

Article

Distribution, Risk Assessment, and Source Identification of Potentially Toxic Elements in the Sediments of the Upper Reaches of Zhanghe River, Haihe Basin

Pengyang Gao ^{1,2,3}, Jingshi Shang ¹, Jinkun Wu ^{2,3}, Zheng Mu ^{2,3}, Meiqin Suo ^{2,3} , Jingjing Fan ^{2,3}, Yunpu Zheng ^{2,3}, Yao Cheng ^{1,2,3,*} and Yuchun Wang ^{1,*} 

¹ State Key Laboratory of Simulation and Regulation of Water Cycle in River Basin, China Institute of Water Resources and Hydropower Research, Beijing 100038, China

² School of Water Conservancy and Hydroelectric Power, Hebei University of Engineering, Handan 056038, China

³ Hebei Key Laboratory of Intelligent Water Conservancy, Hebei University of Engineering, Handan 056038, China

* Correspondence: chengyao@hebeu.edu.cn (Y.C.); wangyc@iwhr.com (Y.W.)



Citation: Gao, P.; Shang, J.; Wu, J.; Mu, Z.; Suo, M.; Fan, J.; Zheng, Y.; Cheng, Y.; Wang, Y. Distribution, Risk Assessment, and Source Identification of Potentially Toxic Elements in the Sediments of the Upper Reaches of Zhanghe River, Haihe Basin. *Sustainability* **2022**, *14*, 15885. <https://doi.org/10.3390/su142315885>

Academic Editors: Miklas Scholz and Shibao Chen

Received: 19 October 2022

Accepted: 26 November 2022

Published: 29 November 2022

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Abstract: The Beijing–Tianjin–Hebei region is mostly located in the Haihe Basin. Studying the distribution and sources of potentially toxic elements (PTEs) and heavy metals in the upper reaches of Zhanghe River, the largest tributary of Haihe runoff, is of great significance to the water security of Beijing–Tianjin–Hebei region, a world-class urban agglomeration. In this study, 32 sediment samples were collected in the upper reaches of Zhanghe River, and the concentrations of eight PTEs were analyzed. The results show that the concentrations of PTEs in sediments ranked are as follows: Mn > Cr > Zn > Cu > Pb > Co > As > Cd. Cr, Cu, Zn, and Cd show a random spatial variation trend; Mn, As, and Pb are mainly distributed in the headwaters of the Zhuozhang River. Ninety percent of samples of Cr, Cu, Zn, Cd, and Pb are under the threshold effect level, and 16% of the Cr samples are above the probable effect level. PTEs in the study area have low to moderate pollution as the enrichment factor and geo-accumulation index showed, and the contribution of anthropogenic sources to the enhancement of PTEs in sediment samples is still at a preliminary stage. Potential ecological risk results indicate that 96% of the upper reaches of Zhanghe River have a low risk level. The three evaluation methods all point out that Cr is the main pollutant in the upper reaches of Zhanghe River, and the Southern Headwater of Zhuozhang River is the main polluted area. Cr, Mn, Co, and Pb originate from mining activities and road dust, while Cu, Zn, As, and Cd originate from agricultural activities.

Keywords: potentially toxic elements; spatial distribution; risk assessment; possible sources; Zhanghe River; Haihe Basin

1. Introduction

With rapid economic development and urban expansion, potentially toxic elements (PTEs) are being discharged increasingly into the aquatic environment from geological sources such as weathered rocks or anthropogenic sources such as industry and agriculture, resulting in the river PTE pollution becoming more and more serious [1,2]. In particular, the toxicity and high bioaccumulation of PTEs have attracted extensive attention from scholars [3]. As the sediment is a source or sink in the aquatic environment [4–6], PTE pollution in the sediment has become a complicated and persistent problem [7]. PTEs discharged into the aquatic environment can accumulate in sediments through adsorption, hydrolysis, and precipitation. Moreover, PTEs in sediments may re-enter the overlying water with the change of environment, causing secondary pollution [8]. These pollutants may even enter the food chain, affecting the survival of aquatic organisms and the safety

of human health [9]. After a long period of cumulative effect, sediments can act as an indicator for pollution levels in rivers, reflecting historical and recent river pollution conditions [10,11].

As the largest and most dynamic region in northern China, the Beijing–Tianjin–Hebei region has attracted more and more attention from China and even the whole world; most of its area is located in the Haihe Basin [12]. Its water environment problem causes a great concern accompanied by the development of industry and urbanization [13,14]. The research on the nine sub-basins of the Haihe Basin found that most of the sediment related to Hg seemed to come from natural sources [15]. There was a moderate risk of Hg in the Da Qing He, Luan He, and Tu-Hai Ma-Xia rivers. The Cd in the sediments of the Haihe Basin was at a high level of pollution and became a severe pollutant of this ecosystem [16]. The study on the three reservoirs in Beijing and Tianjin showed the environmental water quality standard of PTEs, which provided a reference for local water quality assessment in China [17]. However, the ecological risk of PTEs in the Zhanghe River (ZR), which is the source of the Haihe Basin and flows in its tributaries, is seldom studied. Many mathematicians ignored the main factors of ecological risk in the assessment process [18–20].

ZR is located upstream of the southern system of the Haihe Basin, and its upper reaches are an important source of water for industrial and agricultural production and drinking water for Shanxi, Hebei, and Henan provinces [21]. There are many coal and chemical enterprises in this region, and there are also many roads built along the river to transport coal and chemical products. Studies have shown that the exploitation and combustion of fossil fuels and the processing and transportation of ore will bring PTEs into rivers [22–24]. Therefore, to ensure the water safety of the Haihe Basin and understand the distribution, composition, and source of PTEs in the Haihe Basin, the PTE pollution in sediments of the upper reaches of ZR was studied in combination with the local industrial structure.

