Ecological Risk Assessment of Heavy Metals in Sediment from Beijing-Hangzhou Grand Canal

Lijun Wu[1, 2*], Xiangru Li[1, 3], Xin Luo[1, 3] and Jiye Xie[1, 3]
[1] Huadong Eco-Environmental Engineering Research Institute of Zhejiang Province, Hangzhou 311122, Zhejiang, China
[2] College of Environmental and Resource Science, Zhejiang University, Hangzhou 310029, Zhejiang, China
[3] Power China Huadong Engineering Corporation Limited, Hangzhou 311122, Zhejiang, China

Abstract. Sediments contaminated by heavy metals (HMS) pose detrimental effects on both the public health and ecosystem. In our study, sediment samples were collected from Hangzhou Section of Beijing-Hangzhou Grand Canal. Based on heavy metals concentrations measured, the pollution status assessments were conducted adopting three methods namely the Nemerow index (P_N), single factor index (P_i) and potential ecological risk index(RI). The order of concentration of heavy metals investigated is as follows: Zn>Cd>Cu≈As≈Pb≈Ni≈Cr. T2 and T7 sites had high level pollution based on P_N characterized by Zn and Cd accumulation. Based on the findings of the RI assessment, site T2 reached a higher risk level toward the human and ecological environment in which Cd was the chief contributor.

1. Introduction

Urban rivers are susceptible to pollutants discharged along shores, resulting in N, P [1], HMS [2] accumulation in the sediments. The analysis of geochemical materials concentered is of vital importance in understanding river environment. Particularly, the relative consistence of heavy metal render it an effective marker to evaluate the state of the pollution. Accordingly, a large number of assessment methods such as sediment quality guidelines, risk assessment methods, geoaccumulation index have been established to understand the sedimentary conditions of a river so as for efficient countermeasures. The predominant methods adopted can be categorized as single factor indices and integrated indices.[3] The most popular single factor indices method like the P_i was used to identify one heavy metal that mostly related to pollution.[4] However, it ignores the synergistic effects by heavy metals in combination. Therefore integrated indices methods were proposed such as the P_N[5], the pollution load index[6], as well as the degree of contamination [7]. But varied heavy metal contribute to pollution impact to various extend which is not reflected by integrated indices methods. A risk assessment model like RI was developed which not only take into consideration the content of heavy metals, but also links their toxicology with the ecological and environmental impacts.

The Beijing-Hangzhou Canal flows from north to south through Beijing, Tianjin, Hebei, Shandong, Jiangsu and Zhejiang provinces with a local length at 1794km. It runs through five major water systems of China, naming the Haihe River, the Yellow River, the Huaihe River, the Yangtang River, the Qiantang River and a series of lakes. HSBGC, as an inner river played important role in the urban development and local water environmental infrastructures, lie in the east of Hangzhou city. With the booming of local population as well as the rapid development of urban and rural industries, a growing of industrial pollutants, household contaminants were discharged into the Grand Canal water system, directly leading to the decline of the ecological status of the HSBGC and the quality of the water environment. Since the significance of sediment HMS management and urban aqua ecosystem maintenance is realized, the purpose of this study is therefore to assess the level of heavy metal contamination in the sediments from Hangzhou Section of Beijing-Hangzhou Grand Canal (HSBGC) dredging project and to provide baseline data in assisting in contamination monitor and serves as a roadmap for future work.

2. Materials and Methods

2.1. Study Area

Study area of HSBGC is located in Hangzhou of Zhejiang, China. The sites are located in adjacent to industrial areas, residential areas and agricultural lands. As shown in figure 1, it lies between the longitude 30.360479 and 30.497019 and the latitude 120.253644 and 120.319959. Eleven sampling sites were selected within along HSBGC based on accessibility and proximity from potential pollution sources. At a depth of 0~10cm, sediment samples were collected with a grab at each sampling site and were stored in an polyethylene bag and labeled accordingly. 3 samples were taken at each sampling site to form a mixed sample.

*wu_lj2@hdec.com

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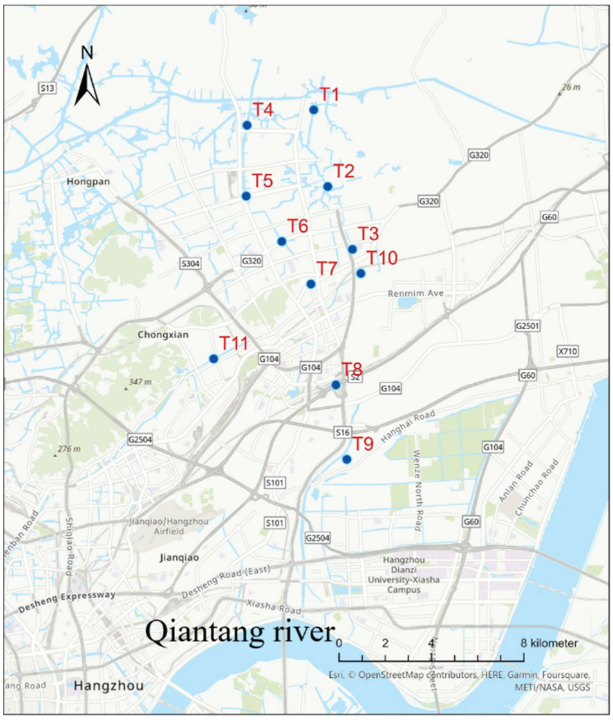

