



Article

# Occurrence of Radionuclides and Hazardous Elements in the Transboundary River Basin Kyrgyzstan-Kazakhstan

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Abstract: Important for irrigation, the transboundary river basin between Kyrgyzstan and Kazakhstan is vulnerable to geochemical and anthropogenic sources of pollution. The use of water use indices, together with measurements of the elemental and radionuclide composition of the water and bottom sediments, provides a means for evaluating the continued use of the water from this region. Recent monitoring shows the highest concentrations of hazardous contaminants include lead and thorium contained in the bottom and banks of the Kichi-Kemin River. These contaminants are likely remnants of an accidental spill at the Aktyuz tailing dump in 1964. The specific activity of the Th-232 of the bottom and banks of the Kichi-Kemin River is 107-189 Bq/kg. There is evidence of anthropogenic sources of additional pollution from uranium in both the bottom sediments and the water in the Oyrandy River. The geochemical origins of uranium and other associated elements in the water of the Shu River are likely the Kamyshanovskoye deposit. Contact between the riverbed and ore bodies in this region likely leads to elevated concentrations of several geogenic contaminants, including lithium, strontium, uranium, and boron (Li, Sr, U, B), increasing by as much as 60–130%. The uranium concentrations in the water of channels that are used for irrigation exceed the maximum allowable contaminant levels by 3.8 times. Future work is needed to evaluate the ecological and human health impacts of these contaminants in irrigation and drinking water.

**Keywords:** hazardous elements; natural radionuclides; Contamination Factor (CF*i*); pollution load index (PLI); enrichment factor (EF*i*); Metal Index (MI)

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# 1. Introduction

As a consequence of the landlocked geography of Kazakhstan, many rivers flow into the country and provide opportunities for understanding water quality issues which cross geopolitical boundaries. One such transboundary river basin is formed by the Shu and Talas Rivers and their tributaries, as well as small rivers originating in the Tian Shen Mountains. The headwaters of this drainage area are located almost entirely in mountainous areas in the territory of Kyrgyzstan. This dense river network in the foothill zone supports thriving agricultural land use for the two neighboring countries, since the availability of irrigation water is a main condition for growing crops. Simultaneously with the development of irrigated farming, mining and processing of minerals has been carried out extensively in the upper reaches of this watershed. Enterprises for the extraction and processing of ore, as well as waste storage sites and mine tailings, are located almost everywhere in this territory.

In the upstream of the Kichi-Kemin River, in the mountainous area in Kyrgyzstan, the Ak-Tyuz mine is located. Since 1942, ore containing Pb, Zn, Th, and rare earth elements

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was mined and processed. Mine waste was stored in three dumps and four tailings [1,2], which contain Pb, Mo, Th, Cu, and Y [3]. Soils in the territory contain uranium and thorium anomalies, with U-238 ranging up to 131.7 Bq/kg and Th-232 up to 323.8 Bq/kg [4–7]. In [5], it was revealed that the content of Pb in the soils of the deposit is 6–7.5 times higher than the allowable concentration. The historical transboundary pollution associated with this mine is also known. A sudden seismic event at the Ak-Tyuz Mine in December 1964 led to the destruction of tailings dam No.2, resulting in the spillage of ~600,000 m³ of waste downstream of the Kichi-Kemin River [6], right up to its confluence with the Shu River in Kazakhstan. This transboundary catastrophe was partially remediated, but scattered contaminated areas remained untouched [4,7–10]. After the accident, it was found that the bottom sediments of the Kichi-Kemin River (in the Kyrgyz part) contain elevated levels of Zn, Y, Zr, Nb, Mo, Pb, Th, U, and natural radionuclides Th-234, Ra-226, Pb-214, Bi-214, Pb-210, and Ac-228 [8–10]. In the territory of Kazakhstan, studies of the consequences of the accident have not been carried out.

The Shu River flows through the territory of several large uranium ore provinces. In a study of the mountainous part of Kyrgyzstan to the territory of Kazakhstan, the concentration of U (and its radionuclides) in water increased [11] along the stream due to groundwater inflow [12]. One of the deposits of this province zone is Kamyshanskoye, which is located near the border zone on the territory of Kyrgyzstan. Studies [11–14] show that the soils in the Kamyshanovskoye village, close to the deposit, contain uranium series radionuclides up to 10 times higher than the background level of this region. More than 90% of the U occurs in mobile forms subject to chemical weathering and subsequent pollution [11,13,14]. Migration from the ore is source of pollution of U and other hazardous elements such as Mo, Zn, As, Pb, and Co in Shu River waters.

