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Sources characteristic of heavy metals and environmental assessments of surface sediments in Xiaoqing River Estuary, eastern China

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Abstract:
A total of 43 surface sediments samples (0-20cm) were collected from Xiaoqing River Estuary (XRE), eastern China, the concentrations of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn and grain size were measured. The mean concentrations of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were 9.36, 0.105, 8.42, 39.33, 9.84, 0.0165, 48.94, 17.31, 13.86, and 43.72 mg·kg^{-1}, respectively. The sources of heavy metals were identified by US-EPA positive matrix factorization (EPAPMF). Three sources of ten heavy metals were identified by EPAPMF, showing that As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn are mainly controlled by natural sources with contributions from 59.8% to 88.1%; agricultural activities is associated with As (27.9%) and Mn (32.4%); 20.3% of Cu and 27.5% of Hg were affected by industrial activities and atmospheric deposition.

Key Word*: estuarine areas; heavy metals; source.*

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I. Introduction

The ecosystem of estuarine areas is vulnerable because these regions are controlled by the land, river and ocean[1,2]. However, the estuarine areas were polluted by heavy metals and the ecological environment suffered serious damage in recent years. The main sources of estuarine heavy metals include natural sources such as weathering of rocks and human sources including agricultural and industrial wastes, which could transfer into estuary through atmospheric deposition and fluvial transportation. Flocculation, adsorption onto inorganic-organic particulates, and subsequent sedimentation are the main process responsible for the trapping and accumulation of metals in estuarine systems[3]. Therefore, the heavy metals were preserved in estuarine sediments and enriched in the organism via the food chain[4]. At present, the heavy metals pollution has attracted the attention of scholars and become a hot topic; meanwhile, the sediments are the main sinks for heavy metals in estuarine aquatic environments. As a result, it is necessary to identify the source of heavy metals for estuarine areas.

Generally, the concentrations of heavy metals in environment are influenced by natural background and anthropogenic activities. Principal component analysis (PCA) is a widely and traditional method of heavy metal sources prediction, which aims to transform multiple indicators into a few comprehensive indicators by dimensionality reduction, each factor as a principal component to explain the source of heavy metals[5]. Then, receptor models, such as absolute principal component score/multiple linear regression (APCS/MLR) and positive matrix factorization (PMF), are used to identify the sources of heavy metals[6,7].

In our study, both EPAPMF was applied to the heavy metal datasets (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn concentrations of 43 surface sediments samples) in Xiaoqing River Estuary (XRE), eastern China.

II. Material and Methods

Study area

Xiaoqing River was located in Shandong Province, eastern China, having drainage basin of 10336 km^2 area with total length of 237 km (Fig.1). And the Xiaoqing River run from Jinan into Laizhou Bay. The whole basin is the temperate monsoon climate with an average temperature ranging from 12℃ to 14 ℃ and annual rainfall of 640.4 mm. Xiaoqing River is important to economy development and the functions include flood drainage, transportation, irrigation and breeding. However, the river was polluted by heavy metals due to human activities. There are many factories in study area including chemical plants, machinery factories and electroplating plants. Meanwhile, application of chemical fertilizer and pesticide in agricultural activities also was an important reason causing heavy metals pollution. Because the physical and chemical properties of sediments, the heavy metals attached to sediments were transported to the estuarine areas and deposited, the estuarine environment was threatened and the development was restricted.

