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Comprehensive Evaluation and Source Apportionment of Potential Toxic Elements in Soils and Sediments of Guishui River, Beijing

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Abstract: This study investigated the concentrations and spatial distributions, ecological risks, and potential pollution sources of potential toxic elements (PTEs) in the soils and sediments collected from the Guishui River (GSR) in Beijing, China. Multiple methods for pollution assessment and source identification of PTEs in the sediments/soils were used, including analysis of the physicochemical properties, Geo-accumulation index (I_{geo}), potential ecological risk index (RI), Pearson correlation, principal component analysis (PCA), and Pb isotopic ratio analysis. The results showed that PTE concentrations in the sediments/soils were similar to the soil background values (BV) of Beijing, except for Cd. Maximum Cd concentrations in soils were far below the guideline of the Environmental Quality Standard for Soils in China. PTE concentrations in the soils were slightly higher than those in the sediments. Upstream to downstream of GSR, PTEs concentrations in the soils and sediments remained stable. Pollution assessment based on I_{geo} and RI indicated that Cd was the main contaminant with moderate pollution levels. PCA results showed that Cd originated from anthropogenic sources, mainly including pesticide and fertilizer residues, while other metals mainly originated from natural sources. Further source identification using Pb isotopic ratios and PCA indicated that Cu, Pb, and Zn in GSR originated from anthropogenic sources (aerosols and coal combustion) and atmospheric deposition was considered as the primary input pathway.

Keywords: soil; sediment; potential toxic elements; risk assessment; source apportionment; Guishui River

1. Introduction

Environmental contamination by potential toxic elements (PTEs) is a serious and worldwide problem due to their toxicity, persistence, and non-degradability [1,2]. With rapid industrialization and urbanization, the accumulation of PTEs in surface soils and sediments is attracting worldwide concern [3]. The soil along rivers is a transitional buffer zone between aquatic and terrestrial ecosystems, as they can retain PTEs for a long time through physical, chemical, and biological effects [3,4]. PTEs in soils can migrate and transfer through natural processes or anthropogenic activities, threatening the safety of water resources, food, and even human health [5,6]. In particular, the PTEs were more likely to accumulate in paddy fields [7]. In water bodies, the sediment, which serves as a sink for PTEs, can reflect the long-term pollution of water bodies by PTEs [8–10]. For example, the water quality of Amvrakikos bay suffered severe degradation caused by PTE pollution in sediment [11]. Moreover, the Kolleru Lake in India, was also affected by PTE (especially chromium) pollution [12]. PTE pollution

in the soils and sediments along rivers is not only harmful to aquatic animals and plants, but can also be released into the environment again [13]. Studying various aspects of the PTEs in different media (i.e., soil and sediment) of a specific watershed, such as sources or geochemical behaviors, helps understand the migration and transformation of metals.

PTEs in the soil enter the surface water when washed by rainfall and tends to precipitate in the sediments [4]. Shore soil is the most basic natural transport in the process of supplying PTEs to sediments [14,15]. Therefore, tracing the source of PTEs is very important for obtaining basic information on the transportation of PTEs across different media. However, many studies have focused on the source of PTEs in a single medium only (i.e., sediment or soil) [16,17], and systematic and integrated research on the source of PTEs in both soils and sediments in a particular river basin has rarely been reported. In recent studies, principal component analysis (PCA) was applied to assist with the identification and analysis of PTE sources [17–19]. PCA was used to highlight the distribution behavior of metals [20], but was unable to distinguish their specific source. However, Pb isotopic ratios are able to determine the source of Pb pollution, which have been employed for several decades [21,22]. Therefore, combined with PCA, Pb isotopic ratios could be used to provide a more comprehensive understanding of the source of PTE pollution.

The Guishui River (GSR) basin is located north of Beijing, the capital of China. It is the venue for the World Horticultural Exposition (2019) and the International Winter Olympics (2022). The environmental quality of the GSR has received extensive attention in recent years. Thus, studying the source of PTEs in the soils and sediments in the GSR basin is of great significance for ensuring the safety of the water quality and quantity and improving the quality of the aquatic ecological environment. The aims of this study were to: (1) investigate the concentrations and distributions of PTEs in the soils and sediments of the GSR; (2) assess the ecological risk of individually toxic PTEs in the soils and sediments; and (3) identify the potential sources of PTE pollution.