One of the largest environmental hazards in this region is posed by the tailing dump of the Kara-Balta Mining Combine, which is located near the city of Kara-Balta. Since 1956, roughly 29.6 million tons of uranium processing waste has been collected and stored in this tailing dump [2,3]. This tailing dump is located upgradient of a transboundary groundwater aquifer [15]. Dissemination of the tailing contaminants has allowed infiltration of wastewater laden with high sulfates, nitrates, heavy metals, and natural radionuclides to enter the underground aquifer [2,3]. This contamination can enter the local aquifer extending toward Kazakhstan and then provide a contaminant source through seepage to canals and rivers, thus posing a significant threat to irrigation water quality.

The history of this region has required numerous radioecological studies to understand the extent of the contamination in Kazakhstan. The study of water quality in such areas is important for ensuring food security because water pollution can lead to the contamination of plant products and affect human health [16,17]. A number of studies [18– 23] have been published based on the results of the governmental monitoring of the main transboundary rivers in Kazakhstan. These publications have highlighted the problems of pollution with hazardous elements of soils and bottom sediments of the main transboundary rivers between Kyrgyzstan and Kazakhstan. Monitoring results provides a basis for evaluating the sustainable use of water in these basins of not only the main channels but also small transboundary rivers. In 2020–2021, authors published detailed studies of these transboundary rivers [24], as well as the Shu River, which flows through the territory of the Kamyshanskoye ore field [25]. The present work is a continuation of the previously published studies. The novelty of this study is conducting an additional assessment of the quality of sediments and surface water with the calculation of evaluation indices that are widely used in the international literature, such as Contamination Factor, Pollution Load Index, and Enrichment Factor for assessing soil and sediment pollution. Water quality assessment was carried out by using Metal Index and the evaluation of uranium isotope ratios. Based on the calculation results, it was possible to determine the type of pollution source and confirm and expand the conclusions obtained earlier. Finally, transboundary water issues are dependent on international agreements specifying the annual transfer of sufficient water quantities to meet downstream needs. This study highlights the

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importance of evaluating downstream water quality for intended uses in transboundary water agreements.

The results are presented in two parts, which reflect the research areas.

#### 2. Materials and Methods

## 2.1. Sampling and Analytical Testing

The field expeditions were conducted along the border of Kazakhstan and Kyrgyzstan to take samples of riverbank soil, floodplain soil, sediments, and surface water. The samples were analyzed in the Center of Complex Environmental Research of the Institute of Nuclear Physics, Kazakhstan, which is accredited for compliance with the International Organization for Standardization of International Electrotechnical Commission ISO/IEC 17025-2019 [26]. The measuring methods that were used included: X-ray fluorescence analysis (XRF) [27] and neutron activation analysis (NAA) [28] for the determination of the elemental composition of the soil and sediment samples; instrumental gamma-spectrometry (IGS) [29] for the determination of the specific activity of Ra-226 and Th-232; mass and optical emission spectrometry with inductively coupled plasma (ICP-MS, ICP-OES) for the determination of the elemental composition of water samples; and radiochemical analysis for the determination of the specific activity of U-234 and U-238 [30].

#### 2.2. Environment Assessment

The measured concentrations of elements and radionuclides were compared with each other in different samples, with the background level [31], and with the maximum allowable concentration (MACi). To assess the quality of the riverbank soil, floodplain soil, sediments, and surface water, several indices were determined.

The degree of contamination of the riverbank soil, floodplain soil, and sediment was evaluated by using the Contamination Factor (CFi) and Pollution Load Index (PLI), as in [32–34], according to the formulas:

$$CFi = \frac{c_i}{B_i} \tag{1}$$

where Ci is the concentration (µg/g) of the i-th element, and Bi is the background level (µg/g) of the i-th element. The CFi is a dimensionless value rated from 1 to 6 [34]: CFi < 1—low pollution; 1 < CFi < 3—moderate contamination; 3 < CFi < 6—considerable contamination; CFi > 6—very high contamination.

$$PLI = \sqrt[n]{CF_1} * CF_2 * \dots CF_n$$
 (2)

where CFi—Contamination Factor of the i-th element and n—number of elements. PLI < 1 classified that there was no pollution, and PLI > 1 classified the pollution [34].

