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Radionuclides and toxic chemical elements in the transboundary Kyrgyzstan–Kazakhstan rivers

V. P. Solodukhin[1] · V. L. Poznyak[1] · G. M. Kabirova[1] · L. A. Ryazanova[1] · S. G. Lennik[1] · A. S. Liventsova[1] · A. N. Bychenko[1] · D. A. Zheltov[1]

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Abstract The paper presents the results of radiation surveying and determination of radionuclide and elemental composition in water objects (soil, bottom sediments, water) of the transboundary rivers Shu, Shor-Koo, Aksu, Karabalta, Toktas as well as of Tasotkel water-storage in Kazakhstan in vicinity of the border with Kyrgyzstan. Increased contents of natural radionuclides of ^{238}U and ^{232}Th series, As, Co, Cs, Cu, Hf, Mo, Pb, Sb, Sc, Zn, Zr and rare earth elements were observed in soil and bottom sediment samples. Increased contents of the following toxic elements were revealed in water samples: B, As, Mo, Ba, U. Negative influence of radiation-hazardous sites in Kyrgyzstan on the contamination of the transboundary rivers with natural radionuclides and toxic elements was revealed.

Keywords Transboundary rivers · Radionuclides · Toxic elements · Ecology

Introduction

In Kyrgyzstan the following radiation-hazardous objects are located in the basins of the transboundary rivers near Kazakhstan: the deposit of polymetals and thorium “Ak-Tyuz”, the uranium deposit “Kamyshanovskoe” and a large uranium processing plant “Kara-Balta” (Fig. 1). It is known that tailings of these facilities Ak-Tyuz and Karabalta contain large amounts of natural radionuclides (NR) and toxic elements (TE) [1, 2].

Active commercial agricultural activity is also performed at these lands intensively involving mineral fertilizers with high contents of NRs [3]. Irrigation system for vegetable and melon fields consists of numerous densely interconnected canals and irrigation ditches fed by water from local rivers. Such situation creates considerable possibilities for contamination of the whole irrigation system with NRs and TEs and for proliferation of these contaminants to the territory of Kazakhstan by the transboundary waters. As it is known, in December 1964 the dam of the tailing pool No. 2 of the Ak-Tyuz mine was damaged by seismic activity in the region. The accident resulted in the release of about 600 thousand m^3 of waste with high concentrations of thorium and TEs into the Kichi-Kemin River. This flow in the form of a radioactive torrent moved down along the riverbed and the valley of Kichi-Kemin for about 40 km till its confluence to the Shu River in Kazakhstan. The consequences of that accident were eliminated for many years, but even now they still have negative impact on the environment and local population [1]. Based on this understanding, we set up a task for radiological surveying and studies of radionuclide and element composition in water objects of the transboundary rivers Shu, Shor-Koo, Aksu, Karabalta, Toktas as well as of Tasotkel water-storage in order to detect the signs of the contamination effect imposed by these radiation hazardous sites at these objects in Kyrgyzstan.

Experimental

Sampling of soil, bottom sediment and water was performed in compliance with the procedures developed in the course of our previous work in 2000–2010 within the international project “Navruz” [4–7].

✉ V. P. Solodukhin
solodukhin@inp.kz

[1] Institute of Nuclear Physics, Ibragimov str.1, 050032 Almaty, Kazakhstan

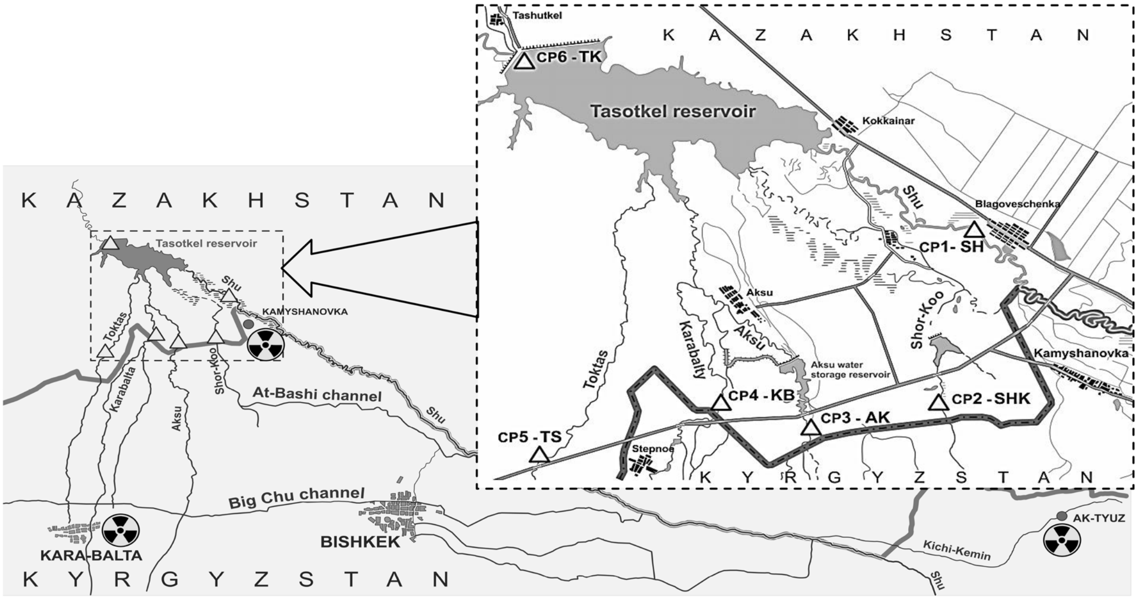

Fig. 1 Radiation survey and environmental sampling layout in the studied water basin

Radiation surveying and sampling of water, bottom sediments, riverside and inundated soil were performed as presented on the map (Fig. 1). Total five control points (SH, SHK, AK, KB, TS) were allocated in the riverbeds of the rivers in vicinity of the state border with Kyrgyzstan. Water composition and bottom sediments were studied there. One control point (TK) was arranged at the Tasotkelsky water reservoir in order to compare water composition and bottom sediments there with the samples taken from all rivers flowing into this reservoir.

