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Article

Pollution and Ecological Risk Assessment of Metal Elements in Groundwater in the Ibinur Lake Basin of NW China

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Abstract: Groundwater pollution by metal elements is a serious issue due to its probable risks to the ecosystem and human health. In the present study, 75 groundwater samples were collected from the Ibinur Lake Basin (ILB) of NW China. The contents of As, Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd were determined. The levels, pollution degrees, and potential ecological risks of metals in groundwater were systematically analyzed for the first time in this area. The potential sources of metals were also discussed. It was observed that the mean contents of metals in groundwater in the ILB were lower than the Class III thresholds of the Standard for Groundwater Quality of China (GB/T 14848–2017), whereas the maximum contents of As, Se, Pb, Cr(VI), and Mn exceeded the Class III thresholds values. The pollution index of each metal and the Nemerow comprehensive index (NPI) caused by the overall pollution by all these metals in groundwater showed the pollution-free level. The single and comprehensive potential ecological risk index of analyzed metals in groundwater showed a relatively low level of potential ecological risk. Additionally, spatial distribution patterns of contents, pollution levels, and ecological risks of metals in groundwater in the ILB were found to be substantially heterogeneous. Furthermore, As and Se in groundwater originated from anthropogenic sources such as agriculture and mining, whereas Mn mainly originated from natural factors, and Pb, Cu, Cr(VI), Zn, and Cd were correlated with both natural and anthropogenic sources. Overall, As was identified as the main pollution factor, while As and Se were identified as the main ecological risk factors in the groundwater in the ILB. These results can provide important information for groundwater management in the ILB and will guide authorities in taking the necessary measures to ensure the safety of groundwater supply in the northwestern arid regions of China.

Keywords: groundwater; metals; pollution; ecological risk; distribution; Ibinur Lake basin

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1. Introduction

Groundwater pollution by metal elements is one of the most serious eco-environmental problems in the world since most people around the world directly depend on groundwater [1]. Groundwater plays a crucial role in the ecological environment through regional water supply. Groundwater is an important type of freshwater resource, especially in areas with a lack of surface water resources, such as in arid regions, and plays a decisive role in regulating hydrological cycles and maintaining ecosystem stability in arid regions [2]. Nearly two-thirds of the world population directly depends on groundwater for daily water use, while about 33% of the world population uses groundwater for drinking requirements [3]. Similarly, about 70% of the population in China depends on groundwater for drinking requirements, while about 40% of cultivated lands in China depend on groundwater for irrigation. However, pollution of groundwater by metals has emerged as a major challenge to the sustainability of groundwater resources in recent years [4]. Metals accumulated in groundwater can cause probable ecological risks due to their potential toxicity and detrimental effects. Pollution of groundwater by metals poses a considerable risk to the ecological environment because metal elements diffuse more quickly in groundwater systems than in soil systems [5]. Therefore, assessment of pollution and probable ecological risk of metals in groundwater is essential for regional environmental protection and groundwater pollution remediation.

Metal elements in groundwater not only affect the function of the groundwater and soil system but also seriously threaten the safety of the entire ecosystem and human health through the circulation between various ecosystems in the Earth Critical Zone [6]. The World Health Organization (WHO, United Nations) reported that approximately 20% of global cancers arise because of the consumption of unfit water, and about 80% of diseases are caused due to pollution of groundwater by metal elements [7,8]. In recent years, therefore, numerous researchers have been focusing on the pollution risks and sources of metals in groundwater worldwide. In China, for example, Wang et al. [9] observed that Pb is the most prominent potential risk factor in drinking groundwater in Ningxia. Wang et al. [10] pointed out that Cr is the main carcinogenic risk factor in groundwater in coal mine areas in southern Jiangsu of China. Qiao et al. [11] investigated metals in groundwater in the Guanzhong Plain in China and found that Cr in shallow groundwater in this region exceeded the Standard for Groundwater Quality of China. Wang et al. [12] indicated that As and Mn in groundwater in the eastern coastal areas of China exceeded the Standard for Groundwater Quality of China. Similarly, Sheng et al. [2] identified that the groundwater of the Zhangye Oasis in the northwest arid region of China is also significantly enriched with As and Mn. Results of numerous studies [13–16] indicated that As, a carcinogenic metalloid, is the major pollution factor in groundwater in different regions of China. Nevertheless, Pan et al. [17] indicated that natural factors, agricultural activities, industry, and atmospheric deposits are the main sources of metal pollution of shallow groundwater systems in the Leizhou Peninsula of China.

Outside of China, Ramos et al. [1] analyzed the probable human health risks of eight toxic metals, including Al, As, B, Cr, Cu, Fe, Mn, and Zn, in groundwater in the Monterrey metropolitan district in northern Mexico, and found a carcinogenic risk of oral consumption of Cr in groundwater. Hullysses et al. [18] reported that the Cr, Mn, and Al contents of the groundwater of the Tamoios coastal area in Brazil surpass the maximum acceptable content of the water quality standards for drinking purposes, introduced in the Canadian Standard 2019. Seyed et al. [19] observed that Pb is the most prominent potential risk element in drinking groundwater in Gayan County of Iran. Ahmed et al. [20] found a probable health risk of As in groundwater in northwestern Egypt. In terms of pollution sources of metals in groundwater, Triassi et al. [21] clarified that the main origins of metals in groundwater in southern Italy include natural sources, human factors, and geochemical activities. John and Francis [22] analyzed metal pollution of groundwater around a sugar factory and found that the increased levels of Pb in groundwater around the sugar factory could potentially become toxic to microorganisms. Their study suggested that the company should implement the use of unleaded fuel to reduce the Pb pollution of groundwater. Luiza et al. [23] investigated metals and emerging pollutants in groundwater in the southern region of Brazil and pointed out that the presence of metals, including Co, Mn, Cr, and Ni, in groundwater can show the impact of agriculture and the inadequate disposal of domestic sewage. Hilary et al. [24] observed the contents and spatial distribution of metal elements in groundwater around selected automobile workshops in the Niger Delta region of Nigeria based on geostatistical modeling and found that the activities in automobile workshops can result in metal pollution of groundwater. In terms of ecological risks of metals in groundwater, John et al. [25] detected significant potential ecological risks of metals, such as As, Cr, Cd, and Pb, in groundwater in southern Nigeria. Other relevant studies [26,27] also assessed the potential ecological and environmental risks of metals in groundwater based on the selected ecological risk indexes. However, the above-mentioned studies showed that metals can accumulate in groundwater owing to various natural origins (soil–water interactions, geochemical background, mineral leaching, etc.) or various anthropogenic sources (agriculture, industry, mining, etc.) that lead to metal pollution of groundwater systems. The ecological risk estimation of metals in groundwater is of high concern due to its direct relation to human life and regional ecological security. Therefore, periodical investigation and monitoring of metals in groundwater is required to identify their potential risks.