2. Materials and Methods

2.1. Study Area

The study area (40°26′–40°29′ N, 115°52′–116°05′ E) was located in Yanqing Country, Beijing (Figure 1). The GSR belongs to a tributary of the Yongding River, and is one of the three largest rivers flowing into the Guanting Reservoir (GTR). The river originates in Yanqing County, passes through the Sanli, Caijia, and Gucheng Rivers, and then flows into the GTR from east to west. The total length and area of the GSR is 18.5 km and 1073.6 km², respectively. The area is controlled by continental depressions in summer and prevailing southerly winds, making the summers hot and humid. The average annual temperature is 8.5 °C and average annual rainfall is 503.8 mm, which is concentrated from June to September. The area is dominated by agricultural land, which is mainly planted with corn, vegetables, and fruit trees.

2.2. Sample Collection and Pretreatment

Five superficial sediments (0–10 cm) and six soil samples (0–10 cm) were collected in the GSR area (Figure 1) in May 2018. Three parallel samples were collected at each sampling site and mixed to form a single sample. All the collected samples were sealed in polyethylene bags and transported to the laboratory where they were stored at 4 °C for further analysis. The samples were divided into two equal groups; one group was naturally air-dried indoors, and impurities such as stones and leaves were removed by hand and sieving. Subsequently, the samples were ground to pass through a 0.10 mm nylon sieve for the soil properties analysis. The other group was frozen, lyophilized at –80 °C, ground in an agate mortar, and passed through a 100-mesh nylon sieve for the total metal analysis.

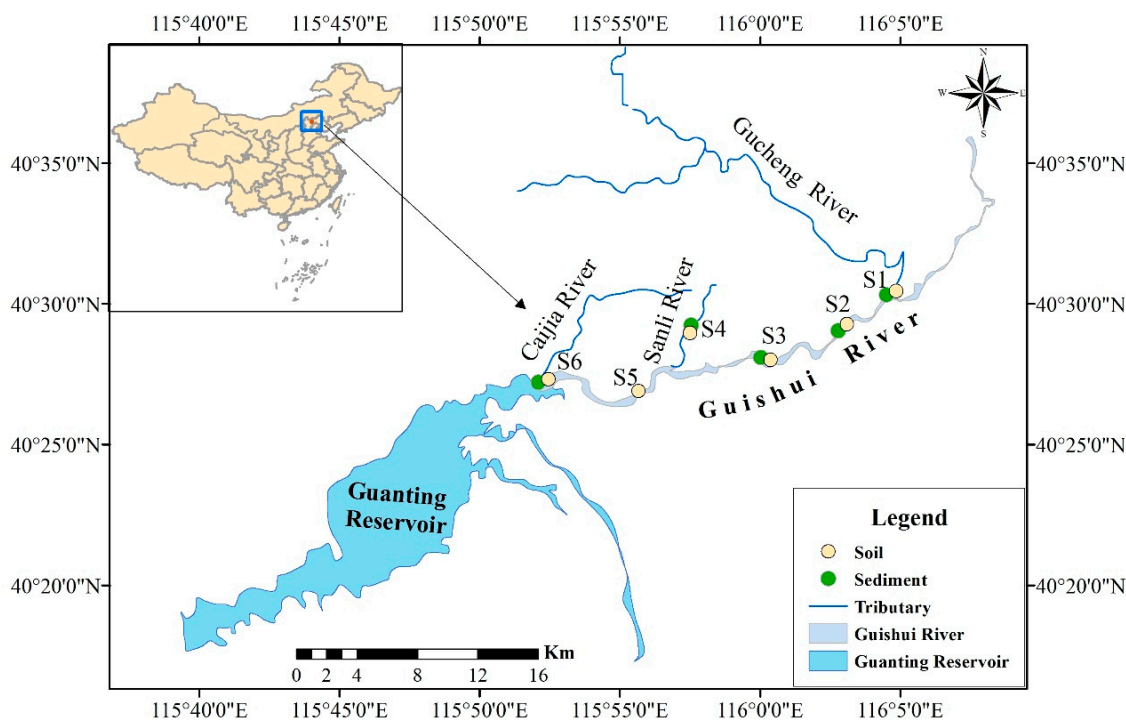


Figure 1. Map of the sampling sites in the soils/sediments of the Guishui River.

2.3. Analytical Methods

The total metal concentrations in the soils/sediments were digested with $\text{HNO}_3\text{--HF--H}_2\text{O}_2$ in a Teflon beaker, according to Gao et al. [23]. The concentrations of metals were measured by inductively coupled plasma mass spectrometry (Elan DRC-e, PerkinElmer, Waltham, MA, USA). The organic matter (OM) content and pH were measured to show the general characteristics of soil/sediment samples. The content of OM was approximately replaced by the weight-loss-on-ignition (LOI), which was determined at a temperature of 550 °C for 16 h, according to the methods of Heiri et al. [24]. The pH was determined from the supernatant that was obtained after shaking the soil/sediment with ultrapure water at a 1:2.5 ratio, according to the Lake Survey Technical Regulations in China [25].