Measurements of the equivalent dose rate (EDR) were performed at each of the checkpoints 1 m above the surface employing the dosimeter-radiometer MKS-AT 1117M. It has been revealed that EDR values for the samples from this basin are within the interval 0.12–0.19 μSv h^{-1}. According to the [8], the state regulatory limit for population is established at the level 1 mSv $year^{-1}$, i.e. 0.114 μSv h^{-1}. Our data demonstrate increased radiation background at all the checkpoints.

The soil samples were taken in accordance with the standard procedures GOST 17.4.3.01-83 and GOST 17.4.4.02-84. These samples were taken near the riverbank at the site not subjected to flooding or economic activity. The sampling was made by the “envelope” method (four sampling points at the corners of a square with 50 m sides and one point in its center). At each point, the surface soil was sampled from the 10 × 10 cm^2 area at the depth of 5 cm. After careful quartering, a bigger integrated sample from these five points was aggregated and placed (1 kg) in the properly labeled plastic bags.

Floodplain soil was sampled from a flat slope of a riverbank at five points 10–15 m from each other and at equal distance (2–3 m) from the water edge. Surface layer of upper 5 cm soil was sampled at each point from the area 10 × 10 cm^2. Upon thorough quartering, each aggregate of samples (1 kg) taken from five points was placed in a double-layer plastic bag and marked.

Bottom sediments were sampled as follows: samples of not less than 1.0 kg were taken several meters from the water edge with a special sampler tool. Upon drying, the samples were placed into plastic bags and stored in special sealed containers.

The water sampling was performed in five places at each checkpoint in compliance with the requirements of the State Standard GOST R51592-2003. Water samples (1 L each) were taken in the places with no algae, floating driftweed or litter; at that a sampling container was placed 50 cm below the water surface. Water was filtered through a 0.3 μm membrane filter, preserved with concentrated nitric acid HNO_3 (3 ml of HNO_3 per 1 L) and sealed in plastic bags.

Instrumental gamma-spectrometry (IGS) was used for determination of the samples’ radionuclide composition; neutron activation analysis (NAA), X-ray fluorescence analysis (XRF) and the inductively coupled plasma mass spectrometry (ICP-MS) methods were used in our studies of element composition in the taken samples [4–7, 9–11].

The method of instrumental γ-spectrometry (IGS)

The IGS technique “Radionuclides activity in bulk samples” No. 5.06.001.98 was used for measuring natural radionuclides (NRs) and ARs in soil and bottom sediments. The samples were dried before measurements and homogenized by grinding in the ball mill up to 150–200 microns. The weighed 200 g samples were collected by quartering from the prepared material and placed in the special glass 70 mm in diameter with the bottom made from 100 microns thick polyethylene film. The measurements were performed at the gamma spectrometer with the semiconductor detector BE-3830 “CANBERRA” during 3 h. The resulting spectra were processed with a software package specifically designed in INP for the gamma-spectrometric analyses; this software has been successfully used for several years. The method allows to assess concentrations of radionuclides from the three natural series (uranium, thorium and actinouranium), as well as concentrations of the natural radionuclide ^{40}K and the artificial radionuclide ^{137}Cs.

As scheduled, this method is verified with geological SRMs at least on a semiannual basis (Soils: IAEA-312, IAEA-326, IAEA-327, IAEA-375, IAEA-Soil-6; Sediments: IAEA-313, IAEA-314, IAEA-SL-2, IAEA-315, IAEA-368) and it has been successfully used in radioecology studies for more than 15 years in Kazakhstan and in international projects [4–7, 9, 10].

Inductively-coupled plasma mass-spectrometry (ICP-MS)

Elemental composition of the natural water samples was determined by the ICP-MS technique employing the mass spectrometer «ELAN 9000» of the «Perkin Elmer SCIEX» Company provided with the PC and the specialized software. The analyses were performed in compliance with the method ISO 17294-2 “Water quality—Application of ICP-MS. Part 2: determination of 62 elements”. Before each series of measurements the sensitivity and stability of the spectrometer (instrument setup) was checked using the specially prepared (based on standard samples) solution. After preparation of the calibration curves, the idle solutions and the natural water samples, either initial or diluted 1/10, 1/100 and so on, we measured. The technique determines the concentrations of many elements within the detection limits from 0.1 to 10 μg/L.

The X-ray fluorescent analysis (XRF)

The technique “Assessment of elemental composition in powder samples of various materials employing the X-ray fluorescence energy-dispersion instrument RLP-21 with the semiconductor detector” No.KZ 07.00.01569 was used to reveal the elemental composition of soil and sediment samples. The low-power X-ray tube provided with two replaceable intermediate targets (Cd, Te) is used in this instrument to excite the characteristic radiation. The preliminary preparation of the bottom sediment samples for XRF includes the standard procedure of drying and homogenization by grinding in a ball mill. Then the samples are placed in a 10-mL cell with the bottom made from 100-micron-thick polyethylene. The instrument is operated by special software that takes into account the matrix effect and change in geometry during the measurements. Utilization of the advanced fundamental parameters method allows us determining element contents without any involvement of standard samples. The technique provides the quantitative assessment over 25 elements in soil and sediment with the detection limit ranging from 5 to 300 μg g^{-1} in compliance with the precision category III.

