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Contamination Status and Potential Ecological Risks of Heavy Metal in Sediments from the Qiantang River

Abstract: Heavy metal sediment contamination can significantly damage the ecological water environment. In this paper, we collected superficial sediment samples at 26 different sampling sites, and then tested and evaluated their contamination status and potential ecological risks. The sediment analysis results showed that Cu, Zn, As, Cd, and Pb contents were excessive compared with local soil background levels. There is a low or moderate potential ecological risk level from heavy metal pollution in sediments in the study area; Cd is the element with the potential to cause the most ecological damage.

Keywords: component, heavy metal, ecological risk, river sediment, Qiantang River.

1 Introduction

With industrial development and population growth, environmental pollution caused by industrial wastewater and domestic sewage has become increasingly serious. Urban river pollution has gradually intensified. River sediment is an important component of the water ecological environment. On the one hand, sediments can absorb pollutants in water and relieve water pollution. However, sediment can also release pollutants back into the water upon external environmental changes and thus cause secondary water pollution [1,2]. Sediment is the main living place and food source for benthos. Pollutants in sediments could access terrestrial biota and human bodies through biological concentration and the food chain [3-5].

Urbanization, industrialization, and intensive agricultural development have increased heavy metal contents in river sediments [6]. Because of their toxicity, durability, and non-degradability [7], heavy metals have become key pollutants that significantly influence sediment quality [8,9] and cause sediment to be a secondary pollution source. Therefore, it is necessary to detect heavy metals in river sediments to evaluate heavy metal pollution levels and corresponding potential risks [10-15]. The results from this study will help develop strategies for river pollution control and the ecological dredging of rivers in the Zhejiang province, China, and will also provide reference information for similar areas.

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2 Materials and methods

2.1 Description of Study Area

In this paper, sampling sites were mainly in Hangzhou and Jiaxing along the Qiantang River. Table 1 shows the spatial distribution of sampling sites.

Table 1: Distribution of Sediment Sampling Sites

Sample Site	Longitude and latitude	
	Longitude	latitude
1	30°39'15"	120°31'49"
2	30°14'49"	120°07'40"
3	30°01'41"	120°01'03"
4	30°01'39"	120°00'28"
5	30°14'50"	120°07'37"
6	30°06'16"	120°12'58"
7	30°06'02"	120°12'49"
8	30°15'33"	120°03'44"
9	30°39'15"	120°31'49"
10	30°04'36"	120°12'03"
11	30°07'49"	120°12'44"
12	30°19'27"	120°08'57"
13	30°09'09"	120°13'52"
14	30°13'48"	120°08'11"
15	29°39'02"	119°04'42"
16	29°27'52"	119°15'28"
17	30°06'43"	120°11'13"
18	30°03'23"	119°57'38"
19	30°03'13"	119°56'52"
20	30°44'38"	121°01'49"
21	30°42'07"	121°16'09"
22	30°04'17"	120°11'07"
23	30°39'58"	120°30'32"
24	30°06'24"	120°14'07"
25	30°16'39"	120°10'54"
26	29°59'22"	119°41'8"

2.2 Sample Collection and Processing

Superficial sediment samples were collected with piston samplers (Fig. 1) and kept in sealed, labelled bags. The samples were naturally air-dried in a cool, ventilated laboratory. Impurities such as gravel and animal and plant residue were removed. Later, the samples were tiled on a piece of solid fiberboard and pressed with a glass

rod. Samples were sifted by a 20-mesh sieve to remove oversized substances. Sifted samples were divided through a quartering sample method, and the samples were ground by an agate mortar until they could be sifted through a 100-mesh sieve. The processed samples were sealed for later tests.

Figure 1: Sample analytical methods

2.3 Assessment of Potential Ecological Risk

The sample analysis process had 2 stages: sample pretreatment and heavy metal detection. The sample pretreatment steps were as follows: first, a weighed, dried sediment sample ($0.4 \text{ g} \pm 0.0002 \text{ g}$) was put into a clean PTFE crucible, and 6 mL hydrochloric acid (HCl [36%]) was added on a hot plate at 100°C until only 2 mL of solution remained. When cooled, a combination of a certain volume of nitric acid (HNO_3 [69%]), hydrofluoric acid (HF [48%]), and 3 mL perchloric acid (HClO_4 [70%]) was added on a hot plate between 120 and 150°C until it was nearly dry. The digested sediment solution was diluted with deionized water and filtered quantitatively into a 50 mL volumetric flask. The heavy metal contents (Ni, Cu, Zn, As, Cd, and Pb) in the sediment samples after pretreatment were detected by ICP-MS.

2.4 Assessment of Potential Ecological Risk

Hakanson developed the Potential Ecological Risk Index [16] to evaluate damage to the environment from heavy metals in the sediment, and to assess heavy metal pollution. It integrates the concentrations of heavy metals, their toxic responses and ecological factors, and shows the combined effect of many types of heavy metals. The potential risk index can be calculated as follows:

$$C_f^i = C_h^i / C_n^i \quad (1)$$

$$E_r^i = T_r^i \times C_f^i \quad (2)$$

$$R = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i \quad (3)$$

where C_f^i is the contamination coefficient for a certain heavy metal, and C_h^i is the measured value of the heavy metal. C_n^i is a reference value for heavy metals. E_r^i is the potential ecological risk index for heavy metal pollution from one metal. T_r^i is the toxic response factor of heavy metals that indicates the hazards of heavy metals on human and aquatic ecosystems, and reflects the levels of heavy metal toxicity and ecological sensitivity to heavy metal pollution. RI represents the potential ecological risk index of multiple heavy metals.

