Heavy Metals and Related Human Health Risk Assessment for River Waters in the Issyk–Kul Basin, Kyrgyzstan, Central Asia

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Abstract: The water resources of Central Asia play an important role in maintaining the fragile balance of ecosystems and the sustainable development of human society. However, the lack of research on the heavy metals in river waters has a far-reaching influence on public health and the sustainable development in Central Asia. In order to reveal the possible sources of the heavy metals and to assess the associated human health risks, thirty-eight water samples were collected from the rivers of the Issyk–Kul Basin during the period with low river flow (May) and the period with high river flow (July and August), and the hydrochemical compositions and major ions of heavy metals were analyzed. No changes in hydrochemical facies were observed between the two periods and the river water type was calcium bicarbonate. Carbonate dissolution and silicate weathering controlled the variation of cations and anions in river waters from the Issyk–Kul Basin. There were some differences in the sources of heavy metals in water bodies between the two periods. During the period with low river flow, heavy metals (Cr) were closely clustered with major ions, indicating that they were mainly affected by water–rock interactions. During the period with high river flow, all heavy metals studied in this paper had different sources of major ions, and the heavy metals maybe influenced by human activities. From the human health risk assessment, the hazard quotients for all samples were less than 1, reflecting that there was no noncarcinogenic risk in the river waters of the Issyk–Kul Basin during the two sampling periods. However, the water samples with carcinogenic risk of arsenic exceeding the threshold \(10^{-4}\) accounted for 21.1% of the total, indicating that there were some certain carcinogenic hazards for human health via water drinking with direct oral ingestion. The results are of certain significance for the utilization and protection of water resources in the basin as well as the protection of public health.

Keywords: heavy metals; human health risk; river waters; Issyk–Kul Basin; Central Asia

1. Introduction

The water resources of Central Asia play an important role in maintaining the fragile balance of ecosystems and the sustainable development of human society [1–3]. The shortage of water resources in Central Asia represented by the Aral Sea crisis has aroused concern worldwide [4,5]. At present, most studies focus on water quantity and water management under the influences of
recent strong fluctuations in climate and increasing human activity in Central Asia [6–10]. For water security in Central Asia, it is also necessary to carry out research focused on water quality [11,12]. The problem of water pollution caused by industrial, agricultural and domestic wastewater is becoming increasingly serious; currently, the impact of water quality on human health in Central Asia had begun to be highlighted [13–15]. Compared with the comprehensive study of water quantity and its influencing factors, research on water quality and its influencing factors needs to be strengthened. Especially, heavy metal, as one of the pollutants in river waters, cause severe threats to humans and the environment [16]. Heavy metal contamination will induce human health risks for direct drinking and via food crop consumption with water irrigation [17,18]. On the one hand, river water resources in Central Asia are mainly used for farmland irrigation [19,20]; on the other hand, according to the field investigation, limited to the level of economic development, some people use surface river water as a direct source of drinking water. Therefore, it is of great practical significance to study heavy metals and their health risks in the rivers of Issyk–Kul Basin.

The Issyk–Kul Basin (22,080 km$^2$) is the largest basin in the Tien Shan Mountains [21], which covers 11.1% of the country’s land area (198,500 km$^2$), and the Issyk–Kul Lake (6236 km$^2$) covers 28.2% of the basin’s surface area [22]. For the Issyk–Kul Basin, the soils in the basin are mainly composed of Haplic Kastanozems and Mollic Leptosols [23]. The hydrochemical composition of rivers not only affects the safety of agricultural irrigation and drinking water but also directly affects the ecological security of Issyk–Kul Lake. However, remarkably little is known about the hydrochemical composition of the basin waters, especially regarding heavy metals. At present, uranium pollution in natural waters [24,25] and heavy metals in surface soils [26] of Issyk–Kul Basin has attracted attention, but other heavy metals in river waters which have potential effects on human health are still uninvestigated. As we know, the problems from heavy metal water pollution [27,28] are becoming increasingly serious, and it is very important to evaluate the sources of heavy metals and perform a related human risk assessment for the river water of the Issyk–Kul Basin.

Based on the above considerations, 38 river water samples were collected from the Issyk–Kul Basin during the period with low river flow ($n = 19$) and the period with high river flow ($n = 19$), and the heavy metals and major ions in river waters were analysed in this study. Specifically, this study aimed to reveal the characteristics of heavy metals in river waters and identify their temporal differences to perform a human health risk assessment. The results are of certain significance for the utilization and protection of water resources in the basin as well as the protection of public health.