Neutron activation analysis (NAA)

The technique «Determination of elemental composition in solid samples employing neutron activation analysis» No KZ 07.00.01.688 was used to reveal elemental composition of soil and sediment samples. The technique has been certified by the Republic of Kazakhstan state Agency for Standards. The internal standardization procedure has been used. Iron is used as an internal standard; iron contents in the studied samples were determined employing XRF method.

Preliminary sample preparation included drying and abrasion of the dried samples in a porcelain mortar down to the size of 40 microns. The analytical samples of 0.2–0.5 g were then taken by quartering from the prepared bulk sample. The selected samples were packed in the double plastic packets, placed in the aluminum container and irradiated during 5 h in the WWR-K nuclear reactor. The neutron flux in the point of irradiation was 9.8×10^{12} neutron cm^{-2} s^{-1}. After 4 days of “cooling down” the irradiated samples were repacked and delivered for measurements. The measurements were performed at the semiconductor gamma spectrometer “CANBERRA”. The spectrum uptake time is 25–30 min. During the first session of the measurements the following was determined: Na, K, Ca, As, Br, Cd, Sb, La, Sm, Au and U. Then, the second session of measurements was performed in 30–32 days. The spectrum uptake time is about 3 h. These measurements determined Sc, Cr, Co, Fe, Zn, Se, Rb, Ag, Cs, Ba, Eu, Tb, Yb, Hf, Ta, Hg and Th. The spectra were processed employing specialized software designed in INP [12]. The technique determines the concentrations of 28 elements within the detection limits from 0.5 to 10 μg/g in compliance with the precision category III.

We verified NAA and XRF analytical techniques at the certified geological reference materials (SRMs) IAEA-SL-1, IAEA-SL-3, IAEA-Soil-7. The obtained results agree well with the certified data, as one can see from [11]. Reliability of our NAA data is confirmed at regular participation of our specialists in the proficiency tests performed by the Forum for Nuclear cooperation in Asia (FNCA) [13].

At analyses samples, the quality is assured by the system of internal quality control which is an integral part of each of the techniques [14]. This internal quality control includes operating control of the procedures during the analyses and control over the consistency of results. The operating control of the procedures is based on precision assessment of the results in each samples' lot employing standard samples similar in their content to the working samples. The consistency control of the analytical results is performed with selective statistical control of the intralaboratory precision and scheduled check-ups of the analytical procedures. The control parameters such as precision, correctness, intralaboratory precision limits are presented in tabular form in the techniques' descriptions.

More details of the procedures in the field and laboratory investigations are presented in [4–7, 9–11].

Results and discussion

Toxic elements in soil and sediments

Contents of the following 34 elements were determined in all taken soil and bottom sediment samples employing the XRF and NAA methods: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Pb, Th, U. Preliminary comparison of the elements' contents in the riverside soil samples and their Clark numbers («Clark» is the average value of element concentration in nature) made it possible to reveal those elements with increased concentrations for the majority of checkpoints (see Table 1).

Table 1 also presents average concentrations for each of the elements over the whole investigated area and the Clark numbers for soil (by Vinogradov A.P.) for most of these elements [15]. When a Clark number was unavailable for soil, the number for lithosphere was used instead (by Beus A.A.) [16]. Also, uncertainties for some of the data and average numbers calculated in compliance with the [14] requirements are presented. One can group the data in the Table 1 based on the rate the contents in the soil exceed the relative Clark number: contents of Ce, La, Nd, Cu, Zn exceed their Clark numbers for (1.1–1.5) times; As, Co, Hf, Pb, Sc, Th—for (1.6–2) times; Cs, U—for (2.7–3) times; Sb—for 6.8 times. This grouping demonstrated considerable concentrations of the following radioactive and highly toxic elements at the investigated lands: As, Co, Cs, Pb, Sb, Th, U. Taking into account uniform distribution of the studied elements over the whole territory, one can link the revealed pattern to the geochemical peculiarities of this area.

Figure 2 below presents graphically the contents of the same elements in riverside and floodplain soils, bottom sediments at all the checkpoints in the studied water basin.

Table 2 presents numerical data for concentrations of these elements in all sample types taken for the detailed analysis of the contamination levels of the floodplain and riverbeds.

The elements with increased contents (uncertainties are taken into account) in the floodplain soils and/or bottom sediments with respect to the riverside contents are presented.

It can be concluded from the Fig. 2 and Table 2 that the highest contents of Hf and Zr are observed in the floodplain soil and bottom sediments of the Shu River. The potential source of this contamination can be the thorium and REM ore field Ak-Tyuz located in the upper Shu River basin in Kyrgyzstan. As indicated in [1], "tailings there content high concentrations of thorium (800–7000 $\mu g\ g^{-1}$) and zirconium (1100–4800 $\mu g\ g^{-1}$)". An accident that took place at this deposit in 1964 resulted in considerable contamination with highly toxic wastes of the riverbed and floodplain of the Kichi-Kemin River (tributary of the Shu River) down to the border with Kazakhstan. We have revealed that the migration of many elements (including Zr) from the tailing to the Kichi-Kemin River takes place now. This fact is based on considerable increase of the elements' contents in the bottom sediments taken in the river downflow the industrial site ($C_{Zr} = 425\ \mu g\ g^{-1}$) over their respective contents in the bottom sediments upflow the deposit ($C_{Zr} = 103\ \mu g\ g^{-1}$) [10]. Hf is a chemical analog for Zr, and their migration capabilities are quite similar. The presented here facts allow us to make an assumption that the revealed high Hf and Zr contents in the bottom sediments and floodplain of the Shu River are stipulated by migration of these elements from the Ak-Tyuz deposit. At the same time, the graphs at the Fig. 2 are not sufficient to make conclusions about increased contents of REM and Th (which is typical for the Ak-Tyuz deposit) in the floodplain soil and bottom sediments of the Shu River. The phenomenon can potentially be related to peculiarities of the elements' migration there.