For the future ecological risk management and water security control of the ZR basin, this study collected 32 sampling sites and measured the concentrations of Cr, Mn, Co, Cu, Zn, As, Cd, and Pb, with the following specific objectives: (1) investigate the concentration level and enrichment degree of PTEs and visualize the pollution situation; (2) evaluate the pollution and risk caused by each PTE, using the ratio of EI to RI to explain the role of PTE toxicity in increasing risk; and (3) combine local industrial structure and multivariate analysis to discuss the possible sources of PTEs.

2. Materials and Methods

2.1. Study Area and Sample Collection

Zhanghe River, flowing through four cities in three provinces, belongs to the Zhangwei South Canal water system of Haihe Basin, including Qingzhang River and Zhuozhang River, two independent water systems [25]. The whole basin is a temperate to warm temperate climate, with four distinct seasons, a short summer and a long winter, and a short frost-free period. The annual precipitation is about 560 mm, and the overall terrain of the basin is high in the northwest, low in the southeast, and relatively flat in the middle. Qingzhang River has many mountains, cliffs, gullies, and steep terrain. Zhuozhang River has rolling hills and a plain. Qingzhang River is divided into the mainstream of the Qingzhang River (MQR) and the headwaters of the Qingzhang River (HQR), such as the eastern headwater of the Qingzhang River (EHQR) and western headwater of the Qingzhang River (WHQR), with a basin area of 5339 km². Zhuozhang River is divided into the mainstream of the Zhuozhang River (MZR) and headwaters of the Zhuozhang River (HZR), such as the western headwater of the Zhuozhang River (WHZR), southern headwater of the Zhuozhang River (SHZR), and northern headwater of the Zhuozhang River (NHZR), with a basin area of 11688 km². It is called the Zhanghe River (ZR) after the convergence of the Zhuozhang River and Qingzhang River.

In September 2019, 32 sampling sites of surface sediments were set up in the upper reaches of ZR (Figure 1), considering the spatial geographical location and accessibility of the study area. To avoid confusion in analyzing the spatial distribution, each tributary was divided into mainstream and headwater, such as ZR, MZR, MQR, HZR, and HQR. S1~S5 belonged to ZR, S9~S13 belonged to MZR, S14~S20 belonged to MQR, S6~S8 and S26~S32 belonged to HZR, and S21~S25 belonged to HQR. Surface sediment samples were taken with a grab sampler. Three samples were taken at each sampling site, mixed thoroughly, put into polyethylene bags with sealed numbers, and stored away from light for immediate transfer to the laboratory. After freeze-drying, stones, tree fragments, and other residues were removed. A mortar was used to grind the sediment samples after impurities were removed, and after passing the ground sediments were passed through a 100-mesh nylon sieve to remove large particles, the processed samples were stored at 4 °C before analysis.

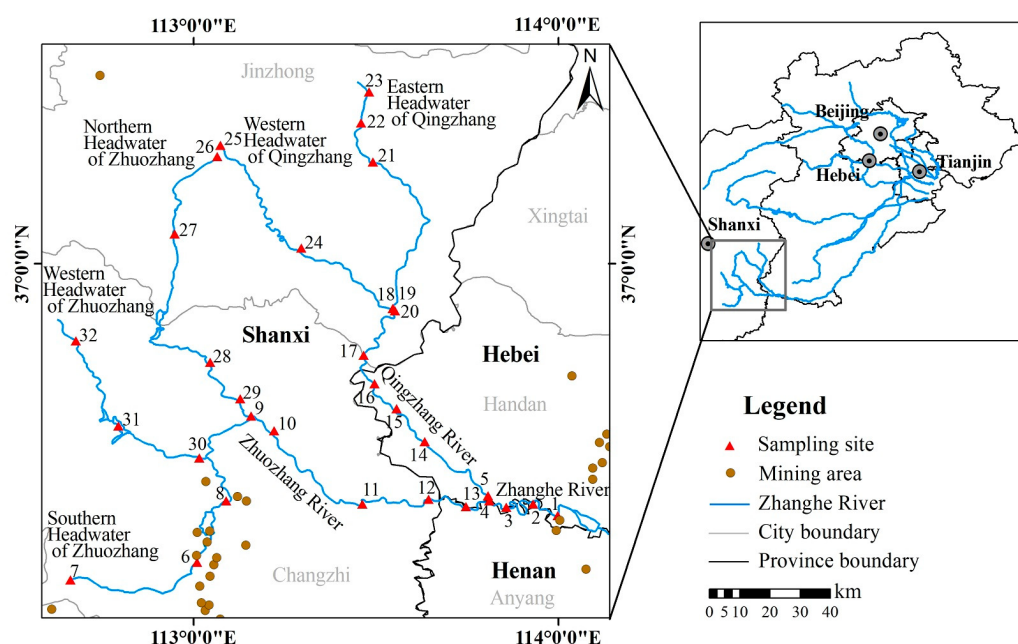


Figure 1. The upper reaches of Zhanghe River and sampling sites.

2.2. Potentially Toxic Elements Analysis

Before the concentrations of PTEs were measured, precisely 0.2 g of the treated sediment sample was weighed and digested with 6 mL HNO_3 and 2 mL HF in a Teflon container (SP-12, Preekem, Shanghai, China). After microwave digestion, an electric heating plate heated to 150 °C was used to drive out acid. After cooling, the residue was diluted with deionized water to 25 mL and the solution was passed through a 0.45 μm membrane. For the measurement of PTE concentrations, inductively coupled plasma mass spectrometry (ICP-MS NeXION 300X, Perkin Elmer, Waltham, MA, USA) was used for the determination of PTEs in the digested solution under routine operation. Quality assurance and quality control were strictly guaranteed in all experiments [26]. The instruments were calibrated with standards before the experiments. The glassware and polyethylene vessels were rinsed with deionized water after a soak in 1 mol/L HNO_3 for more than 24 h; all reagents used were of analytical purity or higher grade. Standard reference materials used to calibrate the accuracy and precision of the analytical procedures were GBW07311 (GSD-11) and GBW07366 (GSD-23). The recoveries ranged from 94% to 103% for total PTEs and 93% to 105% for PTE fractions ((sum of fractions/total PTEs) $\times$ 100). Blank samples were used to eliminate experimental errors, and experiments were repeated to ensure the accuracy of experimental data. Relative deviations were within $\pm 5\%$ for all batches of treated duplicate samples.