2. Materials and Methods

2.1. Sampling and Analysis

In the study area of the Issyk–Kul Basin, samples were collected from 19 sampling points during the low river flow period (May 2017), and 19 were collected from the same points during the high flow period (July and August 2017) (Table 1 and Figure 1), for a total of 38 samples. Due to the influence of mountain topography, the precipitation in Issyk–Kul Lake basin varies greatly from north to south, and the precipitation in the south is significantly higher than that in the north [29], which leads to the long-term interruption of the rivers in the north side of the basin. River water samples that were rinsed three times in situ were collected in 1.5–L polyethylene terephthalate bottles. The subsamples were filtered through a 0.45–µm filter and stored in a polyethylene tube for subsequent laboratory measurements. Before sampling and analysis of cations and heavy metals, samples were mixed with 10% HNO$_3$ and three drops of HNO$_3$ (65%) for subsample acidification (pH < 2). A HI 9828 multiparameter water quality meter (Hanna Instruments, Villafranca Padovana, Italy) was used to measure pH, electrical conductivity (EC) and total dissolved solids (TDS) in situ. HCO$_3$ and CO$_3$ were determined by potentiometric titration using a G20 compact titrator (Mettler Toledo AG, Greifensee, Switzerland). The major ions were measured by a Dionex ICS 900 ionic chromatography system (Thermo Fisher Scientific Inc., Waltham, MA, USA) [30]. The charge balance error (CBE)
percentage [31,32] was used to evaluate the accuracy of the results for the main cations and anions, and the CBE was less than 5%. The contents of dissolved heavy metals in river waters, including zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb), total chromium (Cr) and arsenic (As), were determined by inductively coupled plasma mass spectrometry with an Agilent 8800 system (Agilent Technologies, Santa Clara, CA, USA). The blank solution of 1% nitric acid was measured for 21 consecutive times, and the concentration corresponding to 4.6 standard deviations was used as the detection limit for Zn (0.003 µg L⁻¹), Cu (0.003 µg L⁻¹), Cd (0.003 µg L⁻¹), Pb (0.001 µg L⁻¹), Cr (0.02 µg L⁻¹), and As (0.006 µg L⁻¹). The standard sample was measured 12 times and its precision and accuracy was calculated. Experiments show that the precision of heavy metal elements is between 0.74 % and 3.17 %. The aforementioned analyses were performed at the Research Center for Ecology and the Environment of Central Asia (Bishkek), Kyrgyzstan.

2.2. Human Health Risk Assessment

The noncarcinogenic effects exist [35,36]. If the noncarcinogenic hazard quotient (HQ) < 1, no noncarcinogenic risks are suggested; otherwise, carcinogenic risks are suggested. The noncarcinogenic risk due to the exposure to a heavy metal X is calculated as:

\[
HQ_X = \frac{ADD_X \times CSF_X}{RfD_X} \leq 1
\]

where

- ADD: average daily dose of exposure through water absorption;
- CSF: cancer slope factor;
- RfD: reference value for heavy metals.

Table 1. Geographic information for sampling points in the Issyk–Kul Basin during the period with low river flow (L) and period with high river flow (H).

| NO  | Latitude (°N) | Longitude (°E) | Elevation (m) | River         | Sampling Date (L) | Sampling Date (H) |
|-----|---------------|----------------|---------------|---------------|-------------------|-------------------|
| K01 | 42.03494      | 77.60447       | 2210          | Barskoon      | 21 May 2017       | 05 August 2017    |
| K02 | 42.12865      | 76.58558       | 1935          | Ak-Terek      | 23 May 2017       | 06 August 2017    |
| K03 | 42.18226      | 77.56650       | 1615          | Ak-Terek      | 21 May 2017       | 05 August 2017    |
| K04 | 42.22949      | 77.95718       | 1950          | Juuku         | 20 May 2017       | 04 August 2017    |
| K05 | 42.24544      | 76.35191       | 1850          | Tuura-Suu     | 23 May 2017       | 07 August 2017    |
| K06 | 42.28658      | 78.10559       | 2023          | Chon Kyzyl-Suu| 19 May 2017       | 03 August 2017    |
| K07 | 42.31846      | 76.39488       | 1664          | Tuura-Suu     | 23 May 2017       | 07 August 2017    |
| K08 | 42.31882      | 77.90189       | 1693          | Juuku         | 20 May 2017       | 04 August 2017    |
| K09 | 42.34861      | 77.99841       | 1736          | Chon Kuzul-Suu| 19 May 2017       | 03 August 2017    |
| K10 | 42.43021      | 78.42594       | 1959          | Karakol       | 18 May 2017       | 02 August 2017    |
| K11 | 42.45497      | 78.54606       | 1976          | Ak-Suu        | 18 May 2017       | 01 August 2017    |
| K12 | 42.49698      | 78.37384       | 1722          | Karakol       | 18 May 2017       | 02 August 2017    |
| K13 | 42.51473      | 78.52718       | 1774          | Ak-Suu        | 18 May 2017       | 01 August 2017    |
| K14 | 42.59347      | 78.38598       | 1634          | Jurgalan      | 17 May 2017       | 31 July 2017      |
| K15 | 42.65318      | 78.88481       | 1903          | Jurgalan      | 17 May 2017       | 31 July 2017      |
| K16 | 42.71734      | 77.47164       | 1745          | Chon Ak-Suu   | 15 May 2017       | 29 July 2017      |
| K17 | 42.73564      | 78.83572       | 1857          | Tyup          | 16 May 2017       | 30 July 2017      |
| K18 | 42.73828      | 78.34636       | 1623          | Tyup          | 16 May 2017       | 30 July 2017      |
| K19 | 42.75582      | 77.47808       | 1862          | Chon Ak–Suu   | 15 May 2017       | 29 July 2017      |

Figure 1. Location map of the Issyk–Kul Basin in Kyrgyzstan (A) and the distribution of the river water samples (B).
2.2. Human Health Risk Assessment

Direct oral ingestion is the main pathway of heavy metal exposure from aqueous systems. The human health risk assessment for noncarcinogens was calculated using Equations (1) and (2) [27,33–35]. If the noncarcinogenic hazard quotient (HQ) < 1, no noncarcinogenic risks are suggested; otherwise, noncarcinogenic effects exist [35,36].

\[
ADD = C_h \times \frac{IngR \times EF \times ED}{BW \times AT} \tag{1}
\]

\[
HQ = \frac{ADD}{RfD} \tag{2}
\]

where HQ: noncarcinogenic hazard quotient; ADD: average daily dose of exposure through water absorption; \(C_h\): concentration of heavy metals in river waters, mg L\(^{-1}\); IngR: ingestion rate, 2 L/day [27]; EF: exposure frequency, 350 day/year [27]; ED: exposure duration, 70 years [33]; BW: body weight, 70 kg [27]; AT: average time, 25550 days [33]; RfD: reference value for heavy metals [37].

