

Original Research

Distribution Characteristics, Source Identification and Risk Assessment of HMs in the Communicate Area of Weihe River and Qianhe River, China

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Abstract

With the acceleration of new-type urbanization and beautiful countryside construction, the urban fringe has become one of the main spaces for urban expansion and environmental quality improvement. Water and sediment samples are collected from 8 sites at the intersection of the Weihe River and the Qianhe River in the eastern suburbs of Baoji City. The results show that from the upper reaches to the lower reaches of the river, the HMs concentration of the mainstream is Weihe River>Qianhe River, and the upper stream < the lower stream. The highest concentrations of Cr, Ni, Pb, and Hg in river water exceeded GB3838 Class II standard limits. The HM concentration in sediments from, high to low, is Zn>Cr>Cu>Ni> Pb>As>Cd>Hg. The degree of potential ecological risk from the upper reaches to the lower reaches of the river was: high → considerable → moderate → considerable. However, the ecological risk degree of individual metal elements is Hg>Cd>Pb>Cu>As>Ni>Cr>Zn. The main pollution elements are Hg, Pb, and As, mostly from point-source discharge and upstream tributaries. In the future, point-source emissions should be strictly controlled, and land use planning should be adjusted.

Keywords: Weihe River, Qianhe River, heavy metal, sediment, spatial distribution, ecological risk assessment

Table 2. Evaluation standard of the I_{geo} .

I_{geo}	≤ 0	0~1.0	1.0~2.0	2.0~3.0	3.0~4.0	4.0~5.0	≥ 5.0
Pollution degree	Unpolluted	Unpolluted to moderate	Moderate	Moderate to heavy	Heavy	Heavy to extreme	Extreme

Ecological Hazard Index (RI)

The potential ecological risk index method (RI) [24] is a commonly used method to assess the risk of HMs in water and sediments. It comprehensively considers the toxicity of heavy metals, the sensitivity of the environment to heavy metals, and the synergy of various heavy metals, and sets the toxicity response coefficient to evaluate heavy metals. It is calculated using the following formula:

$$RI = \sum_{i=1}^n E_{ri} = \sum_{i=1}^n T_{ri} \times \left(\frac{C_d}{C_b}\right) \quad (4)$$

Where, RI is the multifactor comprehensive potential ecological risk index, reflecting the potential hazards of all the participating pollutants. E_{ri} is the single-factor hazard index. T_{ri} is the toxicity response coefficient, which reflects the toxicity level of HM and the sensitivity of organisms to pollutants (which can be replaced by the biological toxicity coefficient). It is determined according to various factors such as the HM concentration of surface sediments, sedimentation, affinity for solids, sensitivity of water to metal pollution, and central toxicity level. In this study, the toxicity response coefficients of Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg are 2,5,5,1,10, 30, 5, and 40, respectively, in reference to the research achievements of Zhuang et al. (2016) [25]. The classification of the potential ecological risk coefficient of HMs and the ecological risk index RI are shown in Table 3.

Statistical Analysis

Analysis of Variances (ANOVA) ($p < 0.05$) of heavy metal concentrations in different areas was performed using a one-way ANOVA test. One-way ANOVA can test whether there is a significant difference between the mean values of dependent variables in samples for

Table 3. Classification of potential ecological risk coefficient and ecological risk index (RI) of HMs.

E_r^i	RI	Risk
<40	<150	Low
40~80	150~300	Moderate
80~160	300~600	Considerable
160~320	600~1200	High
>320	>1200	Significantly high

multiple groups affected by a single factor. Zeng et al. (2020) [26] used one-way ANOVA to compare river water quality in different land-use areas.

In this manuscript, Pearson correlation analysis and CA are suitable for checking the influence factors and identifying the sources of heavy metals in water and sediments and are widely used in many reports [27, 28]. Origin Pro 2021 version (OriginLab Corp., Northampton, MA, USA) was applied for clustering analysis and cluster analysis, and SPSS 22.0 version (IBM SPSS Statistics, Version 22) and ArcGIS 10.5 were conducted to make the spatial distribution map of HMs.

Results and Discussion

Water Contamination Analyses

HMs Content in Rivers

The statistical analysis of HMs in water is shown in Table 4. Concentrations of HMs were 0.01~56.46 µg/L with an average content of 8.83 µg/L for Cr, 0.60~24.31 µg/L with an average content of 4.78 µg/L for Ni, 0.17~9.99 µg/L with an average content of 3.31 µg/L for Cu, 6.17~42.34 µg/L with an average content of 26.61 µg/L for Zn, 0.14~4.03 µg/L with an average content of 1.95 µg/L for As, ND (not detected) ~0.59 µg/L with an average content of 0.15 µg/L for Cd, 0.25~30.21 µg/L with an average content of 6.11 µg/L for Pb, 0.04~1.21 µg/L with an average content of 0.30 µg/L for Hg. Compared with GB3838, it was found that the highest concentrations of Cr, Ni, Pb, and Hg exceeded the GB3838 Class II standard limit. The concentration of other HM is below the GB3838 Class II standard limit.