2.3. Assessment of Sediment Pollution

2.3.1. Enrichment Factor

The enrichment factor (EF) can be used to distinguish between anthropogenic or natural geological inputs of PTEs and evaluate the concentration levels of anthropogenic inputs [27]. The reference PTE chosen in this study is Al, which is stable in the process of migration. The following is the equation for calculating EF:

$$EF = [C_i/C_n]_{sample} / [B_i/B_n]_{background} \quad (1)$$

where C_i and C_n are the measured concentrations of the PTE to be assessed and the reference PTE, respectively. B_i and B_n are the background concentrations of the PTE to be assessed and reference PTE, respectively. The relationship between the grades of EF and the degrees of pollution is shown in Table 1.

Table 1. Evaluation criteria for the enrichment factor and geo-accumulation index.

Grade	EF	Enrichment Level	Grade	I_{geo}	Pollution Level
I	1~2	Slightly enriched	I	0~1	Unpolluted to moderately polluted
II	2~5	Moderately enriched	II	1~2	Moderately polluted
III	5~20	Significantly enriched	III	2~3	Moderately to heavily polluted
IV	20~40	Intensely enriched	IV	3~4	Heavily polluted
V	>40	Extremely enriched	V	4~5	Heavily to extremely polluted
VI			VI	>5	Extremely polluted

2.3.2. Geo-Accumulation Index

A previous work [28] proposed the geo-accumulation index (I_{geo}) to evaluate the environmental pollution of PTEs. The following is the equation for calculating I_{geo} :

$$I_{geo} = \log_2[C_i / (k \times B_i)] \quad (2)$$

where C_i and B_i are the same as aforesaid. k is the coefficient that eliminates the difference in background concentration and is typically taken as 1.5 [29]. The relationship between the grades of I_{geo} and the degree of pollution is shown in Table 1 [30].

2.3.3. Potential Ecological Risk Index

Considering the biological toxicity factors of PTEs, the potential ecological risk index (RI) could comprehensively assess the risk of PTEs [31]. The following equations show the calculation process of RI:

$$CF_i = C_i / B_i \quad (3)$$

$$E_r^i = T_r^i \times CF_i \quad (4)$$

$$RI = \sum_{i=1}^n E_r^i \quad (5)$$

where C_i and B_i are the same as aforesaid; E_r^i (EI) and T_r^i are the potential ecological risk factor and biological toxicity factor of PTEs, respectively. RI is the potential ecological risk index of PTEs at the sampling site. PTE biological toxicity factors from largest to smallest are Cd (30), As (10), Co (5), Cu (5), Pb (5), Cr (2), Mn (1), and Zn (1) [32]. The relationships between the RI and the pollution level are listed in Table 2.

Table 2. Evaluation criteria for the potential ecological risk index.

Grade	E_r^i	Risk Level	Grade	RI	Risk Level
I	<40	Low risk	I	<150	Low risk
II	40~80	Moderate risk	II	150~300	Moderate risk
III	80~160	Considerable risk	III	300~600	Considerable risk
IV	160~320	High risk	IV	≥ 600	Very high risk
V	≥ 320	Very high risk			

2.4. Statistical Analysis

SPSS 19.0 (IBM, New York, NY, USA) and Origin 2018b were used for all statistical analyses. The differences in PTE concentrations between mainstreams and headwaters were analyzed using one-way analysis of variance (ANOVA) [33]. To ensure the normal distribution of PTE concentrations, the one-sample Kolmogorov–Smirnov (K-S) normality test was adopted. The possible sources of PTEs were assessed by Pearson correlation analysis and principal component analysis (PCA). The concentration classification and EF classification of PTEs were completed using ArcGIS 10.7.

3. Results and Discussion

3.1. Spatial Distribution of PTEs in the River Sediments

The parameters of PTEs in sediments of the upper reaches of ZR are shown in Table 3. The mean content of PTEs in the study area is as follows: Mn > Cr > Zn > Cu > Pb > Co > As > Cd. The background concentrations of PTEs refer to the original chemical composition and structural characteristics of soil. A comparison of the background concentrations of PTEs with the measured values can be performed to determine whether the sediments in this area have changed greatly due to external influences. The background concentrations of Chinese soil elements are used as a guideline for PTEs [34]. The average contents of Cu, Zn, and Cd are below the background concentrations, while those of Cr, Mn, Co, As, and Pb are above the background concentrations. This is especially the case for Co and Pb, with more than 60% of the samples having higher concentrations than background concentrations, showing the possible pollution of Co and Pb in this area. According to the threshold effect level (TEL) and probable effect level (PEL), it is possible to judge the possible adverse biological effects of PTEs [35,36]. Adverse biological effects occur rarely when PTE concentrations are below the TEL, occasionally when concentrations are between the TEL and PEL, and frequently when concentrations exceeded the PEL [37]. For Cd and Pb, all sample concentrations are less than the TEL, but 16% of the samples have Cr concentrations above the PEL. Cr might cause undesirable biological effects, and care should be taken to prevent the adverse biological impact of Cr in sediments on the ecological environment. It deserves to be mentioned that the background concentrations of Cr and As exceed the corresponding TEL and might still have adverse biological effects even if the concentrations are within the background concentrations.

Table 3. PTE content in sediments of the upper reaches of Zhanghe River.

Descriptive Statistics (mg/kg)	Cr	Mn	Co	Cu	Zn	As	Cd	Pb
Min	44.13	370.34	7.03	12.49	38.74	5.71	0.07	10
Max	175.57	1242.75	14.37	63.41	284.17	21.40	0.36	35.77
Mean	91.51	583.81	10.66	21.93	67.49	9.81	0.12	18.30
SD	24.30	207.90	1.80	10.48	40.82	3.05	0.05	5.43
TEL	43.40	NG	NG	31.60	121	9.79	0.99	35.80
PEL	111	NG	NG	149	459	33	4.98	128
Soil background concentrations	61.80	554.00	9.90	26.90	75.50	9.80	0.13	15.80
<TEL (%)	0	-	-	91	97	59	100	100
>PEL (%)	16	-	-	0	0	0	0	0

TEL: threshold effect level. PEL: probable effect level [38]. NG: no guideline.

