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INFLUENCING FACTORS OF HEAVY METALS IN THE COASTAL AREAS OF YANGTZE RIVER ESTUARY

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Abstract: This study investigates the distribution and influencing factors of six heavy metals (Cr, Zn, Ni, Cu, Pb, Cd) in water and sediments from the coastal areas of the Yangtze River estuary. Field surveys at seven sites revealed that heavy metal concentrations are significantly affected by physicochemical parameters such as temperature, pH, redox potential, salinity, and conductivity. Strong correlations among Cu, Cr, and Ni suggest common sources or pathways. The findings provide insights into heavy metal behavior in estuarine environments and offer technical support for pollution control and water quality management.

Keywords: Heavy metals; physicochemical parameters of water quality; coastal areas; Yangtze River Estuary

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INTRODUCTION

With the rapid development of urbanization and industrialization in the coastal zone, pollution accumulates in aquatic environments, especially in the estuaries due to the discharge of runoff (Gao and Chen, 2012; Ghosh and Maiti, 2018; Jiang et al., 2017). Heavy metals are one of the major pollutants in aquatic environments characterized by degradation-resistant and strong toxicity. After entering the estuaries ecosystem, they accumulate in the sediment mainly through adsorption, precipitation or flocculation, which makes sediment a major sink for heavy metals (Li et al., 2023; Zahra et al., 2014). Under certain conditions, heavy metals could be released from sediment and re-enter into the water making sediment the potential sources of heavy metals in the aquatic environment. The exchanges of heavy metals at the interface of sediment and water not only pose a threat to the health of the ecosystem, but also endanger human health through the food chain and drinking water (Liu et al., 2018; Xie et al., 2021).The study region is part of the coastal areas of the Yangtze River estuary (CAYRE), which is an important area for human production, as well as an ecologically fragile area. It is strongly influenced by sea-land interactions and human activities. On the one hand, in the CAYRE, freshwater and seawater mix, the flow field is complex and influenced by runoff, tide, and wave, which affects the transport process of heavy metals and other substances. On the other hand, intensive human activities occur in the CAYRE. The ports, petrochemical industries, steel plants and shipyards, etc., generate a large amount of industrial wastewater and urban sewage, which affects the water environment in the CAYRE. The industrial and agricultural activities along the Yangtze River are also very intense, and lots of domestic and industrial wastewater is brought into the Yangtze River through outfalls (e.g., the Wusongkou sewage outfall and the South District sewage outfall) and the runoffs such as the Huangpu River. The annual discharge of heavy metals from the Yangtze River estuary into the sea ranges from 20,000 to 30,000 tons. Therefore, figuring out distributions of heavy metal concentrations in the water environment and their behaviors is essential for environmental management and health protection of the Yangtze River estuary region (Li et al., 2021).

According to previous studies, both anthropogenic activities such as industrial wastewater, mining development, domestic sewage, agricultural production, and traffic pollution (Liang et al., 2023; Liu et al., 2018;

Su et al., 2023) and natural processes such as soil erosion, vegetation growth, and rock decomposition, have a great impact on heavy metal concentrations in water environment (Kang et al., 2019; Zhang, 2006), especially that the physicochemical parameters of water quality such as temperature, pH, salinity, suspended sediment concentration, etc. greatly affect the migration and transformation processes of heavy metals (Apau et al., 2022; Attah et al., 2021; Hu et al., 2021a). It has been found that the release process of heavy metals from sediment into water was increased with pH < 7, while the adsorption and precipitation of heavy metals by sediments was enhanced with pH > 7 (Kang et al., 2019; Wang et al., 2018b), and dissolved oxygen in water allows more heavy metals to be bound (Atkinson et al., 2007). The relationship between heavy metal concentrations and physicochemical parameters of water quality was proved. However, the mechanism between them was still not clearly revealed (Ravisankar et al., 2019).