Quality control was performed using certified reference material of stream sediment (GSD-10, GBW07310), produced by the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences. Analytical reagent blanks were prepared with each batch of digestion and then analyzed for the same elements. The results were consistent with the reference values, and the differences were within $\pm 15\%$. The relative error of each element is shown in Table S1. All of the reagents were guaranteed analytical grade or higher. The laboratory glassware (bottles, tubes, etc.) were pre-cleaned by soaking in 20% HNO_3 (v/v) for at least 24 h, followed by soaking and rinsing with deionized water before use.

2.4. Pb Isotopic Measurements

The Pb isotopic analysis was performed according to Gao et al. [26] and Kumar et al. [27], and Pb isotopic composition was measured using ICP-MS (Elan DRC-e, PerkinElmer, Waltham, MA, USA). The average values of the common Pb isotopic standard (NIST SRM-981) were $^{206}\text{Pb}/^{207}\text{Pb} = 1.0925 \pm 0.0011$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.3648 \pm 0.0039$ ($N = 5$), which were in close agreement with the certified standard values (1.0933 and 2.3704, respectively). The analytical uncertainties expressed by the standard deviation (SD) ($N = 5$) for Pb isotopic ratios were generally $< 0.5\%$.

2.5. Assessment Methods

2.5.1. Geo-Accumulation Index (I_{geo})

The I_{geo} was first proposed by Müller [28], and is the most widely used method. The calculation formula is given in Equation (1):

$$I_{geo} = \log_2 \left(\frac{C_i}{1.5B_i} \right) \quad (1)$$

where C_i is the measured concentration of a potential toxic element in the sediment, B_i is Background values (BV) in the soil of Beijing [29], and 1.5 is the background matrix correction factor. The relationship between I_{geo} and pollution level is presented in Table S2 using seven classes ranging from 0 to 6 to indicate pollution status.

2.5.2. Potential Ecological Risk Index (RI)

The potential ecological risk index (RI) was first introduced by Håkanson [30] to evaluate the potential ecological risk of PTEs in soils and sediments. In this method, multiple influencing factors were comprehensively considered to evaluate the potential risk of PTE contamination such as ecological sensitivity, synergy, and toxic levels. The potential ecological risk (E_i) factor of a given metal is defined in Equation (2):

$$E_i = T_i \times \frac{C_i}{C_0} \quad (2)$$

Equation (3) was used to calculate RI of sampling sites as follows:

$$RI = \sum_{i=1}^n (T_r^i \times \frac{C_i}{C_0}) \quad (3)$$

where C_i is the measured concentration of PTEs in the sediment/soil, C_0 is the reference BV, T_r^i is the toxic-response factor of the individual element, which was determined for Cu = Pb = Ni = 5, Zn = 1, As = 10, Cr = 2, and Cd = 30 [30,31], E_i is the potential ecological risk factor of a single metal, and RI is the potential ecological risk index of the PTEs. The degrees of E_i and RI classification are presented in Table S3.

2.6. Statistical Analysis

Data and graphics processing were performed using SPSS 22.0 and Origin 2017 for Windows, whereas, spatial mapping was performed using ArcGIS 10.1 for Windows. Pearson correlation and principal components analyses (PCA) were used to test for significant relationships among PTEs in the soil and sediment samples, and the level of significance was set at $p < 0.05$ (two-tailed).

3. Results and Discussion

3.1. General Properties of the Soils and Sediments

The physicochemical properties of the soils and sediments in the GSR are listed in Table 1. The mean pH of the soils and sediments was 8.10 (7.84–8.56) and 8.13 (7.7–8.37), respectively. These results show that the pH of the soils were similar to that of the sediments, and both of them were slightly weakly alkaline. The OM content in the soils and sediments ranged from 2.3% to 17.3% and 3.3% to 17.7%, with mean values of 5.99% and 8.66%, respectively. The average content of OM in the sediments was higher than that in the soils, but in general, the OM content in the soils was similar to that in the sediments at each sampling site, except for site S3. It should be noted that the sediment samples of site S3 consisted mainly of plant roots or rotting leaves, which resulted in the significant differences in OM content at site S3.

Table 1. The property and location descriptions of sampling sites in GSR.