According to the one-way ANOVA of PTEs, as shown in Figure 2, the concentrations of Cr, Cu, Zn, and Cd in each tributary have no significant difference and are evenly distributed ($p > 0.05$). Mn, As, and Pb are mainly distributed in the HZR, and Co is evenly distributed throughout the upper reaches of ZR ($p < 0.05$). Each PTE was divided into four concentration gradients, which are shown in Figure 3. Cr is the most concentrated; the contents of Cr in the MZR, HZR, and WHQR were over the PEL. As was mainly distributed in the MZR and the HZR. The contents of Cd and Pb are under the TEL in all sampling sites, and in the SHZR, the content of Zn is between the TEL and PEL. Cu is only present in the SHZR at TEL and PEL. The content of Mn is more than twice the background concentration in the WHZR, and the Co contents are all within 1.5 times the background concentration. In general, Cu, Zn, and Cd have low concentrations, while Cr and As have the highest. The pollution is mainly distributed in the MZR and HZR, especially in the SHZR, where all eight PTEs are enriched, showing that the mining activities of SHZR input many PTEs into rivers [36]. S8 is the most seriously polluted site; it is located in Luzhou District, Changzhi City, which covers the smallest area but has a much higher population density than other urban areas. The growing industrial activities might pose a considerable risk to the ecosystem [39]. In contrast, the ZR has low levels of PTE concentrations. According to the Zhangwei Canal Administration Bureau, the ZR basin is rich in coal and petroleum resources, mainly including coal, petroleum, steel, power generation, textile, paper, and various processing enterprises, with a wide distribution of point-source pollution resulting in spatial differences in PTEs [40].

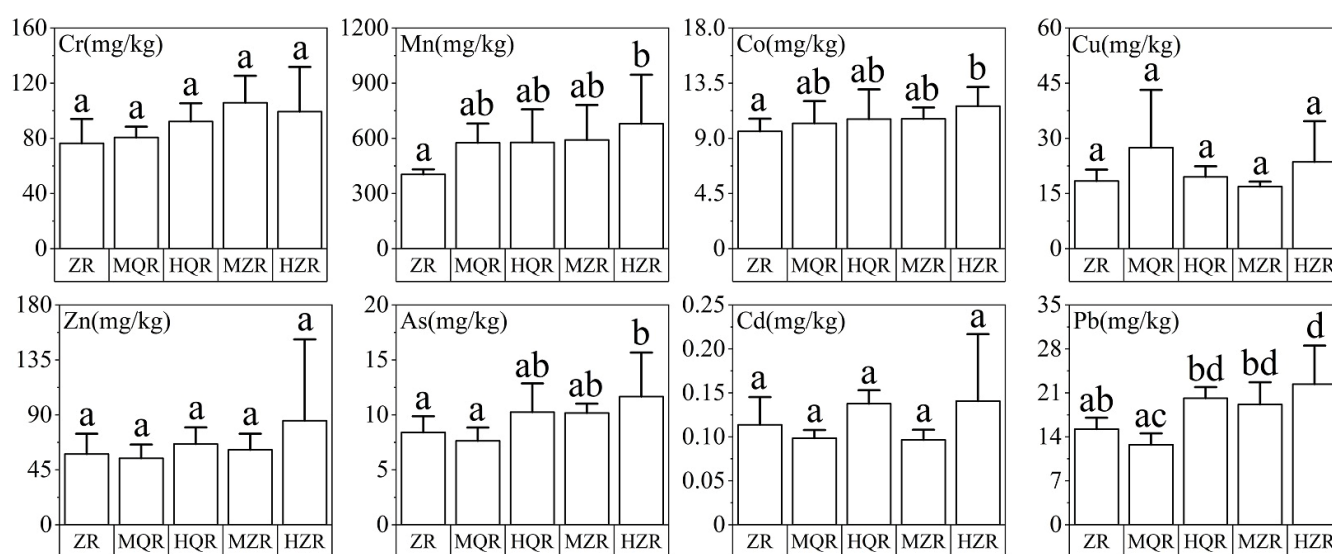


Figure 2. Spatial distribution of sediment PTE concentrations in the upper reaches of Zhanghe River. ZR ($n = 5$), MQR ($n = 7$), HQR ($n = 5$), MZR ($n = 5$), HZR ($n = 10$). There is no significant difference between bars with the same letter, but there is a significant difference between bars with different letters ($p < 0.05$).

The PTE concentrations in the study area were compared with those in other areas in China (Table 4). The upper reaches of ZR have higher Cr concentrations than other rivers except for the Yellow River. In contrast, As and Cd in the upper reaches of ZR have lower concentrations than those in other rivers. Although Pb is at moderate levels compared to other rivers, Pb at low concentrations could also threaten the survival of aquatic organisms [41]. These differences in the concentrations of PTEs might be caused by different industrial structures [20]. Due to the lack of reference information on Mn and Co concentrations in river sediments, it is impossible to make a comprehensive comparison for Mn and Co. Overall, the upper reaches of ZR have low to moderate PTE concentrations in the sediments.