Risks from carcinogens were evaluated by Equation (3) [38], and the acceptable range of CR by the USEPA was \(10^{-6}\) to \(10^{-4}\) [39].

\[
CR = ADD \times CSF \tag{3}
\]

where ADD: average daily dose of exposure through water absorption; CSF: cancer slope factor [37].

3. Results

For the river waters of the Issyk–Kul Basin shown in Tables 2 and 3, the concentration of Zn varied between 0.634 and 9.75 µg L\(^{-1}\), with a mean of 5.43 µg L\(^{-1}\), during the period with low river flow, and the concentration of Zn varied between 0.359 and 26.3 µg L\(^{-1}\), with a mean of 9.60 µg L\(^{-1}\), during the period with high river flow. The Cu concentration varied between 1.08 and 8.51 µg L\(^{-1}\), during the period with low river flow, with a mean of 3.64 µg L\(^{-1}\), and it varied between 0.30 and 12.5 µg L\(^{-1}\) during the period with high river flow, with a mean of 4.23. The Pb level varied between 0 and 2.19 µg L\(^{-1}\), with a mean of 1.01 µg L\(^{-1}\), during the period with low river flow, and from 0 to 4.06 µg L\(^{-1}\), with a mean of 1.52 µg L\(^{-1}\), during the period with high river flow. As varied between 0.461 and 2.08 µg L\(^{-1}\), with a mean of 1.17, during the period with low river flow, and from 0.134 to 3.03 µg L\(^{-1}\), with a mean of 1.25, during the period with high river flow. The Cr value varied between 0.01 and 0.05 mg L\(^{-1}\), with a mean of 0.03 mg L\(^{-1}\), during the period with low river flow, and between 0.01 and 0.07 mg L\(^{-1}\), with a mean of 0.036 mg L\(^{-1}\), during the period with high river flow.
Table 2. Environmental indicators of river water in the Issyk–Kul Basin during the period with low river flow (L, \( n = 19 \)).

| Indicators | Minimum | Maximum | Mean | Median | Standard Deviation | Standard Error |
|------------|---------|---------|------|--------|--------------------|----------------|
| Zn\(^{a}\) (µg L\(^{-1}\)) | 0.634 | 9.75 | 5.43 | 5.06 | 2.13 | 0.49 |
| Cu\(^{a}\) (µg L\(^{-1}\)) | 1.08 | 8.51 | 3.64 | 3.54 | 2.29 | 0.526 |
| Pb\(^{a}\) (µg L\(^{-1}\)) | 0.01 | 2.19 | 1.01 | 0.9 | 0.641 | 0.147 |
| Cr\(^{a}\) (mg L\(^{-1}\)) | 0.01 | 0.05 | 0.032 | 0.03 | 0.011 | 0.003 |
| As\(^{a}\) (µg L\(^{-1}\)) | 0.461 | 2.08 | 1.17 | 1.04 | 0.496 | 0.114 |
| pH | 7.55 | 8.94 | 8.2 | 8.11 | 0.472 | 0.108 |
| TDS (mg L\(^{-1}\)) | 110 | 355 | 204 | 172 | 71.3 | 16.3 |
| EC (µS cm\(^{-1}\)) | 60 | 299 | 145 | 115 | 71.1 | 16.3 |
| Ca\(^{2+}\) (mg L\(^{-1}\)) | 14.7 | 44.6 | 25.2 | 20.9 | 8.8 | 2.02 |
| Mg\(^{2+}\) (mg L\(^{-1}\)) | 0.522 | 8.23 | 2.86 | 1.87 | 2.33 | 0.534 |
| Na\(^{+}\) (mg L\(^{-1}\)) | 1.1 | 2.65 | 1.5 | 1.36 | 0.407 | 0.093 |
| K\(^{+}\) (mg L\(^{-1}\)) | 78.6 | 250 | 140 | 125 | 44.8 | 10.3 |
| HCO\(_3\)\(^{-}\) (mg L\(^{-1}\)) | 8.21 | 53.8 | 23.8 | 17.6 | 13.9 | 3.19 |

\(^{a}\): Dissolved heavy metals of river waters in the Issyk–Kul Basin.

Table 3. Environmental indicators of river water in the Issyk–Kul Basin during the period with high river flow (H, \( n = 19 \)).

| Indicators | Minimum | Maximum | Mean | Median | Standard Deviation | Standard Error |
|------------|---------|---------|------|--------|--------------------|----------------|
| Zn\(^{a}\) (µg L\(^{-1}\)) | 0.359 | 26.30 | 9.60 | 8.2 | 6.79 | 1.56 |
| Cu\(^{a}\) (µg L\(^{-1}\)) | 0.297 | 12.5 | 4.23 | 3.09 | 3.62 | 0.831 |
| Pb\(^{a}\) (µg L\(^{-1}\)) | 0.01 | 0.07 | 0.036 | 0.03 | 0.015 | 0.003 |
| Cr\(^{a}\) (mg L\(^{-1}\)) | 0.134 | 3.03 | 1.25 | 0.869 | 0.889 | 0.204 |
| pH | 7.79 | 8.84 | 8.25 | 8.17 | 0.311 | 0.071 |
| TDS (mg L\(^{-1}\)) | 119 | 392 | 217 | 186 | 89.6 | 20.6 |
| EC (µS cm\(^{-1}\)) | 71 | 352 | 170 | 138 | 88 | 20.2 |
| Ca\(^{2+}\) (mg L\(^{-1}\)) | 17.4 | 53 | 30.7 | 27.3 | 11.9 | 2.72 |
| Mg\(^{2+}\) (mg L\(^{-1}\)) | 1.64 | 13.4 | 5.42 | 4.34 | 3.46 | 0.795 |
| Na\(^{+}\) (mg L\(^{-1}\)) | 0.744 | 9.12 | 3.07 | 1.27 | 2.78 | 0.637 |
| K\(^{+}\) (mg L\(^{-1}\)) | 1.1 | 2.65 | 1.5 | 1.36 | 0.407 | 0.093 |
| HCO\(_3\)\(^{-}\) (mg L\(^{-1}\)) | 0.838 | 2.46 | 1.5 | 1.45 | 0.395 | 0.091 |
| SO\(_4\)\(^{2-}\) (mg L\(^{-1}\)) | 84.3 | 287 | 144 | 111 | 62.4 | 14.3 |
| Cl\(^{-}\) (mg L\(^{-1}\)) | 6.9 | 49.2 | 27.4 | 21.8 | 14.2 | 3.26 |
| Ca\(^{2+}\) (mg L\(^{-1}\)) | 0.471 | 6.37 | 2.23 | 1.13 | 1.9 | 0.437 |