Sample Site	Location	Description	Classification	pH	OM (%dry weight)
S1	115.52° E, 40.27° N	North Road of Binhe, Gucheng River	soil	8.2	2.3
			sediment	8.19	3.3
S2	115.56° E, 40.26° N	North Road of Binhe, Guishui River	soil	8.09	5.8
			sediment	8.04	5.4
S3	115.57° E, 40.28° N	Longshun Road, Guishui River	soil	7.82	4.8
			sediment	7.84	17.7
S4	116.00° E, 40.27° N	Spa Resort, Sanli River	soil	7.7	17.3
S5	116.02° E, 40.27° N	South Road of Huanhu, Guishui River	sediment	8.03	15.6
			soil	8.25	5.6
S6	116.05° E, 40.29° N	The Bridge of Caijia River	soil	8.25	2.5
			sediment	8.56	1.3

3.2. Concentration and Distribution of Potential Toxic Elements in the Soils and Sediments

The concentration range and average value of PTEs in the soils and sediments of the GSR are shown in Table 2. The average PTEs concentrations in the soils followed the order of $Mn \approx Ba > Zn > V > Cr > B > Ga > Li > Ni > Cu > Co > As > Be > Tl > Cd$. The average PTE concentrations were comparable with BV in the soils of Beijing [29], excluding Cd. Meanwhile, the maximum concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn in the soils were significantly lower than the guideline from the Environmental Quality Standard for Soils in China [32]. Compared to the soils around the GTR, the mean concentrations of As, Cr, Ni, Cu, and Pb in the GSR were close to those of the GTR, while Cd was lower and Cr and Zn were higher than that of GTR [33].

The average PTE concentrations in the sediments followed the order of $Mn > Ba > V \approx Zn > Cr > B > Ga > Li > Ni > Cu > Co > As > Be > Tl > Cd$. The mean Cd concentration in the sediments was considerably higher than the BV. In a previous study, Cd in the sediment was reported to be polluting the GSR area [34]. The mean concentrations of Cr, Cu, and Pb in the GSR sediments were close to those found in the GTR, Yanghe River, and Yongding River sediments [34–36]; however, the mean Cd, Ni, and Zn concentrations were slightly lower than that in the GTR, Yanghe River, and Yongding River. When comparing the order of PTE concentrations between the soils and sediments of the GSR, it appears that the source of PTEs in the sediments is comparable to those in the soils. In particular, the average concentration of Cd in the soils and sediments was 3 times and 2.6 times higher than the BV, respectively, indicating that the PTEs in the GSR could be of anthropogenic origin.

The distribution patterns of PTEs in the soils and sediments are shown in Figure S1. Overall, the PTE distribution patterns (from upstream to downstream) in the sediments were similar to that in the soils, and the concentration of PTEs in the soils and sediments were relatively stable, except for site S4. The reason for this difference in S4 was that the sediments were mainly composed of plant residues. In particular, the concentrations of Cd, Cu, Pb, and Zn in the sediments/soils of site S3 were higher than that of other sampling sites. Overall, the content of PTEs in the sediments was higher than that in the soils, because PTEs absorbed in the soils are gradually transferred to the sediments where they accumulate [35]. However, our findings are contrary to those of previous studies [34], which can be attributed to local hydrogeological conditions [37]. Since the 1950s, the rise in temperature and reduced rainfall was clearly observed in the GSR region. The soil water content decreased by about 76% during the period 1980–2000 [38,39], and the reduction in runoff reduced PTE contamination of the sediments. In addition, the spatial distribution of PTEs are also affected by the physicochemical properties of soils and sediments such as pH, OM, and texture [13,40]. As seen from Table S4, the concentrations of Cd, Cu, Pb, and Zn in the soils were positively correlated with OM, but no relationship was observed between PTEs and pH. In contrast, there was no significant correlation between the concentrations of PTEs and OM/pH in the sediments. These results indicate that the concentrations of Cd, Cu, Pb, and Zn in the soils may be affected by the soil properties.

Table 2. The concentration of potential toxic elements in soils/sediments from GSR and other selected soils/sediments around GSR area (mg/kg).