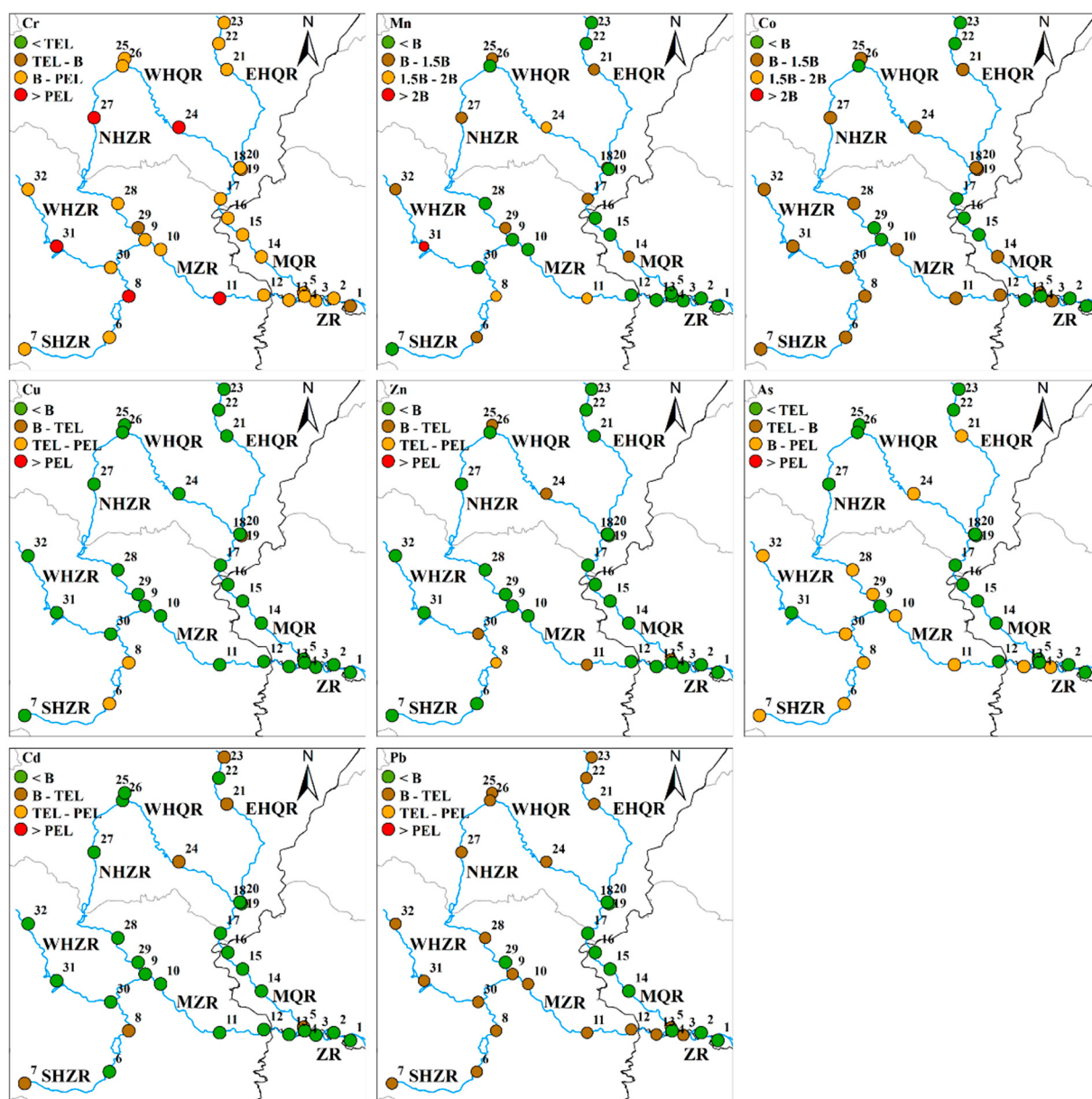


Figure 3. Classification and spatial distribution of PTE concentrations. B indicates background value.

Table 4. The mean concentrations of PTEs in sediments of rivers in China (mg/kg).

Rivers	Cr	Mn	Co	Cu	Zn	As	Cd	Pb	References
Zhanghe River	91.51	583.81	10.66	21.93	67.49	9.81	0.12	18.3	This study
Liaohe River	35.06	-	-	17.82	-	9.88	1.2	10.57	[37]
Songhua River	18.5	-	-	24	59.3	-	4	39	[41]
Yellow River	101.87	-	-	22.47	89.7	-	1.38	8.16	[42]
Huaihe River	-	-	-	31.3	183.57	-	-	53.43	[43]
Changjiang River	84.7	-	-	24.3	89.5	10.3	0.25	21	[44]

3.2. Potentially Toxic Element Pollution Characteristics

EF is used to identify abnormal concentrations of PTEs in sediments so as to better identify the enrichment level in rivers [45]. Figure 4 shows EF values of PTEs in sediments of the upper reaches of ZR. The mean EF values of Cu, Zn, As, and Cd are under 2, and they are slightly enriched, showing a similar spatial distribution. The mean EF values of Cr, Mn, Co, and Pb are over 2; this indicates that the geogenic rock weathering is no longer

the main source and anthropogenic activities may become the dominant factor [46]. Cr is moderately enriched at most sampling sites, indicating the pollution of Cr was prevalent in the area. Overall, ZR, MQR, and MZR have lower enrichment levels. PTEs reached significant enrichment in HZR, and the pollution is more severe than that in the other regions. This is generally consistent with the concentration distribution, indicating that most of the PTEs in HZR come from anthropogenic activities.

