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Accumulation risk and sources of heavy metals in supratidal wetlands along the west coast of the Bohai Sea†

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The heavy metals Al, Cr, Cu, Ni, Pb, Zn, Fe, Mn, As, and Cd in the rainfall-driven supratidal wetlands along the west coast of the Bohai Sea (the areas are named site 1, site 2, site 3, and site 4 from south to north in the gradient in this study) are tested for their accumulation risks and sources. Results show that the distribution and enrichment of the heavy metals in the supratidal wetlands are lower in site 1 than in sites 2–4. The risk indices (RIs) of all sites are less than 150, indicating low–moderate risk. However, the RI values are primarily dominated by the risk indices (E_r^i) of As and Cd. The accumulative contribution values of E_r^i -As and E_r^i -Cd in sites 1, 2, 3, and 4 are 79.05%, 77.80%, 80.54%, and 76.43%, respectively. Additionally, the contamination degree (C_d) and the Nemeru comprehensive pollution index (PN) of the supratidal wetland in site 1 are 6.86 and 0.74 respectively, indicating a low-risk state. By contrast, the C_d and PN values of the other three supratidal wetlands are higher than those of site 1, suggesting an increasing accumulation risk for heavy metals in sites 2, 3 and 4. Our analysis indicates that the heavy metals Al, Cr, Mn, and Fe in all the supratidal wetlands mainly originate from the weathering of rocks and their parent materials. Pb is significantly correlated with anthropogenic activities, while Cu, As, and Cd are likely induced by anthropogenic activities and atmospheric deposition. The sources of Ni and Zn should be determined on the basis of the situation of the wetland and its surrounding areas. For example, Ni is mainly affected by anthropogenic activities in site 2, whereas the origins of Ni are soil parent materials or atmospheric depositions in sites 1, 3, and 4. Our results can provide data to support the utilization strategy and sustainable development plans for marine space resources on the coast of the Bohai Sea.

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1 Introduction

Heavy metal pollution has widely attracted special attention from scientists and environmentalists,^{1,2} mainly because such metals are easily accumulated by organisms, are gradually enriched and magnified along the food chains of ecosystems, and ultimately threaten human health.^{3–5} Heavy metals in soil are often considered a powerful indicator of the effects of human activities given that the origins of heavy metal pollution in the environment are primarily anthropogenic types.⁶

Coastal wetlands generally lie between terrestrial and marine ecosystems and often act as natural filters in removing chemicals and contaminants from surface runoff or river water.⁷ Wetland soils have an important role in transferring chemical contaminants, including organic pollutants and heavy metals, through the physicochemical processes of adsorption, ligand exchange, and sedimentation.⁸ Heavy metals in wetland soils

are mainly determined by their chemical forms and their binding states, and the accumulation, mobility, and toxicity of these heavy metals affect both soils and organisms.⁹ Moreover, the migration and enrichment of heavy metals are affected by soil physicochemical properties, such as pH, soil organic matter (SOM), temperature, and salinity, among others, and they subsequently affect the mobility of heavy metals, further influencing their accumulation in soils.^{10,11} Heavy metals are non-biodegradable or refractory pollutants and can persist in the ecosystem for a long time.¹² Once a certain amount of heavy metals is accumulated in plant tissues, the growth or survival of plants becomes adversely affected, and the wetland ecosystems become unstable.^{13,14} In addition, heavy metals in litter or rotted leaves usually increase in concentration during decomposition and can continue to be deposited in the sediment or transported by water flow to estuarine and coasts,¹⁵ which then increase the pollution risk of these areas.

Heavy metal pollution has become increasingly serious in the past two decades due to various urbanization activities in coastal areas, such as the rapid industrial development of many large river deltas.¹ As for the impact of industrial activities on the accumulation of heavy metals in wetlands, researchers believe that wetland reclamation may lead to the increase in

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metal contents in soil.^{16–18} Other researchers have also suggested that agriculture and aquaculture can increase heavy metal content (*e.g.*, Cd) in lagoon sediments.¹⁹ Studies have also shown that traffic can lead to high deposits of heavy metals in roadside soil.²⁰ The flow-sediment regulation regime of Yellow River has reportedly increased the content of some heavy metals in the estuarine and intertidal wetlands.²¹ Therefore, a comprehensive understanding of the dynamic changes, sources, and input pathways of heavy metals can help build a sustainable utilization strategy for marine space resources and promote the harmonious development of human and nature.

The coastal region of Bohai Sea, which is one of the most active areas in China, has been subjected to considerable environmental pressure due to its dense population and high agricultural, aquaculture, urban construction activities. The categories of heavy metals and their input pathways vary depending on the types of human activities, but an information gap has considerably limited our understanding of the sources and accumulation risk of heavy metals in certain habitats. Studies on heavy metal pollution have been carried out for some coastal wetlands,^{1,2,22,23} but the research on heavy metals in rainfall-driven supratidal wetlands remains to be rare. As we all known, the community in the supratidal habitat often experiences long dry periods and then becomes waterlogged following heavy rainfall.²⁴ Thus, rainfall-driven wetland is often observed in the supratidal zone of Northern China, and its hydrologic regime mainly depends on rainfall events in wet seasons.²⁵ Compared with intertidal wetlands and offshore waters, rainfall-driven supratidal wetlands are more easily disturbed by human activities. This differentiation poses a challenge in investigating the accumulation risk and sources of heavy metals in supratidal wetlands.

The heavy metals of Al, Cr, Cu, Ni, Pb, Zn, Fe, Mn, As, and Cd in the rainfall-driven supratidal wetlands along the west coast of Bohai Sea are tested in this study. The objectives of our study are as follows: (a) learn the distribution and enrichment characteristics of the above mentioned heavy metals in the rainfall-driven supratidal wetlands of Bohai Sea; (b) evaluate the accumulation risk of the heavy metals in the rainfall-driven supratidal wetlands of Bohai Sea; and (c) explore the sources and input pathways of the heavy metals in the different rainfall-driven supratidal wetlands of Bohai Sea.

2 Materials and methods

2.1 Site description

The sites selected for the present study are located along the west coast of Bohai Sea. Bohai Sea, the largest semi-enclosed marginal sea along the continental shelf of China, is mainly composed of Liaodong Bay, Bohai Bay, Laizhou Bay, and the central basin. The major rivers along the coast of Bohai Sea are as follows: Yellow River, Liaohe River, Luanhe River, Haihe River, Jiyunhe River, and Xiaoqinghe River. These rivers carry 1.3×10^9 t of sediments into the sea each year, particularly by Yellow River (1.2×10^9 t), Haihe River (7.0×10^7 t), Liaohe River (5.5×10^7 t), and Luanhe River (2.4×10^7 t).²⁶ Apart from

transporting large volumes of sediments to the sea, the rivers also carry environmental pollutants to the offshore waters and coastal wetlands. For example, heavy metals pollutants enter the rivers *via* surface runoff and then flow to Bohai Sea. In addition, the region around Bohai Sea has one of the densest populations with the highest social and economic development levels in China. However, the rapid economic development of the region has led to environmental problems, and pollution due to heavy metals in the coastal habitats and offshore waters is currently a major environmental issue.

In this study, four study sites in the supratidal regions along the west coast of Bohai Sea are selected. The sites are named site 1, site 2, site 3, and site 4 from south to north in the gradient shown in Fig. 1. The study area includes two of the three bays (Bohai Bay and Laizhou Bay) of Bohai Sea. The number and types of coastal wetlands in the study area are large and diverse, respectively.