Floodplain of the Karabalta River demonstrated the highest concentrations of As (15.7 $\mu g\ g^{-1}$), Co (18.1 $\mu g\ g^{-1}$), Cs (9.25 $\mu g\ g^{-1}$),Cu (61.4 $\mu g\ g^{-1}$), Mo (8.93 $\mu g\ g^{-1}$), Sc (16.3 $\mu g\ g^{-1}$), U (8.12 $\mu g\ g^{-1}$), Zn (102 $\mu g\ g^{-1}$) and increased content of Sb (1.88 $\mu g\ g^{-1}$); these numbers considerably exceed their concentrations in the riverside soils: As (7.62 μg

Table 1 Concentrations of some elements in riverside soils of the surveyed water basin, μg g^{-1}

Element	Checkpoint						Uncertainty	Average	Clark, soil
	SH	SHK	AK	KB	TS	TK			
As[a]	7.60	7.84	8.95	7.67	8.82	8.15	0.90	8.17 ± 0.62	5.0
Ce[a]	62.7	73.2	74.8	64.4	69.1	67.5	11.0	68.6 ± 5.1	60*
Co[a]	11.4	13.3	13.7	12.3	12.8	11.7	1.50	12.5 ± 1.0	8.0
Cs[a]	4.46	5.64	5.82	5.47	5.33	4.93	0.90	5.29 ± 0.53	2.0*
Cu[b]	26.4	23.5	34.4	28.6	27.1	26.3	5.72	27.7 ± 4.0	20
Hf[a]	4.37	6.54	5.02	4.56	5.80	4.79	0.90	5.18 ± 0.88	2.6*
La[a]	34.2	37.9	40.8	32.4	34.2	35.3	4.60	35.8 ± 2.8	25*
Nd[a]	33.4	38.6	39.2	31.7	33.0	32.9	6.20	34.8 ± 3.4	24*
Pb[b]	16.5	18.8	19.3	17.2	16.3	18.0	3.00	17.7 ± 1.3	10
Sb[a]	1.22	1.30	1.48	1.39	1.46	1.25	0.20	1.35 ± 0.12	0.2*
Sc[a]	9.72	11.4	12.7	10.6	11.0	10.5	1.70	11.0 ± 1.1	7.0
Th[a]	10.5	12.2	11.6	10.3	12.0	10.8	1.50	11.2 ± 0.9	6.0
U[a]	3.24	2.72	3.17	2.96	2.83	2.75	0.46	2.98 ± 0.24	1.0
Zn[b]	74.7	63.5	72.6	70.2	62.9	63.4	9.30	67.9 ± 5.6	50

* Due to unavailability of Clark numbers for soil, Clark numbers of lithosphere are presented

[a] NAA

[b] XRF

g^{-1}), Co (12.3 μg g^{-1}), Cs (5.47 μg g^{-1}), Cu (28.6 μg g^{-1}), Mo (1.93 μg g^{-1}), Sc (10.6 μg g^{-1}), U (2.96 μg g^{-1}), Zn (70.2 μg g^{-1}), Sb (1.39 μg g^{-1}). The majority of these elements also demonstrate high concentrations in bottom sediments of this river (see Fig. 2; Table 2). With reference to these results, the observed peculiarity could possibly be explained by the proliferation via the river channel from Kyrgyzstan. In Kyrgyzstan, the source of contamination could most probably be the radioactive waste tailing of the uranium processing Kara-Balta Plant. The data on considerable (except for Th) contents of certain elements in the tailing of this plant are presented in Table 3 [2].

The same work also studied the contents of certain metals in sois at the industrial site of this plant, in its protective and habitation zones. It has been shown that in all these zones the contents of Mo, Pb, Co, Cd and Sb exceed the sanitary limits (the maximal allowable concentrations) set in Kyrgyzstan. The author has revealed considerable contents of U (up to 36 μg L^{-1}), Fe (up to 1.8 mg L^{-1}), Zn (up to 5 mg L^{-1}) and Mo (up to 1.5 mg L^{-1}) in the underground waters at the site of the plant. Migration of this water to the surface reservoirs in contact with the Karabalta River has been proved [2]. These facts prove that the waste storage of the Kara-Balta Plant contaminates the Karabalta River with toxic elements. This statement is also supported by the contamination with such elements as As, Co, Cs, Cu, Sb, Sc, Zn and, particularly, with Mo and U which we have revealed in floodplain soils and bottom sediments of this river in Kazakhstan.

Natural radionuclides in soil and sediments

IGS methods allowed us to identify the average contents of the radionuclides (^{234}Th, ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{210}Pb, ^{228}Ac, ^{224}Ra, ^{212}Pb, ^{212}Bi, ^{208}Tl, ^{235}U, ^{227}Th, ^{40}K, ^{137}Cs) in riverside and floodplain soils as well as in bottom sediments of the whole water basin. Some data are presented in the Table 4 below. The Table 4 contents specific activities of ^{234}Th and ^{226}Ra (^{238}U series); ^{228}Ac and ^{224}Ra (^{232}Th series) and ^{40}K and ^{137}Cs.

As one can see from the table above, specific activity of the artificial radionuclide ^{137}Cs in all studied objects correspond to the level of its global fallout in the region [17]. Increased activity of ^{137}Cs in the riverside soil over the activities measured for the floodplain soils and bottom sediments is quite a normal phenomenon since this radionuclide falls out from the atmosphere and is mainly represented in the upper soil.