In this study, we adopted the environmental background levels of heavy metals from Wang et al. [17] to evaluate the pollution level. Table 2 lists the local background value and the toxic response factor of heavy metals in sediments.

Table 2: The Local Background Value and the Toxic Response Factor of Heavy Metals in Sediments [16,17].

Metals	Ni	Cu	Zn	As	Cd	Pb
C_n^i	41.10	40.80	110.00	10.00	0.21	38.20
T_r^i	1	10	5	5	30	5

3 Results and discussion

3.1 Concentrations and Distribution of Heavy Metals in Sediments

Based on Equation (1), heavy metal concentrations in sediment surfaces (C_h^i) should be measured. Table 3 presents the concentrations of Cu, Zn, Pb, Cd, AS, and Ni in surface sediments. Ni concentrations were lower than the background levels at most sampling sites (except No.18). The Fig. 2 for Cu was also lower than the background levels at most sampling sites (except across 4 sites), but was nearly 10 times higher than the background level at site No.17. On the other hand, the concentrations of other metals (Pb, Cd, As, and Zn) were higher than the background levels at more than half of sampling sites, especially for Cd. The standard exceedance rates of Cu, Zn, As, Cd, and Pb were 4%, 15%, 27%, 50%, 81%, and 58% respectively. The maximum concentrations of Cu, Zn, As, Cd, and Pb were 9.90, 3.86, 2.23, 15.74, and 3.43 times greater than the background values, respectively, while the average concentrations

of Cu, Zn, As, Cd, and Pb were 1.09, 1.28, 1.07, 3.62, and 1.17 times greater than the background values, respectively. Of all the metals, pollution from Cd is the most serious. The pollution levels decrease in the order Cd>Zn>Pb>Cu>As.

Table 3: The Concentrations (mg kg⁻¹) of Heavy Metals in Surface Sediments.

Sampling site	Ni	Cu	Zn	As	Cd	Pb
1	34.02	23.20	62.71	0.01	0.27	32.14
2	37.72	34.52	151.46	10.30	0.91	40.12
3	20.77	29.70	54.21	9.79	1.12	81.80
4	22.66	34.85	105.37	9.55	1.15	87.17
5	17.61	51.61	861.55	10.03	0.75	48.13
6	26.84	35.32	77.72	10.51	1.46	64.46
7	24.02	89.31	256.49	10.66	1.42	50.79
8	34.04	24.49	85.59	14.59	0.28	29.83
9	25.48	24.67	118.72	17.22	0.48	35.29
10	20.90	19.58	65.46	8.42	0.37	28.22
11	21.71	26.00	80.93	13.31	1.21	60.20
12	32.04	25.72	56.95	8.81	0.13	28.36
13	31.96	33.83	107.68	9.20	0.96	67.80
14	27.45	20.50	59.76	9.61	0.20	43.81
15	36.98	78.79	355.70	13.41	2.94	131.01
16	26.03	16.40	78.20	9.96	0.20	23.08
17	25.90	403.75	425.04	16.60	3.31	55.05
18	66.29	29.49	80.89	22.35	0.16	19.96
19	35.98	21.95	94.32	7.05	0.27	26.30
20	29.14	22.39	55.71	6.59	0.25	29.49
21	33.23	24.71	62.46	5.83	0.35	33.48
22	27.12	26.79	123.52	16.73	0.53	34.70
23	13.14	12.84	75.45	8.85	0.37	37.38
24	14.83	8.90	49.56	14.85	0.13	16.43
25	22.56	17.16	50.26	3.81	0.28	30.45
26	30.37	17.81	77.04	11.06	0.25	23.64
mean	28.41	44.40	141.26	10.74	0.76	44.58
standard deviation	1.21	9.07	1.55	4.52	114.05	3.28

Figure 2: Concentrations histograms of Ni(a), Cu(b), Zn(c), As(d), Cd(e), and Pb(f) in surface sediments (mg kg^{-1})

The variation coefficient was used to analyse the spatial distribution of heavy metal content in the surface sediments of the study areas. It can be calculated as follows:

$$CV = S_n / L_n \quad (4)$$

Where, for a certain heavy metal, CV is the variation coefficient, S_n is the standard deviation of the 26 sampling sites, and L_n is the mean value of the 26 sampling sites.

Table 4 lists the variation coefficients of heavy metals in sediments. The variation coefficient decreased in the order of $Cd > As > Cu > Pb > Ni > Zn$. With the exception of Cd, all heavy metals had small variation coefficients. This indicates the spatial distribution of each heavy metal was not uniform, mainly because the rivers suffer from different pollution sources.