The first study site (site 1) is located in the coastal supratidal wetland of Weifang, Shandong Province. All sampling sites (E: $119^\circ 22' - 119^\circ 46'$; N: $37^\circ 03' - 38^\circ 07'$) lie within the experimental area of the Changyi Marine Ecology Special Reserve, which is the only national reserve for *Tamarix chinensis* protection in China. Site 1 has a warm and semi-humid continental monsoon climate. The average annual temperature is approximately 12.9°C , the average annual rainfall is 580–660 mm, and the average annual evaporation is 1764–1859 mm. The soil type is coastal solonchak, and the vegetation types are mainly shrubs and herbs. According to our investigation of site 1, the dominant shrub species are *Tamarix chinensis*, and the dominant herbaceous plants are *Artemisia capillaries*, *Phragmites australis*, and *Setaria viridis*.

The second study site (site 2) is located in the coastal supratidal wetland of Dongying, Shandong Province. All sampling sites (E: $118^\circ 15' - 119^\circ 19'$; N: $37^\circ 24' - 38^\circ 10'$) lie within the experimental area of Yellow River Delta National Nature Reserve. Site 2 is characterized by a warm and semi-humid continental monsoon climate with an average annual temperature of 12.8°C , an average annual precipitation of 556 mm, and an average annual evaporation of 1885 mm. The soil type is coastal solonchak, and the vegetation type is a meadow landscape. Annual and perennial herbs are dominant, whereas woody plants are rare. *Suaeda salsa*, *Phragmites australis*, and *Tamarix chinensis* have high frequencies of occurrence in site 2.

The third study site (site 3) is located in the coastal supratidal wetland of Binzhou, Shandong Province. All sampling sites (E: $117^\circ 50' - 118^\circ 00'$; N: $38^\circ 13' - 39^\circ 00'$) lie within the experimental area of Shell Island and Wetland National Nature Reserve. The climate of site 3 is north temperate continental monsoon. The average annual temperature is 12.0°C , the average annual precipitation is 575.4 mm, and the average annual evaporation is 1213.5 mm. The soil type is coastal solonchak. According to our survey, *Artemisia carvifolia*, *Phragmites australis*, *Cynanchum chinense*, *Caragana korshinskii*, and *Suaeda salsa* are the most popular species in site 3.

The fourth study site (site 4) is located in the coastal supratidal wetland of Tianjin. All sampling sites (E: $117^\circ 30' - 117^\circ 47'$; N: $38^\circ 44' - 39^\circ 13'$) lie within the estuarine region of Yongdingxin River in the Binhai New Area. Tianjin has a warm



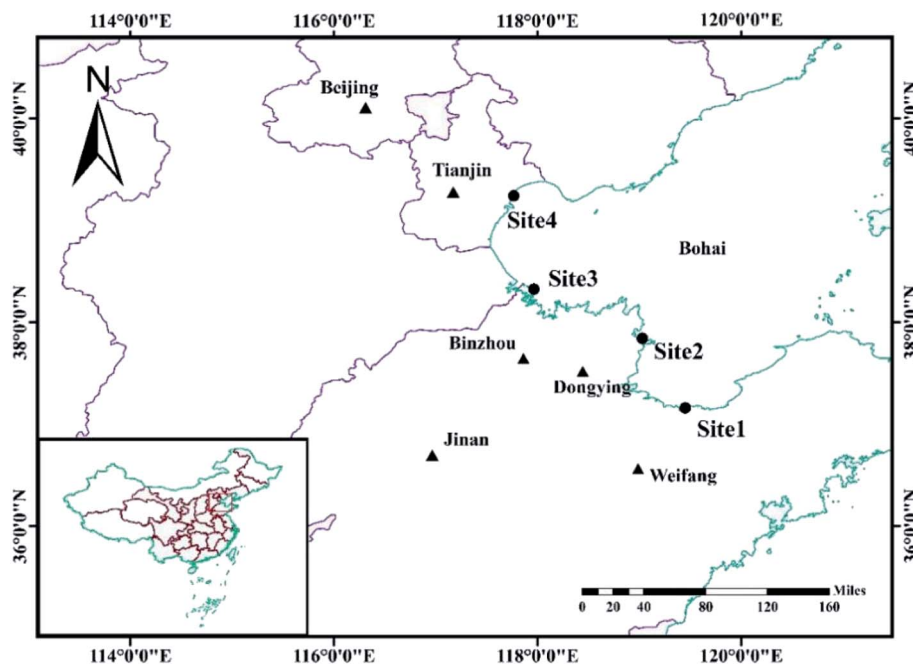


Fig. 1 Map of the coast of Bohai Sea and the location of our study sites. Cities are indicated by triangles, study sites are indicated by dots.

temperate monsoon continental climate with marine climatic characteristics. The average annual temperature is 13.3 °C, the average annual precipitation is 566.0 mm, and the average annual evaporation is 1500 mm. The soil type is coastal solonchak. The most popular herbaceous plants based on the plot survey of site 4 are *Suaeda salsa*, *Setaria viridis*, *Phragmites australis*, and *Salsola collina*, and the woody plant is mainly *Tamarix chinensis*.

2.2 Sampling collection

Samples were collected from the four study sites on August 2014 and August 2015. The seasonal variations of the annual and monthly precipitations are shown in Fig. 2, which can provide the information for waterlogging frequency, duration and water depth in those rainfall-driven wetlands. In this study, each site is

equipped with two sampling strips perpendicular to the coast-line, the distance between the two sampling points in each strip is 50 m, and a quadrat of 3 m × 3 m was performed in each point. Ten to twenty quadrats were set randomly in each study site based on the situation on the field. In particular, 20, 14, 10, and 20 quadrats were plotted in the supratidal wetlands of sites 1, 2, 3, and 4, respectively. The species names and the number of plants were investigated and recorded for each quadrat. Then, soil samples at depths of 0–10, 10–20, and 20–30 cm were collected randomly from five points in a quadrat. Samples of the same layers in each quadrat were mixed and placed inside polyethylene bags and brought to the laboratory for air drying. In this study, a total of 60, 42, 30 and 60 soil samples were collected from sites 1, 2, 3 and 4, respectively. All dried soil samples were ground into fine powder and passed through a 0.149 mm nylon sieve and then sealed in plastic bottles for chemical analysis.

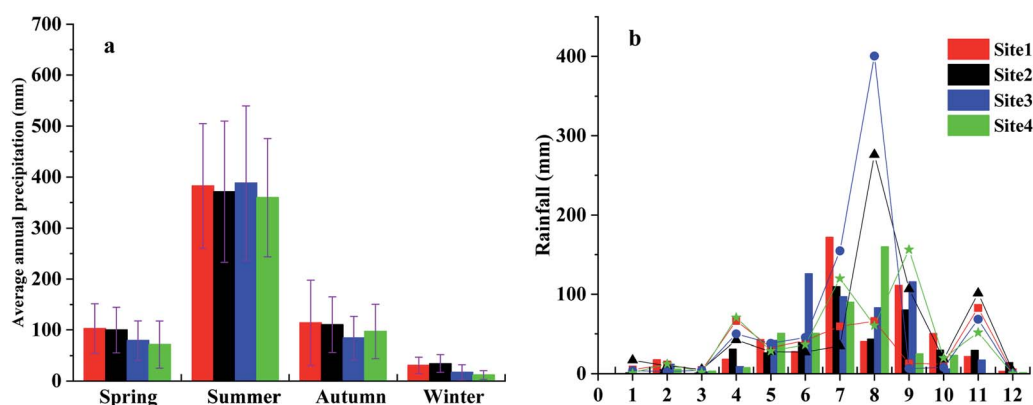


Fig. 2 Seasonal and monthly variation of mean annual precipitation along the west coast of Bohai Sea. (a) Seasonal variation of mean annual precipitation; (b) monthly variation of mean annual precipitation in sampling year (histogram indicates 2014, line indicates 2015).