^{137}Cs migrates from the floodplain with flood and rainwater; its concentration is therefore much lower than in the riverside soils. Bottom sediments are formed by crumbling of riverside soils. At that, the mass of upper soil layers represents just a small fraction of the whole soil collapsed mass. This results in decrease of this radionuclide's concentration in the bottom sediments. Increased values for ^{210}Pb revealed in all objects is also a normal phenomenon since this radionuclide is additionally accumulated in soil being generated by ^{222}Rn delivered to the surface from decompaction and fracturing zones.

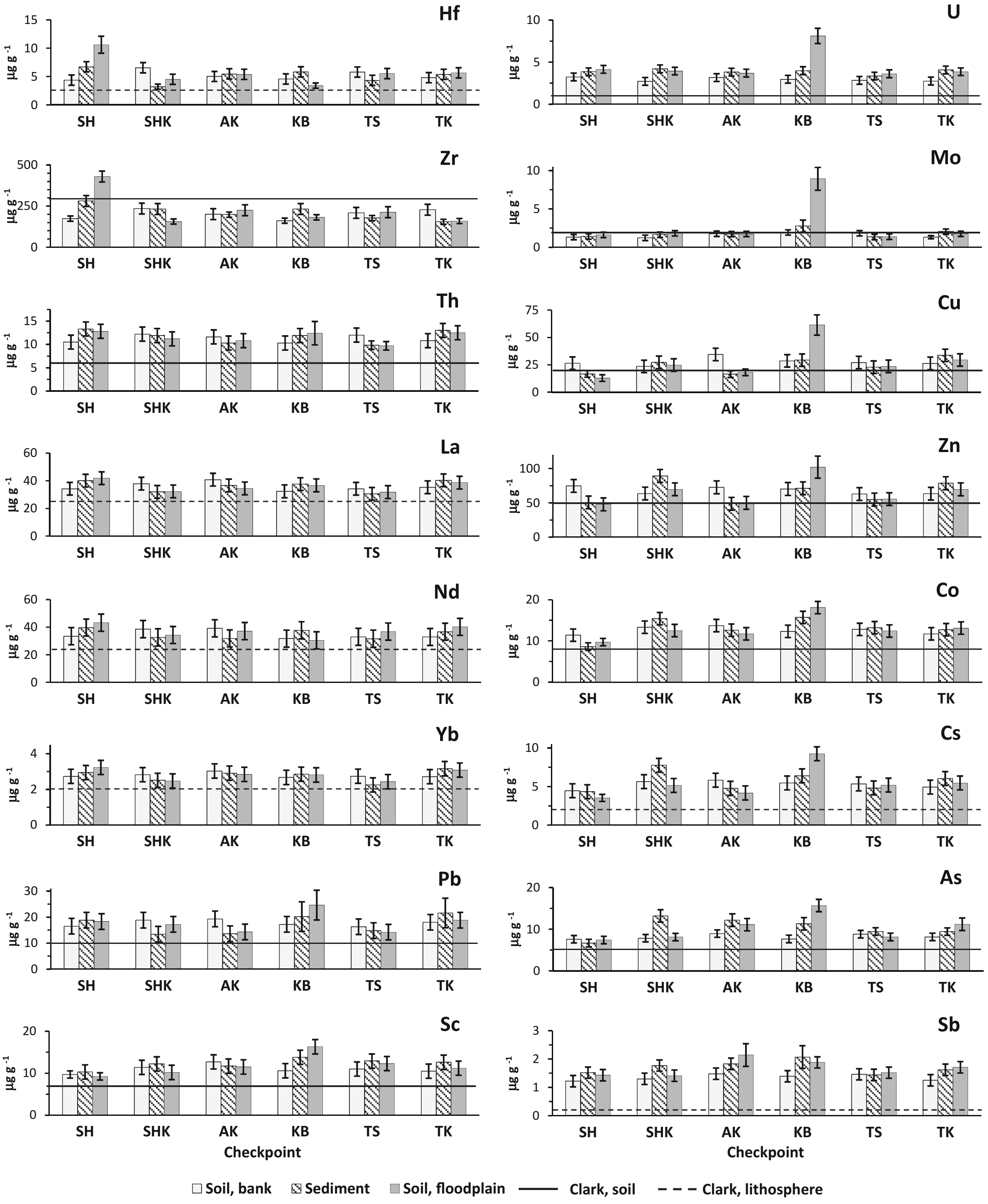

Fig. 2 Concentration of some elements in soil and bottom sediments at various checkpoints of the studied water basin, µg g^{-1}

Contents of natural radionuclides from ^{238}U and ^{232}Th series in all studied objects are explicitly elevated what can be considered as an additional evidence for considerable contents of uranium and thorium in these objects. Besides that, ^{234}Th (daughter product of ^{238}U) average concentrations in the floodplain and bottom sediments (56.3 and 48.1 Bq kg^{-1}, respectively) are much higher than those in the riverside soils (36.9 Bq kg^{-1}) what also confirms the made above statement regarding the mechanism of uranium migration from Kyrgyzstan to Kazakhstan.