In this paper, through the field observations at seven sampling sites along the coastal areas of the Yangtze River estuary, the six heavy metals (Cr, Zn, Ni, Cu, Pb, and Cd) in sediment and water were analyzed. Spearman correlation analysis and multiple linear regression were used together to qualitatively describe the linear relationships between heavy metal concentrations and physicochemical parameters of water quality, through which the key factors affecting the concentration of heavy metals can be revealed. The method proposed in this paper can be easily applied to heavy metal prevention and control in estuaries, which can also provide valuable information and technical support for water environment protection in similar areas.

MATERIALS AND METHODS

Field observations

Four times of field surveys were conducted on July 14th, September 22nd, November 29th in 2021 and January 15th in 2022 to analyze heavy metal concentrations and physicochemical parameters of water quality at seven sampling sites (Fig. 1). From northwest to southeast along the coastline, seven sampling stations are LiuHeKou (LHK), ShiDongKou (SDK), WuSongKou (WSK), ZhuYuan (ZY), SanJiaGang (SJG), ChaoYangNongChang (CYNC) and DaZhiHe (DZH). These sampling points are distributed along the Yangtze River estuary and can reflect changes in heavy metal concentrations with geographical locations in the Yangtze River estuary area.

Six heavy metals (Cr, Zn, Ni, Cu, Pb, and Cd) were analyzed based on the sediment and water samplings. Water samples were collected in middle layer of the water column using a 2.5L Plexiglas water sampler. The water samples were conserved by high-density polyethylene (HDPE) containers, which were rinsed with nitric acid and cleaned with Milli-Q water prior to sampling. Sediment samples of surface sediment (0–5 cm) were collected by plastic shovel, and sealed in a polypropylene bag. Three water samples were collected as parallel samples at each sampling site. The collected sediment and water samples were transported to the laboratory in boxes with ice packs for testing as soon as possible, and all samples were stored at 4 °C before further analysis.

At each site, multifunctional water quality monitor (AP5000, Aqueous) was used to record the physicochemical parameters of water quality on site, including Temperature (Temp), pH, Oxygen redox potential (ORP), Dissolved oxygen (DO), Electrical conductivity (EC), Electrical resistivity (RES), Total dissolved solids (TDS), Salinity (SAL), Cyanobacteria (BGA-PE), and turbidity (NTU). A portable turbidimeter (2100Q, HACH, USA) and a portable pH meter (FiveGo F2-Field Kit, METTLER TOLEDO, Switzerland) were adopted to monitor the turbidity and pH at the same time to verify the validity of data.

Heavy metal concentrations tests

In the pretreatment procedure, the sediment samples were thawed at ambient temperature. Subsequently, a portion of the sample was extracted using a sampling spoon and subjected to drying in a constant temperature blast dryer. The samples dried were ground with a mortar and pestle, and sieved with a 63 μm nylon mesh sieve and subsequently placed in sealed bags for measurement. The collected water samples were promptly filtered through a 0.45 μm microporous membrane using a vacuum extraction device to scrape the suspended particles. The obtained suspended sediment samples were dried in a drying oven, ground uniformly and then bagged for analysis of particulate heavy metals. The filtered water samples were put into clean 50 ml polyethylene bottles, and 2 drops of 10 % HNO_3 were added to inhibit the activity of microorganisms and placed in the refrigerator at 4 °C for further detection of dissolved heavy metals.

The obtained suspended sediment samples were pretreated and then digested by the acid dissolution method (Janaki-Raman et al., 2007). The experimental steps were as follows: 0.1 g of the homogenized mud sample was weighed accurately in a PTFE digestion vessel, and 6 ml HCl, 2 ml HNO_3, 1 ml H_2O_2 and 2 ml of HF were added. The graphite digester was then programmed to perform the digestion: the temperature was ramped up from room temperature to 180 °C for