\(^{a}\): Dissolved heavy metals of river waters in the Issyk–Kul Basin.

During the period with low river flow (May 2017), the pH varied from 7.55 to 8.94, with a mean of 8.20. During the period with high river flow (July and August 2017), the pH varied from 7.79 to 8.84, with a mean of 8.25. The EC ranged between 60 and 299 µS cm\(^{-1}\), with a mean of 144.53 µS cm\(^{-1}\), during the period with low river flow, and from 71 to 352 µS cm\(^{-1}\), with a mean of 170 µS cm\(^{-1}\), during the period with high river flow. The TDS ranged from 110 to 355 mg L\(^{-1}\), with a mean of 204 mg L\(^{-1}\), during the period with low river flow, and the TDS varied from 119 to 392 mg L\(^{-1}\), with a mean of 217 mg L\(^{-1}\), during the period with high river flow.

As seen from the table showing statistics on the concentration of major ions in the river waters, HCO\(_3\)\(^{-}\) was found in the highest concentration. No changes in hydrochemical facies were observed between the two periods. As seen in the Durov diagrams \([40,41]\), the river water type was calcium bicarbonate (Figure 2).
Figure 2. Durov diagram for the water samples from the Issyk–Kul Basin. The grey dots correspond to the samples during the period with low river flow (L, n = 19) and the black crosses correspond to the period with high river flow (H, n = 19).

4. Discussion

In order to determine the detailed factors affecting water chemistry, Gibbs diagrams [42–44] and mixing diagrams [42,45–47] were used. For the Gibbs and mixing diagrams, the concentrations of major ions were transformed to milliequivalents per liter [48] as seen in Figure 3. This suggests that river samples plotted in the dominant area are dominated by rock, which suggests that major ions in river water from the Issyk–Kul Basin are mainly controlled by the process of water–rock interactions. The river samples were located between the two end–members of carbonate and silicate (Figure 3). Figure 3 shows that river water samples from the Issyk–Kul basin had high Ca/Na ratios, indicating that the importance of carbonate dissolution is greater than that of silicate weathering.

The statistical characteristics of hydrochemical data including major ions and heavy metals (Table 2) cannot explain the relationship between various chemical proxies, so we used the hierarchical cluster analysis (HCA) [49] to clarify the possible influences on heavy metals in the river waters of the Issyk–Kul Basin [50–53]. The chemical compositions of the river waters were analysed at different periods using HCA. The results showed that there were some differences in the sources of heavy metals in water bodies between the two periods. During the period with low river flow, the heavy metal element Cr was closely related to calcium, bicarbonate, and potassium ions (Figure 4). This indicates that the heavy metal elements were mainly affected by the interaction between water and rock and mainly arise from the natural weathering of rock. However, the relationship between other heavy metals (Pb, Zn, Cu, and As) and the major ions was more distant, which reflects different ion sources and suggests effects from human activities (Figure 4). For the period with high river flow, heavy metals were clustered far from the major ions, reflecting different natural origins of these major ions (Figure 5). It can be concluded that heavy metals are affected by different factors during different hydrological periods.
In order to determine the detailed factors affecting water chemistry, Gibbs diagrams [42–44] and mixing diagrams [42, 45–47] were used. For the Gibbs and mixing diagrams, the concentrations of major ions were transformed to milliequivalents per liter [48] as seen in Figure 3. This suggests that river samples plotted in the dominant area are dominated by rock, which suggests that major ions in river water from the Issyk–Kul Basin are mainly controlled by the process of water–rock interactions. The river samples were located between the two end−members of carbonate and silicate (Figure 3). Figure 3 shows that river water samples from the Issyk–Kul basin had high Ca/Na ratios, indicating that the importance of carbonate dissolution is greater than that of silicate weathering.

The Issyk–Kul Basin is an important international tourist area, and the number of international tourists visiting this area can be quite high. The noncarcinogenic and carcinogenic risks related to the water in this area have important practical significance in public health. From the calculated results (Table 4), the hazard quotient for noncarcinogenic risk was less than one during the two sampling periods, reflecting that no noncarcinogenic risk was posed by heavy metals in the river waters of the Issyk–Kul Basin; however, the heavy metal Cr was present in concentrations close to the threshold value, which needs more attention. From the carcinogenic risk index, the maximum value of the heavy metal As was more than $10^{-4}$ (maximum was $1.25 \times 10^{-4}$) during the period with high river flow, and the carcinogenic risk exceeding the threshold account for 21.1% of the total samples, which indicates that there is a certain carcinogenic risk to human health (Figure 6). Although it is not more than $10^{-4}$, during the period with low river flow, it is also close to the threshold and needs a high degree of attention.
The statistical characteristics of hydrochemical data including heavy metals in the river waters from Issyk-Kul Basin during the period with low river flow, it is also close to the threshold and needs a high degree of attention.