One should note that radioactive equilibrium between the following genetically related NRs takes place in soil and bottom sediments: ^{238}U–^{234}Th, ^{232}Th–^{228}Ra–^{228}Ac, ^{228}Th–^{224}Ra. Comparing the NAA data (recalculated in

Table 2 Maximal concentrations of the elements in bottom sediments and floodplain soil at the different checkpoints of the studied basin, μg g^{-1}

Element	Checkpoint	Sample			C_s/C_{sb}	C_{sf}/C_{sb}
		Soil, bank (sb)	Sediment (s)	Soil, floodplain (sf)		
As^a	SHK	7.84 ± 0.90	13.2 ± 1.5	8.13 ± 0.90	1.68	
	KB	7.62 ± 0.9	11.3 ± 1.5	15.7 ± 1.5	1.48	2.06
	AK	8.95 ± 0.90	12.2 ± 1.5	11.1 ± 1.5	1.36	
	TK	8.15 ± 0.90	9.43 ± 0.90	11.2 ± 1.5		1.37
Co^a	KB	12.3 ± 1.5	15.7 ± 1.5	18.1 ± 1.5	1.28	1.47
Cs^a	SHK	5.64 ± 0.90	7.76 ± 0.90	5.15 ± 0.90	1.38	
	KB	5.47 ± 0.90	6.39 ± 0.90	9.25 ± 0.90		1.69
Cu^b	KB	28.6 ± 5.7	29.2 ± 5.7	61.4 ± 9.3		2.15
Hf^a	SH	4.37 ± 0.90	6.72 ± 0.90	10.6 ± 1.5	1.54	2.43
Mo^a	KB	1.93 ± 0.35	2.76 ± 0.79	8.93 ± 1.50		4.63
Sb^a	SHK	1.30 ± 0.20	1.77 ± 0.20	1.41 ± 0.20	1.36	
	KB	1.39 ± 0.20	2.07 ± 0.40	1.88 ± 0.20	1.49	1.35
	AK	1.48 ± 0.20	1.83 ± 0.20	2.14 ± 0.40		1.45
	TK	1.25 ± 0.20	1.62 ± 0.20	1.71 ± 0.20		1.37
Sc^a	KB	10.6 ± 1.7	13.8 ± 1.7	16.3 ± 1.7		1.54
U^a	SHK	2.72 ± 0.46	4.20 ± 0.46	3.94 ± 0.46	1.54	1.45
	KB	2.96 ± 0.46	3.98 ± 0.46	8.12 ± 0.90	1.34	2.74
	TK	2.75 ± 0.46	4.07 ± 0.46	3.86 ± 0.46	1.48	1.40
Zn^b	SHK	63.5 ± 9.3	89.2 ± 9.3	69.8 ± 9.3	1.40	
	KB	70.2 ± 9.3	71.3 ± 9.3	102 ± 16		1.45
Zr^b	SH	174 ± 16	281 ± 33	430 ± 33	1.61	2.47
	KB	161 ± 16	232 ± 33	186 ± 16	1.44	

[a] NAA

[b] XRF

Table 3 Contents of the elements in the radioactive waste tailing of Kara-Balta plant [2]

Element	As	Co	Cu	Mo	Pb	Th	U	Zn
C (μg g^{-1})	80–11,000	30–200	100–1300	100–80,000	90–1000	4–18	40–60	20–900

terms of activity) and IGS data we have revealed that all studied samples obey this equilibrium rule for ^{238}U and ^{234}Th, as well as for ^{232}Th and ^{228}Ac. For instance, average U contents in the riverside soils (2.98 ± 0.24 μg g^{-1}, Table 1) corresponds to the specific activity of ^{238}U (36.9 ± 3.6 Bq kg^{-1}), i.e. completely corresponds to the average specific activity of ^{234}Th (36.9 ± 2.1 Bq kg^{-1}) found by IGS method (Table 4). Average Th contents in the riverside soil (11.2 ± 0.9 μg g^{-1}) correspond to the ^{232}Th specific activity (45.8 ± 3.7 Bq kg^{-1}), i.e. corresponds to the average specific activity of ^{228}Ac (46.2 ± 1.2 Bq kg^{-1}) obtained by IGS (Table 4). For activity calculation we used the method described in [17].

Table 4 also presents the specific activity data for ^{228}Ac and ^{224}Ra. These data confirm that the radionuclides in all studied objects are present in the radioactive equilibrium state. Radioactive equilibrium is also observed between ^{234}Th and ^{226}Ra in the riverside soil and bottom sediments. At the same time, considerable difference in specific activities of ^{234}Th (99.2 Bq kg^{-1}) and ^{226}Ra (53.8 Bq kg^{-1}) in the floodplain soil of the Karabalta River is the evidence for violation of the radioactive equilibrium between these NRs. This revealed peculiarity allows us to make an assumption about presence of some artificial (anthropogenic) component and the source of this component could, most probably, be the Kara-Balta Plant.

The Table 5 presents the absorbed dose rates due to radioactive radiation from ^{226}Ra, ^{232}Th(^{228}Ac) and ^{40}K, calculated in compliance with UNSCEAR 2000 [18].

The data in the Table 5 demonstrate that the radiation background at the investigated territory is slightly increased since the absorbed dose rate (ADR) due to

Table 4 Concentration ranges for some of the radionuclides in riverside soil (sb), floodplain soil (sf) and bottom sediments (s) in samples taken at different checkpoints, Bq kg^{-1}