2.3 Chemical analysis

In this study, each soil sample was digested with 9 ml H₂SO₄ and 1 ml HF, then was dissolved by microwave assisted digestion at 160 °C for two hours. Finally, the digested solution was adjusted to 25 ml in a volumetric flask for trace elements measurement. Here, an inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian, USA) was performed to analyze the concentrations of Al, Cr, Cu, Ni, Pb, Zn, Fe, Mn, As, and soil phosphorus (P). Quality assurance (QA) and quality control (QC) were estimated using duplicates, method blanks and national standard reference materials (GSB 04-1767-2004). During measurement, at least one control sample was spiked with each set of samples (1 bank for each 10 samples), and each measurement was replicated three times. The test results were reliable if the repeat sample analysis error was below 5%.²³ Atomic absorption spectroscopy was conducted to test the concentration of Cd in the soils. In this experiment, SOM was measured by the potassium dichromate titration method.²⁷ Soil nitrogen (N) concentration was analyzed by an elemental analyzer (2400II CHNS/O Elemental Analyzer, PerkinElmer, USA). Soil pH was measured by the potentiometric method at the soil–water ratio of 1 : 2.5 (IQ-150 Conductivity Analyzer, Germany). Salinity was measured by the weighing method at the soil–water ratio of 1 : 5. All measurements were repeated thrice to avoid systematic errors, and the arithmetic mean values were used for subsequent data analysis. The physicochemical properties of the soil samples are listed in Table 1. The background values of the heavy metals of Al, Cr, Cu, Ni, Pb, Zn, Fe, Mn, Cu, As, and Cd in Shandong are 66.2 g kg⁻¹, 66 mg kg⁻¹, 24 mg kg⁻¹, 25.8 mg kg⁻¹, 25.8 mg kg⁻¹, 63.5 mg kg⁻¹, 26.9 g kg⁻¹, 644 mg kg⁻¹, 9.3 mg kg⁻¹, and 0.084 mg kg⁻¹, respectively; as for Tianjin, the background values are 73.2 g kg⁻¹, 84.2 mg kg⁻¹, 28.8 mg kg⁻¹, 33.3 mg kg⁻¹, 21.0 mg kg⁻¹, 79.3 mg kg⁻¹, 33.5 g kg⁻¹, 686 mg kg⁻¹, 9.6 mg kg⁻¹ and 0.09 mg kg⁻¹.²⁸

2.4 Enrichment factor

The enrichment factors (EFs) of heavy metals can be calculated by the following formulation:

$$EF = \frac{\left(\frac{C_M}{C_R}\right)_{\text{sample}}}{\left(\frac{C_M}{C_R}\right)_{\text{background}}} \quad (1)$$

where $\frac{C_M}{C_R}$ is the ratio of measured and reference metals of the soil samples and their corresponding background values. In the present work, Al was selected as a reference metal to assess

heavy metals (Cr, Cu, Ni, Pb, Zn, Fe, Mn, Cu, As, and Cd) contamination in soil samples.^{2,23} While Mn was used as the reference metal for the calculation of EF-Al.²⁹ Contamination can be classified on the basis of the following EF values: EF < 2, minor enrichment; 2 ≤ EF < 5, moderate enrichment; 5 ≤ EF < 20, moderately severe enrichment; 20 ≤ EF < 40, severe enrichment; and EF ≥ 40, extremely severe enrichment.³⁰

2.5 Risk index

Ecological risk index (RI) can be estimated by the following equation:

$$RI = \sum_{i=1}^m E_r^i = \sum_{i=1}^m T_r^i \times C_r^i = \sum_{i=1}^m T_r^i \times \frac{C^i}{C_n^i} \quad (2)$$

where E_r^i is the potential ecological risk of a single heavy metal, and T_r^i is the toxic-response factor of the heavy metal, as suggested by Hakanson *et al.*³¹ In the present work, the T_r^i values of the heavy metals of Al, Cr, Cu, Ni, Pb, Zn, Fe, Mn, Cu, As, and Cd were 1, 2, 5, 5, 5, 1, 1, 1, 10, and 30, respectively. In eqn (2), C^i denotes the measured concentration of the i -th heavy metal in the soil sample, and C_n^i denotes the background value of the i -th heavy metal. Contamination can be classified on the basis of the following RI values: RI < 150, low ecological risk; 150 ≤ RI < 300, moderate ecological risk; 300 ≤ RI < 600, considerate ecological risk; and RI ≥ 600, high ecological risk.

2.6 Degree of contamination

Degree of contamination (C_d) can be calculated by the following equation:³¹

$$C_d = \sum_{i=1}^m CF \quad (3)$$

$$CF = \frac{C^i}{C_n^i} \quad (4)$$

where C^i is the measured concentration of the i -th heavy metal in the soil sample (in mg kg⁻¹), and C_n^i is the background value of the i -th heavy metal (in mg kg⁻¹). Contamination can be classified on the basis of the following C_d values: $C_d \leq 8$, low risk; $8 < C_d \leq 16$, moderate risk; $16 < C_d \leq 32$, considerate risk; and $C_d > 32$, high ecological risk.

2.7 Nemerio comprehensive pollution index

In order to quantify the degree of heavy metals contamination, the Nemerio comprehensive pollution index (PN) method was used in this study. Its formula is:

Table 1 Soil physicochemical properties in the four supratial wetlands along the west coast of Bohai Sea

Study site	SOM (g kg ⁻¹)	P (mg g ⁻¹)	pH	Salt (‰)	N (mg g ⁻¹)
Site 1	9.21 ± 0.60	0.38 ± 0.11	8.31 ± 0.35	1.16 ± 0.53	0.48 ± 0.14
Site 2	5.10 ± 1.23	0.53 ± 0.03	8.23 ± 0.11	5.68 ± 2.41	0.74 ± 0.57
Site 3	9.25 ± 1.62	0.45 ± 0.14	8.53 ± 0.12	6.07 ± 1.49	0.86 ± 0.08
Site 4	12.44 ± 6.01	0.49 ± 0.02	8.11 ± 0.20	1.95 ± 0.47	0.90 ± 0.39



$$PN = \sqrt{\frac{\left(\frac{C_i}{S_i}\right)_{\max}^2 + \left(\frac{1}{n} \sum_{i=1}^m \frac{C_i}{S_i}\right)^2}{2}}, \quad (5)$$

where PN is the synthesis evaluation score, C_i is the measured content of the i -th element at a sampling point, and S_i is the evaluation criterion of the i -th element. In this study, the evaluation criterion is based on the China Environmental Quality Standard for soil metals (GB15618-2018) (pH > 7.5). Among them, Al, Fe and Mn are evaluated by the background values of territorial soil elements (Al, Fe and Mn are not specified in GB15618-2018). The PN value was graded into five categories:³² $PN \leq 0.7$, safety; $0.7 < PN \leq 1.0$, guard; $1.0 < PN \leq 2.0$, low pollution; $2.0 < PN \leq 3.0$, moderate pollution; and $PN > 3.0$, severe pollution.