From the carcinogenic risk index, the maximum value of the heavy metal element Cr was closely related to calcium, bicarbonate, and potassium ions (Figure 4). It can be concluded that heavy metals are affected by different factors and ion sources and suggests effects from human activities (Figure 5).

The possible influences of these major ions and heavy metals during the period with high river flow (H) and the period with low river flow (L).

The hierarchical cluster analysis (HCA) [49] to clarify the possible influences of these major ions and heavy metals in the river waters of the Issyk-Kul Lake Basin during the period with low river flow.

For the period with high river flow, heavy metals were clustered far from the major ions, reflecting different ion sources and suggests effects from human activities (Figure 5).

Table 2 cannot explain the relationship between various chemical proxies, so we used the dendrogram using Ward Linkage to analyze the relationship between various chemical indicators (Table 2).

The chemical compositions of the river waters were analyzed at different periods using HCA. The results showed that there were some differences in the sources of the two sampling periods. During the period with low river flow, the carcinogenic risk exceeding the threshold account for 21.1% of the total samples, which indicates that there is a certain carcinogenic risk to human health (Figure 6). Although it is not more than 10⁻³, during the period with high river flow, the carcinogenic risk exceeded the threshold account for 21.1% of the total samples, which needs more attention.

Figure 4. Hierarchical clustering analysis of major ionic and dissolved heavy metal elements in the river waters from Issyk-Kul Basin during the period with low river flow.

Figure 5. Hierarchical clustering analysis of major ionic and dissolved heavy metal elements in the river waters from Issyk-Kul Basin during the period with high river flow.
Table 4. Human health risk assessment including the noncarcinogenic hazard quotients (non. HQ) and carcinogenic risks (Cancer. R) from heavy metals in the river waters of the Issyk–Kul Basin during the period with high river flow (H) and the period with low river flow (L).

| Stage | Heavy Metals | Minimum a | Maximum b | Mean | Median |
|-------|--------------|-----------|-----------|------|--------|
| H     | Zn (non.HQ)  | 3.27 × 10^{-5} | 2.40 × 10^{-3} | 8.76 × 10^{-4} | 7.49 × 10^{-4} |
|       | Cu (non. HQ) | 2.04 × 10^{-4} | 8.59 × 10^{-3} | 2.89 × 10^{-3} | 2.12 × 10^{-3} |
|       | Pb (non. HQ) | 0          | 3.18 × 10^{-4} | 1.19 × 10^{-4} | 1.03 × 10^{-4} |
|       | Cr (non. HQ) | 9.13 × 10^{-2} | 6.39 × 10^{-1} | 3.32 × 10^{-1} | 2.74 × 10^{-1} |
|       | As (non. HQ) | 1.22 × 10^{-2} | 2.77 × 10^{-1} | 1.14 × 10^{-1} | 7.93 × 10^{-2} |
|       | As (Cancer.R)| 5.51 × 10^{-6} | 1.25 × 10^{-4} | 5.12 × 10^{-5} | 3.57 × 10^{-5} |
|       | Zn (non.HQ)  | 5.79 × 10^{-5} | 8.90 × 10^{-4} | 4.96 × 10^{-4} | 4.62 × 10^{-4} |
|       | Cu (non. HQ) | 7.42 × 10^{-4} | 5.83 × 10^{-3} | 2.49 × 10^{-3} | 2.42 × 10^{-3} |
| L     | Pb (non. HQ) | 8.05 × 10^{-7} | 1.72 × 10^{-4} | 7.90 × 10^{-5} | 7.04 × 10^{-5} |
|       | Cr (non. HQ) | 9.13 × 10^{-2} | 4.57 × 10^{-1} | 2.89 × 10^{-1} | 2.74 × 10^{-1} |
|       | As (non. HQ) | 4.21 × 10^{-2} | 1.89 × 10^{-1} | 1.06 × 10^{-1} | 9.48 × 10^{-2} |
|       | As (Cancer.R)| 1.89 × 10^{-5} | 8.53 × 10^{-5} | 4.79 × 10^{-5} | 4.27 × 10^{-5} |

a: The minimum value of heavy metals (C_{b}, Equation (1)) was shown in Table 2. b: The maximum value of (C_{b}, Equation (1)) was shown in Table 2.

Figure 6. Carcinogenic risks (Cancer. R) for the arsenic in the river waters of the Issyk–Kul Basin during the period with high river flow (H, n = 19) and the period with low river flow (L, n = 19).

Arsenic is a Class–A human carcinogen [54], and the exposure to arsenic through direct drinking of arsenic–contaminated water or consumption of arsenic–contaminated edible crops is considered a worldwide life–threatening problem [55–57]. Through human health risk assessment, the heavy metal of Arsenic in river waters has shown some harm to human health. Based on this, the exact material source of arsenic and its migration and transformation in water bodies requires in–depth research. However, based on the existing data and other issues, it is not possible to elaborate on the above issues, and we need to carry out in–depth research in the next step.

Although the risks of noncarcinogenic and carcinogenic effects are low, the heavy metals in river waters may be affected by human activities, especially during wet periods with high river flow. As the Issyk Lake area is an internationally famous area for tourism and one of the main agricultural and livestock production areas in Kyrgyzstan, environmental protection of this area is very important. Thus, the treatment and discharge of sewage and the protection of the aquatic environment need to be given enough attention to avoid repeating the traditional pattern of experiencing pollution problems before solutions are implemented.
5. Conclusions

Based on the concentrations of major ions and heavy metals in river water samples, the possible sources of heavy metals in the Issyk–Kul Basin, Kyrgyzstan, Central Asia, and related human health risks were revealed. The results were as follows:

Carbonate dissolution and silicate weathering accounted for the variation in the major ions of river waters from the Issyk–Kul Basin. No changes in hydrochemical facies were observed between the two sampling periods, and all water samples belong to the type of calcium bicarbonate.