The investigation of the pollution and probable ecological risks of metals in groundwater is crucial for preventing the harm of metal pollution of regional groundwater systems [28,29]. The shortage of water resources caused by water quality degradation is one of the key problems faced by water resources in China, especially in the process of agricultural development [30]. According to the "Annual Report of National Groundwater Monitoring", in 2021, the proportion of groundwater that could be directly used as drinking water sources in China was 14.7%, whereas the proportion of groundwater that could be used for drinking after treatment was 67.9% (Class IV thresholds of the national standard) and 17.4% (Class V thresholds of the national standard), respectively. In recent years, metal contents of groundwater have been increasing in many groundwater systems in the northwestern arid zones of China owing to overexploitation, low groundwater recharge, natural origins, or various human activities that lead to the degradation of regional groundwater quality [2,31]. Over the past several decades, the groundwater storage in most areas in the "economic belt" located on the north slope of the Tianshan Mountains has significantly decreased, with the most severe decline in the Ibinur Lake Basin (ILB) [32]. This has led to pollution of groundwater due to changes in water circulation rate and resulted in increasingly serious ecological and environmental problems in the ILB, which is a major grain production area and also a major petrochemical area in the "economic belt". So far, however, there has been no pursuant discussion about the pollution and probable ecological risk of metals in groundwater in the ILB. Moreover, the priority control metal elements in groundwater in the ILB still remain unclear. Therefore, it is necessary to identify the pollution degrees, ecological risks, and sources of metals in groundwater in the ILB.

The main objectives of the present study are to (1) identify the contents and spatial distributions of eight metal elements, arsenic (As), selenium (Se), lead (Pb), copper (Cu), hexavalent cadmium (Cr(VI)), zinc (Zn), manganese (Mn), and cadmium (Cd), in groundwater in the ILB, (2) assess pollution levels of groundwater using the Nemerow comprehensive index, (3) quantify potential ecological risks of metals in groundwater based on the ecological risk assessment model, and (4) identify potential origins of metals in groundwater based on the multivariate statistical analysis. The results of this study will provide a deeper understanding of the safety status of groundwater in northwestern arid regions of China and help strengthen management practices against the probable risks associated with groundwater systems.

2. Materials and Methods

2.1. Study Area

The ILB is situated in the western parts of the Junggar Basin and on the north slope of the Tianshan Mountains, Xinjiang of NW China. The geographical location of the research area lies between 44°20′–45°10′ N and 80°50′–83°10′ E, with an area of 3727 km^2, including three main regions: Bortala City, Arshang County, and Jing County (Figure 1). The ILB has a population of about 524,000. The climate type of the ILB falls into the continental typical dry type with annual mean precipitation, temperature, and evaporation of 105.27 mm, 7.8 °C, and 2221.3 mm, respectively [33,34].

The terrain of the ILB is relatively low and surrounded by mountains on the west, north, and south sides. The total water yield in the ILB decreased from 831.12 $\times$ 10^6 m^3 in 2010 to 706.78 $\times$ 10^6 m^3 in 2015 and 567.26 $\times$ 10^6 m^3 in 2020. The ILB is in a state of water shortage, with a shortage of irrigation water of about 1.83 $\times$ 10^8 m^3, and the socio-economic water consumption consumes a large amount of water resources in the ILB. The groundwater level in the upper region of the piedmont gravel alluvial fan in the ILB is low. The groundwater level is high in the area around the river terraces in the lower part of the alluvial fan, with a groundwater depth of 1–7 m. In lacustrine plains and lakeside zones, the depth of groundwater is around 1 m [33,34].

The western parts of the ILB (upstream part of the Bortala River) are mainly composed of clastic rock mixed with carbonate rock, while the middle reaches of the Bortala River are composed of loose rock, and the southern parts of the Bortala River are composed of carbonate water-bearing formations. The eastern part of the ILB is composed of loose rock pore-water-bearing formations, with relatively low water abundance. The ILB is mostly Quaternary sediments, and their thickness varies greatly due to the undulation of the basement rocks (Figure 1a). The main types of groundwater in the ILB include the mountain bedrock fissure water as well as the Quaternary loose pore water, while Lake Ibinur is the catchment center for both surface and groundwater in the ILB.