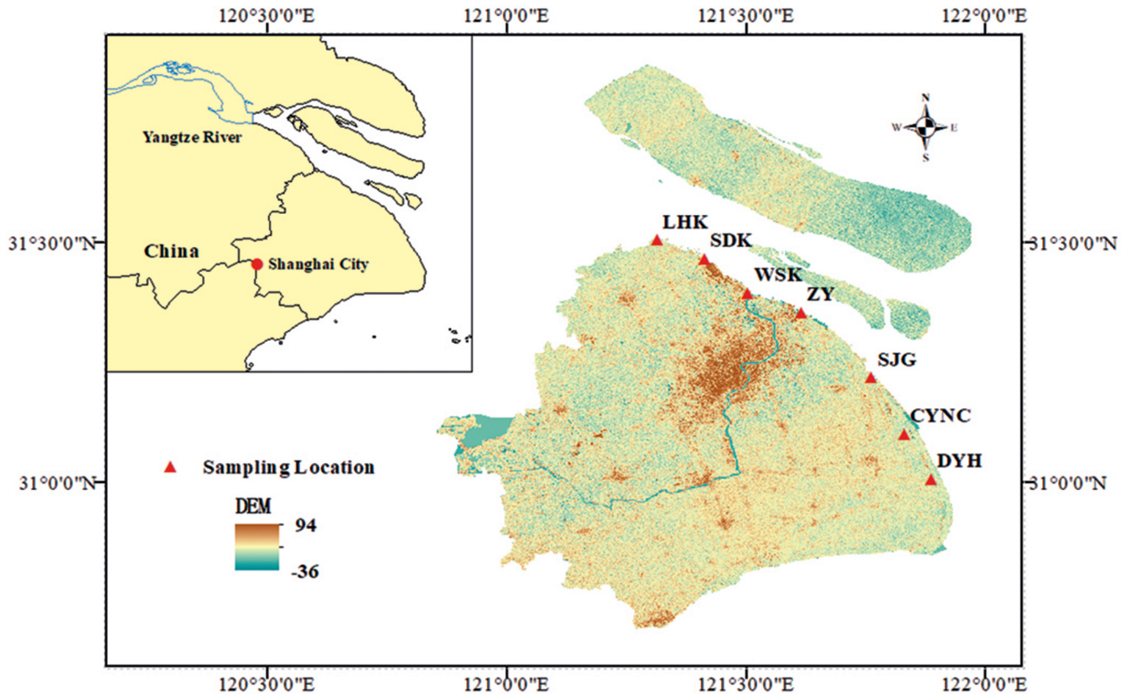


Fig. 1. Study area and sampling stations

30 min and held at 180 °C for 60 min. With the finish of digestion, the sample was placed on the acid catcher until the sediment turned into white crystals. The residue was washed with deionized water and transferred to a centrifuge tube, and placed in the refrigerator to be measured. All samples to be tested were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for the total heavy metal concentrations. To test the reliability of the detection, three parallel sediment and water samples were collected in the vicinity of each sampling site. One sample was randomly selected for five replicate tests during the test of sediment and water samples, and the relative standard deviations of the measured heavy metals (Cu, Zn, Cr, Ni, As, Pb and Cd) were less than 5 %, and the recoveries were in the range of 85 –110 %.