During the period with low river flow, the heavy metal Cr was mainly affected by water–rock interactions, and the sources of other heavy metals were different from the major ions. During the period with high river flow, all heavy metals studied in this paper had different sources of major ions, and the heavy metals were maybe influenced by human activities.

Based on the human health risk, the hazard quotients were less than 1, reflecting no noncarcinogenic risk for the heavy metals in the studied river waters. However, the water samples with carcinogenic risk for arsenic exceeding the threshold (10⁻⁴) account for 21.1% of the total, indicating that there was a certain carcinogenic risk in river water in this area.

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**References**

1. Jin, L.; Chen, F.; Morrill, C.; Otto-Bliesner, B.; Rosenbloom, N. Causes of early Holocene desertification in arid central Asia. *Clim. Dyn.* 2012, 38, 1577–1591. [CrossRef]
2. Chen, Y.; Li, W.; Deng, H.; Fang, G.; Li, Z. Changes in Central Asia’s Water Tower: Past, Present and Future. *Sci. Rep.* 2016, 6, 35458. [CrossRef] [PubMed]
3. Peachey, E.J. The Aral Sea basin crisis and sustainable water resource management in Central Asia. *J. Public Int. Aff.* 2004, 15, 1–20.
4. Wurtsbaugh, W.A.; Miller, C.; Null, S.E.; DeRose, R.J.; Wilcock, P.; Hahnenberger, M.; Howe, F.; Moore, J. Decline of the world’s saline lakes. *Nat. Geosci.* 2017, 10, 816. [CrossRef]
5. Micklin, P.P. Desiccation of the Aral Sea: A Water Management Disaster in the Soviet Union. *Science* 1988, 241, 1170. [CrossRef] [PubMed]
6. Deng, H.; Chen, Y. Influences of recent climate change and human activities on water storage variations in Central Asia. *J. Hydrol.* 2017, 544, 46–57. [CrossRef]
7. Siegfried, T.; Bernauer, T.; Guiennet, R.; Sellars, S.; Robertson, A.W.; Mankin, J.; Bauer–Gottwein, P.; Yakovlev, A. Will climate change exacerbate water stress in Central Asia? *Clim. Chang.* 2012, 112, 881–899. [CrossRef]
8. Li, Z.; Gui, J.; Wang, X.; Peng, Q.; Zhao, T.; Ouyang, C.; Guo, X.; Zhang, B.; Shi, Y. Water resources in inland regions of central Asia: Evidence from stable isotope tracing. *J. Hydrol.* 2019, 570, 1–16. [CrossRef]
9. Guan, X.; Yang, L.; Zhang, Y.; Li, J. Spatial distribution, temporal variation, and transport characteristics of atmospheric water vapor over Central Asia and the arid region of China. *Global Planet. Chang.* 2019, 172, 159–178. [CrossRef]
10. Zou, S.; Jili, A.; Duan, W.; Maeyer, D.P.; De Voorde, V.T. Human and Natural Impacts on the Water Resources in the Syr Darya River Basin, Central Asia. *Sustainability* 2019, 11, 3084. [CrossRef]
11. Gozlan, R.E.; Karimov, B.K.; Zadereev, E.; Kuznetsova, D.; Bruket, S. Status, trends, and future dynamics of freshwater ecosystems in Europe and Central Asia. *Inland Waters* 2019, 9, 78–94. [CrossRef]
12. Boboev, H.; Djainbekov, U.; Bekchanov, M.; Lamers, J.P.A.; Toderich, K. Feasibility of conservation agriculture in the Amu Darya River Lowlands, Central Asia. *Int. J. Agric. Sustain.* 2019, 17, 60–77. [CrossRef]
13. Bekturganov, Z.; Tussupova, K.; Berndtsson, R.; Sharapatova, N.; Aryngazin, K.; Zhanasova, M. Water Related Health Problems in Central Asia—A Review. Water 2016, 8, 219. [CrossRef]

14. Zhang, W.; Ma, L.; Abuduwaili, J.; Ge, Y.; Issanova, G.; Saparov, G. Distribution Characteristics and Assessment of Heavy Metals in the Surface Water of the Syr Darya River, Kazakhstan. Pol. J. Environ. Stud. 2020, 29, 979–988. [CrossRef]

15. Törnqvist, R.; Jarsjö, J.; Karimov, B. Health risks from large-scale water pollution: Trends in Central Asia. Environ. Int. 2011, 37, 435–442. [CrossRef][PubMed]

16. Cheng, S. Heavy metal pollution in China: Origin, pattern and control. Environ. Sci. Pollut. Res. 2003, 10, 192–198. [CrossRef]

17. Khan, M.U.; Malik, R.N.; Muhammad, S. Human health risk from Heavy metal via food crops consumption with wastewater irrigation practices in Pakistan. Chemosphere 2013, 93, 2230–2238. [CrossRef]

18. Wongsasuluk, P.; Chotpantarat, S.; Siri Wong, W.; Robson, M. Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand. Environ. Geochem. Health 2014, 36, 169–182. [CrossRef]

19. Saiko, T.A.; Zonn, I.S. Irrigation expansion and dynamics of desertification in the Circum–Aral region of Central Asia. Appl. Geogr. 2000, 20, 349–367. [CrossRef]