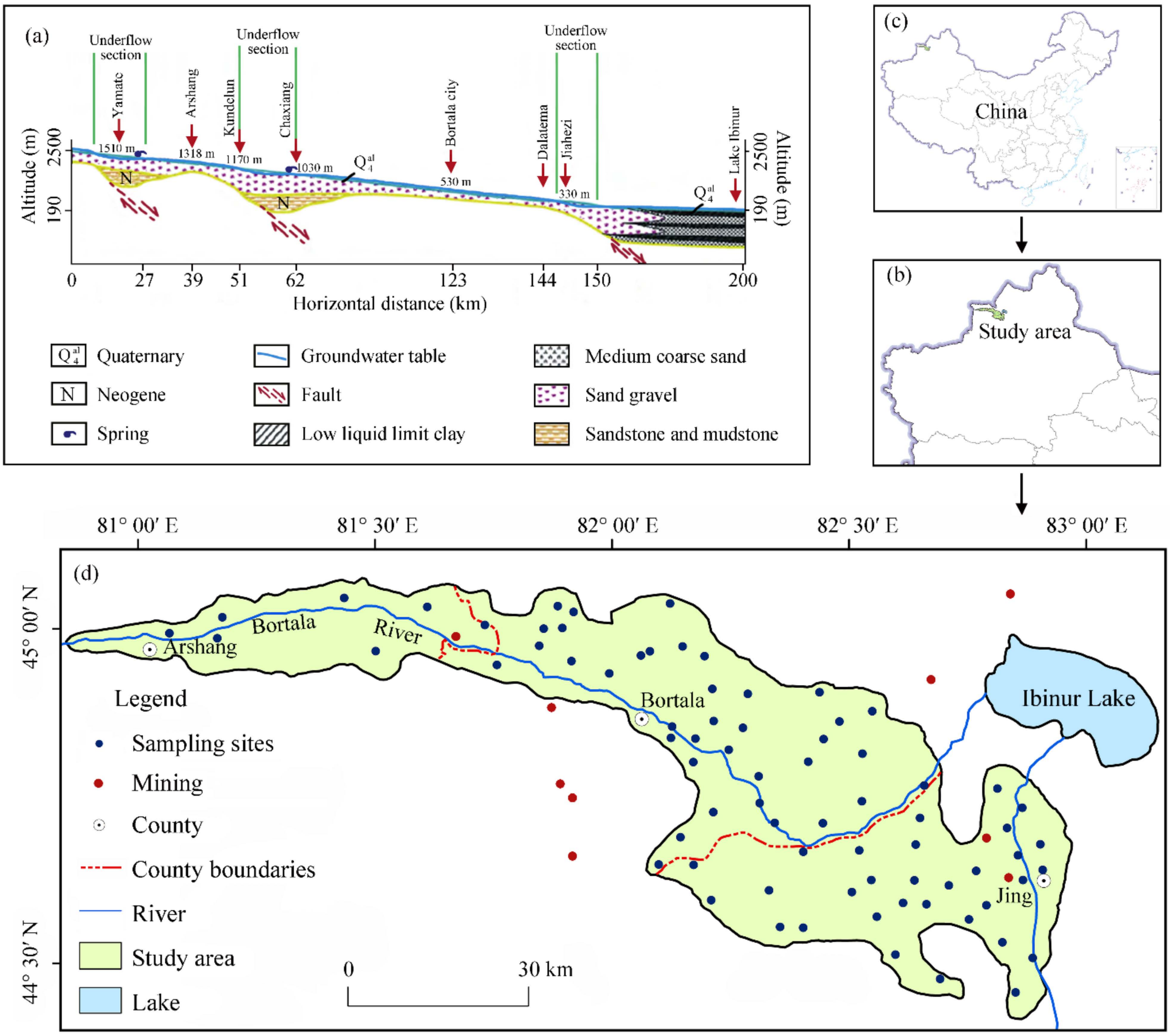

Figure 1. Location map of the ILB. (**a**) Hydrogeology of the ILB; (**b**) NW China; (**c**) Map of China; (**d**) Locations of the ILB and the groundwater sampling sites.

2.2. Sample Collection and Determination

Based on the Technical Specifications for Environmental Monitoring of Groundwater (HJ/T 164–2004) [35], 75 groundwater samples were collected from the ILB in May of 2023. Locations of the groundwater sampling sites are illustrated in Figure 1. Groundwater samples for mainly irrigation, drinking, and other daily uses were collected from irrigation wells or pumping wells. Before sampling, the selected wells were pumped for about three minutes to reduce the possible impacts of stagnant water. Then, 500 mL polyethylene bottles were pre-cleaned using deionized water, about 500 mL groundwater was collected, then the bottle cap was tightened to ensure that the groundwater samples did not come into contact with air. Groundwater samples were stored in a portable refrigerator at 4 °C and then transferred to the laboratory.

In the laboratory, the collected groundwater samples were all syringe-filtered (10 mL disposable syringe, filter pore size 0.45 μm) and stored in pre-cleaned 50 mL polypropylene bottles. The contents of As, Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd were determined as per the national standard of China detailed in GB/T 5750.6–2006 [36]. The contents of Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd were tested using an inductively coupled plasma–mass spectrometer (ICP–MS, Perkin Elmer, Waltham, MA, USA), and the contents of As were tested using an atomic fluorescence spectrophotometer (BAF–4000, Baode, Beijing, China). To ensure the quality of the measured data, calibration curves were produced for assessing data from each set of collected groundwater samples. The contents of metals in each groundwater sample were measured three times, the standard deviation coefficient (SD) of the three measurements was ±5%, and then the mean value was taken as the final content. The detection limits for As, Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd are 1.0 μg/L, 0.09 μg/L, 0.07 μg/L, 0.09 μg/L, 0.09 μg/L, 0.80 μg/L, 0.06 μg/L, and 0.06 μg/L, respectively. The recovery rates were 94.37%, 96.56%, 102.88%, 97.23%, 104.12%, 95.39%, 104.16%, 103.81%, and 96.18% for As, Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd elements, respectively.

2.3. Pollution Assessment

The pollution index (P_i) and the Nemerow comprehensive index (NPI) [37], the enrichment factor (EF) [38], the bioaccumulation factor (BF) [38], and the heavy metal pollution index (HPI) [39] are commonly used methods for pollution assessment of groundwater. Among them, the Nemerow comprehensive index can be used to assess both single and overall pollution degrees of metals in groundwater. In the present study, P_i and NPI methods were adopted, which are calculated as follows:

$$P_i = C_i/B_i \tag{1}$$

$$NPI = \sqrt{\left({P_{max}}^2 + {P_{mean}}^2\right)/2} \tag{2}$$

where C_i and B_i represent the measured concentration and evaluation standard of metal i in groundwater, respectively. The Class III thresholds of the Standard for Groundwater Quality of China (GB/T 14848–2017) were selected as the evaluation standard in this study [40]. The Class III thresholds of the national standard refer to the groundwater suitable for domestic drinking purposes as well as industrial and agricultural water use. P_{max} and P_{mean} represent the maximum and mean values of P_i, respectively.

2.4. Potential Ecological Risk Assessment

The Håkanson ecological risk index (RI) [41] is adopted to reflect the potential ecological risks of metals in groundwater. The RI is calculated as follows:

$$P_i = C_i/B_i \tag{3}$$

$$E_i = C_i \times T_i \tag{4}$$

$$\mathrm{RI} = \sum_{i=1}^{n} E_i \tag{5}$$

where E_i represents the probable ecological risk index for a single metal element, and RI represents the comprehensive probable ecological risk index caused by the overall pollution by all investigated metals in groundwater. C_i, B_i, and P_i are the same as above. T_i represents the coefficient of toxicity for metal i, and the coefficients of toxicity for As, Se, Pb, Cu, Cr, Zn, Mn, and Cd are 10, 15, 5, 5, 2, 1, 1, and 30, respectively [41]. The classification standards for the pollution degree of P_i and NPI, and for the ecological risk degree of E_i and RI, are shown in Table 1 [37,41].

Table 1. Classification of pollution degree and ecological risk degree.

Pollution Degree [37]	P_i	NPI	Ecological Risk Degree [41]	E_i	RI
Pollution-free	$P_i \leq 1$	NPI < 1	Low risk	$E_i < 40$	RI ≤ 150
Low pollution	$1 < P_i \leq 2$	1 ≤ NPI < 2.5	Moderate risk	$40 < E_i \leq 80$	150 < RI ≤ 300
Moderate pollution	$2 < P_i \leq 3$	2.5 ≤ NPI < 7	High risk	$80 < E_i \leq 160$	300 < RI ≤ 600
Heavy pollution	$P_i > 3$	NPI ≥ 7	Extremely high risk	$160 < E_i \leq 320$	RI > 600

2.5. Statistical Analysis

The IBM Statistical Package for the Social Sciences (SPSS) 25.0 was used for the statistical analysis of groundwater data. Basic statistical parameters such as maximum, minimum, mean, standard deviation (SD), coefficient of variation (CV), skewness, and kurtosis were computed. The correlation analysis was implemented to identify the relationships among the analyzed metals, and principal component analysis (PCA) was implemented to explore the possible sources of metals. A GIS-based inverse distance weight interpolation (IDW) was adopted to map the spatial distribution of the contents, pollution levels, and ecological risk degrees of investigated metals in groundwater. The IDW method is suitable for geographic data that are spread over irregular intervals, according to "Tobler's First Law of Geography" [42].

