study area in this experiment is the Panjin Red Beach Wetland, which is adjacent to oilfields and rice paddies. Therefore, it is speculated that the total PAHs content in the sediments of the Red Beach Station B in 2020-2021 is higher than that of Station A, possibly due to the accumulation of PAHs associated with petroleum extraction and biomass burning in the nearby water bodies flowing into the sea.

The main environmental medium for the migration of PAHs is the atmosphere. High and medium molecular weight PAHs such as Fla and BgP can adsorb onto particles and settle on the Earth's surface through atmospheric deposition. They can also re-enter the atmosphere through evaporation with increasing temperatures. The distribution of PAHs in the atmosphere is more extensive than in soils and water bodies, and it is influenced by factors such as wind direction, wind speed, and seasons, which affect the deposition of PAHs (Kong et al., 2012). Some PAHs can easily adsorb onto aquatic plants and sediments, but these associations are not stable. When disturbances occur in the water body, particulate-bound PAHs can re-enter the water, causing re-pollution of the marine environment. Another portion of PAHs can be directly ingested by benthic and planktonic organisms (Hong, 2008).

Conclusion

(1) A total of 16 priority-controlled PAHs were detected in the sediment of Red Beach during the years 2020-2021. Among the detected PAHs, Fla, Pyr, and BgP showed relatively high concentrations. Temporally, the total PAH concentration at Site A exhibited a decreasing trend, while the PAH concentration at Site B showed an increasing trend during the years 2020-2021. Spatially, the analysis of spatial distribution showed that the total PAH concentration in the sediment of Red Beach gradually increased from Site A to Site B during the years 2020-2021.

(2) In the water at Site A of Red Beach, a total of 16 priority-controlled PAHs were detected during the years 2020-2021, with higher concentrations of Nap and Pyr. At Site B, a total of 15 priority-controlled PAHs were detected in 2020, and 14 were detected in 2021, with higher concentrations of Nap, Pyr, and BgP. Temporally, the highest total PAH concentration in the water at Site A was observed in July 2021, while the lowest was observed in September 2020. The PAH concentration increased with the transition to higher temperatures. In contrast, at Site B, the highest total PAH concentration was observed in November 2020, and the lowest was observed in July 2021, showing a decreasing trend over time. Spatially, the total PAH concentration in the seawater at Red Beach gradually increased from Site A to Site B during the years 2020-2021.

(3) In 2020, a total of 16 priority-controlled PAHs were detected in the roots, stems, and leaves of *Suaeda heteroptera* at Site B of Red Beach, with higher concentrations of Pyr, Fla, and BgP. In 2021, 14 priority-controlled PAHs were detected in the *Suaeda heteroptera*, with higher concentrations of Nap and Pyr. Temporally, the total PAH concentration in the *Suaeda heteroptera* showed a decreasing trend, with the root concentration decreasing at a slower rate than the stem and leaf concentrations.

(4) Ecological risk assessment of the sediment in the study area was conducted using sediment quality guidelines and sediment quality standards, revealing relatively low ecological risks. However, the potential ecological risks should not be ignored. Ecological risk assessment of the seawater in the study area using the quotient method showed a low ecological risk. Carcinogenic risk assessment of polycyclic aromatic hydrocarbons in *Suaeda heteroptera* using toxic equivalent factors indicated a certain potential carcinogenic risk, highlighting the need for attention.

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