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# Assessment of the radionuclide and chemical composition of the Irtysh River water at the Republic of Kazakhstan territory

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The transboundary Irtysh River flows through the territory of three states: China, Kazakhstan and Russia. Industrial enterprises are located in the Irtysh River basin at the territory of Kazakhstan. Also, the Semipalatinsk nuclear test site can affect the state of the Irtysh River water. For this reason, researches were carried out to determine the content of natural and anthropogenic radionuclides, macro-, microcomponents and heavy metals in the Irtysh River water. According to the results, no anomalous deviations in the concentration of radionuclides have been established. Except the radionuclide $^{3}H$, which almost constantly inputs in small quantities to the various components of the Irtysh River ecosystem with the Shagan River waters. In terms of the macrocomponent composition, only the $Cl^{-}$ content and the degree of water hardness exceed the standards of the Republic of Kazakhstan. In terms of heavy metals and microcomponents (a total of 16 elements were identified), near the Ust-Kamenogorsk city the Fe content is 1.2–2 times higher than the MPC. Results of the calculations of the comprehensive water pollution index (CWPI) of the Irtysh River water at the Kazakhstan territory correspond to standard clean water.

## 1 Introduction

The problem of the shortage of fresh drinking water has been viewed since the 20th century as a global problem of our time. The world's population is growing rapidly, while the need for clean drinking water is increasing. One of the main problems is the pollution of fresh water, which significantly reduces the already existing reserves. This pollution is caused by industrial emissions and runoff, the washing away of fertilizers from fields, and the intrusion of salt water into aquifers due to groundwater pumping. Aquatic ecosystems are currently subject to the simultaneous impact of different sources of pollution.[1,2] Therefore, one of the most important issues in ecology is the problem of the state of water resources, and the identification of sources of pollution of aquatic ecosystems.

Although the Republic of Kazakhstan belongs to the water-scarce regions of the world, East Kazakhstan is one of the richest regions of the Republic in terms of water resources. This is determined by its natural and climatic conditions. The water fund of the region includes rivers, lakes, swamps, ponds and reservoirs, groundwater and glaciers.[3] The central place in the hydrographic network of the region is occupied by the transboundary Irtysh River, with more than 2.5 million people living in the basin. The Irtysh River flows through the territory of three states: China, Kazakhstan and Russia. The river is a water body of special national importance. The river length before it flows into the Ob River is 4248 km. The total catchment area of the Irtysh River is 1 643 000 km$^2$. Only part of the river, which is 1700 km long, flows through the Kazakhstan territory. In the Irtysh River basin, there are more than 700 tributaries, of which 4 large rivers (Bukhtarma, Uba, Kurchum and Ulba) are more than 200 km long, the rest belong to the category of small rivers with a total length of 17 700 km. The right-bank tributaries of the Irtysh River (in addition to the indicated 4 large rivers) include the rivers of the Southern Altai with lower water content, the largest of which are the Kaba, Alkabek, Kalzhir, Naryn. The rivers on the Irtysh River left bank, especially the Zaisan Lake basin – Kenderlyk, Uydene, Kandysu, Bukon, Shar, Kokpekty, are characterized by even lower water content. The Irtysh River flow is regulated by a cascade of reservoirs – Bukhtarminskoye, Ust-Kamenogorskoye and Shulbinskoye.[4,5] The river provides water to the population and economy not only within its basin, but also to a large area of water-scarce Central Kazakhstan through the Irtysh-Karaganda Canal (Fig. 1).[6] As the river is transboundary, its rational use is not only economically and ecologically important, but also of great political and international importance.

The main sources of anthropogenic contamination of surface and ground water in the Irtysh River basin at the Republic of Kazakhstan territory are associated with the activities of mining

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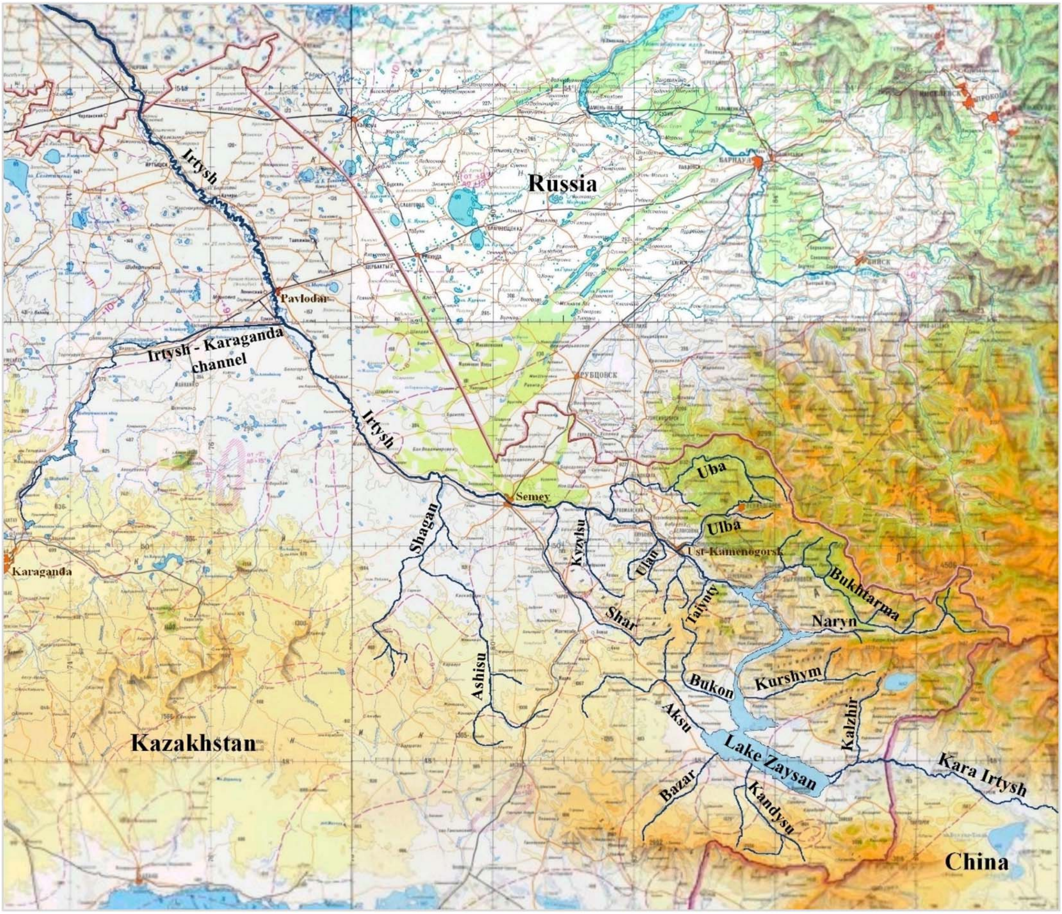