3. Results

3.1. The Contents of Metals in Groundwater

Table 2 indicates that the mean contents of As, Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd in the groundwater in the ILB are 5.50, 4.19, 3.62, 10.20, 7.34, 99.79, 33.77, and 0.53 μg/L, respectively. The mean contents of these eight metals in the groundwater were all below the corresponding Class III thresholds of the GB/T 14848–2017. Meanwhile, the maximum contents of Cu, Zn, and Cd in the groundwater were also below the corresponding national standard. Meanwhile, the mean contents of these eight metals were below the maximum allowable value recommended by the WHO (2017) [43], while the maximum contents of Se, Cu, Zn, Mn, and Cd were also below the corresponding allowable value.

Table 2. Metal contents of the groundwater in the ILB.

Metals	As n = 59	Se n = 67	Pb n = 73	Cu n = 75	Cr(VI) n = 75	Zn n = 75	Mn n = 73	Cd n = 29
Min (μg/L)	1.08	0.27	0.24	0.14	0.14	0.07	0.01	0.01
Max (μg/L)	24.20	12.20	18.50	154.0	147.0	671.0	423.0	3.56
Mean (μg/L)	5.50	4.19	3.62	10.20	7.34	99.79	33.77	0.53
Median (μg/L)	3.18	3.19	1.85	1.45	1.89	46.7	5.65	0.17
SD (μg/L)	5.70	3.24	4.16	25.64	19.34	133.27	69.83	0.83
CV	1.04	0.77	1.15	2.51	2.63	1.34	2.07	1.58
Skewness	2.15	1.01	1.92	3.90	5.79	1.83	3.53	2.52
Kurtosis	4.24	0.16	3.03	16.63	38.48	4.03	15.16	6.33
* National standard (μg/L) [40]	10	10	10	1000	50	1000	100	5
Standard-exceeding ratio (%)	10.17	7.46	9.59	0	2.67	0	10.96	0
** Max. permissible level WHO (2017) (μg/L) [43]	10	40	10	2000	50	5000	1000	5

Notes: * The Standard for Groundwater Quality of China (GB/T 14848–2017). ** The maximum permissible level recommended by WHO.

However, the maximum contents of As, Se, Pb, Cr(VI), and Mn in the groundwater were 24.20, 12.20, 18.50, 147.0, and 423.0 μg/L, respectively, which were 2.42, 1.2, 1.85, 2.94, and 4.23 times the corresponding national standard. In addition, 10.17% (As), 7.46% (Se), 9.59% (Pb), 2.67% (Cr(VI)), and 10.96% (Mn) of the collected groundwater samples in the ILB surpassed their corresponding Class III thresholds (As: 10 μg/L; Se: 10μg/L; Pb: 10 μg/L; Cr(VI): 50 μg/L; Mn: 100 μg/L). Furthermore, the maximum contents of As, Pb, and Cr(VI) were 2.42, 1.85, and 2.94 times the maximum allowable value recommended by the WHO. It indicates that As, Se, Pb, Cr(VI), and Mn are likely the primary pollutants in groundwater in the ILB (Table 2).

The standard deviations (SDs) of the contents of the analyzed metals in groundwater in the ILB were relatively high. The CV values for all metals showed a strong variability (CV > 0.50), as listed in Table 2. It indicates that the contents of eight metals have higher spatial variability, and their contents varied significantly from one sampling point to another. The skewness and kurtosis coefficients for Cu, Cr(VI), and Mn contents in the groundwater were relatively high (Table 2), indicating a high enrichment level of these three metals in the collected groundwater samples. It can be seen that Cu, Cr(VI), and Mn in groundwater are likely to be affected by various anthropogenic factors.

3.2. Spatial Distribution of Metal Contents

GIS-based geostatistical analysis is an effective method to analyze the spatial distribution of metal contents in groundwater [1,11,12,14,19]. A GIS-based IDW method was applied to identify the spatial distribution of metal contents in groundwater in the ILB (Figure 2). As illustrated in Figure 2, the spatial distributions of the contents of the eight metals in groundwater were substantially heterogeneous, with the distribution of the high-content area of each metal showing a "dotted-distribution" pattern.

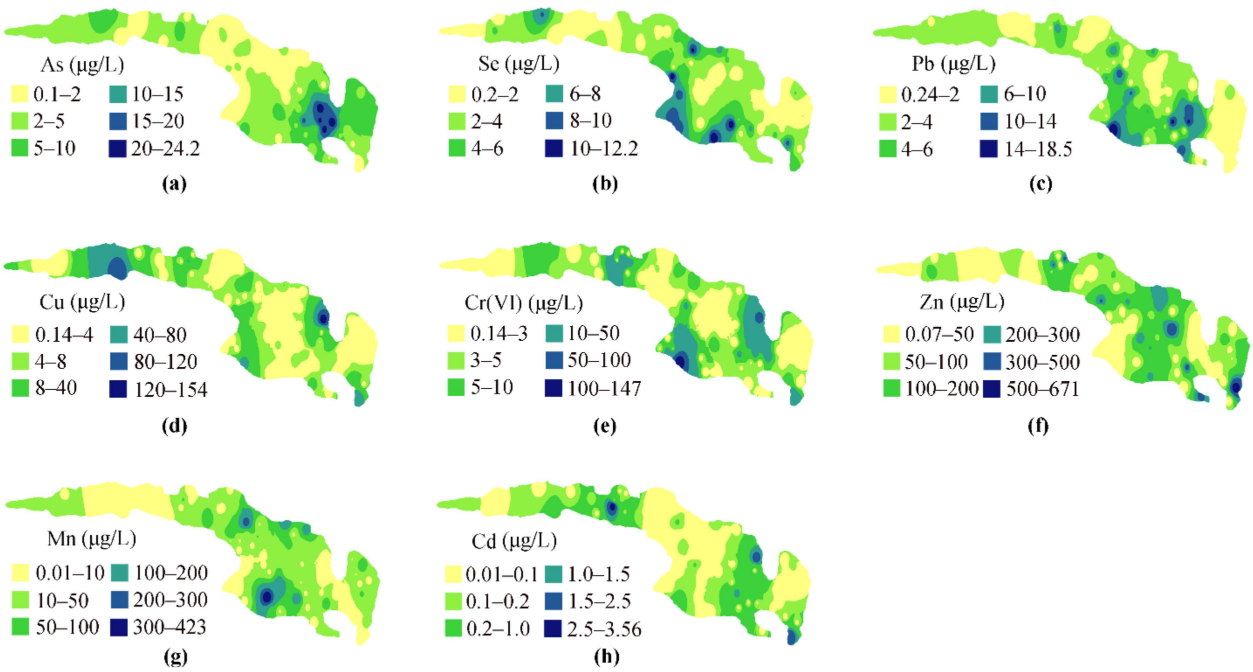

Figure 2. Spatial distribution of metal contents of the groundwater in the ILB. (**a**) As; (**b**) Se; (**c**) Pb; (**d**) Cu; (**e**) Cr(VI); (**f**) Zn; (**g**) Mn; (**h**) Cd.