Fig. 1. Map of sediment sampling sites in HSBGC

Samples in the study area were collected between September to November (the dry season in Hangzhou) in 2022. The effect of rain season on sediment HMS qualities were presumed to be weak.

2.2. Sampling and Analysis

Samples were air dried and remove large size impurities like the fragments of plants. It is then milled in an agate mortar and passed through 2 mm sieve to rid of the coarse sand. It is then followed by acid digestion. 0.25g of the sieved sample was weighted in Teflon vessel, with 5mL of HNO_3 and 5mL of HF added. It was allowed to stand for 30 min for reaction subsided. After that, the samples were then heated at 118°C for 2 min before 5~10ml of 30% H_2O_2 was added droplet. Afterwards, heating the solutions to evaporate till 5 ml and cooling to room temperature, then add 2~5 mL of saturated boric acid before diluted to 25 ml. The resulting digest was filtered and sealed. After the pretreatment, the heavy metals concentrations were measured using atomic absorption spectrophotometer as detailed in “Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products” (HJ332-2006). atomic absorption spectrophotometer calibration standard was prepared by diluting standard(1000ppm) and ultrapure deionsed water was used.

2.3. Single Factor Index

The single factor index suggested by Hakanson is considered to be a simple and effective tool of monitoring HMS contamination. The pollution index for a single pollutant was given by:

$$P_i = \frac{C_i}{S_i} \quad (1)$$

In which P_i is the single pollution index; C_i represents the mean measured concentration of heavy metal; S_i is the standard value of the heavy metal. In this study, S_i were taken using the background value in soils of Hangzhou City. The degree of pollution can then be divided as polluted ($Pi>1$) or unpolluted($Pi\leq1$), and the higher Pi the more polluted.[7]

2.4. Nemerow Index

The Nemerow index which developed by Nemerow and Sumitomo denoted the most polluting factor while also taking the contributions of other factors into account in the assessment process. The Nemerow index (P_N) was defined as following:

$$P_N = \sqrt{\frac{P_{i(avg)}^2 + P_{i(max)}^2}{2}} \quad (2)$$

Where, $P_{i(avg)}$ is the average of the pollution indices for all heavy metals, $P_{i(max)}$ is the highest pollution indice of the heavy metals. The degree of pollution can be classified as: safe ($P_N\leq0.7$), precaution ($0.7 < P_N\leq1.0$), mildly polluted ($1.0 < P_N\leq2.0$), moderate pollution ($2.0 < P_N\leq3.0$), and serious pollution ($P_N > 3.0$)[8].

2.5. The Potential Ecological Risk Index(RI)

The potential ecological risk index was a method created by Hankanson which assumes that the sensitivity of the aquatic system is determined by its productivity. The ecological risk index of a certain heavy metal can be computed from the single contamination factor and toxic-response factor values of the heavy metals. The potential ecological risk index (RI) was defined as following:

$$\mathrm{RI} = \sum E_r^i = \sum_{i=1}^{n} \left(T_r^i \times \frac{C_D^i}{C_B^i} \right) \quad (3)$$

Where, E_r^i is the single pollutant contamination factor, C_D^i is the measured heavy metal concentration of the samples, C_B^i is the heavy metal concentration in the soil, T_r^i represents the toxicological response factor of individual heavy metal as follows: Cd = 30, As =10, Ni = Cu = Pb = 5, Cr = 2 and Zn = 1[9].

Table 1. Criteria of HMS contamination and RI levels

E_r^i		RI	
Threshold interval	Classification	Threshold interval	Classification
$E_r^i<40$	Low contamination	RI<150	Low risk
$40\leq E_r^i<80$	Medium contamination	150≤RI<300	Medium risk
$80\leq E_r^i<160$	Higher contamination	300≤RI<600	Higher risk
$160\leq E_r^i<320$	High contamination	600≤RI<1200	High risk
$E_r^i\geq320$	Severe contamination	RI≥1200	Severe risk

3. Discussions

3.1. Heavy Metal Pollutions Assessment by P_i and P_N

The statistical results for heavy metals in HBHGC sediments are demonstrated in Table 2. The concentrations of Cd, Pb, Cu and Zn exceed the highest background values (HBV) of HMS in topsoil of Hangzhou.[10]