Fig. 1 The Irtysh River basin.

and processing enterprises, as well as enterprises of the chemical, oil refining, engineering industries and non-ferrous metallurgy. On the Irtysh River tributaries are the tailings of the former Belogorsk combine, overburden dumps Tishinsky quarry from which is a partial leaching of ore, Irtysh Chemical and Metallurgical Plant in Pervomaysky village. Other sources of contamination in the river's tributaries are mine water from the former Berezovsky mine, about 8 million tons of low-oxidized rocks containing polymetals from the Chekmar mine, and effluent from the Snegirikhinsky mine, which, due to its launch and operation, receives zinc, copper and lead in water in excess of the maximum permissible concentrations (MPC) many times over.[7,8]

On the Irtysh River there are large industrial centers of Kazakhstan – the cities of Ust-Kamenogorsk, Semey and Pavlodar, whose industrial enterprises can have a negative impact on the ecological state of the river.

In Ust-Kamenogorsk city such enterprises include the landfill of chlorine-containing waste of the Titanium–Magnesium Plant, sludge reservoirs of the former Lead and Zinc Plant (now the LLP "Kazzinc"), radiation waste dump of the Ulba Metallurgical Plant, tailings of the Condenser Plant, *etc.* About 77% of the total volume of discharges of the Ust-Kamenogorsk falls on the effluents of the left-bank treatment facilities of the "Oskemen-Vodokanal". Such effluents contain substances characteristic of both domestic human activities and the waste water of various industrial industries.[9,10] At the same time, researches were previously carried out to determine the content of heavy metals in the Irtysh River water in the area of the cities of Semey[11,12] and Pavlodar,[13] which are located downstream of the Irtysh River at a distance of 200 and 530 km, respectively, from Ust-Kamenogorsk city.

Nuclear weapons testing at the Semipalatinsk test site (STS) may have had a significant impact on the contamination of the Irtysh River ecosystem with anthropogenic radionuclides. The part of the nuclear test traces spreads in the catchment area of the Irtysh River basin. The main concern, in terms of possible radioactive contamination, is the place of the confluence the Shagan River into the Irtysh River. The Shagan River flows along the eastern border of the "Balapan" test site, extends beyond the STS and is a left-bank tributary of the Irtysh River. Because of nuclear tests at the STS, the valley of the Shagan River was subjected to radioactive contamination.[14] At present, the main radionuclide contaminant of the river is tritium ($^3$H). The source of contamination is groundwater flowing into the surface water of the river from the "Balapan" test site. The underground nuclear tests were carried out at this site in vertical boreholes.[15,16] Also, in the area of the "Balapan" test site there is a research reactor where experimental studies with $^3$H were carried out.[17] As a result of previous researches, in 2010 quantitative values of $^3$H were fixed for the first time at the place of the confluence of the Shagan River into the Irtysh River, where the specific activity of

$^{3}$H in water was 400 Bq L$^{-1}$.[18] In 2011, the fact of $^{3}$H transfer to the Irtysh River with the Shagan River water at the level of 50 Bq L$^{-1}$ was confirmed and the transfer was fixed practically during the whole spring-summer period.[19]

In recent years, there are more and more new works on the research of anthropogenic loads on the Irtysh River,[20] including a study of the river's biodiversity,[21] determination of toxicological indicators,[22] determination of heavy metals in soil,[23] and research of thermal pollution from operation of hydroelectric power plants located on the river.[24] However, to date there is no research a wide range of macro- and microelements, natural and anthropogenic radionuclides in the Irtysh River water. Some modern publications cover the ecological situation of the Irtysh River, based on official statistics.[25,26] At local monitoring stations in assessing the quality of surface waters in most cases they determine 16 chemical indicators, among which only 9 are inorganic chemical elements: B, Mn, Cr, Fe, Cu, Zn, Hg, Cd,[27,28] or individual heavy metals in the Irtysh River water, such as Zn,[29] Cu[30] and Cd,[31] and these researches were carried out about 20 years ago. At the same time, there are no data on the content of natural and anthropogenic radionuclides in water.

The purpose of this work was to determine the levels of natural and anthropogenic radionuclides, heavy metals, macro- and microelements in the Irtysh River water.

## 2 Materials and methods

For an estimation of the ecological state of the river the sites with the greatest anthropogenic influence were chosen: in the area of the large industrial center – Ust-Kamenogorsk city and in the place of the confluence the Shagan River into the Irtysh River. The scheme of the research sites is shown in Fig. 2.

The water sampling points were located as follows:

- Site 1: before the river passes through Ust-Kamenogorsk city; in the city on the right and left banks; and after Ust-Kamenogorsk city;

- Site 2: before the confluence, at the confluence and after the confluence of the Shagan River into the Irtysh River.

The scheme of the sampling points is shown in Fig. 2 and the data for the water sampling points are shown in Table 1.

Water samples were taken in the summer and autumn seasons from the bottom layer with a volume of at least 20 L, and in areas after Ust-Kamenogorsk city and after the confluence of the Shagan River – with a volume of 120 L.

The preliminary preparation of water samples after arrival at the laboratory consisted of filtration and preservation with concentrated nitric acid to pH = 2, except for a part of samples to determine the chemical composition.

Then radionuclide analysis was carried out to determine the content of natural ($^{40}$K, $^{232}$Th, $^{226}$Ra, $^{210}$Po, $^{238}$U) and anthropogenic ($^{3}$H, $^{137}$Cs, $^{241}$Am, $^{90}$Sr, $^{239+240}$Pu) radionuclides, chemical analysis was performed to determine the macrocomponent content, and elemental analysis was performed to determine the heavy metals and microcomponents.

As noted above, the main contaminating anthropogenic radionuclide at the confluence of the Shagan River into the Irtysh River is $^{3}$H, therefore additional researches were carried out, including in winter. Research in winter is due to the fact that at the confluence of the Shagan River (p. 6) the small section of the waterway does not freeze even in severe frost. The water samples were taken at regular intervals at this p. 6, where the $^{3}$H content was determined. In order to estimate indirectly the redistribution of $^{3}$H in the ecosystem components of the Irtysh River at Site 2, research of this radionuclide in snow cover during the winter period was conducted. For this purpose, 3 sample sites were chosen at each point (pp. 5–7) and snow samples were taken in layers: from the lower (bottom) layer and from the upper (surface) layer. A total of 18 snow samples were taken and analysed for $^{3}$H content.