20. O’Hara, S.L. Lessons from the past: Water management in Central Asia. Water Policy 2000, 2, 365–384. [CrossRef]

21. De Grave, J.; Glorie, S.; Buslov, M.M.; Stockli, D.F.; McWilliams, M.O.; Bataley, V.Y.; Van den haute, P. Thermo–tectonic history of the Issyk–Kul basement (Kyrgyz Northern Tien Shan, Central Asia). Gondwana Res. 2013, 23, 998–1020. [CrossRef]

22. Hofer, M.; Peeters, F.; Aeschbach–Hertig, W.; Brennwald, M.; Holocher, J.; Livingstone, D.M.; Romanovski, V.; Kipfer, R. Rapid deep–water renewal in Lake Issyk–Kul (Kyrgyzstan) indicated by transient tracers. Limnol. Oceanogr. 2002, 47, 1210–1216. [CrossRef]

23. FAO. Harmonized World Soil Database (Version 1.2); FAO: Rome, Italy; IIASA: Laxenburg, Austria, 2012.

24. Torgoev, I.A.; Aleshyn, U.G.; Havenit, H.B. Impact of Uranium Mining and Processing on the Environment of Mountainous Areas of Kyrgyzstan. In Uranium in the Aquatic Environment; Springer: Berlin/Heidelberg, Germany, 2002; pp. 93–98.

25. Palemski, S.; Nikolaeva, I.; Saprykin, A.; Gavshin, V. Assessment of contamination of the Issyk–Kul’valley natural waters with uranium mine wastes. J. Phys IV (Proc.) 2003, 107, 1013–1015.

26. Ma, L.; Abuduwaili, J.; Li, Y.; Ge, Y. Controlling Factors and Pollution Assessment of Potentially Toxic Elements in Topsoils of the Issyk–Kul Lake Region, Central Asia. Soil Sediment. Contam. 2018, 27, 147–160. [CrossRef]

27. Liang, B.; Han, G.; Liu, M.; Yang, K.; Li, X.; Liu, J. Distribution, Sources, and Water Quality Assessment of Dissolved Heavy Metals in the Jiulongjiang River Water, Southeast China. Int. J. Environ. Res. Public Health 2018, 15, 2752. [CrossRef] [PubMed]

28. Dong, J.; Xia, X.; Zhang, Z.; Liu, Z.; Zhang, X.; Li, H. Variations in concentrations and bioavailability of heavy metals in rivers caused by water conservancy projects: Insights from water regulation of the Xiaolangdi Reservoir in the Yellow River. J. Environ. Sci. 2018, 74, 79–87. [CrossRef]

29. Ma, L.; Jilili, A.; Li, Y. Spatial differentiation in stable isotope compositions of surface waters and its environmental significance in the Issyk–Kul Lake region of Central Asia. J. Mt. Sci. 2018, 15, 254–263. [CrossRef]

30. Ma, L.; Abuduwaili, J.; Li, Y.; Abdymahparuulu, S.; Mu, S. Hydrochemical Characteristics and Water Quality Assessment for the Upper Reaches of Syr Darya River in Aral Sea Basin, Central Asia. Water 2019, 11, 1893. [CrossRef]

31. Talib, A.M.; Tang, Z.; Shahab, A.; Siddique, J.; Faheem, M.; Fatima, M. Hydrogeochemical Characterization and Suitability Assessment of Groundwater: A Case Study in Central Sindh, Pakistan. Int. J. Environ. Res. Public Health 2019, 16, 886. [CrossRef]

32. Rotiroti, M.; Bonomi, T.; Sacchi, E.; McArthur, J.M.; Stefania, G.A.; Zanotti, C.; Taviani, S.; Patelli, M.; Nava, V.; Soler, V.; et al. The effects of irrigation on groundwater quality and quantity in a human–modified hydro–system: The Oglio River basin, Po Plain, northern Italy. Sci. Total Environ. 2019, 672, 342–356. [CrossRef]
33. Xiao, J.; Wang, L.; Deng, L.; Jin, Z. Characteristics, sources, water quality and health risk assessment of trace elements in river water and well water in the Chinese Loess Plateau. *Sci. Total Environ.* 2019, 650, 2004–2012. [CrossRef] [PubMed]

34. Rakotondrabe, F.; Ndám Nguépayou, J.R.; Mfonka, Z.; Rasolomanana, E.H.; Nyangono Abolo, A.J.; Ako Ako, A. Water quality assessment in the Bétaré–Oya gold mining area (East–Cameroon): Multivariate Statistical Analysis approach. *Sci. Total Environ.* 2018, 610–611, 831–844. [CrossRef] [PubMed]

35. Ma, L.; Abuduwaili, J.; Smanov, Z.; Ge, Y.; Samarkhanov, K.; Saparov, G.; Issanova, G. Spatial and Vertical Variations and Heavy Metal Enrichments in Irrigated Soils of the Syr Darya River Watershed, Aral Sea Basin, Kazakhstan. *Int. J. Environ. Res. Public Health* 2019, 16, 4398. [CrossRef] [PubMed]

36. Ma, Y.; Egodawatta, P.; McGree, J.; Liu, A.; Goonetilleke, A. Human health risk assessment of heavy metals in urban stormwater. *Sci. Total Environ.* 2016, 557–558, 764–772. [CrossRef]

37. De Miguel, E.; Iríbarren, I.; Chacón, E.; Ordoñez, A.; Charlesworth, S. Risk–based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). *Chemosphere* 2007, 66, 505–513. [CrossRef]

38. Santos, M.S.; Metzker, M.C.R.M.; Rodrigues, G.L.; Corrêa, L.R.S.; Silva, M.L.V.; Barbosa, A.L.G.; Faria, M.C.S.; Rodrigues, J.L. Risk Assessment of the Drinking Water Samples in the Rural Area from MG, Brazil. *Int. J. Environ. Res. Public Health* 2018, 12, 965–971. [CrossRef]