The coefficient of variation (CV) reflects the degree of disturbance of water physicochemical characteristics by anthropogenic activities [29]. CV scores showed low variability (lower than 15%), medium variability (15%~36%) and high variability (higher than 36%) [30]. The order of coefficients of variation (CV) of the HMs in descending order was Cr>Ni, Pb>Cd>Hg>Cu>As>Zn. It was obvious that the coefficient of variation of HMs was greater than 36% except for Zn and As. On the whole, the HMs of river water bodies is greatly affected by human activities, especially the centralized discharge of unclean water and traffic.

The comparison of HMs concentrations in water bodies with those in other rivers is shown in Table 5 [31-35]. The concentration of HMs in QW was basically consistent with that in the middle section of Weihe Pass, the Baoji section, and the Yellow River Estuary.

Cu content appeared at the Cross-River Bridge (W6) ($0.74\ \mu\text{g/L}$), and the single factor pollution index evaluation result indicated no pollution. The content of the remaining seven elements followed a pattern of initially increasing, then decreasing, and then increasing [37]. In particular, the content of Pb and Hg in Section W8 exceeded the GB3838 Class II standard limit, and the P_{\max} was as high as 12.24. The pollution degree was heavy and gradually decreased in the downstream due to the dilution of water flow. The investigation found that there are important transportation hubs such as the railway station (Wolong Temple Station) and the Baoji Transit Highway (G2034) near W8, with large traffic flow. In addition, factors such as urban coal-fired heating, industrial enterprises, treated sewage discharge, urban renewal and construction, and agricultural production in irrigation areas in the north may lead to excessive HMs content in water. The Hg pollution index of W7 was 7.63 (heavy pollution). There were more than 30 metal material manufacturing, petroleum, and petrochemical enterprises on both sides of the upstream river, and the impact of urban main road and railway transportation cannot be ignored [38].

HM Potential Ecological Risk in Rivers

We used the potential ecological hazard index method to calculate the potential ecological risk of water HM, and the results are shown in Table 6. The HMs of the Thousand Rivers had only a slight potential ecological risk, and the variation of the hazard index (RI) was not significant (17.30~17.55). Because of the admission of centralized sewage discharge, the exceedance of HMs near W8 was relatively high, and the value of RI was as high as 976.55, which indicates a high potential ecological risk. The potential ecological risk level of the rivers in the study area from upstream to downstream was: high \rightarrow considerable \rightarrow moderate \rightarrow considerable. While calculating the potential hazards of HM, this method has obvious shortcomings such as subjectivity and unclear weights of multiple HM, so a single HM pollution index and risk index often affect the calculation results [29].

Sediment Contamination Analyses

HMs Content in Sediments

The concentration distribution of HMs in river sediments in the study area is shown in Fig. 3.

Table 6. Potential ecological risks and comprehensive potential ecological risks of HM in the river.

Sites	Ni	Cu	Zn	As	Cd	Pb	Hg	Cr	RI
W1	1.71	0.05	0.04	0.81	1.31	5.76	120.24	0.35	128.56
W2	0.45	0.01	0.03	0.49	0.59	1.32	32.00	0.16	34.60
W3	0.15	0	0.03	0.55	0.53	0.19	32.00	0.16	33.45
W4	0.20	0	0.04	0.49	0.71	0.59	32.00	0.16	33.99
W5	0.56	0.02	0.03	0.36	0.57	1.09	237.50	0.16	239.73
W6	0.23	0	0.02	0.14	0.03	0.26	182.50	0.16	183.11
W7	0.19	0.03	0.02	0.03	0	0.12	305.00	0.16	305.42
W8	6.08	0.01	0.06	0.26	3.52	15.10	967.76	1.37	988.08

Table 7. Potential ecological risks and comprehensive potential ecological risks of HM in the river.