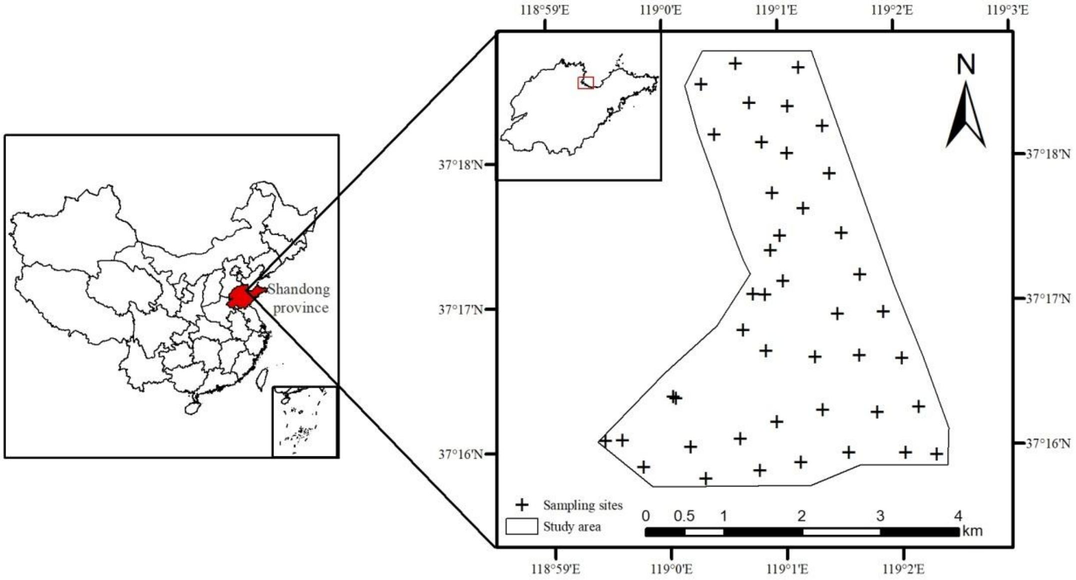

Fig. 1. Location of study area with sampling sites

Sampling and chemical analysis

The sampling routes were predesigned according to the characteristics of XRE. A total of 43 samples were collected and composed 7 profiles paralleling the coast. In the process of the field sampling, if the designed point was unavailable for sampling, an alternative location could be adjusted appropriately based on the actual situation. Because the water level of Xiaoqing River mouth was deep, sampling by boat was adopted. Surface sediment samples were sampled with clamshell sampler and individually packed in sealed polyethylene bags; the original mass of the sample was more than 1kg. The actual geographic coordinate of sampling sites was acquired using a handheld global positioning system (GPS). Locations of 43 samples are shown in Fig. 1. The air-dried samples were ground to 0.149mm for the chemical determination; 5g of samples were used to granulometry.

The concentration of Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, and Li were analyzed by inductively coupled plasma emission spectrometer (ICP-AES) after digestion with $HClO_4$-HNO_3-HF; but the Atomic Fluorescence Spectrometer was applied to analyze As and Hg contents with the digestion of H_2SO_4-HNO_3-$KMnO_4$. The recovery level of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn was 100%±10 and he accuracy could meet the requirement.

The organic matter (OM) and Carbonate were removed by 10% H_2O_2 and 10% HCl; then add plasma water to dilute the solution to neutral; before the test, a10ml $(NaPO_3)$ 6 solution with a concentration of 0.05mol/L, after 24 hours standing, use Malvern 3000 laser particle sizer to test the particle size of the sample, the measurement range is 0.01μm-3500μm, and the repeated measurement error is less than 3%.

Analytical methods of data

Positive matrix factorization (PMF) is widely used to source of heavy metals in soil, sediment and dust[7,8]. In this study, PMF was performed in EPAPMF 5.0 program developed by EPA (US Environment Protection Agency, 2014). The basic idea behind PMF can be expressed:

$$X=G\,F+E \qquad (7)$$

where $X(m\times n)$ is the initial data matrix, $G\ (m\times p)$ represents factor contribution matrix, $F\ (m\times n)$ is factor profile matrix, and $E\ (m\times n)$ represents the residual error matrix. E can be written as:

$$e_{ij}=\sum_{k=1}^{p} g_{ik} f_{kj} - x_{ij} \qquad (8)$$

where the i is the sample from 1 to m, j indicates the heavy metals from 1 to n, k is the sources from 1 to p.

The model is based on the weighted least square method to limit and calculate iteratively. The optimal matrix G and F are obtained. The optimal objective is to minimize the objective function Q. The objective function Q is calculated as follows:

$$Q=\sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{e_{ij}}{u_{ij}}\right)^{2} \qquad (9)$$

where represents the uncertainty of the *j* th chemical element for sample *i*, and is calculated based the element-specific method detection limit (MDL) and error percent measured by standard reference materials.