Location		As	B	Ba	Be	Cd	Co	Cr	Cu	Ga	Li	Mn	Ni	Pb	Tl	V	Zn	Reference
Soil	Range	5.41–10.60	24.37–49.37	472.79–542.25	1.52–2.49	0.10–0.27	7.13–11.96	36.27–58.56	12.54–29.86	25.20–28.16	18.67–29.28	400.90–617.22	15.43–27.84	18.90–36.01	0.50–0.62	51.45–78.08	46.12–162.05	This study
	Mean	8.57	39.58	513.48	1.84	0.16	10.44	52.04	20.04	26.55	24.40	513.68	23.24	25.25	0.57	67.77	75.17	
	Std	2.03	7.98	30.08	0.32	0.06	1.85	7.61	5.97	1.00	4.07	100.75	5.11	6.00	0.05	9.92	39.64	
Soil around Guanting reservoir (N = 61)	Mean	8.67	/	/	/	0.32	/	37.9	16.8	/	/	/	18.3	20.1	/	/	59.4	[33]
Sediment	Range	5.81–8.11	33.12–40.95	351.70–609.54	1.59–2.00	0.09–0.22	10.00–11.02	46.72–53.98	15.97–21.17	21.64–29.80	22.80–23.71	391.27–882.73	19.92–23.65	19.57–25.62	0.47–0.58	59.54–73.54	56.39–91.80	This study
	Mean	6.81	36.72	492.98	1.75	0.14	10.48	50.45	17.95	25.88	23.39	631.74	21.78	22.42	0.55	66.95	66.76	
	Std	1.02	3.54	106.27	0.17	0.06	0.46	3.58	2.30	3.35	0.40	204.71	1.55	2.48	0.05	5.77	16.91	
Sediment of Guanting reservoir (N = 5)	Mean	/	/	/	/	0.205	/	64.6	36.1	/	/	/	38.4	33.5	/	/	104	[34]
Sediment of Yanghe River (N = 14)	Mean	/	/	/	/	0.34	/	59.91	30.64	/	/	/	30.85	39.51	/	/	129.27	[35]
Sediment of Yongding River (N = 11)	Mean	/	/	/	/	0.25	/	47.61	24.71	/	/	/	40.45	35.47	/	/	94.75	[36]
Background values in soil of Beijing		9.4	43.5	522	1.35	0.0534	15	66.7	23.1	17	34.3	688	28.2	24.7	0.452	77.4	97.2	[29]
Environmental quality standard for soils in China (pH > 7.5)		≤20	/	/	/	≤0.8	/	≤350	≤200	/	/	/	≤190	≤240	/	/	≤300	[32]

Note: Std means Standard deviation; “/” means “no data”.

3.3. Risk Assessment of Potential Toxic Elements

3.3.1. Geo-Accumulation Index

The I_{geo} values for PTEs in the soils and sediments are presented in Figure 2. Overall, the average I_{geo} values for PTEs in the soils and sediments occurred within class 0, except for Cd and Ga. Specifically, the mean I_{geo} value for Cd was 0.58 (ranging from 0.14 to 1.43) and 0.92 (ranging from 0.61 to 1.77) in the sediments and soils, respectively. Thus, Cd qualified for class 2, indicating moderate pollution levels in the GSR area (i.e., sediments and soils). The average I_{geo} values for Ga were -0.52 and 0.06 in the sediments and soils, respectively; thus Ga qualified for class 1, indicating uncontaminated to moderately contaminated pollution levels.

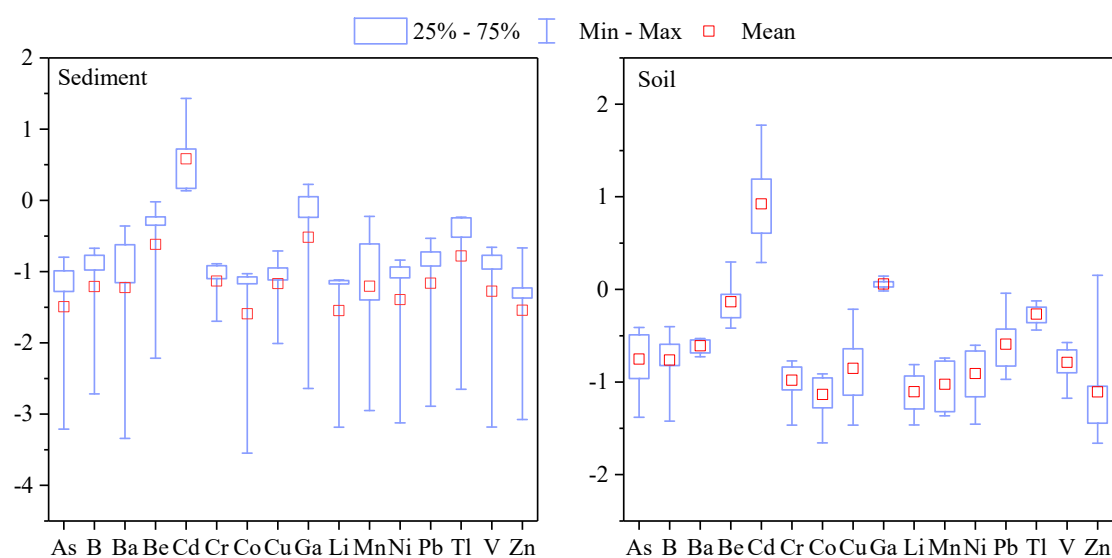


Figure 2. The evaluation results of I_{geo} for potential toxic elements in soils/sediments of the Guishui River (whisker-box).