RESULTS AND DISCUSSION

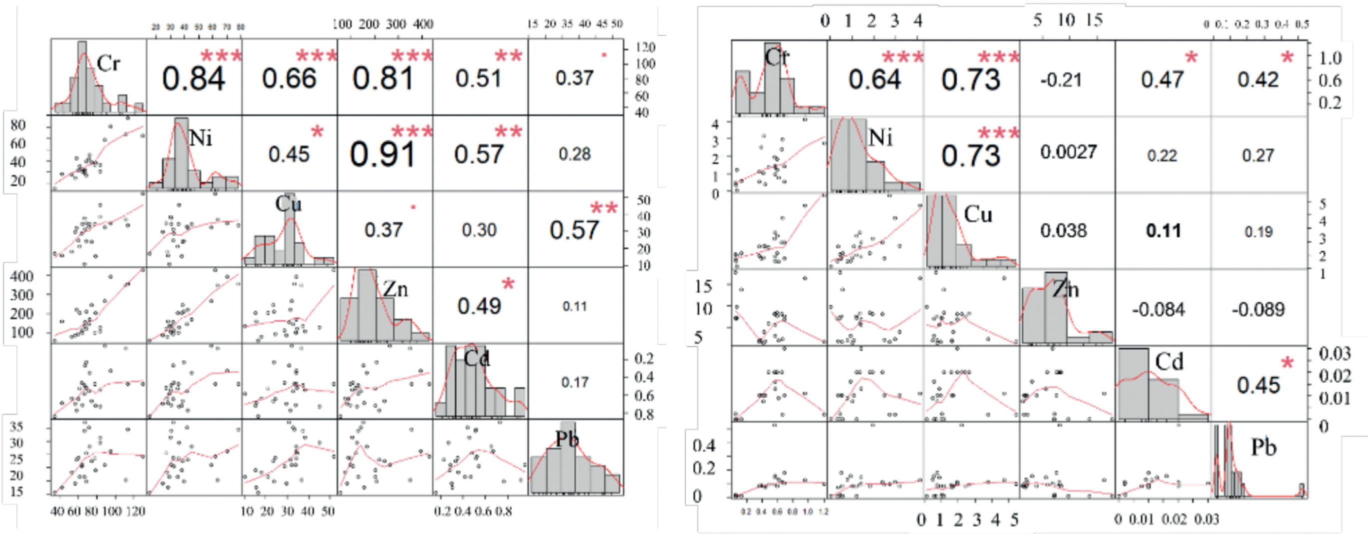
Correlations between heavy metals

Correlations between heavy metals in sediment and water samples were shown in Fig. 2. For sediment samples, Cr concentration was positively correlated to Ni, Cu, Zn and Cd at 0.01 significant level, and to Pb at 0.05 significant level. Ni concentration was positively correlated to Zn and Cd at 0.01 significant level, and to Cu at 0.05 level. Cu concentration was positively correlated to concentrations of Pb at 0.01 significant level and to Zn at 0.05 level. Zn concentration was positively related to Cd at 0.05 significant level. Overall, Cr, Ni, Cu, Cd and Zn were positively related to each other. There were no significant relationships between Pb concentration and most other heavy metals (except Cu).

For water samples, Cr concentration was positively correlated to Ni and Cu at 0.01 significant level, and to Cd and Pb at 0.05 significant level. Ni was positively correlated to Cu at 0.01 significant level. Cd had significant positive correlations with Pb at 0.01 significant level. The positive correlation between heavy metals suggests a potential source or similar environmental pathways for the heavy metals, indicating shared geological, industrial, or anthropogenic influences that contribute to their concurrent presence. Similar to sediment samples, significant correlations were found between Cr, Ni, Cu, which indicates the similar sources of them. Pb and Cd were poorly correlated to other heavy metals but significant relationship was found between them. Zn had no significant correlation with other heavy metals. In sediment and water samples, there is a significant correlation among Cu, Cr, and Ni. However, the correlation between other heavy metal elements varies. Dissolved organic compounds in sediments and microorganisms in the water may influence this process.

Relationships between heavy metal concentrations and physicochemical parameters of water quality

The chemical interactions of heavy metals in sediment and water samples are affected by the physical and chemical properties of water. In order to discuss the linear relationship between the physical and chemical