III. Result and discussion

Descriptive statistics of ten heavy metals

The descriptive statistics of heavy metals distributions of XRE were summarized in Table no 1. The mean concentrations of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were 9.36, 0.105, 8.42, 39.33, 9.84, 0.0165, 48.94, 17.31, 13.86, and 43.72 mg·kg^{-1}, respectively. The contents of As, Cd, Cr, Cu, Hg, Pb and Zn were below level Ⅰ of Marine Sediment Quality standard (MSQS) of China (China's General Administration of Quality Supervision, Inspection and Quarantine, 2002), which applied to industrial areas and marine entertainment areas directly related to human. The average concentrations of As, Cd, and Mn were exceeded corresponding the sediment background values of China offshore[9], suggesting that these three heavy metals were clearly influenced by human activities. The high values of the CV of Cd, Cu, Hg, and Zn indicate that the data distributions of these four elements were not uniform and contained some outliers due to anthropogenic input. The enrichment factor (EF) can be used to distinguish human source from a natural source. Li was selected as the reference element. The sediments background values of Chinese offshore were selected as background concentration. The EFs of ten heavy metals were 2.49, 3.16, 1.41, 1.29, 1.28, 1.25, 2.11, 1.45, 1.40, and 1.34, respectively, indicating that the accumulation trend of all heavy metals. In particular, the EFs of As, Cd and Mn was over 2, suggesting that the anthropogenic accumulation in outliers. The sources of ten heavy metals have to further analyze owning to the background values of offshore are different between XRE and a total China.

Table no 1: Descriptive statistics of heavy metals in sediments of XRE (n=43, unit= mg·kg^{-2})

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Minimum	6.60	0.069	7.14	25.84	5.97	0.009	460.95	11.68	11.84	29.52
Maximum	11.61	0.213	10.92	58.71	21.13	0.037	708.73	25.05	17.88	75.23
Mean	9.36	0.105	8.42	39.33	9.84	0.016	548.94	17.31	13.86	43.72
Median	9.58	0.091	8.26	37.9	8.57	0.014	533.95	16.65	13.65	41.41
SD	1.09	0.037	0.83	6.24	3.65	0.006	53.4	2.46	1.23	9.57
CV (%)	11.6	35.3	9.9	15.9	37.0	36.9	9.7	14.2	8.9	21.9
Skewness	-0.46	1.77	1.33	1.37	1.87	1.77	1.17	1.47	0.97	1.4
Kurtosis	-0.04	2.42	1.8	2.39	2.86	3.51	1.72	3.12	1.65	2.01
Chinese offshore sediments	7.7	0.065	12	61	15	0.025	530	24	20	65
Level Ⅰ of MSQS	20	0.5	-	80	35	0.2	-	-	60	150

SD: standard deviation; CV: Coefficient of variation; SMSQ: Marine Sediment Quality standard (GB18668-2002)

The sources interpretation of heavy metals

In this study, we selected three factors as the optimal solutions for EPAPMF model (Table no 4). The accuracy of two models was assessed by the ratio of predicted to observed and R^2. The Predicted/Observed values was close to 1 and the R^2 values were varied from 0.79 to 1.0, indicating that satisfactory fits. In the EPAPMF modeling, Factor 1 (F1) on As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn ranged from 59.8% to 88.1%. there are 27.9% of As and 32.4% Mn were associated with Factor 2 (F2), Factor 3 (F3) controlled 27.5% of Hg and 20.3% of Cu.

F1 was related to As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn, which indicated that they had the common source. The mean concentrations of Co, Cr, Cu, Hg, Ni, Pb, and Zn were below the sediments background value of China offshore. Commonly, the concentration of Cr and Ni influenced by human activities was weaker than parent materials in soil and sediments. Fei et al.[10] reported that Cr in the soil of Shanghai was natural sources. Lv et al.[11] find that Co, Cr, Ni, Mn, As, and Cu were controlled by geological background. In the study of heavy metal sources of Tigris estuary in Turkey, Varol[12] indicated that Fe and Mn originated from the parent rocks. In the research of Yiyuan heavy metals, Wang et al.[13] suggesting that As, Cd, Co, Cr, Cu, Mn, Ni, and Zn are mainly from natural sources. Therefore, F1 represented natural sources.