2.8 Data analysis

One-way ANOVA was used to test the differences of the heavy metals and the other soil properties from the four study sites. Multiple-comparison tests were carried out. In particular, the Games–Howell method (Levene's test) was performed for variances assumed to be heterogeneous, while the Tukey's method was carried out for homogeneous variances. Spearman's correlation analysis was used to test the relationships between the physicochemical characteristics of the soil samples and the heavy metals. Correlation coefficients were depicted as bar graphs. Principal component analysis (PCA) was performed for the concentrations of all heavy metals and the physicochemical properties of the soil samples (salinity, pH, soil N, soil P, and SOM). PCA was also performed to identify the main sources of the heavy metals, which then can explain the behavior and input pathways of these heavy metals in the supratidal wetlands of Bohai Sea. All statistical analyses in this study were conducted with SPSS 21.0 for Windows, and all figures were constructed by the Origin 8.5 software.

3 Result and discussion

3.1 Distribution of heavy metals

The mean concentrations of Al, Cr, Cu, Fe, and Mn are lower than their local background values (Fig. 3a–c, g and h), implying the absence of enrichment of these heavy metals in the coastal sediments of Bohai Sea. The mean concentration of Ni (40.91 mg kg⁻¹) in the supratidal wetland of site 2 is higher than its local background value (Fig. 3d), which indicates that Ni concentration in this particular habitat may have been affected by other external factors. Wen *et al.*³³ have reported a similar result (*i.e.*, Ni with a mean concentration of 44.9 mg kg⁻¹) for the same region of the Yellow River Delta. By contrast, the concentrations of Ni in the supratidal wetlands of sites 1, 3, and 4 are lower than their local background values (Fig. 3d). The concentrations of Pb in the supratidal wetlands of sites 1 and 2 are lower than their local background values, whereas those of sites 3 and 4 (mean values of 30.43 mg kg⁻¹ and 21.04 mg kg⁻¹, respectively) are significantly higher than their local background values (Fig. 3e). The findings indicate that Pb in these habitats has not originated from pedogenic weathering and instead may have stemmed from

anthropogenic activities. The result of the present study is supported by the findings of Zhang *et al.*⁵ and Wen *et al.*³³ who analyzed Shell Bay (site 3) and Yongdingxin River Watershed (site 4). In those studies, the mean values of Pb were as high as 34.4 mg kg⁻¹ for Shell Bay and 38.5 mg kg⁻¹ for the Yongdingxin River Watershed, the reported values are higher than the local background values in this study.

The mean concentrations of Zn in the supratidal wetlands of sites 2, 3, and 4 are 66.94 mg kg⁻¹, 75.12 mg kg⁻¹, 108.13 mg kg⁻¹, respectively (Fig. 3f), which are higher than their background values. This finding suggests that the Zn concentrations in these habitats are influenced by anthropogenic activities. By contrast, the concentration of Zn in the supratidal wetland of site 1 is lower than its local background value (Fig. 3f). Notably, previous studies^{5,23–35} have consistently reported that Zn concentrations are higher than their local background values in the coastal areas of Bohai Sea. The enrichment of Zn seems to be higher in Bohai Bay than in Laizhou Bay.

The mean concentrations in the supratidal wetlands of sites 1, 2, 3, and 4 are 12.98 mg kg⁻¹, 21.43 mg kg⁻¹, 27.46 mg kg⁻¹, and 24.39 mg kg⁻¹ for As and 0.087 mg kg⁻¹, 0.14 mg kg⁻¹, 0.14 mg kg⁻¹, and 0.11 mg kg⁻¹ for Cd (Fig. 3i and j), respectively. As and Cd have been proven to be the major heavy metal pollutants in previous case studies.^{2,23,36} In the present research, the concentrations of As and Cd are higher than their local background values, which suggest that As and Cd are highly affected by external sources (*i.e.*, anthropogenic activities and atmospheric deposition).

3.2 Assessment of heavy-metal potential ecological risk

EF values are generally used to evaluate the external input of heavy metal in soils.³⁷ Our results show that the EF values of Al, Fe, and Mn in all four sites are less than 2, which suggest that these heavy metals have not been contaminated. 38.10% and 92.86% of EF-Cr and EF-Ni in the supratidal wetland of site 2 are greater than 2 (Fig. 4), indicating a certain degree of accumulation of Cr and Ni and their potential risks in the habitat. By contrast, the EF values of Cr and Ni in the supratidal wetlands of sites 1, 3, and 4 are all less than 2, indicating minimal enrichment levels in the three habitats. 24.56% and 24.00% of the EF-Pb values in the supratidal wetlands of sites 1 and 3 are greater than 2 (Fig. 4), suggesting a certain degree of accumulation of Pb and potential ecological risks. By contrast, the EF-Pb values in the supratidal wetlands of sites 2 and 4 are less than 2, indicating minimal enrichment levels. 64.00% and 62.07% of the EF-Zn values in the supratidal wetlands of sites 3 and 4 are greater than 2 (Fig. 4), suggesting that Zn has been enriched in the two habitats. The mean EF-Zn values in the supratidal wetlands of sites 1 and 2 are also greater than 2 (Fig. 4), but Zn has only been slightly enriched (*i.e.*, Zn concentration has not yet reached the pollution level). The EFs with values greater than 2 in the supratidal wetlands of sites 1, 2, 3, and 4 are 61.40%, 47.62%, 88.00%, and 74.14% for As concentrations and 59.65%, 95.24%, 92.00%, and 48.28% for Cd concentrations, respectively. The results suggest varying degrees of As and Cd accumulation and enrichment in the habitats along the west coast of Bohai Sea.