Table 4: Variation Coefficients of Heavy Metals in Sediments

Ni	Cu	Zn	As	Cd	Pb
0.04	0.20	0.01	0.42	150.07	0.07

Fig. 3 presents the distribution of heavy metals in the sediments of the study areas, and RI (Table 5) was used to present the pollution level. Based on the above analysis, we divided this part of the river into three ecological function areas: upstream, midstream, and downstream. It is necessary to take steps to control heavy metals upstream (Cu, Zn, As, Cd, and Pb) and midstream (Ni, Cu, Zn, As, Cd, and Pb).

Figure 3: Distribution of heavy metals in sediment (RI)

3.2 Potential Ecological Risk of Heavy Metals in Sediments

Table 5 presents the result of the calculations of the single potential ecological risk index (E_i^r) and the integrated potential ecological risk index (RI) based on equations (2) and (3). It also lists the values of E_i^r and RI at each sampling site. The relation

between E_r^i , RI, and degree are listed below (Table 6), and the potential ecological risk assessments in the study areas are shown in Fig. 4.

Table 5: The Potential Ecological Risk Assessment for Heavy Metals in Sediments

Sampling sites	E_r^i						RI
	Ni	Cu	Zn	As	Cd	Pb	
1	4.14	2.84	0.57	0.01	38.64	4.21	50.42
2	4.59	4.23	1.38	10.30	130.25	5.25	156.00
3	2.53	3.64	0.49	9.79	160.55	10.71	187.70
4	2.76	4.27	0.96	9.55	164.41	11.41	193.36
5	2.14	6.32	7.83	10.03	106.96	6.30	139.59
6	3.26	4.33	0.71	10.51	208.86	8.44	236.11
7	2.92	10.94	2.33	10.66	203.26	6.65	236.77
8	4.14	3.00	0.78	14.59	40.45	3.90	66.86
9	3.10	3.02	1.08	17.22	68.66	4.62	97.70
10	2.54	2.40	0.60	8.42	53.51	3.69	71.16
11	2.64	3.19	0.74	13.31	173.11	7.88	200.86
12	3.90	3.15	0.52	8.81	18.79	3.71	38.88
13	3.89	4.15	0.98	9.20	137.81	8.87	164.89
14	3.34	2.51	0.54	9.61	29.12	5.73	50.86
15	4.50	9.66	3.23	13.41	420.39	17.15	468.34
16	3.17	2.01	0.71	9.96	28.03	3.02	46.91
17	3.15	49.48	3.86	16.60	472.20	7.21	552.51
18	8.06	3.61	0.74	22.35	22.90	2.61	60.28
19	4.38	2.69	0.86	7.05	38.30	3.44	56.71
20	3.55	2.74	0.51	6.59	35.59	3.86	52.83
21	4.04	3.03	0.57	5.83	50.43	4.38	68.28
22	3.30	3.28	1.12	16.73	75.68	4.54	104.66
23	1.60	1.57	0.69	8.85	53.15	4.89	70.76
24	1.80	1.09	0.45	14.85	18.17	2.15	38.51
25	2.74	2.10	0.46	3.81	40.08	3.99	53.18
26	3.69	2.18	0.70	11.06	35.05	3.09	55.78

Table 6: The Relation Between E_r^i , RI, and Degree [16]

E_r^i and degree		RI and degree	
$E_r^i < 40$	low	$RI < 150$	low
$40 \leq E_r^i < 80$	moderate	$150 \leq RI < 300$	moderate
$80 \leq E_r^i < 160$	higher	$300 \leq RI < 600$	severe
$160 \leq E_r^i < 320$	high	$RI \geq 600$	serious
$E_r^i \geq 320$	serious

Figure 4: The potential ecological risk assessment for heavy metals in the study areas

Most potential ecological risk indexes (E_i^p) for Cd exceeded 40 (Fig. 3), and nearly half of them exceeded 80 and fell into the higher risk category. The E_i^p values for Ni, Zn, As, and Pb were less than 40, and indicated low risk. The E_i^p of Cu ranged from 1 to 10 (except one in 49.98), which indicated low risk. The potential ecological risk values (E_i^p) decreased in the order of $Cd > As > Pb > Cu > Ni > Zn$. RI values ranges from 30 to 600, and around half of them were higher than 150, which indicated that the integrated potential ecological risk at nearly 13 sampling sites was moderate. The average contribution proportions of E_i^p of Ni, Cu, Zn, As, Cd, and Pb to RI were 2.55%, 4.02%, 0.95%, 7.93%, 80.24%, and 4.31%, respectively. Of these, Cd contributed the most. These results show that Cd is the element with the potential to cause most ecological damage.

4 Conclusions

1. According to heavy metal distribution in sediments, we divided this part of the river into three ecological function areas: upstream, midstream, and downstream. It is necessary to take steps to control heavy metals in the upstream (Cu, Zn, As, Cd, and Pb) and midstream (Ni, Cu, Zn, As, Cd, and Pb) portions of the Qiantang River, China.

2. Comparison shows that pollution from Cd is more severe than the pollution from other metals, with an average concentration 3.62 times higher than the background levels. The risk from Cu is slight/medium, while the risks from Ni, Zn is low.

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