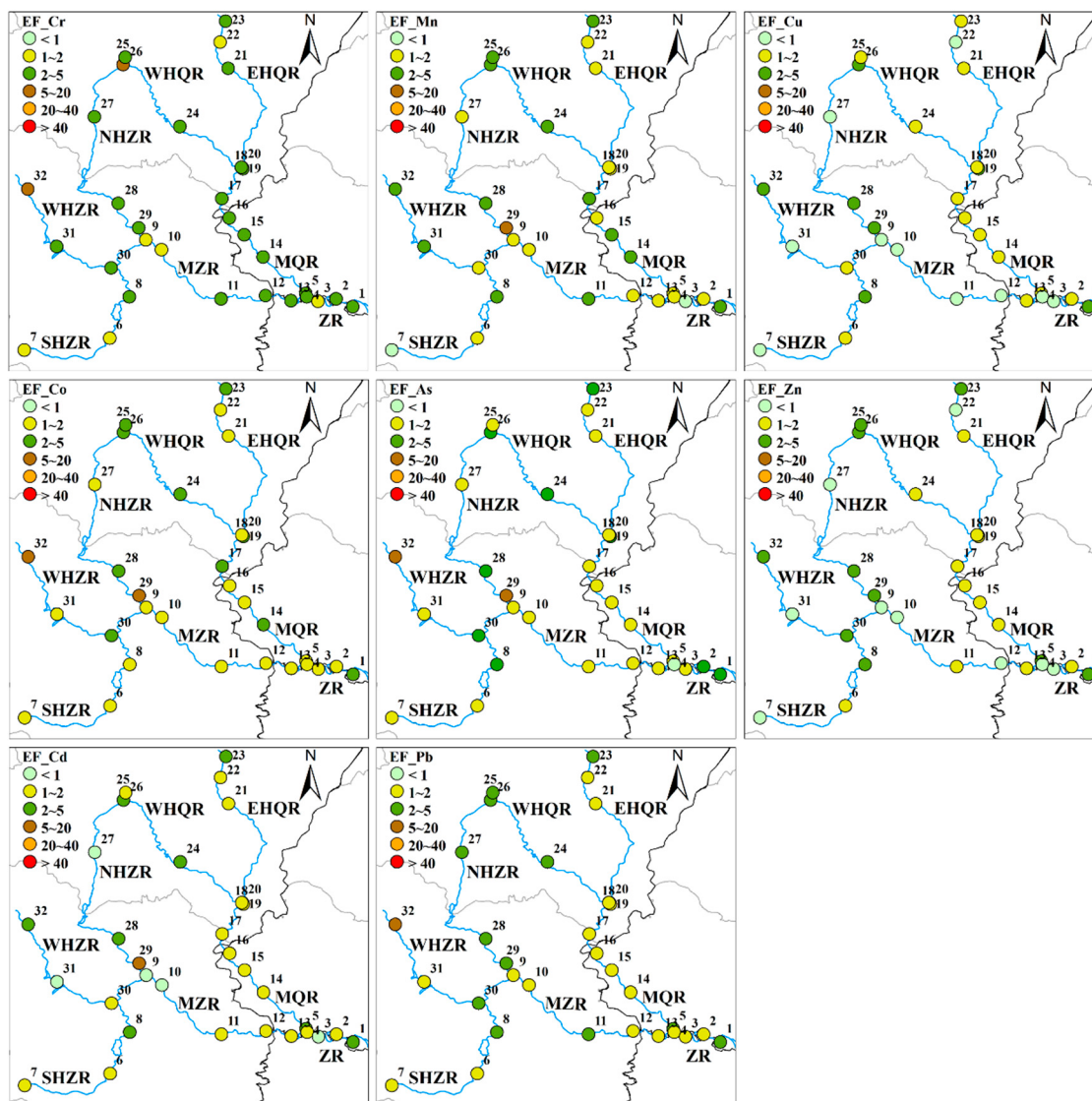


Figure 4. The EF spatial distribution of PTEs in the upper reaches of Zhanghe River.

The pollution levels of PTEs were evaluated by I_{geo} ; Figure 5 shows the I_{geo} values of PTEs in the sediments of the upper reaches of ZR. The pollution of PTEs ranges from practically unpolluted to moderately polluted. The mean I_{geo} values of all PTEs do not exceed 0 and belong to practically unpolluted. The I_{geo} value of Cr with the most serious pollution level does not exceed 2, showing this PTE does not pollute the upper reaches of ZR for the time being. It is worth noting that the PTEs in S8 have abnormally high I_{geo} values, and the most elevated, for Zn, reaches 1.33, which is in the state of no pollution to moderate pollution. This means anthropogenic activities have given rise to PTE pollution [47]. The results of the EF and I_{geo} show consistency, both pointing to Cr as the primary pollutant, with pollution distributed at the HZR.

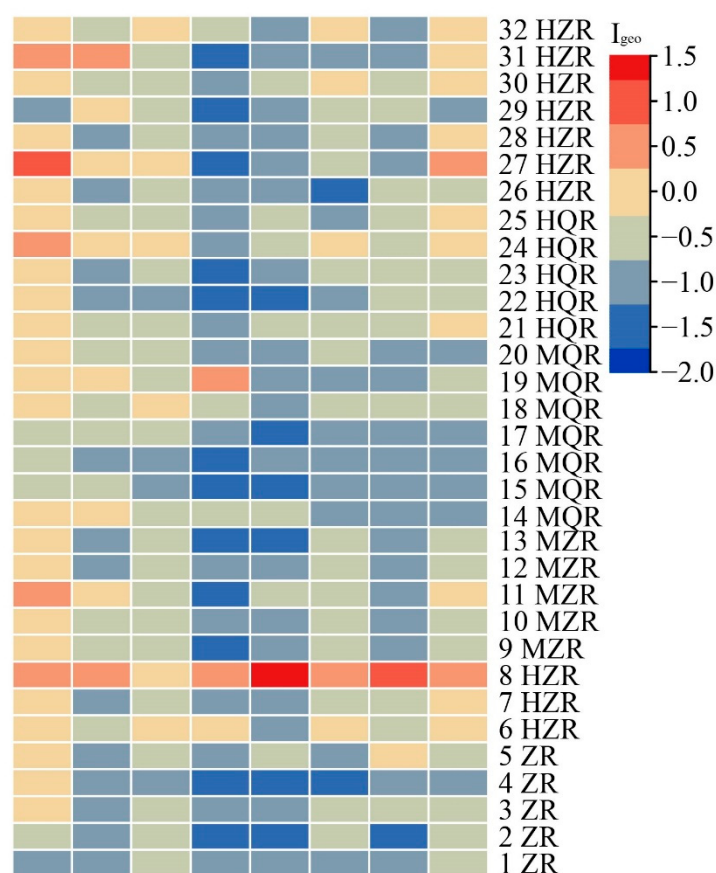


Figure 5. The PTEs I_{geo} values in the upper reaches of Zhanghe River.