Determination of the natural radionuclides content in water was performed from 10 L samples, which were evaporated to a dry residue in advance and then measured on an γ-spectrometer by "ORTEC". The $^{210}$Po content in 2 L samples was performed after radiochemical separation and autodeposition on copper disks, using α-spectrometer measurements by "Canberra Co". The $^{238}$U content in water was determined in 0.02 L samples using the quadrupole mass-spectrometer with inductively coupled plasma Agilent 7700x (by "Agilent Technologies"), which allows the analysis of element ultra-trace content. Determination of $^{3}$H content in water samples of 0.02 L volume was carried out by the β-spectrometric method using a low-background liquid spectrometric radiometer SL-300 by "Hidex". To determine the $^{137}$Cs, $^{241}$Am, $^{90}$Sr, and $^{239+240}$Pu contents, 100 L water samples were preconcentrated by evaporation to a volume of 10 L. Then all 10 L water samples were concentrated using the co-precipitation method: $^{241}$Am and $^{239+240}$Pu with iron(III) hydroxide, $^{90}$Sr with calcium carbonate, $^{137}$Cs with copper hexacyanoferrate. Further, the $^{137}$Cs and $^{241}$Am contents were measured on the γ-spectrometer by "ORTEC". Determination of $^{90}$Sr content was performed by the β-spectrometric method using the daughter $^{90}$Y after preliminary radiochemical extraction followed by measurement on the TRI-CARB β-spectrometer (by "PerkinElmer, Inc"). Determination of $^{239+240}$Pu content was performed using the α-spectrometric method after extraction-chromatographic extraction and electrolytic precipitation followed by measurement on the α-spectrometer by "Canberra Co".

To determine the chemical–physical parameters and the macrocomponents in water, a general chemical analysis of water from 2 L samples was carried out using standard methods: pH level, salinity and hardness, macrocomponents of the basic composition ($Na^{+}$, $K^{+}$, $Ca^{2+}$, $Mg^{2+}$, $Cl^{-}$, $HCO_3^{-}$, $SO_4^{2-}$). Determination of the heavy metals and microcomponents were carried out by measuring a 0.5 L water sample on the mass-spectrometer with inductively coupled plasma Agilent 7700x (by "Agilent Technologies"), as well as by atomic emission spectrometry with inductively coupled plasma using an iCap 6300 Duo spectrometer (by "Thermo Scientific").

The ratios of the stable isotopes $^{2}$H/$^{1}$H and $^{18}$O/$^{16}$O were measured using an LGR 912-0008 laser spectrometer (by "Los Gatos Research, Inc."). The international standard "VSMOW-2" (Vienna Standard Mean Ocean Water, IAEA) was used as a calibration standard.

 

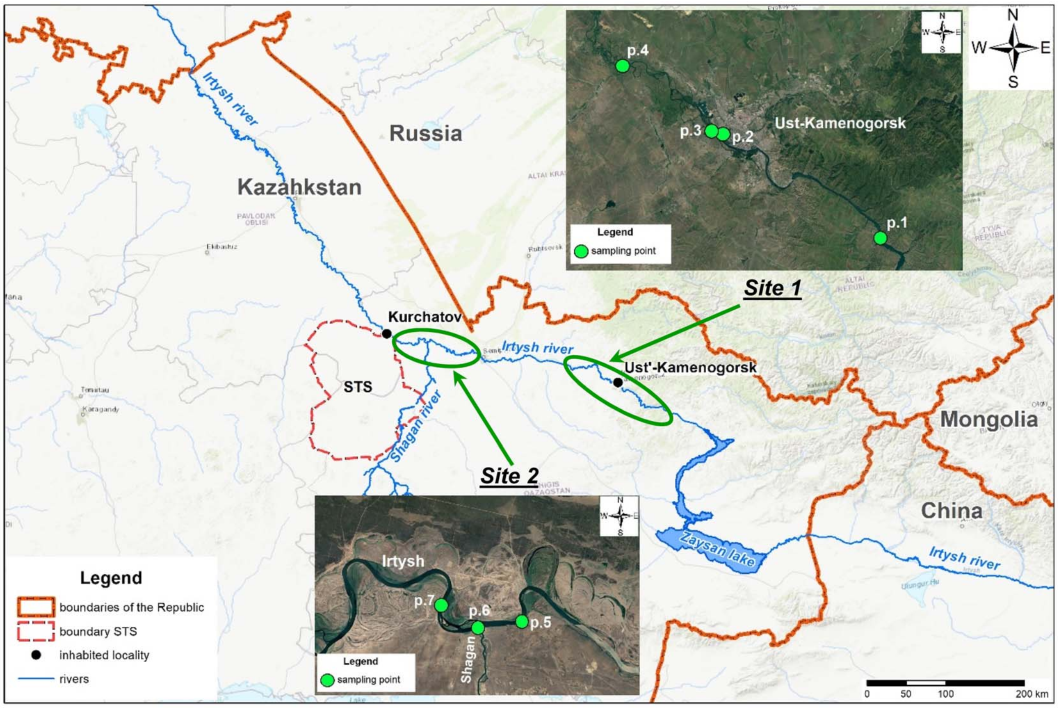


Fig. 2 Scheme of research sites and sampling points locations on the Irtysh River.

Table 1 Data on water sampling points

| No. | Sampling site description | Sampling point | Coordinates | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Latitude | | | Longitude | | |
| 1 | Irtysh River before Ust-Kamenogorsk city | p. 1 | 49 | 54 | 13.4 | 82 | 43 | 44.4 |
| 2 | Within the city limits of Ust-Kamenogorsk, right bank | p. 2 | 49 | 58 | 23.4 | 82 | 33 | 16.4 |
| 3 | Within the city limits of Ust-Kamenogorsk, left bank | p. 3 | 49 | 58 | 14.8 | 82 | 33 | 8 |
| 4 | Irtysh River after Ust-Kamenogorsk city | p. 4 | 50 | 2 | 27.5 | 82 | 25 | 12.5 |
| 5 | Before the confluence of the Shagan River into the Irtysh River | p. 5 | 50 | 36 | 9.1 | 79 | 25 | 51 |
| 6 | The place of the confluence the Shagan River into the Irtysh River | p. 6 | 50 | 37 | 57.8 | 79 | 15 | 39 |
| 7 | After the confluence of the Shagan River into the Irtysh River | p. 7 | 50 | 38 | 21.3 | 79 | 12 | 58.9 |

# 3 Results and discussion

## 3.1 Determination of natural and anthropogenic radionuclides in the Irtysh River water

The results of the analyses for the determination of natural and anthropogenic radionuclides in water are presented in Tables 2 and 3.