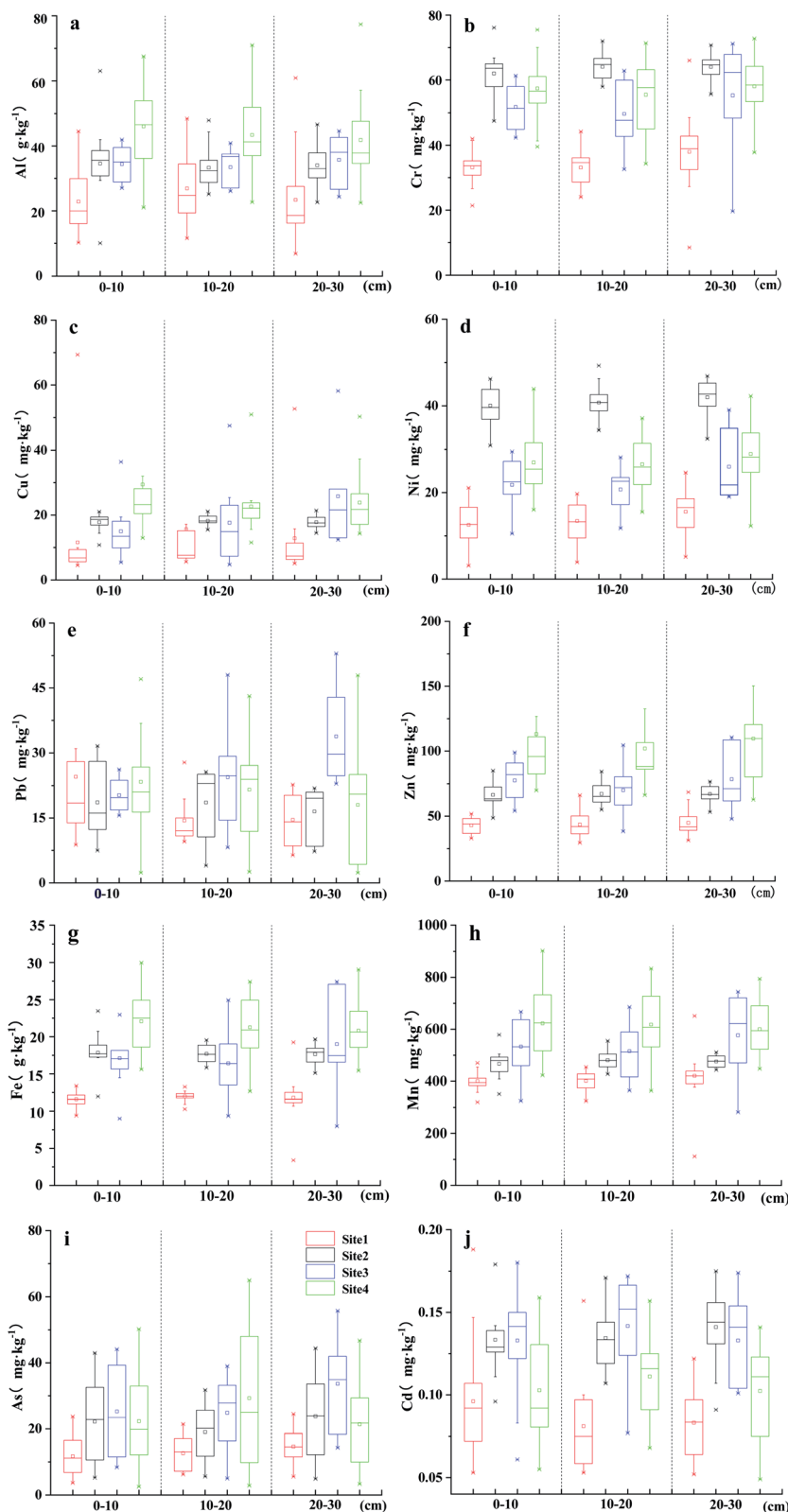


Fig. 3 Spatial distribution for soil heavy metals in the four supratidal wetlands along the west coast of Bohai Sea.

Ecological RI is widely used to determine the ecological risk of heavy metals in soils and sediments.^{1,38} The RI of the supratidal wetland in site 1 is 57.27, which is significantly

lower than the RIs of the other supratidal wetlands (Fig. 5). According to the ecological risk assessment, the RIs of all study sites are less than 150, suggesting a low accumulation



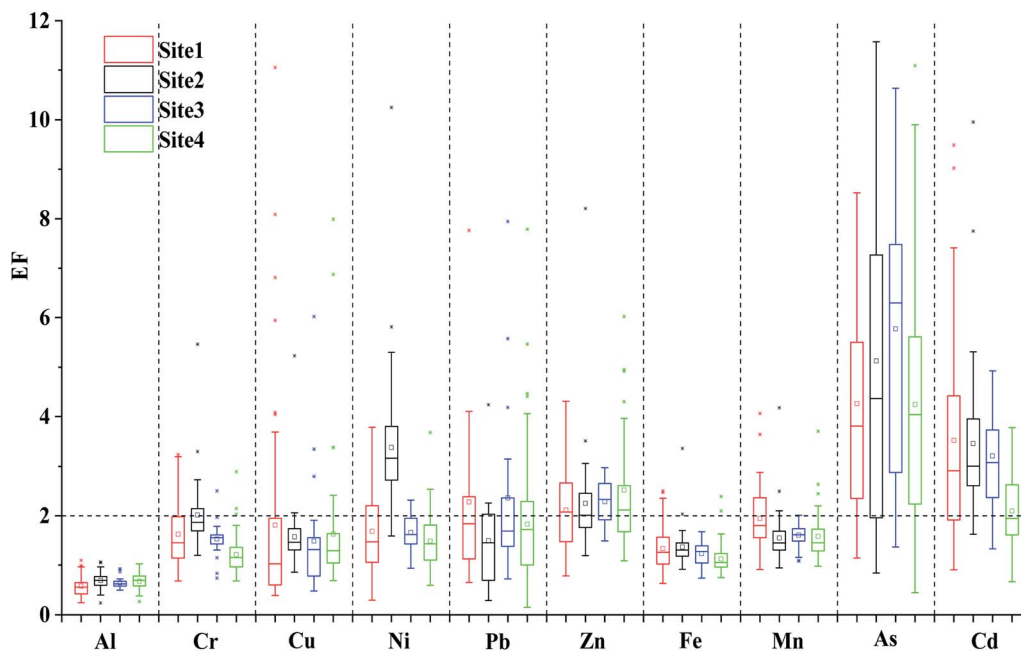


Fig. 4 Enrichment factors (EF) of heavy metals in the four supratidal wetlands along the west coast of Bohai Sea.

risk in the habitats. However, the values of RI are primarily dominated by the risk indices (E_r^i) of As and Cd. The sums of the E_r^i -As and E_r^i -Cd of the supratidal wetlands of sites 1, 2, 3, and 4 are 45.27, 63.49, 78.03, and 59.64, while the corresponding contribution percentages of the sums of Cd and As to the overall potential ecological risks are 79.05%, 77.80%, 80.54%, and 76.43%. The result of the degree of contamination (C_d) of the supratidal wetland of site 1 is $6.86 < 8$ (Fig. 5), which is a low-risk state. While, the C_d values of the three other supratidal wetlands are higher than 8, indicating moderate ecological risk. In this study, we use another contamination index of PN to evaluate the degree of heavy metals contamination, the result show that PN of the supratidal wetland of site 1 is 0.74, which indicates that the level of heavy metals pollution in the soil is on the alert. However, the PN values of the three other supratidal wetlands lie between 1 and 2 (Fig. 5), indicating a low pollution risk. Regardless of the differences between C_d and PN, the accumulation risk of site 1 is lower than that of sites 2, 3 and 4. This phenomenon may be due to the selected study area (site 1) having been surrounded by macrophanerophytes of *Tamarix chinensis*, which have a barrier function against heavy metals. However, the other three sites locate outside of the nature reserve area, which may have been influenced by the local industrial and agricultural development in these areas. For example, many agricultural and tourist facilities are found in the neighbouring regions of sites 2 and 3, as an impurity in phosphate ores, Cd is often found in phosphate fertilizers.³⁹

3.3 Correlation and homology analysis for heavy metals

In general, those closely related heavy metals in soils may be homologous and come from similar sources.² In this study, Al, Fe, Mn, Cr and Zn in the supratidal wetland of site 1 are

positively correlated with one another or multiple heavy metals (Table 2), suggesting that these metals might originated from common source. In addition, the conservative elements of Al and Fe are stable in the crust and often used as reference metals in many studies.^{2,40} Here, those strongly correlated metals of Al, Fe, Mn, Cr and Zn in site 1 are classified as one group (Fig. 6a), which might come from natural sources. However, Cu, Ni, Pb, As and Cd are found no significant correlations with Al, Fe and/or Mn in site 1 (Table 2), which indicate that these heavy metals are affected by exogenous input factors.