Specifically, the high-content areas (standard-exceeding areas) for As were primarily observed in the central irrigation areas of Jing County in the ILB (Figure 2a). The spatial distributions of Se, Pb, Cr(VI), and Mn contents in groundwater in the ILB were similar (Figure 2b,c,e,g). The high-content areas (standard-exceeding areas) of these four metals were mainly distributed in the western parts of Jing County. The distribution patterns of Cu and Cd in groundwater were also similar (Figure 2d,h), with the high-content areas of these two metals mainly detected in the eastern and western parts of Bortala City. The high-content areas of Zn in groundwater were primarily observed in Jing County, with a "dotted-distribution" pattern (Figure 2f).

Obviously, there were basically no high-content areas of metals in the groundwater in Arshang County, whereas many of the high-content areas of metals were observed in

Jing County. This is because Jing County is the oldest agricultural reclamation area in the ILB, with intensive agricultural activities and shallow groundwater depth. Based on our field investigation in the ILB, the metal contents of groundwater near the national roads, railways, residential areas, agricultural lands, and areas with shallow groundwater table were relatively higher, which likely a clear indication that pollution emissions from agricultural activities and transportation influence the accumulation of metals in groundwater in the ILB.

3.3. Pollution of Metals in Groundwater

Two approaches, P_i and NPI, were used to determine the pollution levels of all analyzed metals to better identify the natural and anthropogenic origins of metals in groundwater in the ILB. As shown in Table 3, the mean P_i values of metals in the collected groundwater samples in the ILB can be ranked as: As (0.56), Se (0.42), Pb (0.36), Mn (0.34), Cr(VI) (0.15), Cd (0.11), Zn (0.10), and Cu (0.01), with greater P_i values indicating higher pollution degrees. Based on the classification standard of P_i (Table 1), each metal in groundwater in the ILB showed a pollution-free level. It is noteworthy that the maximum P_i value of Mn in groundwater fall into the heavy pollution level, while the maximum P_i values of two carcinogenic metals, As and Cr(VI), fall into the moderate pollution level, and the maximum P_i values of Se and Pb also fall into the moderate pollution level.

Table 3. Pollution levels of metals in groundwater in the ILB.

Statistics	P_i								NPI
	As	Se	Pb	Cu	Cr(VI)	Zn	Mn	Cd	
Min	0.1080	0.0269	0.024	0.0001	0.0028	0.0001	0.0001	0.0017	0.097
Max	2.42	1.22	1.85	0.15	2.94	0.67	4.23	0.71	3.02
Mean	0.56	0.42	0.36	0.01	0.15	0.1	0.34	0.11	0.67

Specifically, As in two groundwater samples, Se in five groundwater samples, Pb in seven groundwater samples, Cr(VI) in one groundwater sample, and Mn in six groundwater samples fall into the low pollution level. Meanwhile, As in four groundwater samples and both Cr(VI) and Mn in one groundwater sample showed a moderate pollution level. Furthermore, Mn in one groundwater sample showed a heavy pollution level.

The NPI values of metals in the collected groundwater samples in the ILB were in the range of 0.097–3.02, with a mean value of 0.67, at the pollution-free level. According to the classification standard of NPI (Table 1), twelve and one groundwater sample exhibited low and the moderate pollution levels, respectively. As a whole, the pollution level of metals in groundwater in the ILB was relatively low but groundwater in some specific areas was polluted by metals to varying degrees with point source pollution. However, As is the main pollution factor in the groundwater in the ILB.

The spatial distributions of the P_i and NPI values of the metals in groundwater in the ILB are shown in Figure 3. Here, a relatively high level of As pollution of groundwater was situated in the central regions of Jing County, at low and moderate pollution levels (Figure 3a). The P_i value of As in groundwater in other areas in the ILB showed a pollution-free level. The distribution patterns of P_i values of Se, Pb, Cr(VI), and Mn in groundwater in the ILB were quite similar (Figure 3b,c,e,g). Among them, metals in groundwater in the eastern part of Arshang County, the western part of Jing County, and the surrounding areas of Bortala City showed low pollution by Se, while Se in groundwater in other areas showed a pollution-free level. Metal elements in groundwater in the central and western parts of Jing County and the eastern parts of Bortala City showed low pollution by Pb, while Pb in groundwater in the other areas showed a pollution-free level. Meanwhile, the areas with low or moderate pollution of Cr(VI) were mainly observed in the western part of Jing County, while Cr(VI) in groundwater in other areas showed a pollution-free level. Moreover, the pollution area of groundwater by Mn was the biggest, with the areas with the heaviest pollution by Mn primarily observed in the western parts of Jing County.