The content of natural radionuclides in the Irtysh River water was below the detection limit (DL) for $^{40}$K, $^{232}$Th and $^{226}$Ra, the $^{210}$Po content ranged from $(0.7 \pm 0.2) \times 10^{-3}$ to $(2.5 \pm 0.4) \times 10^{-2}$ Bq L$^{-1}$, for $^{238}$U – from $<1.3 \times 10^{-4}$ to $0.12 \pm 0.01$ Bq L$^{-1}$. The obtained data on the $^{210}$Po and $^{238}$U contents in water are 2–3 orders of magnitude lower than the intervention level (IL) with water, according to the Hygienic standards established in the Republic of Kazakhstan (RK).[32]

The contents of the anthropogenic radionuclides $^{3}$H, $^{137}$Cs, $^{241}$Am, $^{90}$Sr and $^{239+240}$Pu in water were below the DL. Except for the place of the confluence of the Shagan River into the Irtysh River, where the $^{90}$Sr content is $0.07 \pm 0.01$ Bq L$^{-1}$, which is 2 orders of magnitude lower than the IL, and the $^{3}$H content is $9 \pm 4$ Bq L$^{-1}$, which is 3 orders of magnitude lower than the IL.[32]

## 3.2 Determination of $^{3}$H contamination of the river ecosystem components at the place of the confluence of the Shagan River into the Irtysh River

The $^{3}$H content in the water at Site 2 and the sampling date are presented in Table 4.

At the confluence of the Shagan River and the Irtysh River (p. 6) in winter the numerical values of the $^{3}$H content are fixed at

Table 2 The activity concentrations of the natural radionuclides in water

| | Activity concentration, Bq L$^{-1}$ | | | | |
|---|---|---|---|---|---|
| Sampling point | $^{40}$K | $^{232}$Th | $^{226}$Ra | $^{210}$Po | $^{238}$U |
| **Summer** | | | | | |
| p. 1 | <5.4 × 10$^{-2}$ | <1.6 × 10$^{-2}$ | <2.0 × 10$^{-2}$ | (0.9 ± 0.2) × 10$^{-3}$ | (2.3 ± 0.5) × 10$^{-2}$ |
| p. 2 | <5.5 × 10$^{-2}$ | <1.4 × 10$^{-2}$ | <1.7 × 10$^{-2}$ | (1.5 ± 0.4) × 10$^{-3}$ | <1.3 × 10$^{-4}$ |
| p. 3 | <6.2 × 10$^{-2}$ | <1.7 × 10$^{-2}$ | <1.6 × 10$^{-2}$ | (2.1 ± 0.6) × 10$^{-3}$ | (2.1 ± 0.5) × 10$^{-2}$ |
| p. 4 | <3.7 × 10$^{-2}$ | <1.6 × 10$^{-2}$ | <1.3 × 10$^{-2}$ | (0.7 ± 0.2) × 10$^{-3}$ | (2.3 ± 0.3) × 10$^{-2}$ |
| p. 5 | <5.1 × 10$^{-2}$ | <2.1 × 10$^{-2}$ | <1.7 × 10$^{-2}$ | (2.1 ± 0.4) × 10$^{-3}$ | (2.1 ± 0.5) × 10$^{-2}$ |
| p. 6 | <6.3 × 10$^{-2}$ | <3.1 × 10$^{-2}$ | <3.4 × 10$^{-2}$ | (2.2 ± 0.5) × 10$^{-3}$ | (4.8 ± 0.6) × 10$^{-2}$ |
| p. 7 | <3.7 × 10$^{-2}$ | <1.5 × 10$^{-2}$ | <1.1 × 10$^{-2}$ | (1.8 ± 0.5) × 10$^{-3}$ | (2.0 ± 0.3) × 10$^{-2}$ |
| **Autumn** | | | | | |
| p. 1 | <3.5 × 10$^{-2}$ | <9.4 × 10$^{-3}$ | <1.0 × 10$^{-2}$ | (7.6 ± 1.2) × 10$^{-3}$ | (2.9 ± 0.3) × 10$^{-2}$ |
| p. 2 | <7.0 × 10$^{-2}$ | <2.0 × 10$^{-2}$ | <1.9 × 10$^{-2}$ | (2.7 ± 0.4) × 10$^{-3}$ | (2.1 ± 0.1) × 10$^{-2}$ |
| p. 3 | <1.1 × 10$^{-1}$ | <3.1 × 10$^{-2}$ | <3.4 × 10$^{-2}$ | (2.5 ± 0.4) × 10$^{-2}$ | 0.12 ± 0.01 |
| p. 4 | <3.8 × 10$^{-2}$ | <1.1 × 10$^{-2}$ | <1.1 × 10$^{-2}$ | (1.2 ± 0.5) × 10$^{-2}$ | (2.4 ± 0.1) × 10$^{-2}$ |
| p. 5 | < 6.4 × 10$^{-2}$ | < 1.6 × 10$^{-2}$ | < 2.0 × 10$^{-2}$ | (7.3 ± 1)×10$^{-3}$ | (2.4 ± 0.1)×10$^{-2}$ |
| p. 6 | < 5.0 × 10$^{-2}$ | < 1.4 × 10$^{-2}$ | < 1.7 × 10$^{-2}$ | (6.1 ± 1.1)×10$^{-3}$ | (1.4 ± 0.1)×10$^{-2}$ |
| p. 7 | <6.0 × 10$^{-2}$ | <1.6 × 10$^{-2}$ | <1.6 × 10$^{-2}$ | (5.6 ± 0.9) × 10$^{-3}$ | (2.8 ± 0.1) × 10$^{-2}$ |
| Intervention level | — | 0.6 | 0.49 | 0.11 | 3 |