3.3. Potential Ecological Risk

In this study, RI was used to assess ecological risks. The RI is formed by the EI accumulation of each PTE, as shown in Figure 6. The RI of all samples is under 150, indicating that the upper reaches of ZR present a low ecological risk. The RI of S8 is 143.26, which is higher than that of other sites. The rest of the samples range from 41.57 to 74.97. Since this method emphasizes the role of toxicology, the ratio of EI and RI is adopted in this study to explain the role of toxicity of PTEs in increasing risks. Although the content of Cd is the lowest, it provides the highest risk, followed by As, and while the content of Mn is the largest, it provides a more negligible risk. Although concentration is one of the indicators to calculate ecological risk, the toxicity of PTEs plays a leading role, and high biological toxicity factors cause high ecological risk [48]. Therefore, Cd and As should receive more attention. The results of RI show that the PTEs are generally of low risk in the sediments of the upper reaches of ZR, but pollution control, especially the comprehensive treatment of PTEs with high biological toxicity factors, is still needed in some aspects.

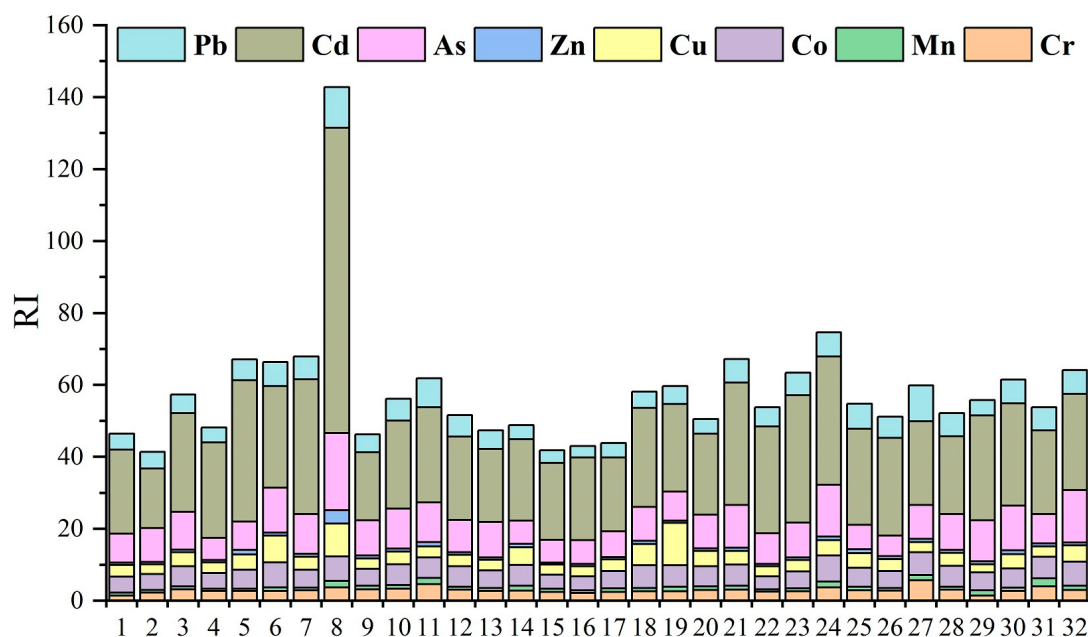


Figure 6. The PTE RI in the upper reaches of the Zhanghe River.

3.4. Possible Sources of PTEs

Discussing the source of PTEs is an essential step in formulating pollution control strategies [49,50]. Both natural and anthropogenic sources can release PTEs into rivers. Natural sources include volcanic eruptions, forest fires, and rock weathering, while major anthropogenic sources include industrial discharge, agricultural activities, domestic sewage, and fossil fuel burning [26,51]. The interrelationships between PTEs were analyzed using Pearson correlation analysis. Correlations between PTEs might reveal the sources and distribution of metals in specific environments [52]. Significant correlations between PTEs indicate that their behavior is driven by similar factors [8], and relatively weak correlations suggest a complex source of PTEs due to industrial activities [47]. Cr, Mn, Co, and Pb are correlated significantly ($p < 0.01$), indicating a possible same source (Figure 7). PCA was used to reveal the potential sources of PTEs in this study. The results show that the concentrations of Mn, Co, As, and Pb are normally distributed ($p < 0.05$), while the contents of Cr, Cu, Zn, and Cd do not pass the normality test, indicating anthropogenic emissions existed in some areas [53]. The varimax rotation method is used for rotation in the process of PCA. The result of the KMO value is 0.73, while the Bartlett sphericity test result is < 0.001 , which determines the applicability of the data of this study to the PCA. Two principal components whose eigenvalues exceeded 1 were determined, and 72.867% of the total variance was explained (Table 5).

The first principal component (PC1), which includes Cr, Mn, Co, and Pb, explained 39.704% of the total variance, agreeing with the Pearson correlation analysis. These four metals are spread throughout almost the whole upper reaches of ZR (Figure 2). Cr in nature is mainly derived from the crust [54,55], in forms such as weathering products and in association with Fe and Mn mineral deposits [56]. Co is commonly found in Mn and Pb ores. Considering that the mean EF of these metals is over 2, it is unlikely that natural activity represents a source for these metals. There are abundant mineral resources in the upper reaches of ZR, and the high pollution caused by long-term mining operations has caused tremendous damage to the ecological environment of the basin. It has been documented that in the mining process, PTEs exposed at the surface ground are finally washed into the river by rain [57,58], eventually accumulating in sediments. Therefore, these PTEs are likely to be imported into the river after being exposed to dust and rocks on the ground during mining activities. On the other hand, there are many roads built along the river. Due to road construction and mining, there are still millions of tons of

PTE dust particles, including Cr and Pb from vehicle traffic, Mn from rock, and soil parent material [59], which enter rivers through atmospheric deposition, runoff erosion, and street-cleaning [60]. Thus, these PTEs might also reflect the accumulation of road dust and historical pollution levels in the past. Combining EF analysis, Pearson correlation analysis, and PCA, PC1 is derived from mining activities and road dust, indicating that the PTEs in rivers are controlled by the natural mineral composition of sediments and anthropogenic activities [61].