Table 2. Statistical description of HMS concentrations in HBHGC sediments

Items	Cd (mg/kg)	As (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cr (mg/kg)
Mean	0.34	9.0	35.7	40.0	32.9	217	84.3
Min	0.10	5.4	22.1	20.4	23.0	82	59.5
Max	1.90	16.4	58.9	118.0	47.0	719	142.1
SD	0.52	3.5	12.0	29.7	8.0	199	28.6
HBV	0.21	15	35	35	40	100	90

The P_i and P_N calculated by Eqs. (1) and (2) for each hevay metal in eleven locations are illustrated in Fig. 2. The Pi of all HMS at sites T1, T5, T6 and T9 are below 1, showing that none of the sites had been polluted. Severe pollution occurred at downstream of Ting Toe Harbour (T3) and Wo Fung Harbour (T7) in addition to the confluence of rivers such as T2 and T10. The concentration levels of HMS decreases in the same order of Zn>Cd>Cu≈As≈Pb≈Ni≈Cr for those severe polluted sites indicating a similar source of contamination.

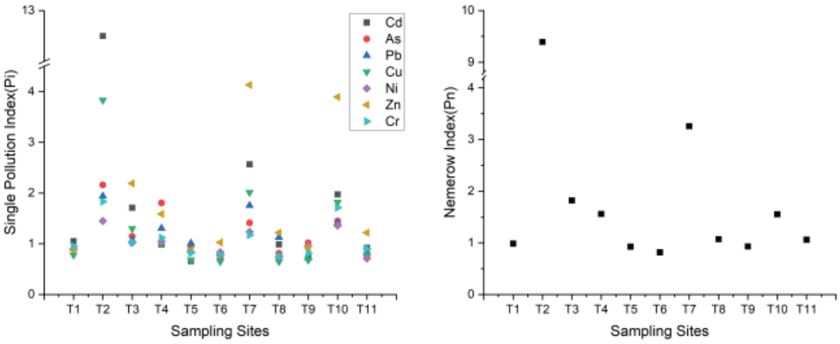

Fig. 2. The P_i (left) and P_N (right) of the samples

In respect to P_N, the pollution degree of T2 and T7 were of high value, at 9.4 and 3.3 separately. The P_N of T3, T4 and T10 were between 1.5 and 2, showing slight pollution. Other Six sites, T1, T5, T6, T8, T9 and T11, were rated at precautionary level.

3.2. Heavy Metal Ecological Risk Assessment by RI

The HMS risk assessment by RI properly integrate toxicology with ecological impacts. In this study, calculated results of the single elements (E_r^i) and the overall RI are listed in Table 3.

Table 3. Statistical descriptions on HMS risk assessment of HBHGC sediments

Sampling Sites	E_r^i							RI
	Cd	As	Pb	Cu	Ni	Zn	Cr	
T1	31.58	8.96	4.57	3.90	4.48	4.42	1.91	59.8
T2	375.00	21.61	9.69	19.16	7.25	38.73	3.66	475.1
T3	51.32	11.46	5.35	6.49	5.09	10.95	2.06	92.7
T4	29.61	18.05	6.53	5.03	5.25	7.93	2.24	74.6
T5	19.74	9.46	5.05	3.41	4.17	4.37	1.65	47.8
T6	23.68	7.13	4.08	3.25	4.17	5.12	1.55	49.0
T7	76.97	14.10	8.78	10.06	6.17	20.66	2.35	139.1
T8	29.61	8.12	5.63	3.25	3.70	6.09	1.52	57.9
T9	21.71	10.17	3.63	3.41	4.78	4.58	1.62	49.9
T10	59.21	14.49	7.07	9.09	6.79	19.47	3.43	119.6
T11	27.63	7.48	4.14	3.90	3.55	6.09	1.80	54.6
Mean	67.82	11.91	5.87	6.45	5.04	11.68	2.16	110.9

As demonstrated in Table 3, the scope of the mean E_r^i for each metal ranges from 2.16 to 67.82, indicating low to medium contamination. E_r^i for HMS declined in the order Cd>As>Zn >Cu > Ni > Pb > Cr. Heavy metal Cd posed a severe contamination at site T2 while low to medium contamination at other sites. The contamination according to E_r^i of other metals were all less than 40, belonging to low contamination level. For the overall RI, the mean of all sites was 110.9 denoted that the comprehensive ecological risk was minimum. However, site T2 has reached a higher risk level in which Cd was the key contributor.

4. Conclusions

The concentrations of HMS in the sediments from HBHGC were determined based on which the extent of pollution and the potential risk of HMS were evaluated in this research. Zn, Cd and Cu is ranked top in concentration but only Cd contributed to potential ecological risk in our study. Apart from T2, all other sites were found to be low in contamination and potential ecological risk.

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