Table 3 The activity concentrations of the anthropogenic radionuclides in water

| | Activity concentration, Bq L$^{-1}$ | | | | |
|---|---|---|---|---|---|
| Sampling point | $^{3}$H | $^{137}$Cs | $^{241}$Am | $^{90}$Sr | $^{239+240}$Pu |
| **Summer** | | | | | |
| p. 1 | <4 | <0.01 | <0.02 | <0.01 | <1.3 × 10$^{-4}$ |
| p. 2 | <4 | <0.01 | <0.02 | <0.01 | <4.6 × 10$^{-4}$ |
| p. 3 | <4 | <0.01 | <0.03 | <0.01 | <4.8 × 10$^{-5}$ |
| p. 4 | <4 | <0.01 | <0.02 | <0.01 | <1.4 × 10$^{-4}$ |
| p. 5 | <4 | <0.01 | <0.01 | <0.01 | <1.1 × 10$^{-4}$ |
| p. 6 | 9 ± 4 | <0.01 | <0.02 | <0.01 | <8.3 × 10$^{-5}$ |
| p. 7 | <4 | <0.01 | <0.02 | <0.01 | <8.4 × 10$^{-5}$ |
| Autumn | | | | | |
| p. 1 | <4 | <0.02 | <0.02 | < 0.01 | <1.1 × 10$^{-4}$ |
| p. 2 | <4 | <0.02 | <0.02 | <0.01 | <1.1 × 10$^{-4}$ |
| p. 3 | <4 | <0.03 | <0.02 | <0.01 | <1.5 × 10$^{-5}$ |
| p. 4 | <4 | <0.003 | <0.04 | <0.01 | <1.0 × 10$^{-4}$ |
| p. 5 | <4 | <0.03 | <0.01 | <0.01 | <1.1 × 10$^{-4}$ |
| p. 6 | <4 | <0.03 | <0.01 | 0.07 ± 0.01 | <1.1 × 10$^{-4}$ |
| p. 7 | <4 | <0.004 | <0.03 | <0.01 | <1.3 × 10$^{-5}$ |
| Intervention level | 7600 | 11 | 0.69 | 4.9 | 0.55 |

levels up to 20 ± 4 Bq L$^{-1}$, in contrast to autumn, where the $^{3}$H concentration below the DL. Probably, in autumn, water is diluted with precipitation (rain), but in winter this effect is absent, and only $^{3}$H contaminated waters enter the watercourse. In spring and summer period, the presence of $^{3}$H in water is due to the leaching of the radionuclide by melt water from the contaminated area of the STS and partial dilution. In the place before and after the confluence of the Shagan River, the $^{3}$H content in the water is below the DL.

The of $^{3}$H content in the snow cover is presented in Table 5.

At the confluence of the Shagan River and the Irtysh River, in the section of the nonfreezing waterway (p. 6), high $^{3}$H concentrations in the snow cover of up to 290 ± 40 Bq L$^{-1}$ were detected. However, at some distance from this point, in the places before and after the confluence of the Shagan River, no numerical values of $^{3}$H were detected.

The isotopic composition of water is expressed in relative values $\delta^2$H and $\delta^{18}$O in ‰:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000‰ \quad (1)$$

where $R_{\text{sample}}$ and $R_{\text{standard}}$ relations $^2$H/$^1$H and $^{18}$O/$^{16}$O in the measured sample and the standard. The standard is the mean ocean water "SMOW" (Standard of Mean Ocean Water, IAEA). To analyse the conditions for water and snow formation, the measurement results are plotted on the $\delta^{18}$O − $\delta^2$H diagram with the Local Meteoric Water Line (LMWL), which is built on the basis of the Global Meteoric Water Line, taking into account stable isotopes in the atmospheric precipitation of the research region. The results of analysis of the ratios of stable isotopes $^2$H/$^1$H and $^{18}$O/$^{16}$O in water and snow are presented in Fig. 3.

The isotopic composition of water varies from −111‰ to −96.9‰ for $\delta^2$H, from −15.7‰ to −12.1‰ for $\delta^{18}$O, snow from −158.4‰ to −120.2‰ for $\delta^2$H, from −20.6‰ to −15.4‰ for

Table 4 The activity concentration of $^{3}$H in water

| Sampling point | Sampling date | Activity concentration $^{3}$H, Bq L$^{-1}$ |
|---|---|---|
| p. 5 | May 14, 2021 | <4 |
| p. 6 | February 12, 2021 | 20 ± 4 |
| | February 26, 2021 | 13 ± 4 |
| | March 13, 2021 | 15 ± 4 |
| | May 14, 2021 | 9 ± 4 |
| | June 30, 2021 | 9 ± 4 |
| | October 23, 2021 | <4 |
| p. 7 | May 14, 2021 | <4 |

 

Table 5 Activity concentration of $^{3}H$ in snow cover

| Sampling point | Sampling place | Activity concentration $^{3}H$, Bq $L^{-1}$ | |
|---|---|---|---|
| | | Lower cover | Upper cover |
| p. 5 | 5/1 | <4 | <4 |
| | 5/2 | <4 | <4 |
| | 5/3 | <4 | <4 |
| p. 6 | 6/1 | <4 | 110 ± 20 |
| | 6/2 | <4 | 15 ± 4 |
| | 6/3 | 290 ± 40 | <4 |
| p. 7 | 7/1 | <4 | <4 |
| | 7/2 | <4 | <4 |
| | 7/3 | <4 | <4 |

$\delta^{18}O$. It was found that the isotopic composition of winter precipitation is much lighter than the isotopic composition of the Irtysh River surface waters. According to the comparative analysis, it was revealed that the Irtysh River water is located mainly in the zone of influence of regional atmospheric precipitation, formed during the spring and winter periods (February, March). Solid precipitation is the main source for river waters, that is, river water is fed mainly during spring snowmelt. Seasonal variations in the isotopic composition of the river's surface waters are not observed. This indicates the interannual stability of the water supply structure. Consequently, the absence of $^{3}H$ in water in autumn is associated with the dilution of the Shagan River water by precipitation (rain). In winter, the watercourse receives only underflow water, which is contaminated with $^{3}H$ coming from the nuclear test site territory.

According to the obtained data on radionuclide contamination of the Irtysh River water, it follows that the anthropogenic radionuclides $^{137}Cs$, $^{90}Sr$ and $^{239+240}Pu$ do not enter the river from the STS territory, unlike $^{3}H$. The obtained quantitative $^{3}H$ concentration in the environmental components (water and snow) and their territorial confinement to p. 6 indicate the input of this radionuclide with the Shagan River water into the Irtysh River even in winter.