Cluster analysis results show that the five elements of Pb, Cu, Cd, As and Ni in site 1 are subdivided into three groups (Fig. 6a), which suggest that the exogenous heavy metals are complex in

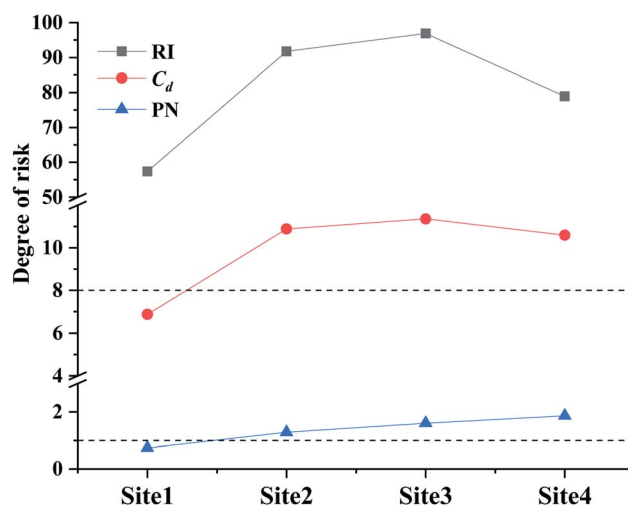


Fig. 5 Potential ecological risk index (RI) and degree of contamination (C_d) in the four supratidal wetlands along the west coast of Bohai Sea.



Table 2 Correlation analysis for heavy metals in the supratidal wetlands of site 1 and site 2 along the west coast of Bohai Sea^a

	Al	Cr	Cu	Ni	Pb	Zn	Fe	Mn	As	Cd
Al		0.156	-0.042	-0.059	0.245	0.243	0.684**	0.547**	0.13	-0.205
Cr	0.29		0.069	0.473**	-0.061	0.485**	0.548**	0.570**	0.235	0.264
Cu	0.28	0.711**		0.133	-0.234	0.057	0.1	0.141	0.048	0.076
Ni	-0.20	0.16	0.09		0.089	0.169	0.15	0.146	0.443**	0.17
Pb	-0.25	-0.30	-0.42	-0.36		0.244	0.106	0.137	-0.018	-0.07
Zn	-0.16	0.571**	0.630**	0.23	-0.28		0.418**	0.427**	-0.099	0.116
Fe	0.727**	0.673**	0.683**	0.039	-0.389	0.245		0.811**	0.109	-0.125
Mn	0.296	0.855**	0.814**	0.131	-0.491*	0.640**	0.714**		0.147	-0.084
As	-0.21	-0.01	-0.15	0.07	0.28	0.28	-0.25	-0.06		0.12
Cd	-0.02	-0.01	-0.04	-0.06	0.18	-0.03	-0.09	0.05	0.21	

^a The upper triangular part of the matrix displays the correlation coefficients for heavy metals in site 1, while the lower triangular part indicates the correlation coefficients for heavy metals in site 2. *Correlation is significant at the 0.05 level (2-tailed), **Correlation is significant at the 0.01 level (2-tailed).

their sources and input pathways. In the supratidal wetland of site 2, Al, Cr and Mn have positive correlations with Fe (Table 2), suggesting that these heavy metals are homology and similarity in their sources.⁴¹ Additionally, the cluster analysis results also support our deduction for those heavy metals in site 2 (Fig. 6b). In this study, Cu and Zn have no significant correlations with Fe, but they are positively and significantly correlated with Cr and Mn in site 2 (Table 2). In some previous studies, Mn had been selected as a reference element due to its robust relationships with other heavy metals.^{25,29} Thus, Cu and Zn in site 2 may have similar sources with Mn. However the cluster analysis have shown that the two heavy metals belonging to different categories (Fig. 6b). Ni, As and Cd have no significant correlations with other heavy metals (Table 2), indicating that the three

kinds of heavy metals may be influenced by unpredictable exogenous input. In most cases, these heavy metals might come from atmospheric deposition, wastewater discharge and/or agricultural activities.¹⁹

In this study, Cr, Cu, Ni, Zn, Fe and Mn are positively and significantly correlated with Al in site 3 (Table 3), indicating that those heavy metals are less affected by external input factors.²⁹ Pb, As and Cd have no significant correlations with Al and Fe in site 3, they may come from different sources and develop without affecting each other. The cluster analysis show that the classification of the ten heavy metals is consistent with the correlation result (Fig. 6c). In the supratidal wetland of site 4, all heavy metals except Cd are positively and significantly correlated with Al, Fe and/or Mn (Table 3), which

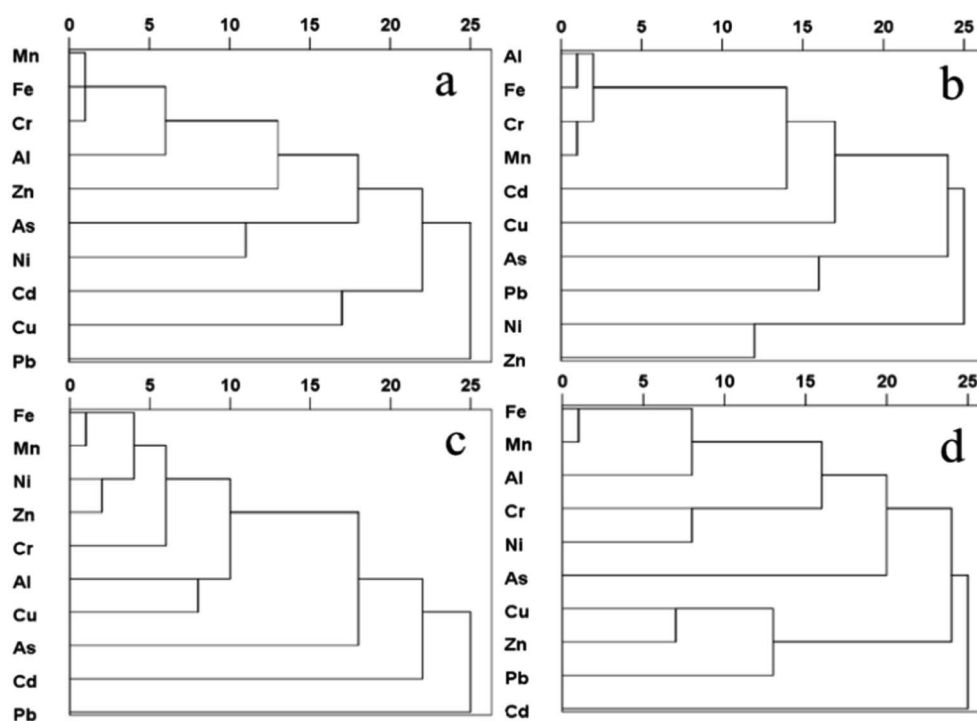


Fig. 6 Cluster analysis for heavy metals in the four supratidal wetlands along the west coast of Bohai Sea. (a) Site 1; (b) site 2; (c) site 3; (d) site 4.



Table 3 Correlation analysis for heavy metals in the supratidal wetlands of site 3 and site 4 along the west coast of Bohai Sea^a

	Al	Cr	Cu	Ni	Pb	Zn	Fe	Mn	As	Cd
Al		0.622**	0.506**	0.737**	0.075	0.689**	0.681**	0.775**	0.31	0.25
Cr	0.241		0.410*	0.723**	-0.024	0.621**	0.788**	0.762**	0.18	0.16
Cu	0.177	0.444**		0.657**	0.216	0.382	0.482*	0.444*	0.31	0.05
Ni	0.02	0.661**	0.408**		-0.059	0.800**	0.715**	0.695**	0.20	0.37
Pb	0.061	0.215	0.392**	0.118		-0.319	-0.013	0.154	-0.10	-0.472*
Zn	0.113	0.494**	0.672**	0.553**	0.329*		0.704**	0.621**	0.30	0.566**
Fe	0.683**	0.478**	0.542**	0.245	0.266*	0.413**		0.874**	0.20	0.18
Mn	0.557**	0.571**	0.532**	0.387**	0.260*	0.478**	0.911**		0.18	0.17
As	0.398**	0.14	0.18	0.012	0.05	0.17	0.464**	0.457**		-0.01
Cd	0.08	0.18	0.14	0.183	0.05	0.19	0.19	0.18	-0.05	

^a The upper triangular part of the matrix displays the correlation coefficients for heavy metals in site 3, while the lower triangular part indicates the correlation coefficients for heavy metals in site 4. *Correlation is significant at the 0.05 level (2-tailed), **Correlation is significant at the 0.01 level (2-tailed).

indicate that these heavy metals have similar sources or they are affected by the same factors.⁴¹ However, the cluster analysis result show that all heavy metals are classified into four categories (Fig. 6d), which indicate that Cd, Zn, Cu, Pb and As

have different sources with Al, Cr, Mn, Fe and Ni in spite of their correlations. In this study, other quantitative ecological method, such as PCA, should be used to explore the sources and input pathways of heavy metals.