F2 was associated with As and Mn. The agricultural activities of Jinan, Binzhou, Zibo and Weifang are concentrated. Fertilizer and organic fertilizer were overused for the normal growth of crops. The average application amount of chemical fertilizer was more than 300kg·hm^{-2} but the utilization ratio was 15% - 35%[14]. Phosphate fertilizer was regarded as the source of As in many researches[13]. According to statistics, the mean use of organic fertilizer in agricultural soil of Jinan, Binzhou, Zibo and Weifang were 16165.5, 30432, 29014.5 and 24994.5 kg/hm^2, respectively, and chemical fertilizer was 1076.2, 1948.8, 1362.5 and 1837.8 kg/hm^2, respectively. Generally, As was used as additive in animals' food to prevent disease, and lack of Mn in crops would lead to chlorosis. However, As entered animal wastes through incomplete absorption. Therefore, animal wastes were an important source for As and Mn[6,15,16]. Luo et al.[17] showed that 8% - 25% and 5% - 30% of As in agricultural soil in China came from livestock manure and chemical fertilizer every year. Meanwhile, the source of As and Mn was pesticides. The studies by Kelepertzis et al.[18] in Argolida reported that these two elements originated from pesticides. Consequently, As and Mn in sediments originated from agricultural activities.

Table no 2: Percentage contribution of ten heavy metals (%)

	F1	F2	F3	Predicted/Observed	R^2
As	69.5	27.9	2.7	0.88	0.87
Cd	85.3	7.7	6.9	0.97	0.99
Co	84.4	15.6	0.0	0.93	0.86
Cr	87.0	5.3	7.8	0.94	0.95
Cu	79.7	0.0	20.3	1.01	1.00
Hg	71.1	1.4	27.5	0.99	1.00
Mn	59.8	32.4	7.7	0.86	0.90
Ni	88.1	6.3	5.6	0.93	0.95
Pb	79.9	10.1	10.0	0.84	0.79
Zn	83.8	7.2	9.0	0.99	0.99

F3 had the correlation with Cu and Hg. The CV of Cu and Hg were 37.0% and 36.9%, respectively, suggesting that the content was influence by various human inputs. Many industrial mining enterprises, including electroplating plants, Machine-Building Plants and chemical plants, were located in Xiaoqing River Basin. Coal fired power plants and industrial activities with coal as the main energy source were important sources of Hg. Although the dedusting equipment can capture most of the Hg^{2+}, there was still Hg^0 escaping to the environment. Therefore, coal fired power plants and industrial activities with coal as the main energy source were important sources of Hg. the accumulation of Cu in sediments was related with industrial activities. The studies by Xiao et al.[19] and Nguyen et al.[20] suggesting that the Cu was influenced by human activities including mining of copper, copper smelt industry and transport emission. Consequently, industrial emission, along with coal burning might be the important pathway of the input of Cu and Hg to the sediments.

Table no 3: Descriptive statistics of grain size at XRE

	Clay <0.004mm	Silty sand 0.004-0.063mm	Sand 0.063-2 mm
Minimum/%	4.70	9.94	12.34
Maximum/%	21.82	65.84	85.35
Mean/%	7.67	25.50	66.83
SD	2.69	13.04	15.27
CV/%	35.0	51.1	22.9
Skewness	3.48	1.52	-1.71
Kurtosis	17.40	1.70	3.04

IV. Conclusion

The mean concentration of As, Cd, and Mn were higher than the BV of Chinese Offshore sediments and exhibited significant accumulation sediments. The distributions of heavy metals were influenced by grain size of sediment in XRE. The areas with high Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn contents mainly occur in the central parts of the study area, which corresponded to high value area of silt sand content. Three sources of ten heavy metals was determined with EPAPMF, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn were mainly controlled by natural sources, with contribution rates of 69.5%, 85.3%, 87%, 79.7%, 71.1%, 59.8%, 88.1%, 79.9% and 83.8%, respectively. The contribution of agricultural activities to As and Mn was 27.9% and 32.4%, respectively; 20.3% of Cu and 27.5% of Hg were affected by industrial activities and atmospheric deposition. Heavy metals in the XRE were affected by human activities, which should be paid special attention.

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