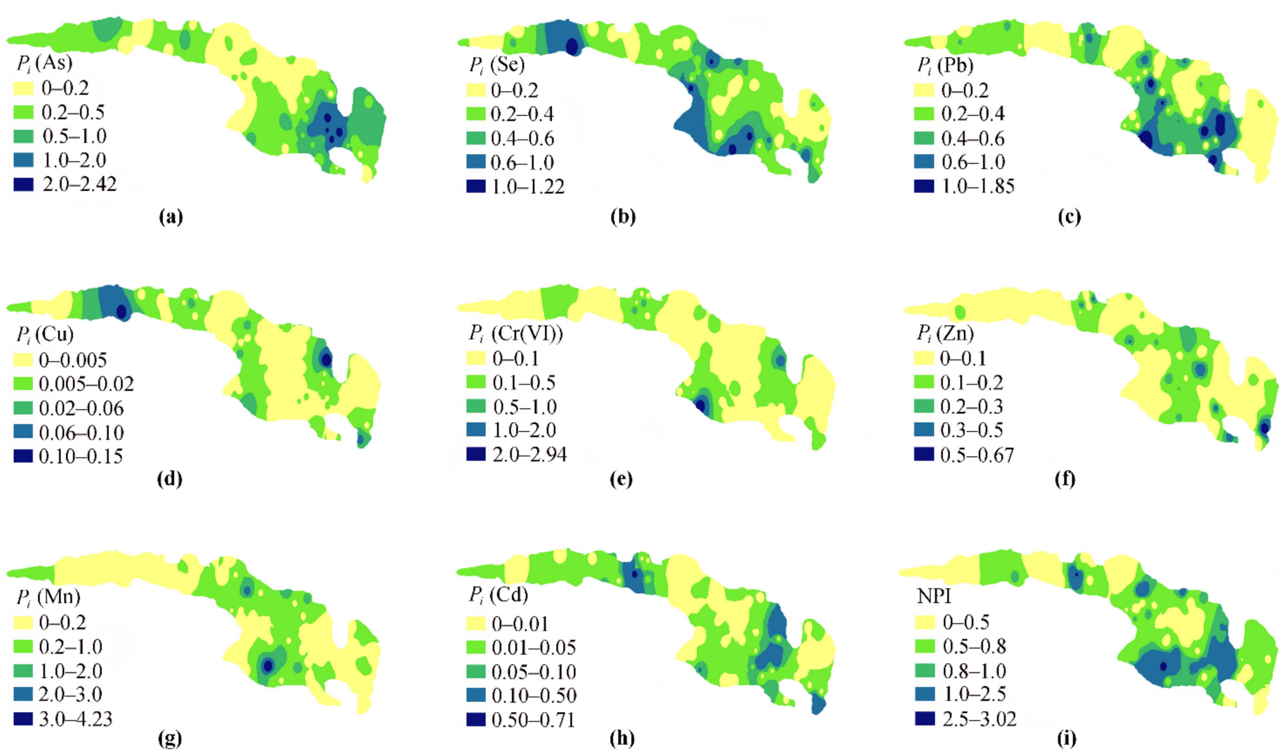

Figure 3. Spatial distributions of pollution levels of metals in the groundwater in the ILB. (**a**) As; (**b**) Se; (**c**) Pb; (**d**) Cu; (**e**) Cr(VI); (**f**) Zn; (**g**) Mn; (**h**) Cd; (**i**) NPI.

However, the spatial distribution of the P_i value of Cu, Zn, and Cd in the groundwater in the whole ILB showed a pollution-free level (Figure 3d,f,h). Among them, relatively higher P_i values of Cu in the groundwater were observed in the eastern parts of both Bortala City and Arshang County, while a relatively higher P_i value of Zn was distributed in the eastern regions of Jing County, and the relatively higher P_i value of Cd was primarily detected in the surrounding areas of Bortala City.

As illustrated in Figure 3i, the NPI values of the metals in groundwater in the western parts in Jing County showed a moderate pollution level, whereas the NPI values of metals in groundwater in the central and western parts of Jing County and the surrounding areas of Bortala City showed a low pollution level. Overall, the spatial distributions of the P_i value of As element and the NPI value of all analyzed metals were very similar, further proving that As is the main pollution metal in groundwater in the ILB.

3.4. Ecological Risk of Metals in Groundwater

More knowledge on the pollution risk induced by metals in the groundwater is necessary for the reasonable management of the groundwater environment in the ILB. Therefore, two approaches, E_i and RI, were used to assess the probable ecological risk of metals in the ILB. As given in Table 4, the mean E_i value of metals in groundwater in the ILB decreased in the following order: Se (5.78), As (4.28), Pb (1.76), Cd (1.37), Mn (0.33), Cr(VI) (0.29), Zn (0.10), and Cu (0.05), with greater E_i values representing higher ecological risk degrees. According to the classification standard of E_i (Table 1), each metal in groundwater in the ILB belonged to the low ecological risk level. In addition, although the maximum E_i values of As (24.20), Se (18.30), and Cd (21.36) were also at the low ecological risk level, they reached a relatively high risk level.

Table 4. Potential ecological risk of metals in the groundwater in the ILB.

Statistics	E_i								RI
	As	Se	Pb	Cu	Cr(VI)	Zn	Mn	Cd	
Min	0.10	0.40	0.05	0.00	0.01	0.00	0.00	0.05	2.31
Max	24.20	18.30	9.25	0.77	5.88	0.67	4.23	21.36	39.87
Mean	4.28	5.78	1.76	0.05	0.29	0.10	0.33	1.37	13.96

The RI values of investigated metals in groundwater in the ILB were in the range of 2.31–39.87, with a mean value of 13.96, at the low ecological risk level. The contribution rates of E_i values of As and Se to the RI were 30.66% and 41.40%, respectively. It indicates that As and Se are the main potential ecological risk factors in groundwater in the ILB. Overall, the ecological risk of metals in groundwater in the ILB was relatively low. However, groundwater in some specific areas showed relatively higher ecological risk levels due to point source pollution of groundwater.

The spatial distributions of the E_i values of metals in groundwater in the ILB indicated that there are significant spatial differences in the potential ecological risks of each metal, and the higher ecological risk areas of each metal showed a "dotted-distribution" pattern (Figure 4).