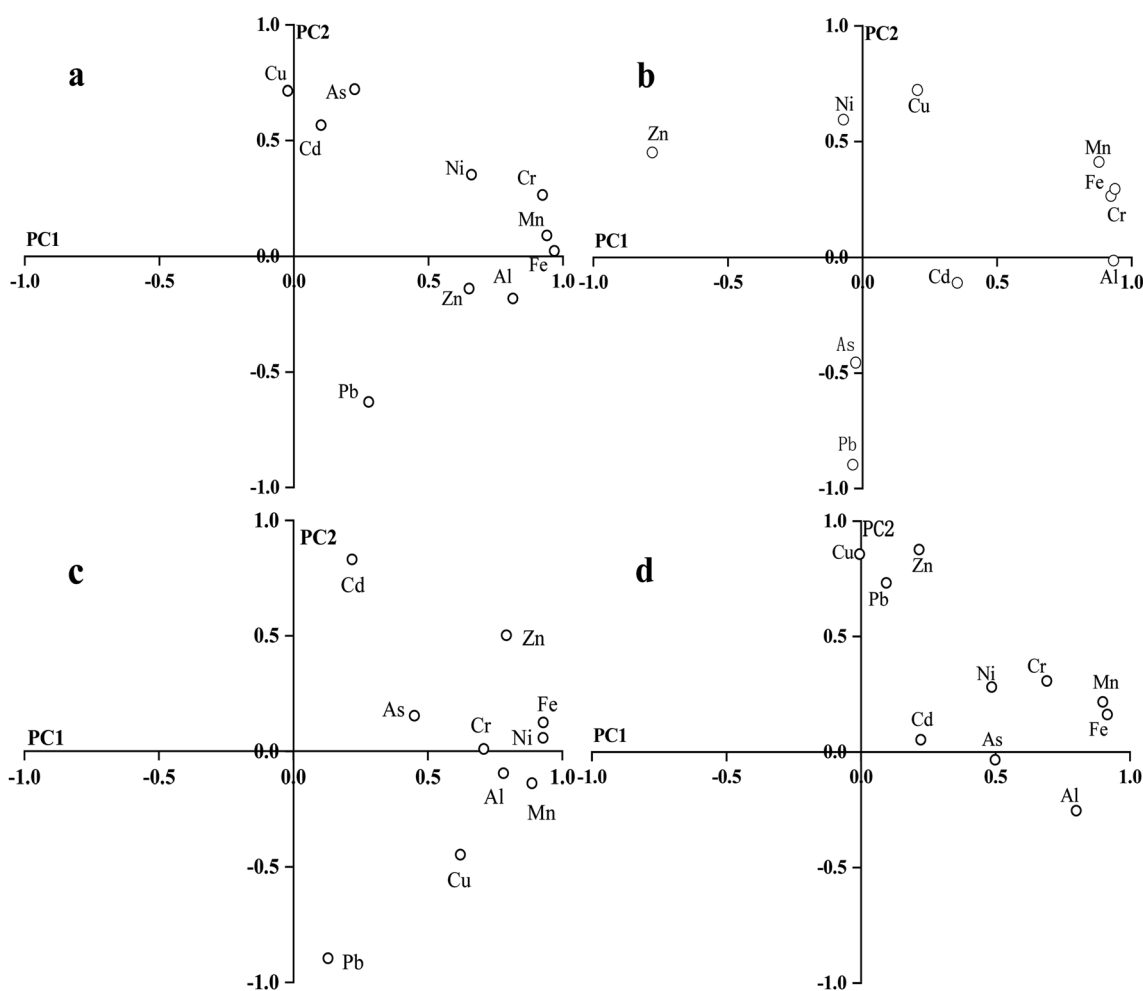


Fig. 7 Principal component analysis (PCA) for heavy metals in the four supratidal wetlands along the west coast of Bohai Sea. (a) Site 1; (b) site 2; (c) site 3; (d) site 4.



3.4 Sources of heavy metals

Two principle components (PCs) can explain 63.42% of the total variance in the supratidal wetland of site 1. In particular, PC1 and PC2 can explain 43.93% and 19.49% of the total variance, respectively (Table S1†). Fang *et al.*⁴² and Jiao *et al.*⁴³ have suggested that PC1 of the biplot is likely correlated with natural factors. In the present research, PC1 is strongly and positively correlated with Al, Cr, Fe, Ni, Zn, and Mn (Fig. 7a), which indicate that the sources of these heavy metals may have originated from natural sources. Additionally, the heavy metals of Cr, Fe, Zn, and Mn in site 1 are positively correlated with soil P, but no significant correlations with soil N and pH (Fig. 8a) have been established. Therefore, Al, Cr, Fe, Zn, and Mn may have primarily originated from parent materials because P is a rock-derived element of the earth's crust.⁴⁴ A significant correlation is found between Ni and soil N (Fig. 8a), which suggests that Ni originates from nitrogen deposition. PC2 represents the anthropogenic activities and relevant factors reported in many studies.^{17,42,43} In the present study, PC2 is positively correlated with Cu, Cd, and As. However, these heavy metals are not correlated with the physicochemical properties of the soil samples, and we suppose that these heavy metals may have primarily originated from the emissions of nearby factories. PC2 is negatively correlated with Pb, which suggests that Pb may

have originated from other anthropogenic activities other than industrial sources. Our finding further indicates that Pb may have originated from embankment constructions or from gasoline and diesel combustion related to agricultural machineries.