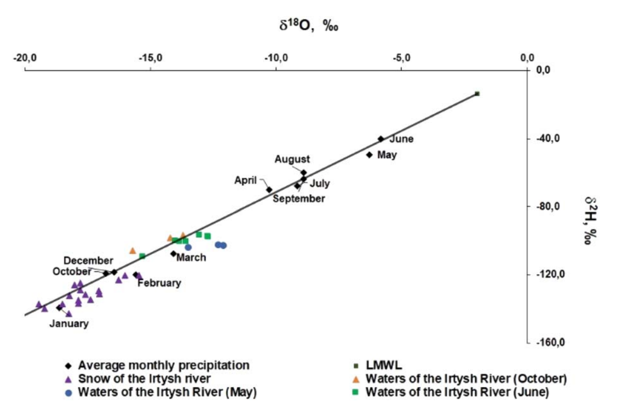


Fig. 3 The results of analysis of stable isotopes $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratio in water and snow.

### 3.3 Determination of heavy metals, macro- and microelements in the Irtysh River water

The results of determining the chemical composition of the Irtysh River water are presented in Table 6.

Chemical analysis of the Irtysh River water showed that the pH of the water was neutral (7.0–7.5) and slightly alkaline (7.6–8). As for other parameters (with the exception of p. 6), water is fresh in terms of the degree of salinity, and soft in terms of the degree of hardness. According to these parameters, water is suitable for use for economic purposes, in accordance with the Hygienic Standards established in RK.[34]

The Shagan River waters are characterized as very hard (up to 30 mmol $L^{-1}$) and salty (up to 20 g $L^{-1}$).[18] When the Shagan River water enter the Irtysh River, dilution occurs. But nevertheless, in this area at the confluence of the Shagan and the Irtysh Rivers (p. 6), in summer water belongs to the category of medium hardness, and in autumn – in terms of the degree of salinity they are brackish, in terms of the degree of hardness – hard, and according to these parameters water is not suitable for use for economic purposes, in accordance with the Hygienic Standards of RK.[34]

The comparative analysis of the macrocomponent composition of the Irtysh River water, sampled in summer and autumn, is presented in the form of histograms in Fig. 4.

According to the present data, the macrocomponents content of the Irtysh River water in autumn exceeds its content in summer. This is due to the dilution of river waters with melt water in spring and precipitation (rain) at the beginning of summer. If we compare the macrocomponents content in water at different sampling points, then their highest content was fixed at p. 6 at the confluence of the Shagan River into the Irtysh River, regardless of the season. At the same time, the $Cl^{-}$ content in water in autumn exceeds the maximum permissible concentration (MPC) by 1.3 times according to Hygienic standards. In summer, due to more dilution, the macrocomponents content does not exceed the Hygienic standards.[34]

The chemical composition of the Irtysh River water is presented in the Piper diagram (Fig. 5). This diagram consists of two triangular fields: the left represents the cation composition, the right represents the anion composition. The diamond-shaped field in the center represents the cations and anions composition, that are present in water. The Piper diagram allows for a more detailed classification of waters according to the main cations and anions.[35]

According to the Piper diagram in summer by the cation composition of the Irtysh River water in p. 2 and p. 5 belong to the $Na^{+} + K^{+}$ type, pp. 1, 3, 4, 6, 7 – mixed, there is no dominant cation; by the anionic composition pp. 1, 3, 4, 7 – hydrocarbonate type, p. 2 – sulfate waters, p. 5 and p. 6 – mixed. In autumn, by the cation composition in pp. 2, 5, 6, 7 – $Na^{+} + K^{+}$ type; pp. 1, 3, 4 – mixed, no dominant cation; by anion composition p. 6 is chloride water, all the rest are hydrocarbonate.

To visually depict the chemical composition of the water, the Kurlov formula was used. This formula is a pseudo fraction (a false fraction, since the division operation is not performed), in

Table 6 Chemical composition of the Irtysh River water

| | | | | Cation content, mg $L^{-1}$ | | | Anion content, mg $L^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Sampling point | pH | Salinity, mg $L^{-1}$ | Hardness, mmol $L^{-1}$ | $Na^+ + K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $HCO_3^-$ | $SO_4^{2-}$ |
| Summer | | | | | | | | | |
| p. 1 | 7.7 | 136 | 1.75 | 30 | 25 | 5 | 5 | 105 | 55 |
| p. 2 | 7.1 | 95 | 0.65 | 30 | 10 | 1 | 2 | 50 | 50 |
| p. 3 | 7.5 | 140 | 1.7 | 30 | 20 | 10 | 5 | 105 | 50 |
| p. 4 | 7.2 | 130 | 1.8 | 30 | 20 | 10 | 5 | 110 | 50 |
| p. 5 | 7.9 | 205 | 1.8 | 45 | 25 | 5 | 15 | 105 | 75 |
| p. 6 | 8 | 580 | 4.9 | 110 | 45 | 30 | 130 | 135 | 180 |
| p. 7 | 7.7 | 170 | 1.8 | 30 | 25 | 10 | 10 | 100 | 50 |
| **Autumn** | | | | | | | | | |
| p. 1 | 7.0 | 160 | 2.0 | 20 | 15 | 15 | 35 | 100 | 15 |
| p. 2 | 7.5 | 240 | 2.2 | 60 | 20 | 15 | 40 | 200 | 20 |
| p. 3 | 7.3 | 110 | 1.5 | 15 | 10 | 10 | 20 | 70 | 20 |
| p. 4 | 7.5 | 180 | 2.0 | 30 | 15 | 15 | 35 | 100 | 30 |
| p. 5 | 7.0 | 285 | 2.5 | 65 | 25 | 15 | 55 | 200 | 20 |
| p. 6 | 7.5 | 1250 | 10 | 245 | 110 | 55 | 450 | 300 | 145 |
| p. 7 | 7.5 | 265 | 2.0 | 60 | 25 | 10 | 60 | 150 | 20 |
| MPC[34] | 6–9 | 1000 | 7.0 | — | — | — | 350 | — | 500 |

the numerator of which the content of anions (in %-eq.) is written in descending order, and in the denominator of cations (in %-eq.). In front of the fraction abbreviately indicate the value of mineralization $M$ (in g $L^{-1}$), and at the end of the fraction – pH. Below is a general "passport" for the seasons of the Irtysh River water at the Kazakhstan territory according to Kurlov's formula:

Summer

$$M(95-1000)\frac{HCO_3(25-60)SO_4(35-55)Cl(5-40)}{Na+K(40-65)Ca(25-40)Mg(5-30)}$$

$$pH(7.1-8.0)$$

Autumn

$$M(110-1250)\frac{HCO_3(25-70)Cl(25-60)SO_4(10-20)}{Na+K(30-54)Mg(20-50)Ca(20-30)}$$

$$pH(7.0-7.5)$$

The results of determining the microelement composition of the Irtysh River water are presented in Table 7.