River	Cr	Ni	Cu	Zn	As	Cd	Pb	Hg
This study	23.70~71.29	17.43~68.73	16.53~89.96	54.53~133.28	0.35~8.45	0.13~0.83	20.31~34.98	0.07~1.61
Weihe River [39]	109.98	41.47	52.37	103.47	29.16	-	24.22	-
Yellow River [40]	47.52	-	11.78	46.56	8.29	0.15	10.65	-
Liaohe River [41]	90.30	26.50	37.90	-	12.30	0.49	32.90	0.14
Haihe River [42]	75.27	33.07	34.01	102.55	8.47	0.17	25.32	0.11
Zhujiang River [43]	56.40	-	39.00	-	5.24	1.40	59.40	1.40
Huaihe river [44]	79.9	34.6	44.7	149.0	10.8	0.61	33.4	0.25
Surma River [45]	-	92.34	2.68	6.12	-	0.06	11.73	-

background and man-made sources, with contribution rates of 45% and 55%, respectively. Industrial sources affect the accumulation of Hg in urban river sediments. Saiful et al. (2022) [56] found that severe man-made pressure and urbanization had significant impacts on the soil environment in the capital of ancient Pundranagar, Bangladesh. The Ga-Selati River sediments in South Africa had the highest accumulation of chromium and nickel, and pollution levels in the middle reaches were much higher than at upstream and downstream sites, mainly from mining, wastewater/sewage, and agricultural discharges [57]. In addition to natural factors, human activities such as agricultural production and fossil fuel utilization also significantly affected the spatial distribution of HMs in river sediments in the Beijing-Tianjin area [58]. However, Setia et al. (2020) [59] emphasize that non-point sources of HM concentrations, such as agricultural surface runoff and soil erosion in urban areas, should not be ignored due to their complexity and difficulty in analysis.

The research analysis showed that river ecological environment protection and pollution control in Baoji should be carried out from the perspectives of source control, path control, and terminal treatment [60]. Firstly, strengthen the production level of key industrial enterprises (such as BAOTI Group Co., Ltd., and other metal smelting and processing enterprises) and strictly control the discharge of pollutants. Pollutants generated by industrial production and transportation are discharged into sewage treatment plants for treatment in accordance with the requirements and then discharged after meeting the specified standards (W8) so as to reduce the concentrated discharge of pollutants from the source. Strengthen the detection of river water quality and pay attention to the upstream water situation in Baoji so as to prevent the import of foreign pollutants. Secondly, focus on strengthening the control of river HMs pollution, combined with the construction and protection of Qianweizhihui National Wetland Park, optimizing waterways through the reasonable layout of water conservancy projects, and reducing the accumulation of HMs in sediments. In addition, it was necessary to reasonably plan traffic routes, strengthen urban vehicle management, and ensure transportation on the basis of reducing pollution discharge as much as possible. Moreover, in the construction of intensive, high-standard farmland, it was important to strictly control the use of pesticides and fertilizers containing HMs, scientific irrigation, and the non-point source pollution of farmland into urban rivers [61]. In particular, in the study area, the use of biological agents and the planting of hyper enrichment plants require human intervention to control the polluted water and sediment. This study can improve public awareness of soil heavy metal pollution and provide important information for further control and reduction of soil heavy metal pollution.

Conclusions

On the basis of the HMs investigation of water and sediment in the confluence of the Qianhe River and the Weihe River in Baoji City, according to the current analysis results, we can draw the following conclusions:

(1) The results of the Nemerov comprehensive pollution index and ground accumulation index showed that the HM concentration showed a pattern of main stream>tributary, upstream<downstream. The highest concentrations of Cr, Ni, Pb, and Hg in river water exceeded GB3838 Class II standard limits, while the HM concentration in sediments was Zn>Cr>Cu>Ni>Pb>As>Cd>Hg from high to low.

(2) Because of the contribution of pollutants from urban point sources and tributaries, the ecological risk levels of HMs in each river reach were different. The degree of potential ecological risk from the upper reaches to the lower reaches of the river was: high → considerable → moderate → considerable. However, the ecological risk degree of individual metal elements is Hg>Cd>Pb>Cu>As>Ni>Cr>Zn. Due to the different toxicity coefficients of different elements, the ecological risk assessment method will affect the potential ecological risk assessment results while considering the types and contents of pollutants.

(3) The river HMs mainly come from centralized wastewater discharge, transportation (railway and highway hubs), metallurgy, industrial enterprises (metal material manufacturing), and agricultural production. For this, the monitoring analysis strictly requires centralized wastewater discharge to meet the standards before discharge. The application of pesticides and fertilizers in intensive, high-standard farmland construction is controlled to minimize the discharge of agricultural non-point source pollution into rivers. The enhancement of riverside transportation vehicles, station waste disposal, and river wetland pollution restoration and treatment are the key directions of urban river HMs treatment in the future.

Limitations and Future Research Directions

There are still the following shortcomings in this paper: This paper only studies part of the Weihe River in Baoji City. Further studies on the distribution and risk of HMs on a larger scale or even within a basin are needed in the future. To investigate the migration and accumulation mechanism of HMs to aquatic organisms and even in ecosystems.

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