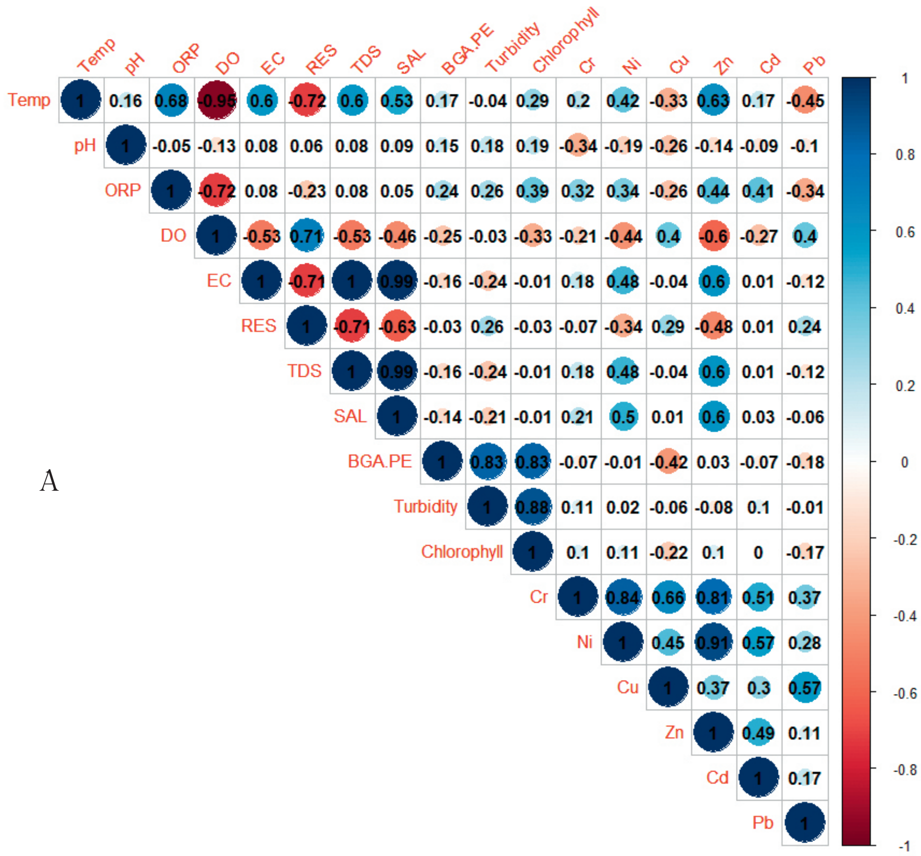
A B

Fig. 2. Correlation among heavy metal concentrations: A — Sediment samples; B — Water samples

properties of water and the concentration of heavy metals, Spearman correlation analysis and Multiple linear regression were conducted.

Spearman correlation analysis was used to describe the correlations between heavy metal concentrations and physicochemical parameters of water quality (Fig. 3). For sediment samples, most heavy metal concentrations were positively correlated with Temp. The rise in temperature promotes the hydrolysis of fats, sugars, and proteins into small molecules, causing heavy metals to lose their binding sites and be released, which are adsorbed by sludge particles and deposited into sediment. pH was negatively correlated with the concentration of most heavy metals. This was due to the fact that heavy metal ions can form precipitates or complexes with other substances at higher pH values. ORP had positive correlations with most heavy metals. Heavy metals were commonly present in aquatic systems in the form of ions. Cr, Ni, Cd, and Zn ions exhibited high electron transfer capabilities, enabling them to act as effective oxidants in redox reactions. Consequently, the oxidation-reduction potential (ORP) increased with the rising concentration of these heavy metals. Most heavy metals exhibited negative correlations with dissolved oxygen (DO). Heavy metal ions can react with oxygen in the aquatic environment, forming insoluble precipitates, thereby reducing the concentration of DO in water. EC was positively correlated to most heavy metals, while RES was negatively correlated to most heavy metals. When the concentration of heavy metal ions increased, the conductivity of the water also increased accordingly, resulting in an increase in the EC value. The increase in salinity could modify the solubility of heavy metal ions. Certain heavy metal ions were more readily soluble under high salinity conditions, as the increasing salt concentration provided a greater number of ions to stabilize the dissolved state of these ions. There was no significant correlation between most heavy metals and BGA, NTU and Chlorophyll. In general, water quality physicochemical parameters of Temp, PH, ORP, DO, EC, RES, TDS and SAL had relatively stronger influences on heavy metals in sediments.