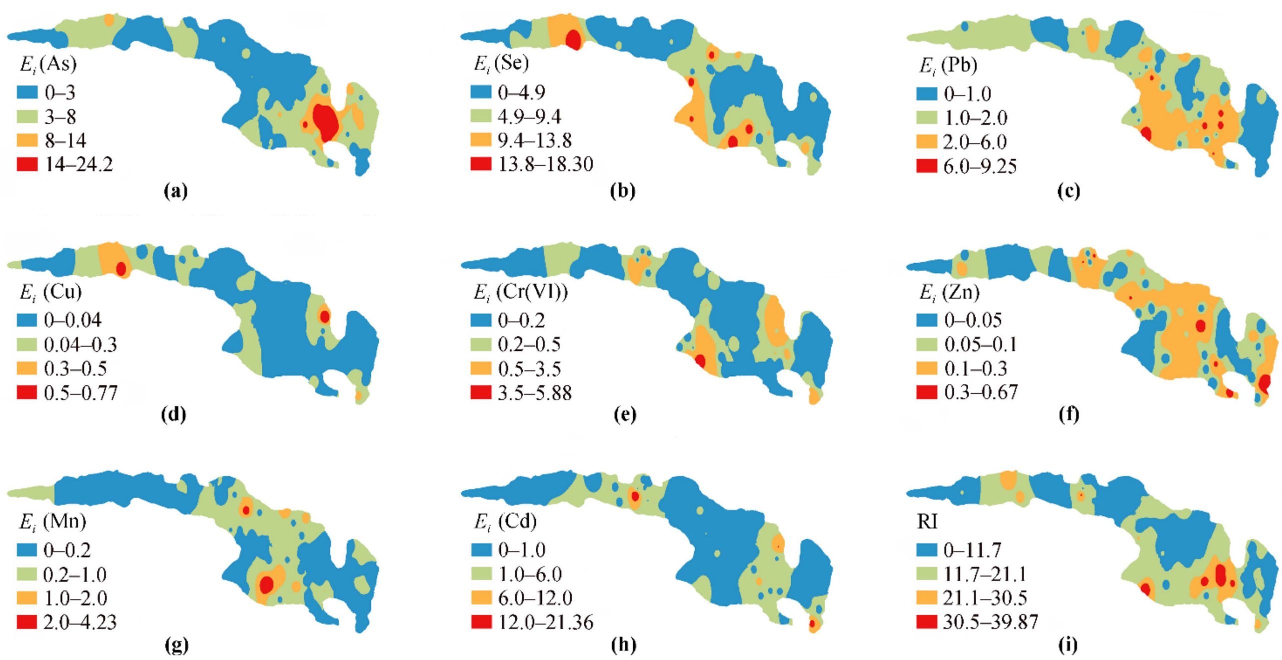

Figure 4. Spatial distribution of ecological risk of metals in groundwater in the ILB. (**a**) As; (**b**) Se; (**c**) Pb; (**d**) Cu; (**e**) Cr(VI); (**f**) Zn; (**g**) Mn; (**h**) Cd; (**i**) RI.

Among them, the areas with the higher E_i values of As in groundwater in the ILB were observed in the central parts of Jing County (Figure 4a), while the higher ecological risk areas of Se were distributed in the western part of Jing County and the eastern parts of Arshang County (Figure 4b). The higher ecological risk areas of Pb were distributed in the central and western parts of Jing County (Figure 4c), while the higher ecological risk areas of Cu were located in Arshang County and the eastern parts of Bortala City (Figure 4d). Meanwhile, the higher ecological risk areas of both Cr(VI) and Mn were mainly situated in the western parts of Jing County (Figure 4e,g), while the higher ecological risk area of Zn was mainly observed in the eastern parts of Jing County (Figure 4f), and the higher ecological risk areas of Cd were distributed in the west of Bortala City (Figure 4h).

Overall, as shown in Figure 4i, the higher RI values of metals in groundwater were mainly distributed in the central and western parts of Jing County. The spatial distribution pattern of the RI was quite similar to that of the spatial distribution pattern of the E_i of As and Se. It further indicates that As and Se are the main potential ecological risk factors in the groundwater in the ILB.

4. Discussion

Metal elements in groundwater originate from either anthropogenic sources or natural sources. Correlation analysis and principal component analysis (PCA) have been widely implemented to explore the origins of metals in groundwater [2,14]. The correlation between metals in groundwater in a watershed can reflect that the sources of these metals may be the same. Results of correlation analysis, as illustrated in Figure 5, indicated that a strong positive correlation between As and Pb, Pb and Cr(VI), Cu and Cr(VI) and Cd, and Cr(VI) and Cd was found, with significance at the 0.01 level ($p \leq 0.01$). A relatively strong correlation between As and Se, Se and Cu, Pb and Zn, and Cu and Zn was also found, at the $p \leq 0.05$ level. Positive correlations between the analyzed metals in the groundwater reflect that they may have common origins. In addition, no correlation was found between Mn and other metals in groundwater, indicating that the origins of Mn in groundwater in the ILB are different from other metals.

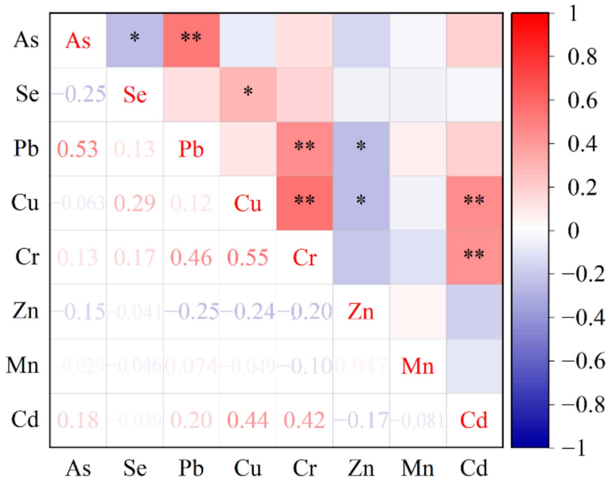

Figure 5. Pearson correlation of metals in groundwater in the ILB. * $p \leq 0.05$; ** $p \leq 0.01$; Cr represents Cr(VI) here.

In the present study, the mean contents of the eight metals in the groundwater in the ILB were lower than the Class III thresholds of the Standard for Groundwater Quality of China (GB/T 14848–2017), indicating that anthropogenic activities have no obvious effects on the enrichment of metals in groundwater [16]. Therefore, natural sources (geological background) are likely the main controlling factor for metals in groundwater in the ILB. However, the spatial distribution of contents, pollution levels, and potential ecological risks of the eight metals showed a "dotted-distribution" feature, indicating that anthropogenic activities in some specific areas may have significant impacts on the metal enrichment of groundwater.

Principal component analysis (PCA) is a method for taking high-dimensional data by compressing the wide range of analyzed data into correlated variables based on the dependencies between the variables [20]. In the present study, the PCA was used to further identify the possible origins of metals in groundwater in this study. Table 5 shows the loadings of rotational factors based on the varimax Kaiser normalization, and the percentages of total variance and cumulative variance for all groundwater samples are also given. As shown in Table 5, three eigenvalues (higher than 1) were identified in the 75 groundwater samples for eight metals that represent 62.435% of the total variance.

Table 5. Results of principal component analysis.

Variables	As	Se	Pb	Cu	Cr(VI)	Zn	Mn	Cd	% of Variance	Cumulative %
PC1	0.381	0.233	0.652	0.687	0.809	−0.477	−0.117	0.653	30.242	30.242
PC2	0.797	−0.602	0.466	−0.498	−0.149	−0.086	0.151	−0.043	18.966	49.207
PC3	−0.033	0.513	0.397	−0.057	0.007	−0.015	0.690	−0.396	13.228	62.435

PC1 is the most important principal component with 30.242% of the whole variance. PC1 comprised six metals including Pb, Cu, Cr(VI), Zn, and Cd, with relatively higher positive loading values of Pb (0.652), Cu (0.687), Cr(VI) (0.809), and Cd (0.653), as well as weak negative loading with Zn (−0.477). Both the mean and maximum contents of Cu, Zn, and Cd in the PC1 were lower than the corresponding Class III threshold values of the GB/T 14848–2017, indicating possible natural sources of these metals. However, the maximum contents of Pb and Cr(VI) in PC1 surpassed the corresponding Class III threshold values, indicating possible point source pollution of these metals. The spatial distribution pattern of these metals in PC1 showed a "dotted-distribution" feature. It indicates that these five metals in PC1 are likely correlated with anthropogenic factors in some specific sampling sites. Related studies indicate that the possible sources of Cu and Cd in groundwater are often related to agricultural activities, such as fertilizers, pesticides, insecticides, and herbicides [17,21]. Also, Pb in groundwater is considered as an anthropogenic metal [17,20,42]. Origins of Cr in groundwater are also related to human activities such as agricultural or industrial wastewater [44]. Based on this, PC1 can be identified as having a natural and anthropogenic composite source.