Checkpoint	Object	Radionuclide						
		^{234}Th	^{226}Ra	^{210}Pb	^{228}Ac	^{224}Ra	^{40}K	^{137}Cs
SH	sb	39.4 ± 2.8	37.5 ± 4.6	67.4 ± 6.6	45.4 ± 3.5	46.8 ± 5.3	761 ± 38	4.72 ± 0.62
	sf	52.7 ± 3.7	53.6 ± 6.8	54.8 ± 5.3	53.2 ± 3.9	54.4 ± 6.2	878 ± 46	0.75 ± 0.22
	s	47.1 ± 3.5	49.2 ± 5.1	51.1 ± 4.9	54.5 ± 4.0	55.6 ± 6.2	862 ± 44	0.77 ± 0.22
SHK	sb	34.6 ± 2.8	36.3 ± 4.5	83.8 ± 8.0	47.3 ± 3.6	45.7 ± 5.1	717 ± 39	6.04 ± 1.10
	sf	47.3 ± 3.6	46.5 ± 4.9	93.1 ± 9.1	46.8 ± 3.5	47.3 ± 5.4	669 ± 35	1.14 ± 0.30
	s	51.4 ± 3.8	48.6 ± 5.2	123 ± 11	48.2 ± 3.6	52.4 ± 6.1	521 ± 28	1.22 ± 0.31
AK	sb	38.7 ± 2.7	35.9 ± 4.5	82.9 ± 8.1	46.0 ± 3.5	47.2 ± 5.5	772 ± 39	8.12 ± 1.34
	sf	46.8 ± 3.7	46.6 ± 4.8	50.8 ± 5.0	44.7 ± 3.4	46.2 ± 5.2	781 ± 42	0.61 ± 0.21
	s	46.2 ± 3.8	45.4 ± 4.7	53.2 ± 5.2	42.7 ± 3.2	45.3 ± 5.1	786 ± 42	<0.3
KB	sb	37.5 ± 2.6	36.5 ± 4.4	83.6 ± 8.1	46.4 ± 3.5	44.8 ± 4.9	743 ± 38	7.38 ± 1.32
	sf	99.2 ± 7.6	53.8 ± 6.6	57.3 ± 5.7	51.6 ± 3.8	50.5 ± 6.2	938 ± 48	0.88 ± 0.23
	s	50.6 ± 3.8	47.4 ± 5.0	53.9 ± 5.2	49.2 ± 3.7	46.8 ± 5.1	794 ± 41	0.63 ± 0.22
TS	sb	36.2 ± 2.9	37.8 ± 4.6	84.3 ± 7.8	47.6 ± 3.6	45.2 ± 5.0	715 ± 39	6.45 ± 1.28
	sf	43.9 ± 3.2	45.2 ± 4.7	47.0 ± 4.4	38.8 ± 3.0	39.9 ± 4.5	765 ± 40	0.72 ± 0.22
	s	42.3 ± 3.3	43.4 ± 4.7	38.7 ± 3.7	39.3 ± 3.0	41.8 ± 4.6	826 ± 41	<0.3
TK	sb	35.0 ± 2.8	36.2 ± 4.3	79.3 ± 7.8	44.7 ± 3.4	42.9 ± 4.8	745 ± 37	8.76 ± 1.52
	sf	48.1 ± 3.6	49.0 ± 5.1	53.7 ± 5.2	52.3 ± 3.8	50.8 ± 6.1	781 ± 40	0.78 ± 0.23
	s	50.8 ± 3.7	47.8 ± 4.9	54.2 ± 5.1	53.5 ± 3.9	53.3 ± 6.2	836 ± 42	<0.3
$\overline{C}$	sb	36.9 ± 2.1	36.7 ± 0.8	80.2 ± 6.9	46.2 ± 1.2	45.4 ± 1.6	742 ± 24	6.91 ± 1.56
	sf	56.3 ± 22.0	49.1 ± 4.0	59.5 ± 17.9	47.9 ± 5.9	48.2 ± 5.3	802 ± 99	0.81 ± 0.26
	s	48.1 ± 3.8	47.0 ± 2.3	62.4 ± 17.0	47.9 ± 6.3	49.2 ± 5.7	770 ± 133	<0.50

radioactive radiation from the riverside soil (75.9 nGy h^{-1}) is for 27 % higher than its world average value (60 nGy h^{-1}). One should also note that the average ADR rates due to floodplain soils (85.1 nGy h^{-1}) is much higher and exceed the world average values for 42 %. Besides, it should be emphasized, that the greatest ADR rates (85–95 nGy h^{-1}) correspond to the bottom sediments and floodplain soils of Shu and Karabalta rivers and the Tasotkel water-storage. This further indicates the presence of NRs migration mechanism acting from the Kyrgyzstan to Kazakhstan territory along the transboundary Shu and Karabalta rivers.

Toxic elements in water

The ICP-MS method was used to study element composition of water samples taken at all the checkpoints. Some characteristic data are presented in Table 6 below. For these elements in the table above, we presented the corresponding maximal allowable concentrations for drinking water as specified in the international sanitary standard and recommended by the World Health Organization (MAC$_{\mathrm{WHO}}$) [19]. According to Table 6, the highest concentration of Ba (72.8 µg L^{-1}) was observed in the Toktas River. Water from the Shor-Koo River demonstrated the highest concentrations of B (217 µg L^{-1}) and Sb (1.56 µg L^{-1}). The highest concentrations of As (7.87 µg L^{-1}), Mo (37.5 µg L^{-1}) and U (38.7 µg L^{-1}) were revealed in the Karabalta River. One should particularly note that the uranium contents in all studied water objects exceed the MAC$_{\mathrm{WHO}}$ level of 15µg L^{-1}.

Based on the sanitary rules of the Republic of Kazakhstan [20], we have calculated the hazard limiting coefficients K_{HL} for water in all studied sources. At that, the limited list of the 1st and 2nd hazard class elements (B, As, Mo, Sb, Ba and U) was then considered. The results are presented at Fig. 3 below.

One can see that for all studied rivers and the Tasotkel water reservoir the K_{HL} index in water (even for just 6 elements) exceeds the sanitary limit of 1.0.