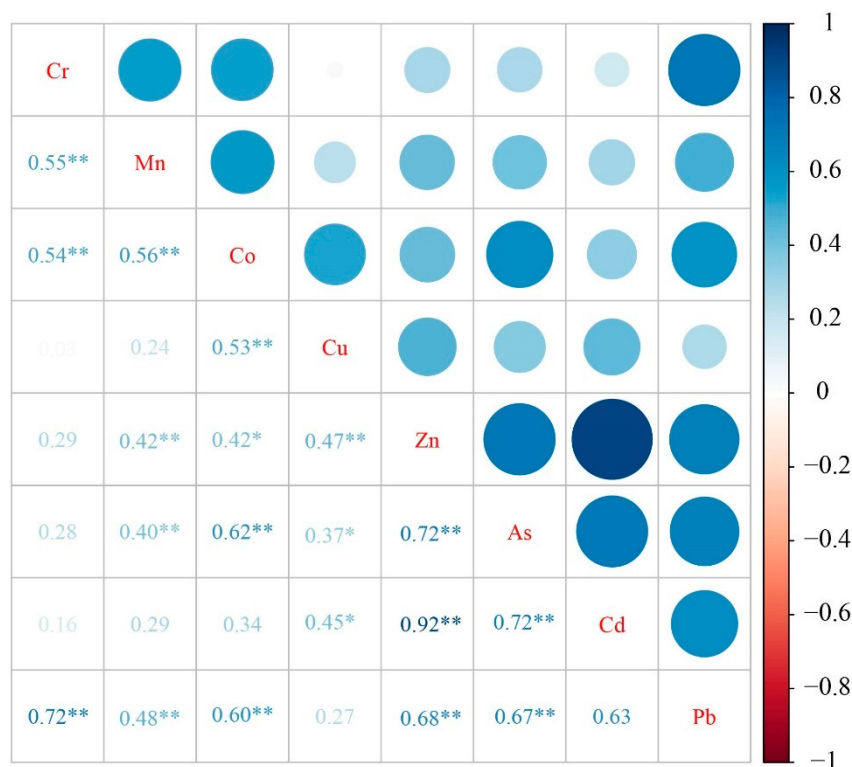


Figure 7. Correlation matrix for PTEs in the upper reaches of Zhanghe River. * and ** represent significant correlations at the levels of 0.05 and 0.01.

Table 5. The PCA results for PTEs in the upper reaches of the Zhanghe River.

Potentially Toxic Elements	Component	
	1	2
Cr	−0.031	0.926
Mn	0.199	0.755
Co	0.407	0.698
Cu	0.666	0.063
Zn	0.882	0.290
As	0.765	0.393
Cd	0.919	0.146
Pb	0.511	0.728
Eigenvalues	3.120	2.709
% of variance	39.704	33.863
% of cumulative	39.704	72.867

Rotation method: varimax rotation. Rotation converged in three iterations.

The second principal component (PC2), which includes Cu, Zn, As, and Cd, explained 33.863% of the total variance, agreeing with the Pearson correlation analysis. In China, livestock manure, fertilizers, pesticides, and plastic films are widely used in agricultural soils. Unreasonable large-scale application of pesticides and fertilizers not only causes waste of pesticides and fertilizers but also pollutes surface water and groundwater through

loss and infiltration. Therefore, excessive application of pesticides or fungicides causes Cu and Zn accumulation in sediments [62]. In addition, Cd in the environment might be caused by long-term abuse of phosphate fertilizers and pesticides [32]. It is mainly used as a component of pesticides, herbicides, and fertilizers, and it migrates in suspension [18]. The PTEs released by these agricultural activities might eventually accumulate in the sediments through rainfall. It is reported that as the components of fertilizers and pesticides, As, Cd, and Zn also cause pollution of surface water [63]. Therefore, PC2 is derived from agricultural activities, indicating that agricultural production might cause ecological pollution of rivers. Therefore, PTE pollution in the upper reaches of ZR is mainly affected by mining activities and road dust, followed by the use of pesticides and fertilizers in agricultural production.

4. Conclusions

In this study, the pollution of eight PTEs from the upper reaches of ZR was analyzed. The results show that the concentration of Mn in river sediments is the highest and that of Cd is the lowest. Ninety percent of Cr, Cu, Zn, Cd, and Pb samples are under the TEL, and 16% of the Cr samples are above the PEL, which indicates potential adverse biological effects on the study area. The distribution of Cr, Cu, Zn, and Cd is relatively uniform; there is no obvious difference in concentration among the tributaries. In addition, compared with other major rivers in China, the concentration of PTEs in sediments in the upper reaches of ZR is at a low level. The average EF of Cr, Mn, Co, and Pb exceeds 2, indicating that these PTEs may come from human activities. The PTE enrichment levels of ZR, MQR, and MZR are low. PTEs in HZR also reached significant enrichment. The average I_{geo} of all PTEs is less than 0, and there is almost no pollution. I_{geo} outliers generally appear in S8, where there are human activities. I_{geo} shows that Cr is the main pollutant, and the pollution is distributed in the HZR. The RI results indicate that 96% of the upper reaches of ZR have a low risk level. Cd content is the lowest, but the risk is the greatest, followed by As. Mn content is the highest, but the risk is even negligible. PCA analysis indicates that Cr, Mn, Co, and Pb originate from mining activities and road dust, while Cu, Zn, As, and Cd originate from agricultural activities.

Author Contributions: Writing—original draft, P.G.; investigation and formal analysis, J.S., J.W., Z.M., M.S., J.F. and Y.Z.; conceptualization, and methodology, Y.C. and Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (U1802241, U204021, 920472045, and 52209013) and Open Research Fund of State Key Laboratory of Simulation and Regulation of Water Cycle in River Basin, China Institute of Water Resources and Hydropower Research (IWHR-SKL-202214).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data generated during the study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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