39. Rodríguez-Protea, R.; Grant, R.L. Toxicity Evaluation and Human Health Risk Assessment of Surface and Ground Water Contaminated by Recycled Hazardous Waste Materials. In *Water Pollution: Environmental Impact Assessment of Recycled Wastes on Surface and Ground Waters; Risk Analysis*; Kassim, T.A., Ed.; Springer: Berlin/Heidelberg, Germany, 2005; pp. 133–189. [CrossRef]

40. Kim, J.H.; Kim, K.H.; Thao, N.T.; Batsaikhan, B.; Yun, S.T. Hydrochemical assessment of freshening saline groundwater using multiple end–members mixing modeling: A study of Red River delta aquifer, Vietnam. *J. Hydrol.* 2017, 549, 703–714. [CrossRef]

41. Ntanganedzeni, B.; Elumalai, V.; Rajmohan, N. Coastal aquifer contamination and geochemical processes evaluation in Tugela Catchment, South Africa–Geochemical and statistical approaches. *Water* 2018, 10, 687. [CrossRef]

42. Qu, B.; Zhang, Y.; Kang, S.; Sillanpää, M. Water quality in the Tibetan Plateau: Major ions and trace elements in rivers of the “Water Tower of Asia”. *Sci. Total Environ.* 2019, 649, 571–581. [CrossRef]

43. Dehbandi, R.; Moore, F.; Keshavarzi, B. Geochemical sources, hydrogeochemical behavior, and health risk assessment of fluoride in an endemic fluorosis area, central Iran. *Chemosphere* 2018, 193, 763–776. [CrossRef]

44. Weynell, M.; Wiechert, U.; Zhang, C. Chemical and isotopic (O, H, C) composition of surface waters in the catchment of Lake Donggi Cona (NW China) and implications for paleoenvironmental reconstructions. *Chemosphere* 2014, 435, 92–107. [CrossRef]

45. Gaillardet, J.; Dupré, B.; Louvat, P.; Allègre, C.J. Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 1999, 159, 3–30. [CrossRef]

46. Tenorio, G.E.; Vanacker, V.; Campforts, B.; Álvarez, L.; Zhiminaicela, S.; Vercruysse, K.; Molina, A.; Govers, G. Tracking spatial variation in river load from Andean highlands to inter–Andean valleys. *Geomorphology* 2018, 308, 175–189. [CrossRef]

47. Wen, B.; Zhou, A.; Zhou, J.; Liu, C.; Huang, Y.; Li, L. Coupled S and Sr isotope evidences for elevated arsenic concentrations in groundwater from the world’s largest antimony mine, Central China. *J. Hydrol.* 2018, 557, 211–221. [CrossRef]

48. Jasaitis, D.; Wohlt, J.; Evans, J. Influence of feed ion content on buffering capacity of ruminant feedstuffs in vitro. *J. Dairy Sci.* 1987, 70, 1391–1403. [CrossRef]

49. Pacheco Castro, R.; Pacheco Ávila, J.; Ye, M.; Cabrera Sansores, A. Groundwater Quality: Analysis of Its Temporal and Spatial Variability in a Karst Aquifer. *Groundwater* 2018, 56, 62–72. [CrossRef] [PubMed]

50. Wei, H.; Yu, H.; Zhang, G.; Pan, H.; Lv, C.; Meng, F. Revealing the correlations between heavy metals and water quality, with insight into the potential factors and variations through canonical correlation analysis in an upstream tributary. *Ecol. Indic.* 2018, 90, 485–493. [CrossRef]

51. Wang, X.; Zhao, L.; Xu, H.; Zhang, X. Spatial and seasonal characteristics of dissolved heavy metals in the surface seawater of the Yellow River Estuary, China. *Mar. Pollut. Bull.* 2018, 137, 465–473. [CrossRef]

52. Zhang, J.; Hua, P.; Krebs, P. Influences of land use and antecedent dry–weather period on pollution level and ecological risk of heavy metals in road–deposited sediment. *Environ. Pollut.* 2017, 228, 158–168. [CrossRef]
53. Hong, Z.; Zhao, Q.; Chang, J.; Peng, L.; Wang, S.; Hong, Y.; Liu, G.; Ding, S. Evaluation of Water Quality and Heavy Metals in Wetlands along the Yellow River in Henan Province. *Sustainability* **2020**, *12*, 1300. [CrossRef]

54. Li, Z.; Yang, Q.; Yang, Y.; Xie, C.; Ma, H. Hydrogeochemical controls on arsenic contamination potential and health threat in an intensive agricultural area, northern China. *Environ. Pollut.* **2020**, *256*. [CrossRef][PubMed]

55. Shakoor, M.B.; Nawaz, R.; Hussain, F.; Raza, M.; Ali, S.; Rizwan, M.; Oh, S.E.; Ahmad, S. Human health implications, risk assessment and remediation of As–contaminated water: A critical review. *Sci. Total Environ.* **2017**, *601–602*, 756–769. [CrossRef] [PubMed]

56. Chen, Y.; Wu, F.; Liu, X.; Parvez, F.; Lolacono, N.J.; Gibson, E.A.; Kioumourtzoglou, M.-A.; Levy, D.; Shahriar, H.; Uddin, M.N.; et al. Early life and adolescent arsenic exposure from drinking water and blood pressure in adolescence. *Environ. Res.* **2019**, *178*. [CrossRef][PubMed]

57. He, J.; Charlet, L. A review of arsenic presence in China drinking water. *J. Hydrol.* **2013**, *492*, 79–88. [CrossRef]