As for the supratidal wetland of site 2, the first two PCs can explain 65.90% of the total variance (Table S2†). PC1 (43.60%) is positively correlated with Al, Cr, Fe, and Mn (Fig. 7b). Given that Al is a geological element in the earth's crust,² we conclude that the heavy metals of Al, Cr, Fe, and Mn may have mainly originated from the weathering of parent materials. PC1 is positively related to Cd but not conspicuously as showing of Al and Fe (Fig. 7b), indicating sources differentiation. Here, Cd may have mainly originated from atmospheric deposition. PC2 (22.30%) is positively correlated with Cu and Ni (Fig. 7b), implying that these two heavy metals are related to anthropogenic activities in the habitat. Cu is positively correlated with soil P but negatively correlated with salinity (Fig. 8b), indicating that Cu and Ni may have originated from agricultural activities (wetland reclamation and/or phosphate fertilizers). As and Pb are negatively correlated with PC2, but no significant correlations are found between these two heavy metals and the physio-chemical properties of their soils (Fig. 7b and 8b). Anthropogenic activities, such as automobile exhaust, industry exhaust, and port

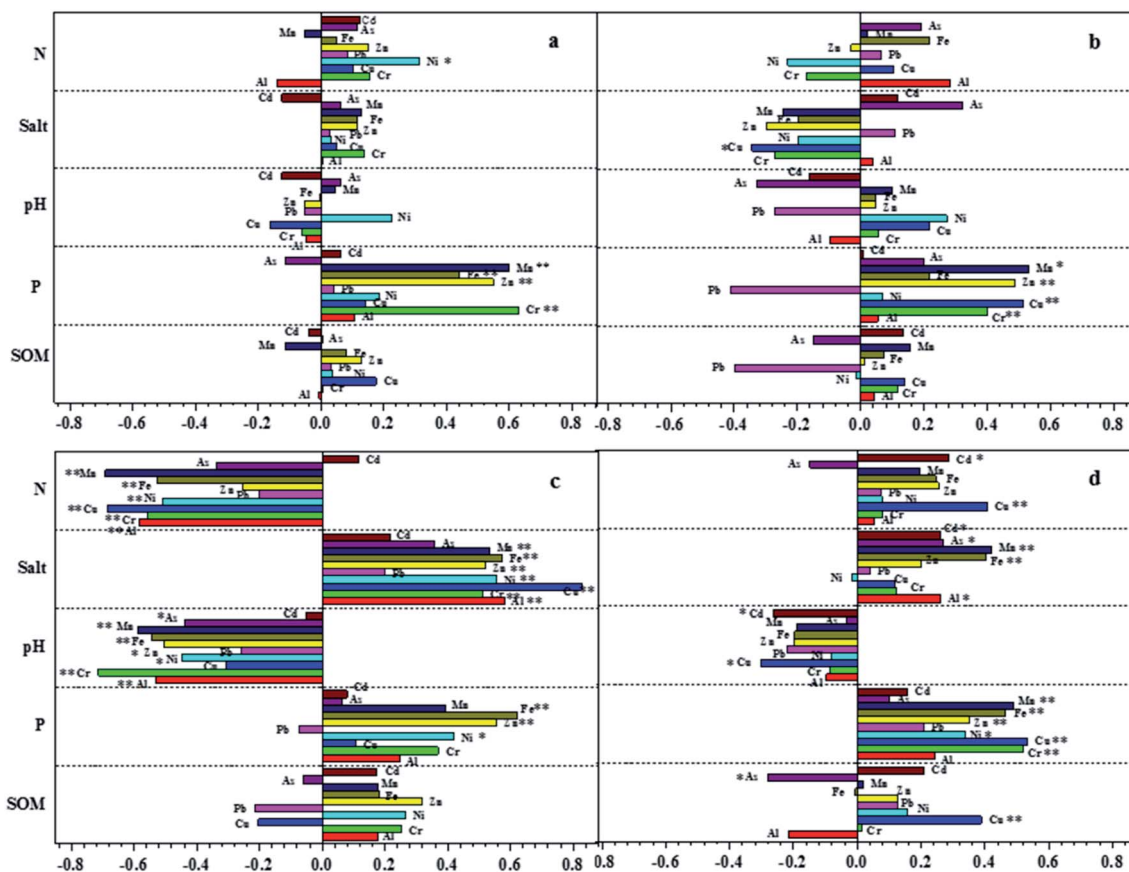


Fig. 8 Correlation coefficients between heavy metals and soil physicochemical properties in the four supratidal wetlands along the west coast of Bohai Sea. (a) Site 1; (b) site 2; (c) site 3; (d) site 4. * correlation is significant at the 0.05 level (2-tailed), ** correlation is significant at the 0.01 level (2-tailed).



construction, may have been the sources of As and Pb in the habitat. Zn lies between PC1 and PC2 (Fig. 7b), implying that Zn is influenced by anthropogenic activities and natural factors. However, Zn is somewhat close to the PC1 axis (-0.781). Soil P is positively correlated with Zn (Fig. 8b), suggesting that Zn has mainly originated from acid deposition (phosphoric acid).

As for the supratidal wetland of site 3, the first two PCs can explain 69.17% of the total variance (Table S3†). PC1 (49.22%) is positively correlated with Al, Cr, Fe, Ni, and Mn (Fig. 7c). The heavy metals of Cr, Ni, and Fe are positively correlated with soil P but negatively correlated with soil N (Fig. 8c), which suggest that parent materials are the major sources of Al, Cr, Fe, Ni, and Mn in this habitat.⁴⁵ PC1 is closely related with As and Zn but not with Al and Fe (Fig. 7c). The negative correlation of As and Zn with soil pH (Fig. 8c) suggests that the heavy metals may have originated from atmospheric acid deposition. Cu lies between the two axes of PC1 and PC2 but much closer to the PC1 axis (0.621). Cu is positively correlated with Al, Cr, Fe, Ni, and Mn (Fig. 7c), suggesting that Cu may have originated from rock weathering or the parent materials of soil in this habitat. PC2 (19.95%), which can be defined as the anthropogenic factors in site 3, is positively correlated with Cd but negatively correlated with Pb (Fig. 7c). We suppose that Pb and Cd are mainly related to the different human activities. Combined with the actual situations in the wetland, we suggest that Cd may be associated with the emissions of existing or historical industries, and Pb may have originated from vehicle exhausts (*e.g.*, tourist buses and engineering vehicles).⁴⁶

As for the supratidal wetland of site 4, the first two PCs can explain 57.11% of the total variance (Table S4†). PC1 (37.48%) is positively correlated with Al, Cr, Fe, Ni, and Mn (Fig. 7d), and all heavy metals in addition to Al are positively correlated with soil P (Fig. 8d), suggesting that Cr, Fe, Ni, and Mn in this habitat not only originate from parent materials but also from atmospheric acid deposition (phosphoric acid).^{47,48} As and Cd are closely related to PC1 (Fig. 7d), and Cd is positively correlated with N (Fig. 8d), suggesting that As and Cd may have originated from atmospheric acid deposition (nitric acid).⁴⁹ PC2 (19.64%) is positively correlated with Cu, Zn, and Pb in this habitat (Fig. 7d). Given that Cu is positively correlated with SOM, soil N, and P (Fig. 8d), we conclude that Cu, Zn, and Pb are likely controlled by wetland reclamation and agricultural activities (*e.g.*, fertilization and sewage water irrigation).

4 Conclusion

The distribution and accumulation risk of heavy metals are higher in the middle and northern regions than in the southern region along the west coast of Bohai Sea. The ecological RIs of all heavy metals indicate that As and Cd are the most widespread pollutants among the heavy metals in the rainfall-driven supratidal wetlands of Bohai Sea. The source analysis of all habitats suggests that Al, Cr, Mn, and Fe mainly originate from soil parent materials and rock weathering. Thus, these heavy metals can be neglected in the formulation of environmental protection policies and monitoring programs. Pb is closely related to human activities in the coastal area of Bohai Sea, and

the major focuses should be on the waste discharge of Pb-related enterprises, the transportation industry, and the over-development of agricultural activities. Cu, Cd, and As can be attributed to human activities, and they may also be related to atmospheric deposition. Hence, we should also pay attention to the waste discharge of related enterprises and the over-development of agricultural activities. Furthermore, the heavy metals of Cu, Cd, and As in the atmosphere should be supervised and monitored. Ni and Zn are correlated with human activities in some habitats and may have originated from soil parent materials or atmospheric deposition in other habitats. Appropriate measures should be taken according to the actual conditions in the coastal wetlands.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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