The estimates of the sources of the elements in the soil were based on the dimensionless Enrichment Factor (EF<sub>i</sub>), as was performed in [35], according to the formula:

$$EF_i = \frac{C_i / C_{ref}}{B_n / B_{ref}} \tag{3}$$

where Ci—is the concentration ( $\mu g/g$ ) of the i-th element in the sample;  $C_{ref}$ —is the concentration ( $\mu g/g$ ) of the reference element in the sample; Bn—is the concentration ( $\mu g/g$ ) of the i-th element in the background;  $B_{ref}$ —is the concentration ( $\mu g/g$ ) of the reference element in the background. The reference element for calculation, as in [36], is Fe. If EFi < 1, it classified a natural source of an element in the soil. If 1 < EFi < 10, the source was natural with some anthropogenic influence. If EFi > 10, the source was anthropogenic.

The extent of surface water pollution was evaluated by using a dimensionless Metal Index (MI) [37,38], which takes into consideration the possible effects of heavy metals on

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human health to evaluate the overall quality of drinking water. The calculation is according to the formula:

$$MI = \sum_{i=1}^{N} \frac{C_i}{MAC_i} \tag{4}$$

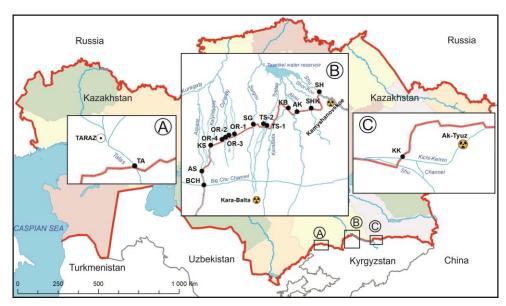
where MAC*i* indicates the maximum allowable concentration (μg/L) of the *i*-th element, and C*i* is the mean concentration (μg/L) of the *i*-th of each element in the sample water. The MI index is calculated by using elements of hazard classes 1 and 2. The evaluation of water quality compared concentrations with the maximum allowable level recommended by the World Health Organization (WHO) for drinking water (MACwho) [39]. For elements for which the MACwho was undetermined or not available, the concentrations were compared with the MAC*i* permitted in drinking water for Kazakhstan (MACkz) [40]. Based on the calculation of the MI index, water is classified as follows [37,38]: <0.3—very pure; 0.3–1.0—pure; 1.0–2.0—slightly affected; 2.0–4.0—moderately affected; 4.0–6.0—strongly affected; >6.0—seriously affected. MI > 1 is a warning threshold [37,38].

The assessment of the radionuclide levels in water included comparing radionuclide activity with the hygienic standards (intervention level—IL) of Kazakhstan [41]. To help evaluate the sources of uranium (natural or anthropogenic), a method was used to assess the isotope ratios of U-234 (Bq/L) to U-238 (Bq/L) activity (U-234/U-238). Dissolved uranium becomes enriched during weathering in U-234 because of alpha-recoil [42], and the main sources can be characterized by the following boundary criteria: if the ratio of activities U-234/U-238 > 1, then the uranium is of natural origin. Lower U-234/U-238 ratios (234/U-238  $\leq$  1) typically derived from ore bodies and may indicate input from anthropogenic uranium.

#### 3. Results

# 3.1. Research in a Transboundary River Basin

The transboundary basin includes the 11 rivers and Big Chu Canal. Riverbank sediment, floodplain soil, bottom sediment, and surface water were taken at 16 sample points: Kichi-Kemin (KK), Shu (SH), Shor-Koo (SHK), Aksu (AK), Karabalta (KB), Toktas (TS-1, TS-2), Sargou (SG), Oirandy (OR-1, OR-2, OR-3, OR-4), Kayindysay (KS), Aspara (AS), Talas (TA), and Big Chu Canal (BCH) (Figure 1 [24]).