3.3.2. Potential Ecological Risk Index

Individual PTEs with high biotoxicity were selected for the RI assessment (Table 3). Overall, the mean RI values in both the soils and sediments were less than 150, except for site S3, indicating that there was no obvious pollution in the GSR area. However, the average E_i value for Cd was 87.1 and 71.5 in the soils and sediments, indicating that Cd exhibited moderate risk and considerable risk in the soils and sediments, respectively. These results further show that Cd was the main contaminant in the GSR area.

Table 3. Potential ecological risk assessment results of potential toxic elements in soils/sediments from GSR.

Sampling Site		E_i							RI
		Cr	Ni	Cu	Zn	As	Cd	Pb	
S1	sediment	1.4	3.5	3.6	0.6	6.2	74.2	4.5	94.1
	soil	1.1	3.0	2.8	0.5	5.8	55.1	3.8	72.0
S2	sediment	1.6	3.9	3.9	0.6	8.6	61.8	4.5	84.9
	soil	1.6	4.7	4.7	0.7	10.4	103.4	5.2	130.7
S3	sediment	1.6	4.2	4.6	0.9	7.6	121.3	5.2	145.4
	soil	1.7	4.9	6.5	1.7	9.0	153.9	7.3	185.0
S4	sediment	0.9	0.9	1.9	0.2	1.6	49.4	1.0	55.9
	soil	1.6	4.6	4.8	0.6	9.8	68.5	4.6	90.9
S5	soil	1.5	2.7	2.7	0.5	6.6	73.0	3.9	120.2
S6	sediment	1.4	3.8	3.5	0.6	6.6	50.6	4.0	70.4
	soil	1.6	4.1	4.1	0.7	11.3	68.5	5.9	96.3

3.4. Identification of Pollution Sources in Sediments and Soils

3.4.1. Correlation Analysis

The results of the correlation analysis among PTE concentrations are presented in Table S4. For the soils, the concentration of Cd was significantly correlated with Mn, Cu, Zn, and Pb, however, the concentration of Li was significantly correlated with all PTEs, except B, Cu, Zn, Pb, and Cd. There were significantly positive correlations between Cd–Cu (0.812) and Cd–Pb (0.798) at $p < 0.05$ and between Pb–Cu (0.851), Pb–Zn (0.903), and Cd–Zn (0.876) at $p < 0.01$. This indicates that Cd, Cu, Zn, and Pb might originate from a common source, as might As, Li, Be, V, and Ga. Compared to the soils, the concentrations of PTEs in the sediments were significantly correlated except for Cd. This indicates that most of the PTEs in the sediments were from a common source except for Cd. Therefore, Cd in the sediments may come from an external source.

3.4.2. Principal Component Analysis

The PCA was used to identify the source of PTEs in the soils and sediments (Table 4). The rotated principal components (PCs) were extracted with eigenvalues >1 , accounting for 86.931% of the total variance. Factor one (PC1) was dominated by all of the PTEs except for Cd, and explained 75.833% of the total variance (Table 4). As mentioned in Section 3.2, the concentrations of these PTEs were similar to the BVs. Moreover, the results of the I_{geo} and RI assessments indicated that the pollution levels of these PTEs presented a low or zero potential ecological risk. Thus, it could be inferred that PC1 is a natural source of PTEs. In contrast, factor two (PC2) was dominated by Cd, and accounted for 11.098% of the total variance. In general, Cd concentrations are mainly considered to originate from anthropogenic sources [41,42]; thus, it may be considered that PC2 is mainly an anthropogenic source.

Table 4. Rotated component matrix for data of mix soils/sediments in GSR.