For water samples, positive correlations between temperature and most heavy metals were observed. As the temperature increases, the solubility of water also increases, which makes it easier for heavy metal ions to dissolve in water, resulting in an increase in concentration. EC was positively correlated to most heavy metals, and RES was negatively correlated to most heavy metals, which were similar to those for sediment sample. TDS and SAL showed positive correlations to most heavy metals. In Yangtze River estuary, most heavy metals in water were in particulate form (Yin et al., 2016). The increase in TDS, EC, and SAL resulted in the enrichment of negative charges on the surface of clay particles (Nieto et al., 2007). The surface charges and deposits were capable of precipitating fine particle-associated heavy metals through adsorption and flocculation reactions, and formed oxides, hydroxides, carbonates and phosphates in the surrounding environment (Sun et al., 2018). Therefore, the concentration of heavy metals in water samples increased. The sedimentation of fine particles was greatly affected by the physicochemical parameters of water quality at salty and fresh water mixing areas (study region in present paper). NTU was negatively correlated with most heavy metals in water. In general, the water quality physicochemical parameters of Temp, pH, ORP, EC, RES, TDS and SAL were more strongly related to heavy metals in water.



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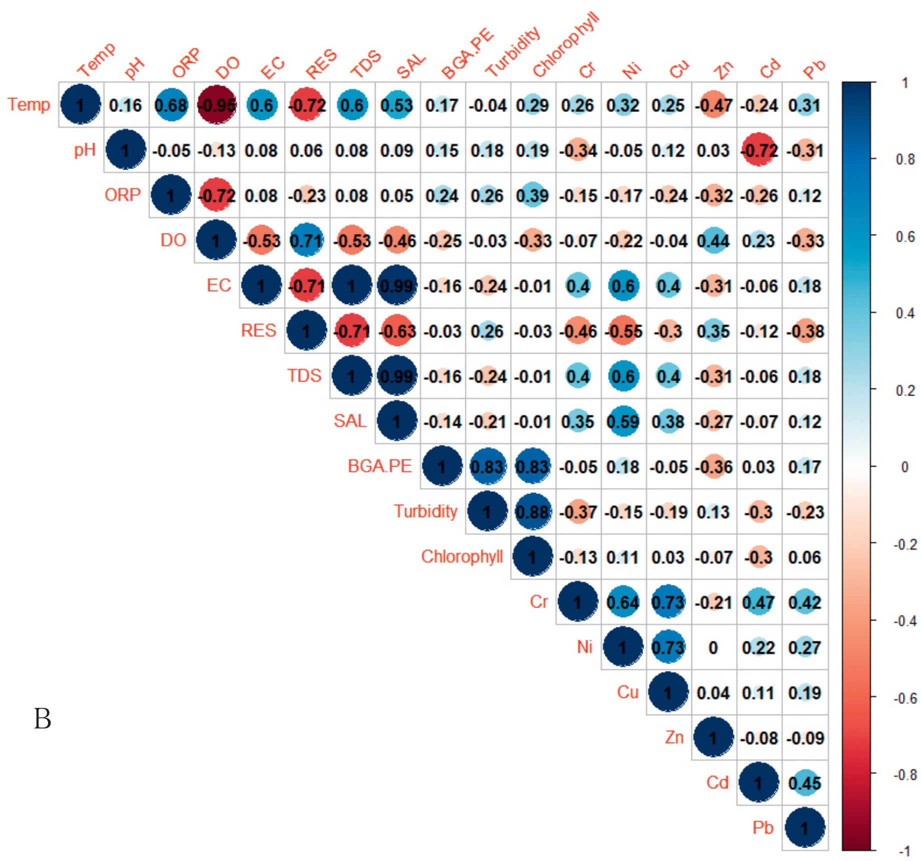

B

Fig. 3. Spearman correlation analyses between heavy metal concentrations and water quality physicochemical parameters. A — sediment samples; B — water samples

CONCLUSIONS

In this study, six heavy metals were investigated in surface sediment and water samples at seven sampling stations in the Yangtze River estuary. By analyzing the relationship between heavy metal concentrations and physicochemical parameters of water quality, it was found that Temp, pH, ORP, EC, RES, TDS and SAL significantly correlate with heavy metal concentration in sediment samples, and Temp, PH, ORP, DO, EC, RES, TDS and SAL are related to heavy metal concentration in water samples. The results in this study provide significant information and technical support for environmental protection and management in coastal areas of Yangtze River estuary and other similar areas.

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