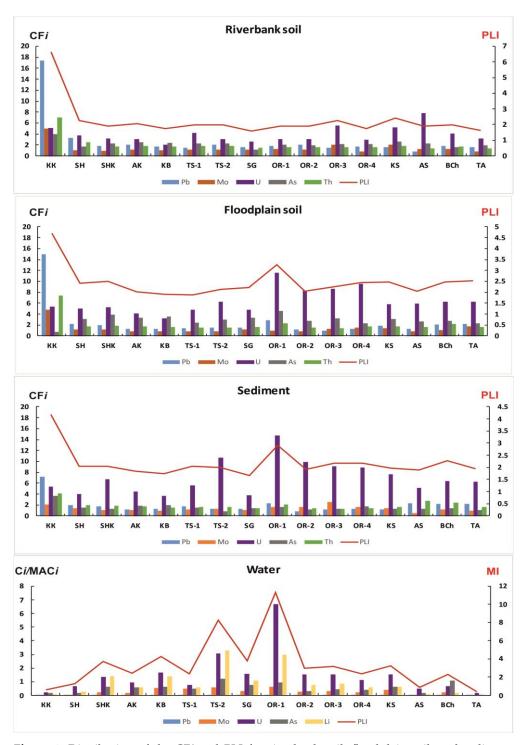


**Figure 1.** Scheme of sampling sites in the transboundary rivers "Kyrgyzstan-Kazakhstan" and the Big Chu Canal [24]. (A) - on the Talas River; (B) - on the Kichi-Kemin River, (C) - other studied rivers.

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During the analysis of the previous results of riverbank soil, floodplain soil and sediment, it was determined that the following hazardous elements are of the greatest interest for research: Pb, Mo, U, As, Th, and Li.

Figure 2 shows the results calculation of the CF*i* and PLI-index for riverbank and floodplain soils and sediment and (C*i*/MAC*i*) and MI for surface water. Th was not considered in the MI calculation, while Li was included in CF*i* and PLI.



**Figure 2.** Distribution of the CF*i* and PLI for riverbank soil, floodplain soil, and sediment and C*i*/MAC*i* and MI for surface water in sample points.

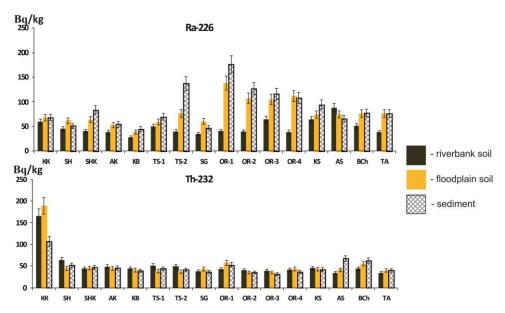
The present levels in riverbank, floodplain soil, and bottom sediments belong to the "considerable contamination" (3 < CFi < 6) category. The highest PLI of most elements

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occurs in riverbank soil and floodplain soil and sediment of the Kichi-Kemin (KK) River. The concentration of Pb in the riverbank soil exceeded the background level by 17.5 times, while other elements exceeded the background level as follows: Th: 7.1 times, Mo: 5.1 times, and Zn: 3.7 times. The elevated concentrations of U (CFi > 6) are consistent with "very high contamination" in the floodplain soil and sediment of most rivers, especially the Oyrandy (CR-1, CR-2, CR-3, CR-4) and CR-10 (in floodplain soil) Rivers.

In river water, the concentrations of U exceeded the established MACi in almost all control points. The concentration of U (Figure 2) in the water of the Shor-Koo (SHK), Karabalta (KB), Sargou (SG), Kayindysay (KS), Oyrandy (OR-1), and Toktas (TS-2) Rivers significantly exceeded the corresponding value of the MACwho (30 µg/L). The concentration of this hazardous element in the water of OR-1 exceeds the permissible level by 6.7 times, and by 3.1 times in TS-2. The lowest U concentrations were found in the water of Talas (TA) (6.25 µg/L) and in the Kichi-Kemin (7.25 µg/L) Rivers. Generally, the distribution of the concentrations of elements was as follows: Pb (µg/L)—from 0.1 (KB, AS) to 0.44 (KK); Mo (µg/L)—from 2.91 (TA) to 46.6 (OR-1); U (µg/L)—from 6.25 (TA) to 201.03 (OR-1); Li (µg/L)—from 3.04 (KK) to 100 (TS-2); As (µg/L)—from 0.75 (TA) to 12.2 (TS-2).

The distribution of the specific activity of Ra-226 (Bq/kg) and Th-232 (Bq/kg) in the riverbank, floodplain soil, and bottom sediments is presented in Figure 3.