Elements	PC1	PC2
Li	0.938	−0.272
Be	0.829	−0.341
B	0.910	−0.095
V	0.963	−0.220
Cr	0.894	0.081
Mn	0.748	0.009
Co	0.974	−0.060
Ni	0.965	0.073
Cu	0.848	0.476
Zn	0.683	0.680
Ga	0.903	−0.300
As	0.892	−0.135
Cd	0.597	0.733
Ba	0.798	−0.241
Tl	0.960	−0.228
Pb	0.927	0.260
Eigenvalue	12.133	1.776
Percentage of variance (%)	75.833	11.098
Cumulative variance (%)	75.833	86.931

Previous research confirms that Cd pollution originates from the abuse of phosphate fertilizers in agriculture [43], and that pesticides may be another source of Cd [44–46]. As the GSR is located in Yanqing County, which is dominated by agricultural land [47,48], the high Cd concentrations found in the soils and sediments from the GSR may have originated from agricultural practices such as pesticides and fertilizers used in farming. Similar conclusions could be also available in other countries. For example, the abandoned Kettara mine, in Morocco, is the primarily responsible for soil

contamination by metals [49]; In Vietnam, the enrichment of Cd, Pb and Cu in rice paddy soils was seriously affected by the open pit coal extraction activities. This is mainly due to the mobility of PTEs in the soil is greatly improved by mining and ore processing [50,51]; In addition, the human impacts such as tourist activities, boat navigation, and car fuel combustion products, were contributed to the accumulation of PTEs in beach sediments of Sharm El-Sheikh, Egypt [52]. This means that the impact of human activities is a major factor in the source of PTEs.

It can be also seen in Table 4 that Cu, Pb, and Zn were positive and accounted for some of assignment value in PC2. Moreover, Cu, Pb, and Zn were positively correlated with each other, both in the soils and sediments. Therefore, Cu, Pb, and Zn may have a common source. The concentrations of Cu, Pb, and Zn in the sediments and soils were similar to those in the BVs, which suggests that these PTEs originate from natural sources. However, they may also originate from anthropogenic sources based on the assignment value in PC2. In general, Cu, Pb, and Zn are considered to originate from industrial sources [53]; thus, in this study, sources of Cu, Pb, and Zn were further examined using Pb isotopic ratios, as these have been successfully applied in previous studies [21,22].

3.4.3. Pb Isotopic Ratios

The Pb isotopic ratios were 1.15–1.18 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.45–2.57 for $^{208}\text{Pb}/^{207}\text{Pb}$ in the soils and 1.16–1.18 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.45–2.47 for $^{208}\text{Pb}/^{207}\text{Pb}$ in the sediments (Figure 3). Thus, the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of the sediments were similar to those of the soils, indicating that Pb in the sediments and soils has the same origin. Currently, a generally accepted view is that the geochemical background Pb with low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (<1.19) could indicate potential anthropogenic sources [54,55]. Combined with the results of the PCA, this indicates that Pb concentrations in the soils and sediments in this study originated from both natural and anthropogenic sources.