Table 5 External exposure rates calculated from the radionuclide concentrations in riverside soil (sb), floodplain soil (sf) and bottom sediment (s), at different checkpoints, nGy h^{-1}

Checkpoint	Object	Absorbed dose rate			
		^{226}Ra	^{232}Th (^{228}Ac)	^{40}K	D
SH	sb	17.3 ± 2.1	27.4 ± 2.1	31.7 ± 1.6	76.4 ± 3.4
	sf	24.8 ± 3.1	32.1 ± 2.4	36.6 ± 1.9	93.5 ± 4.4
	s	22.7 ± 2.4	32.9 ± 2.4	35.9 ± 1.8	91.5 ± 3.8
SHK	sb	16.8 ± 2.1	28.6 ± 2.2	29.9 ± 1.6	75.3 ± 3.4
	sf	21.5 ± 2.3	28.3 ± 2.1	27.9 ± 1.5	77.7 ± 3.5
	s	22.5 ± 2.4	29.1 ± 2.2	21.7 ± 1.2	73.3 ± 3.5
AK	sb	16.5 ± 2.1	27.8 ± 2.1	32.2 ± 1.6	76.5 ± 3.4
	sf	21.4 ± 2.2	27.0 ± 2.1	32.6 ± 1.8	81.0 ± 3.5
	s	21.0 ± 2.2	25.8 ± 1.9	32.8 ± 1.8	79.6 ± 3.4
KB	sb	16.9 ± 2.0	28.0 ± 2.1	31.0 ± 1.6	75.9 ± 3.3
	sf	24.9 ± 3.0	31.2 ± 2.3	39.1 ± 2.0	95.2 ± 4.3
	s	21.9 ± 2.3	29.7 ± 2.2	33.1 ± 1.7	84.7 ± 3.6
TS	sb	17.5 ± 2.1	28.8 ± 2.2	29.8 ± 1.6	76.1 ± 3.4
	sf	20.9 ± 2.2	23.4 ± 1.8	31.9 ± 1.7	76.2 ± 3.3
	s	20.0 ± 2.2	23.7 ± 1.8	34.4 ± 1.7	78.1 ± 3.3
TK	sb	16.7 ± 2.0	27.0 ± 2.1	31.1 ± 1.5	75.6 ± 3.3
	sf	22.6 ± 2.4	31.6 ± 2.3	32.6 ± 1.7	86.8 ± 3.7
	s	22.1 ± 2.3	32.3 ± 2.4	34.9 ± 1.8	89.3 ± 3.7
$\overline{D}$	sb	17.0 ± 0.4	27.9 ± 0.7	31.0 ± 1.0	75.9 ± 1.3
	sf	22.7 ± 1.8	28.9 ± 3.6	33.5 ± 4.1	85.1 ± 5.7
	s	21.7 ± 1.1	28.9 ± 3.8	32.1 ± 5.5	82.7 ± 6.8
Worldwide average		15	27	18	60

Table 6 Contents of some toxic elements in water samples taken from various water sources, μg L^{-1}

Water object	Element					
	B	As	Mo	Sb	Ba	U
SH	125 ± 19	2.20 ± 0.28	6.43 ± 0.78	0.72 ± 0.13	59.8 ± 5.4	19.4 ± 2.0
SHK	217 ± 33	4.87 ± 0.63	13.3 ± 1.7	1.56 ± 0.25	44.2 ± 4.0	28.6 ± 2.8
AK	186 ± 28	6.21 ± 0.81	17.8 ± 2.2	0.98 ± 0.17	58.5 ± 5.3	22.7 ± 2.3
KB	172 ± 26	7.87 ± 1.04	37.5 ± 4.5	1.21 ± 0.20	60.7 ± 5.5	38.7 ± 3.7
TS	125 ± 19	5.26 ± 0.69	14.5 ± 1.8	1.12 ± 0.18	72.8 ± 6.6	20.6 ± 2.0
TK	119 ± 18	3.54 ± 0.47	8.74 ± 1.12	0.82 ± 0.14	66.4 ± 6.0	18.8 ± 1.9
MAC$_{\mathrm{WHO}}$	500	10	70	20	700	15

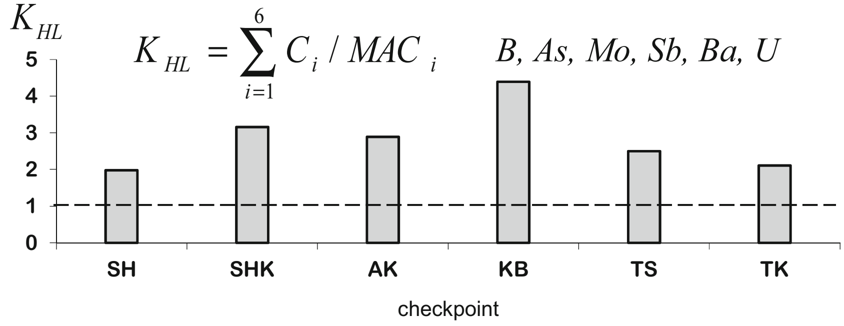

Fig. 3 Values of the hazard limiting coefficient for water sampled at different checkpoints of the studied water basin

Conclusions

There has been performed the radiological surveying with assessment of radionuclide and element composition in water objects (soil, bottom sediments, water) of the transboundary rivers Shu, Shor-Koo, Aksu, Karabalta, Toktas and in the Tasotkel water reservoir in Kazakhstan in the vicinity of the border with Kyrgyzstan. The survey revealed the increased radiation background at the territory of this water basin. Increased contents of the following natural radionuclides and toxic elements were revealed in soil and bottom sediment samples: ^{238}U and ^{232}Th series, As, Co, Cs, Cu, Hf, Mo, Pb, Sb, Sc, Zn, Zr and rare earth elements. Water samples taken at all surveyed objects in this basin demonstrated increased contents of the following toxic elements: B, As, Mo, Ba, U. Uranium content in water of all studied objects exceeds the maximum allowable concentration values set for drinking water recommended by the WHO.

The revealed anomalies in the environmental objects demonstrate negative influence from radiation-hazardous sites in Kyrgyzstan (Ak-Tyuz and Karabalta) on the contamination with natural radionuclides and toxic elements revealed in the investigated transboundary rivers. Further studies of the rate and mechanisms of this phenomenon are required.

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