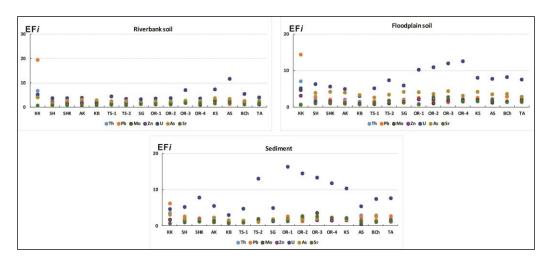


**Figure 3.** Distribution of specific activity of Ra-226 and Th-232 (Bq/kg) in riverbank soil, floodplain soil, and sediment in sample points.

The highest Th-232 activity was found in the riverbank soil and sediment of the Kichi-Kemin (KK) river. In comparison, the specific activity of this radionuclide in the riverank, floodplain soils, and sediment of the Kichi-Kemin (KK) river ranged from 107 to 189 Bq/kg, and in other rivers, it ranged from 31.8 to 67.3 Bq/kg. In the riverbank soil, the range of the values of the specific activity of Th-232 was (165–189 Bq/kg), and in the sediment, it was 107 Bq/kg. An increased activity of Ra-226 was recorded in the Toktas (TS-2) (49.6–69.4 Bq/kg) and Oyrandy (OR 1-4) (38.4–176 Bq/kg) Rivers in comparison with other rivers. The content of Ra-226 in riverbank, floodplain soils and sediments generally follow the uranium distribution (Figure 2).

The calculation of the EF*i* (Figure 4) for soils and sediment helps identify the pollution sources, while the origin of uranium in water can be assessed by plotting the U-234/U-238 isotope ratios (Figure 5).

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**Figure 4.** Distribution of the EF<sub>i</sub> in riverbank soil, floodplain soil and sediment in sample points.

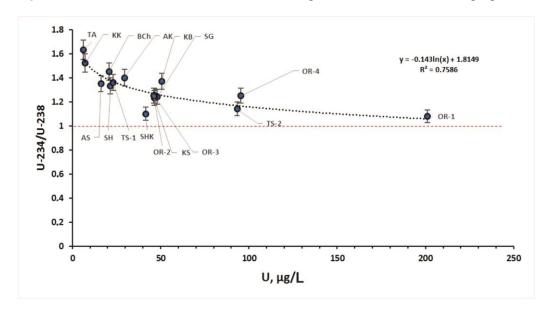


Figure 5. Dependence of the isotopic ratio of U-234/U-238 to the U ( $\mu$ g/L) concentration.

The calculation of the EFi (Figure 4) suggests that the hazardous elements present in most of the samples are from geochemical sources with an anthropogenic influence (1 < EFi < 10). The presence of elevated U in the floodplain soil of the Oyrandy River (OR 1-4) and Pb in riverbank and floodplain soils of the Kichi-Kemin (KK) River is likely due to anthropogenic sources (EFi > 10).

The uranium activity ratios (Figure 5) indicate the degree of disequilibrium between U-234 and U-238 in surface water, with higher values expected from the preferential leaching of U-234 due to the formation of a recoil atom (Th-234) from the alpha decay of U-234 [43]. In some instances, an activity ratio near secular equilibrium (U-234/U-238 = 1.00) has been associated with anthropogenic sources such as phosphate fertilizer or uranium ore [42,44]. The lowest values (1.08–1.25) of isotope activity ratios correspond to the waters of the Oyrandy (OR-1, OR-2, OR-3, OR-4), Shor-Koo (SHK), Kayindysay (KS), Sargou (SG), and Toktas (TS-2) rivers and suggest anthropogenic uranium sources.

## 3.2. Shu River Water Quality across the Kamyshanskoye Ore Body

Surface water samples were researched for 15 sampling points along the Shu River (SH-1, SH-2, SH-3, SH-4, SH-5, SH-6, SH-7, SH-8, SH-9) and the irrigation hydrochannel (CH-1, CH-2, CH-3, CH-4, CH-5, CH-6) (Figure 6 [25]).

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Figure 6. Water sampling scheme in the territory of the Kamyshanovskoye deposit [25].

The distribution of the concentrations of the elements in the surface water at the sampling points located along the hydrochannel (CH) and the Shu River (SH) is shown in Figure 7 [25].