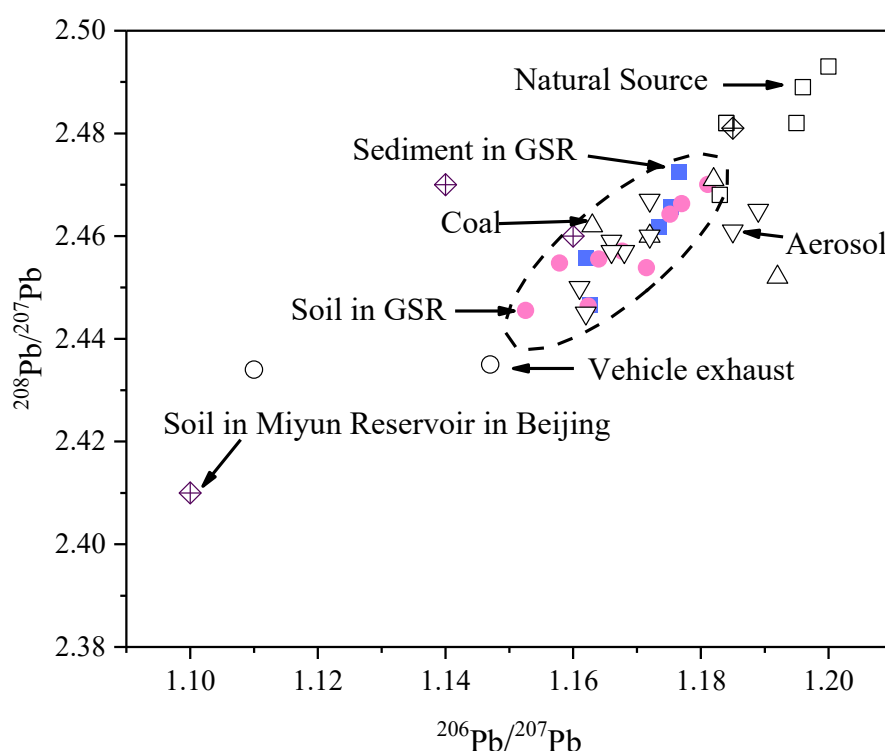


Figure 3. Comparison of Pb isotope ratios between bank soils and sediments of GSR, and other possible Pb emission sources: coal [56–59], Chinese vehicle exhaust [60], aerosol from regional cities in China [55,57,60–64], and soil in Miyun Reservoir in Beijing [22] and natural soils [55,65–68].

To determine the specific origin of Pb, the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios were compared between the soils and sediments from the GSR and environmental samples, including coal [56–59], vehicle exhaust gases [60], aerosols [55,57,60–64], natural soils [55,65–68], and soil in Miyun Reservoir in Beijing [22] (Figure 3). It can be seen from Figure 3, the isotopic ratios of Pb in the sediments is similar to that in the soils, indicating that Pb in the sediments and soils have a common source. Compared with the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.16–1.19) of the stream sediment from mining/smeltering district [69,70], it can be inferred that coal mine was another source of Pb in the sediments of the GSR. Meanwhile, the isotopic ratios of Pb in both the sediments and soils fell within the scope of aerosols, reflecting that aerosols might be the main anthropogenic source, and atmospheric deposition might be the major input pathway.

In recent years, $\text{PM}_{2.5}$ (i.e., pollution due to particulate matter [PM] with an aerodynamic diameter of 2.5 μm) was at a relatively high level in China, especially in the capital of Beijing [71]. Furthermore, the main categories of source apportionment for $\text{PM}_{2.5}$ in Beijing were identified as coal combustion and vehicle emissions [72]. Currently, most of the coal used for industries and heating, especially in cities such as Beijing and Tianjin, northern China [73]. Thus coal combustion may be another source of Pb in this study (Figure 3). Pb was more enriched in fly ash [74] and coal combustion dust [59]. Chen et al. [60] proved that the major Pb source of aerosols was the stationary industrial contribution of coal use. Thus, coal combustion may be another source of Pb in the soils and sediments in the GSR area. In addition, Pb, Cu, and Zn have also been identified in coal [22]. Meanwhile, Pb, Cu, and Zn were positively correlated in both the sediments and soils, as mentioned in Section 3.4.1. Thus, aerosols and coal combustion are the likely sources of Pb, Cu, and Zn enrichment in the soils and sediments, and atmospheric deposition was considered the main input pathway.

4. Conclusions

In this study, the pollution characteristics, risk assessment, and source identification of PTEs in the soils and sediments from the GSR were investigated. Overall, the physicochemical properties of the sediments were similar to that of the soils. The pH of the soils and sediments were weakly alkaline. The concentrations of PTEs in the sediments were slightly higher than that in the soils. Among the PTEs, only the mean Cd concentration in the soils and sediments was 3 times and 2.6 times higher than the BV; the others were similar to the BVs. However, the maximum concentration of Cd in the soils was considerably lower than the guideline of the Environmental Quality Standard for Soils in China. Meanwhile, Cd concentrations in the soils and sediments of the GSR were slightly lower than that in other areas around the GSR basin (the Guanting Reservoir, Yanghe River, and Yongding River). Assessment results based on I_{geo} and RI indicated that Cd was the main pollutant and at moderate pollution levels both in the soils and sediments. The results of the PCA showed that the PTEs in the sediments and soils have a common source. Cd mainly originated from anthropogenic sources, and fertilizer and pesticide applications were identified as the major contributor. The remaining metals were mainly derived from natural sources; however, Cu, Pb, and Zn concentrations were also considered to originate from human sources i.e., aerosols and coal combustion, which was confirmed by Pb isotopic identification. Atmospheric deposition was considered the main input pathway of Cu, Pb, and Zn. In conclusion, the contributions of aerosols and coal combustion to PTEs contamination in the sediments and soils of the GSR cannot be ignored. These sources, including pesticide and fertilizer applications, need to also be taken into consideration in future research.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/11/9/1847/s1>, Figure S1: Concentration variation of potential toxic elements in soils and sediments of the Guishui River, Table S1: The relative error of each element in certified reference material of stream sediment (GSD-10, GBW07310), Table S2: Values of I_{geo} and the pollution level, Table S3: Category of potential ecological risk factor, Table S4: Pearson correlation analysis.

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