PC2 accounted for 18.966% of the entire variance. It comprised two metals, As and Se, with relatively higher positive loading values of As (0.797), as well as negative loading with Se (−0.602). The maximum contents of As and Se in PC2 surpassed the corresponding Class III threshold values of the GB/T 14848–2017, indicating possible point source pollution of these metals. Related studies indicate that the possible sources of As and Se in groundwater are often related to anthropogenic activities, such as agriculture, industry, and mining [20,45,46]. However, the highly polluted areas of As and Se were observed around the central parts and western of Jing County and the eastern areas of Arshang County, where the main mining areas in the Ibinur Lake Basin are located, as illustrated in Figures 1 and 3. Therefore, PC2 can be identified as having an anthropogenic source.

PC3 accounted for 13.228% of the entire variance, with relatively higher positive loading values of Mn (0.690). Mn in groundwater is mainly controlled by natural factors, based on previous studies [15,16]. The Ibinur Lake Basin is a fluvial sedimentary system, mainly composed of silty clay and sand, containing silicate, alumina, and permanganate [47]. The Mn in the rock is weathered and infiltrates into the groundwater under the influences of irrigation water and precipitation in the ILB. Therefore, PC3 can be identified as having a natural composite source.

In recent years, metal pollution of groundwater in the northwest arid zones of China has attracted more attention due to its impacts on the oasis stability and environmental safety of groundwater resources. The ecological security of the ILB is closely related to the sustainable development of the "economic belt" on the northern slope of the Tianshan Mountains. Results of present study pointed out that the levels of pollution and potential ecological risk caused by metals in groundwater in the ILB are not very high. However, in some specific areas in the ILB, the groundwater has been polluted to varying degrees due to significant enrichment of metals. Especially, the pollution level and potential ecological risk of As in groundwater in the ILB have reached a relatively high level. As is a carcinogenic metal element with high toxicity and was recognized as a Class I carcinogen by the International Agency for Research on Cancer (IARC) of the WHO in 2017. The Ministry of Ecology and Environment of China (MEE) listed As and arsenic compounds in the "List of Toxic and Harmful Water Pollutants (the First Batch)". As is also identified as the only carcinogen by the U.S. Environmental Protection Agency (US EPA) that causes cancer through drinking water [48]. High-arsenic groundwater, however, has become a serious problem worldwide due to arsenic poisoning by long-term consumption of it. Therefore, the pollution and probable ecological risks of As in the groundwater in the ILB should be paid special attention, considering its higher levels and pollution risks in this region.

Moreover, Xinjiang is one of the high-arsenic groundwater distribution areas in the NW arid zone of China. The Junggar Basin and the eastern and western parts of the Tarim Basin of Xinjiang are typical high-arsenic groundwater areas in China [49]. The standard-exceeding ratio of As in groundwater in the Changji, Karamay, and Chochek districts in Xinjiang is higher than 10% [50]. The Kuitun district of Xinjiang is also a main and typical high-arsenic groundwater distribution area, with about 73% of the groundwater being high-arsenic water [51]. Furthermore, As content in rural drinking water in the Aksu region of Xinjiang is also at a high level and posing a potential health risk of As poisoning caused by drinking water intake [52]. As contents in groundwater in the Manas River Basin of Xinjiang are very high, with high-arsenic groundwater in this basin accounting for about 62.9% [53]. Nevertheless, the high-arsenic groundwater distribution area in the deep confined aquifer of the alluvial plain in the Shihezi region of Xinjiang is about 276 km^2 [54]. It can be seen that under the influences of relatively higher geological background and intensive anthropogenic activities, the pollution risk of As in the groundwater in Xinjiang is becoming increasingly prominent, which is threatening the ecological security and the sustainable agriculture of the northwestern arid zones of China to a certain extent.

Overall, the present study indicated that As is the main pollution factor, while As and Se are the potential ecological risk factors in groundwater in the Ibinur Lake Basin. The future increase in population loads in the ILB will make its groundwater susceptible to pollution through increased agricultural activities, urbanization, industrialization, and sewage discharge. However, it is suggested that seasonal studies of groundwater in the ILB are needed for more accurate risk assessment of metals and their sources. Combining geochemical and isotopic characterization of the groundwater can provide deeper insights into the origins of metals. Further, the use of advanced water treatment technology for metals, especially for As, can help mitigate the probable pollution risk posed by hazardous metals in groundwater in the basin.

5. Conclusions

Metals in groundwater are a potential threat to the ecosystem and humans. Due to extensive anthropogenic activities, the Ibinur Lake Basin (ILB) in the northwest arid zone of China has faced an environmental problem of metal pollution of groundwater. In the present study, the detailed analyses showed that the mean contents of As, Se, Pb, Cu, Cr(VI), Zn, Mn, and Cd in groundwater in the ILB are all below the Class III thresholds of the GB/T 14848–2017. However, the maximum contents of As, Se, Pb, Cr(VI), and Mn in groundwater were equal to 2.42, 1.2, 1.85, 2.94, and 4.23 times the corresponding national standard. The mean P_i value of metals in groundwater in the ILB can be ranked as: As > Se > Pb > Mn > Cr(VI) > Cd > Zn > Cu, at the pollution-free level for each metal. The mean NPI values of analyzed metals in groundwater in the ILB showed a pollution-free level. The mean E_i value of the investigated metals in groundwater can be ranked as: Se > As > Pb > Cd > Mn > Cr(VI) > Zn > Cu. The RI values of metals in groundwater were in the range of 2.31–39.87, with a mean value of 13.96, at the probable low ecological risk level.

Distribution of contents, pollution levels, and probable ecological risks of metals in groundwater in the ILB were found to be substantially heterogeneous, according to the "dotted-distribution" patterns of them. As and Se in groundwater in the ILB originated from anthropogenic sources, whereas Mn mainly originated from natural factors, and Pb, Cu, Cr(VI), Zn, and Cd were correlated with both natural and anthropogenic sources. On the whole, As was selected as the main pollution factor, while As and Se were selected as the main ecological risk factors in groundwater in the ILB. Finally, groundwater in some specific areas in the ILB showed relatively higher ecological risk levels due to point source pollution of groundwater. Therefore, human activities, especially agriculture and mining, in the ILB should be cautious. Results of this study highlight the importance of a regular monitoring of metals in groundwater in the Ibinur Lake Basin.

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