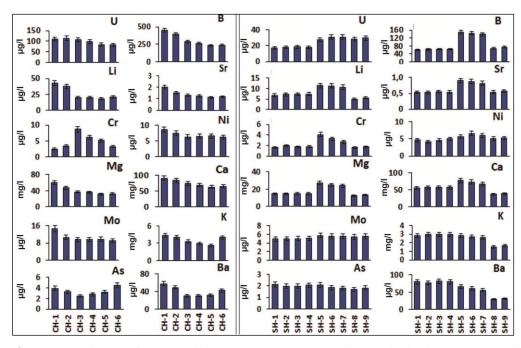
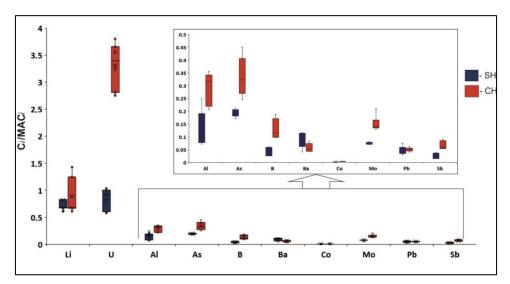


Figure 7. Distribution of individual elements in waters ( $\mu g/L$ ) along the hydrochannel (CH) and the Shu River (SH) [25].

Downstream from CH-1 to CH-6 across the ore bodies, the water composition does not reflect increased concentration for most of the elements, except for Cr. On the contrary, the concentration of Li, Mg, Mo, B, Sr, Ca, K, and Ba is reduced in sample points from CH-2 to CH-4. The distribution of element concentrations along the Shu River shows that between SH-1 – SH-4, the concentration of most elements in the water is not change. Further downstream, between SH-5–SH-7, there is a difference in the concentration of Ca, Ni, Li, Sr, U, Mg, Cr, and B elements in the water by about 28%, 30%, 55%, 61% 66%, 71%, 86%, and 130%, respectively. After SH-8 concentrations, most elements decrease, suggesting dilution from another water source.

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Because of the active agricultural activity in this area, the water quality assessment provides an indication of the safety of the river water for irrigation. Figure 8 shows a graph of the distribution of (*Ci/MACi*), and Figure 9 presents the MI calculation results for the hydrochannel (CH) and the Shu River (SH).



**Figure 8.** Graph of the distribution of the ratio (Ci/MACi) for Li, U, Al, As, B, Ba, Co, Mo, Pb, and Sb for waters in the hydrochannel (CH) and the Shu River (SH).

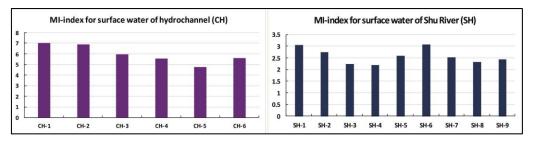


Figure 9. MI for water of hydrochannel and Shu River.

The ratio *Ci/MACi* for most hazardous elements is within acceptable limits, with the possible exceptions of U and Li. The concentration of U in the water of the hydrochannel (CH) is higher than in the Shu River (SH) and exceeds MACwho by up to 3.8 times. The MI for water from the hydrochannel (Figure 9) is in the range of 4–7 ("strongly and seriously affected", VI–V classes), in comparison with the Shu River 2–3 ("moderately affected", IV class). Overall, uranium levels are of the most concern with respect to MI.

# 4. Discussion

The highest PLI and the least MI is found in the Kichi-Kemin (KK) River, with the largest contributor of Pb (Figure 2). The bottom and sediments are most heavily polluted (CFi > 6, "very high contamination"), while the overlying water is relatively safe (MI < 1). EF(Pb) > 10. The EFi (Figure 4) suggests the presence of riverbank floodplain and soils affected with anthropogenic source of Pb. The high Th-232 (31.8–67.3 Bq/kg) activity (Figure 3) was found in samples of the riverbank soil and bottom sediment of this river. This contamination is likely a legacy of the catastrophic spill that occurred in 1964 at the Ak-Tyuz mine. Pb and Th and other associated elements were contained in the waste from the collapsed tailing [3] and remain at the bottom and banks of the river. The low MI can be explained by a decrease in snow melt from glaciers in mountainous areas during the summer period, leading to reduced or nonexistent flow in the river channel across the Kyrgyzstan border. Indeed, the dry riverbed is used mainly as an irrigation canal transferring water from the nearby Shu River during the growing season. At the same time, the

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observed differences in the concentration of Pb in the water of the Kichi-Kemin (KK) and Shu (SH) rivers may also be related to the uranium contamination and should be explored.

The high PLI in the floodplain soil and sediment of the Oyrandy (OR) River and high MI for this river (especially at OR-1) are mainly due to the elevated level of uranium (Figure 2). Ra-226 activity (Figure 3) follows U (Figure 2). Both the EF (U) > 10 (Figure 4) and isotope activity ratios (1.08–1.25) (Figure 5) suggest anthropogenic sources of U in the water of this river. In addition, signs of pollution with U and other hazardous elements in other rivers were found from a geochemical source with anthropogenic influence (1 < EFi < 10). The source of pollution in the channel and water of these rivers remains to be clarified with subsequent studies.

In previous studies [42,44], it has been reported that a uranium activity ratio near secular equilibrium (U-234/U-238 =1.00) can be associated with uranium from phosphate fertilizer or groundwater in contact with uranium ore. In this region, seepage of groundwater previously in contact with uranium ore may provide a source of technogenic uranium from Kyrgyzstan into Kazakhstan in this region [45]. The authors also note that both U and Li concentrations exceed the MACi only in river water downstream from the Kara-Balta mining region. These rivers may be replenished from groundwater high in uranium that is potentially leached from the tailing dump of the Kara-Balta Combine mining plant. Confirmation of this explanation would require additional sampling of both surface and groundwater from this area, as well as an evaluation of the groundwater flow. The evaluation of leaching and irrigation return flow over phosphate-fertilized soils may also be considered as described in [44]. The differences between the concentrations of elements in the floodplain, riverbank soils, sediment, and water may also help explain apparent migration of elements in riverbeds and require further study.

These results support previous work suggesting that the uranium concentrations in the Shu River are influenced by uranium mining in the area [12]. In a segment of the Shu River, where the ore deposits are located closest to the river flow, SH-5–SH-7, the concentrations of Ca, Ni, Li, Sr, U, Mg, Cr, and B increase by about 28–130% with distance downstream (Figure 7). Such an uneven distribution of the concentration of these elements suggests that groundwater seepage may be contributing to the water composition. The composition of the hydrochannel suggests that it does not receive inflow; however, the concentration of U in the water of the hydrochannel at CH-1 is higher than that at CH-6, which may indicate a contribution from further upstream.

The elevated MI > 1 for all samples from the Shu River, particularly in the hydrochannel (Figure 9), is a concern for the use of this water for the irrigation of food crops. The concentration of U in the hydrochannel exceeds MACwho by 3.8 times (Figure 8). The water is regularly used for irrigation, returns via this hydrochannel, and ultimately flows back into the Shu River, providing multiple opportunities to concentrate hazardous elements in this water. The risk from continued irrigation with water from this hydrochannel and the Shu River should be evaluated in future investigations.

#### 5. Conclusions

This study describes modern contaminant levels in river water, soils, and sediment which will affect the intended uses of an important transboundary river basin in southern Kazakhstan. The results suggest that a legacy of pollution is present from a 50-year-old waste spill, which led to elevated Pb, Th, U, and other related elements at the bottom and bank of the river in Kichi-Kemin. The highest radioactivity of Ra-226 and uranium concentrations were measured in samples from the bottom sediments and riverbanks of the Oyrandy and Shu Rivers. Sources for the enrichment of dissolved hazardous elements and uranium, potentially from uranium-enriched groundwater seepage or irrigation return from phosphate-fertilized soils, should be considered in future investigations of this area. The results suggest a strong influence of mining from the regional Kamyshanovskoye ore deposit on the water composition of the Shu River. Elevated

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concentrations of uranium were measured in the irrigation hydrochannel, though the likely sources are unknown.

A more complete radioecological understanding of this region will undoubtedly require more detailed studies, the purpose of which would be to study the mechanisms of the pollution of transboundary rivers with natural radionuclides and hazardous elements and migration processes, as well as to assess the risks for the continued use of these rivers for irrigation and, potentially, human consumption. The Institute of Nuclear Physics plans to continue its work to understand water and environmental quality issues in the region.

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