According to the obtained data, the contents of the microelements V, Co, Ni, Cd and Pb in the water is below the DL (<0.05 μg $L^{-1}$, <0.05 μg $L^{-1}$, <0.5 μg $L^{-1}$, <0.1 μg $L^{-1}$ and <0.01 μg $L^{-1}$, respectively), except for p. 6 at the confluence of the Shagan River into the Irtysh River, where V content was $3.2 \pm 0.02$ μg $L^{-1}$. It should be noted that in autumn, numerical values for Cr, Cu, Zn, As, Mo were recorded, compared to summer, when their content in water was below the DL (<0.1 μg $L^{-1}$, for all listed microelements).

On the right bank of the Irtysh River in Ust-Kamenogorsk city (p. 2), in summer increased values were recorded for Al and Fe, while the Fe content was 1.2 times higher than the MPC according to the Hygienic standards.[34] In autumn, high contents of Al, Fe and Zn were recorded at the same point, where the Fe content was 2 times higher than the MPC. However, these element contents do not exceed the standard values established by the World Health Organization (WHO).[36]

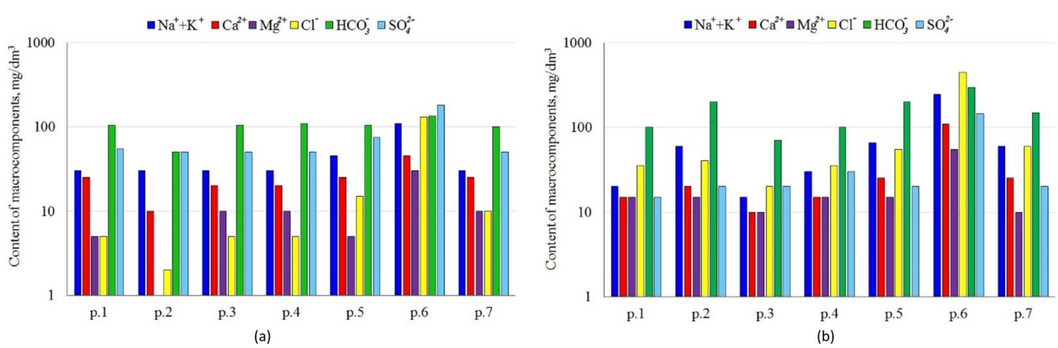


Fig. 4 The macro-component composition of the Irtysh River water: (a) summer; (b) autumn.

 

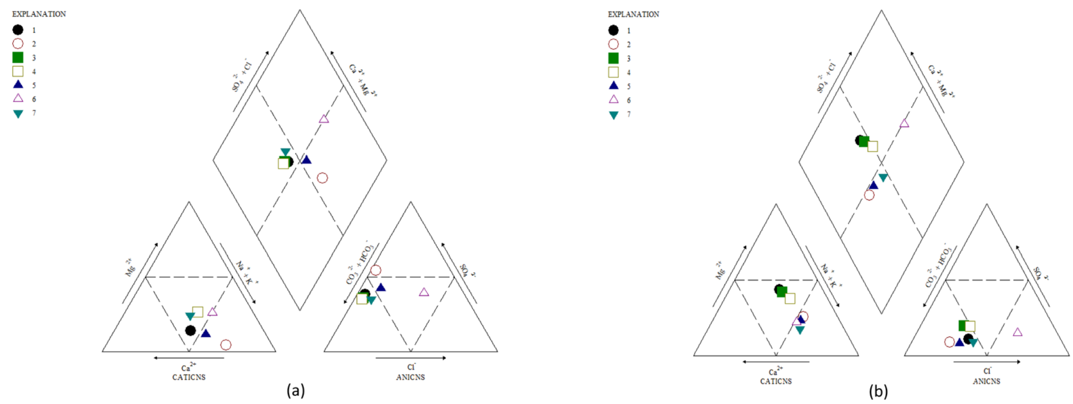


Fig. 5 The chemical composition of the Irtysh River water on the Piper diagram: (a) summer; (b) autumn (points numbers correspond to sampling points in Table 1).

At the confluence of the Shagan River with the Irtysh River (p. 6), increased values of Sr and U were fixed compared with other sites, but did not exceed the MPC.

To reveal features of the Irtysh River water element composition, decreasing series are prepared for their average values toward average river water composition around the globe, using the data:[37,38]

$$U_{38} > Sr_{6,4} > Ba_{2,1} > Mo_{1} > Mn_{0,75} > Cr_{0,44} > As_{0,33} > Zn_{0,28} > Cu_{0,2} > Fe_{0,17} > Al_{0,14}$$ – according to ref. 37;

$$Zn_{9,4} > Sr_{5,4} > U_{4,1} > Mo_{2,4} > Fe_{1,7} > As_{1,1} > Cu_{0,94} > Ba_{0,91} > Cr_{0,63} > Mn_{0,16}$$ – according to ref. 38.

The concentrations of the studied elements exceeded the average values for river waters of the world, for uranium – tens of times. This series also reflects the characteristic elements for the Irtysh River – U, Zn, Sr, Mo and Ba.

The Complex Water Pollution Index (CWPI) is widely used in domestic and foreign practice as an integral indicator for assessing water quality.[33,39] This index is a typical additive coefficient and represents the average share of exceeding MPC for a certain number of components: by the group of heavy metals ($CWPI_{HM}$) and by the group of main ions – macrocomponents ($CWPI_{MI}$), considering the correction for the hazard category.[40] These indexes were determined for parameters that exceed their own MPC and were calculated as:

Table 7 The microelements composition of the Irtysh River water

| | Elements content, μg L$^{-1}$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sampling point | Al | Cr | Mn | Fe | Cu | Zn | As | Sr | Mo | Ba | U |
| **Summer** | | | | | | | | | | | |
| p. 1 | 35 ± 11 | <DL | 1.9 ± 1.5 | 38 ± 2 | <DL | <DL | <DL | 170 ± 12 | <DL | 15.0 ± 3.2 | 1.8 ± 0.3 |
| p. 2 | 460 ± 68 | <DL | 5.8 ± 1.5 | 36 ± 3 | <DL | <DL | <DL | 73 ± 7 | <DL | 18.0 ± 3.2 | <DL |
| p. 3 | 32 ± 13 | <DL | <DL | 370 ± 18 | <DL | <DL | <DL | 170 ± 12 | <DL | 20.0 ± 2.7 | 1.9 ± 0.4 |
| p. 4 | 47 ± 17 | <DL | 1.7 ± 0.4 | 55 ± 10 | <DL | <DL | <DL | 180 ± 12 | <DL | 18.0 ± 2.4 | 1.8 ± 0.3 |
| p. 5 | 26 ± 16 | <DL | 2.1 ± 0.9 | 25 ± 2 | <DL | <DL | <DL | 200 ± 13 | <DL | 19.0 ± 5.0 | 2.0 ± 0.7 |
| p. 6 | 35 ± 11 | <DL | 5.0 ± 1.3 | 28 ± 2 | <DL | <DL | <DL | 720 ± 54 | <DL | 30.0 ± 7.9 | 3.7 ± 0.7 |
| p. 7 | 25 ± 4 | <DL | 3.3 ± 0.9 | 23 ± 2 | <DL | <DL | <DL | 190 ± 14 | <DL | 21.0 ± 2.0 | 1.8 ± 0.3 |
| Average value | 94.3 | — | 3.3 | 82.1 | <DL | <DL | <DL | 243.3 | <DL | 20.1 | 2.2 |
| **Autumn** | | | | | | | | | | | |
| p. 1 | 34 ± 4 | 1.3 ± 0.1 | 2.7 ± 0.2 | 70 ± 6 | 2.3 ± 0.3 | 3.5 ± 0.3 | 1.4 ± 0.1 | 160 ± 14 | 3.2 ± 0.2 | 18 ± 1.2 | 1.9 ± 0.1 |
| p. 2 | 290 ± 31 | 1.3 ± 0.1 | 7.9 ± 0.5 | 590 ± 47 | 3.3 ± 0.4 | 55.0 ± 5.2 | 0.7 ± 0.05 | 140 ± 12 | 1.4 ± 0.09 | 21 ± 1.4 | 1.1 ± 0.07 |
| p. 3 | 22 ± 2 | <no | 24.0 ± 1.6 | 44 ± 4 | 1.8 ± 0.2 | 2.8 ± 0.3 | 1.2 ± 0.09 | 160 ± 14 | 1.8 ± 0.1 | 24 ± 1.6 | 2.2 ± 0.1 |
| p. 4 | 23 ± 2 | 1.5 ± 0.2 | 3.4 ± 0.2 | 39 ± 3 | 1.6 ± 0.2 | 4.0 ± 04 | 1.1 ± 0.08 | 190 ± 17 | 1.3 ± 0.08 | 17 ± 1.2 | 2.3 ± 0.2 |
| p. 5 | 73 ± 8 | <DL | 7.5 ± 0.5 | 98 ± 8 | 2.4 ± 0.3 | 4.2 ± 0.4 | 1.1 ± 0.08 | 170 ± 15 | 1.0 ± 0.07 | 25 ± 1.7 | 1.7 ± 0.1 |
| p. 6 | 28 ± 3 | <DL | 5.3 ± 0.4 | 31 ± 2 | 3.1 ± 0.4 | 2.9 ± 0.3 | 1.9 ± 0.1 | 1800 ± 160 | 3.8 ± 0.3 | 26 ± 1.8 | 9.3 ± 0.6 |
| p. 7 | 72 ± 8 | 1.1 ± 0.1 | 3.2 ± 0.2 | 190 ± 15 | 4.2 ± 0.5 | 5.9 ± 0.6 | 1.1 ± 0.08 | 180 ± 16 | 0.9 ± 0.06 | 20 ± 1.3 | 1.9 ± 0.1 |
| Average value | 77.4 | 1.3 | 7.7 | 152 | 2.6 | 11.2 | 1.2 | 400 | 1.9 | 21.6 | 2.9 |
| MPC[34] (hazard category) | 500 (2) | 50 (3) | 100 (3) | 300 (3) | 1000 (3) | 1000 (3) | 50 (2) | 7000 (2) | 250 (2) | 100 (2) | — |
| WHO guideline values[36] | — | 50 | 80 | — | 2000 | — | 10 | — | — | 1300 | 30 |
| Average value in river waters[37] | 400 | 1 | 7 | 670 | 7 | 20 | 2 | 50 | 1 | 10 | 0.04 |
| Average value in river waters[38] | — | 0.7 | 34 | 66 | 1.48 | 0.60 | 0.62 | 60 | 0.42 | 23 | 0.37 |

Table 8 Classification of water according to the degree of pollution based on the results of calculating the CWPI[40]

| | Water pollution values | |
|---|---|---|
| The degree of pollution | CWPI | CWPI considering the hazard category |
| Normatively clean | ≤1 | ≤2.0 |
| Moderate level of pollution | 1.1–3.0 | 2.1–6.0 |
| High level of pollution | 3.1–10.0 | 6.1–10.0 |
| Extremely high levels of pollution | ≥10.1 | ≥10.1 |

$$\mathrm{CWPI}_j = \frac{1}{n}\left(\sum_{i=1}^{n}\frac{C_i}{\mathrm{MPC}_i c_{\mathrm{h}i}}\right)$$

where $\mathrm{CWPI}_j$ – Complex Water Pollution Index for group $j$ (heavy metals or main ions); $C_i$ – concentration of the $i$-th component, μg $L^{-1}$ or mg $L^{-1}$; $\mathrm{MPC}_i$ – maximum permissible concentration of the $i$-th component, μg $L^{-1}$ or mg $L^{-1}$; $c_{\mathrm{h}i}$ – hazard category coefficient of the $i$-th component; $n$ – number of components used to calculate the index.

According to the obtained calculations from the data of chemical and elemental analysis of the water samples, the $\mathrm{CWPI}_{\mathrm{HM}}$ for the Irtysh River water was 0.42 in summer and 0.65 in autumn, which corresponds to normatively clean water for the heavy metals group (Table 8). The $\mathrm{CWPI}_{\mathrm{MI}}$ was 0.32 in autumn, which corresponds to normatively clean water for the group of main ions (Table 8).

This may be due to the fact that water sampling was not linked to the source of industrial wastewater. According to earlier studies, due to dilution even at a distance of 100 m from the source of input, the concentration of heavy metals was reduced from 10 to 100 times and did not exceed the MPC, except for Fe.[12]

## 4 Conclusions

As a result of the research, the levels of natural ($^{40}$K, $^{232}$Th, $^{226}$Ra, $^{210}$Po, $^{238}$U) and anthropogenic ($^{3}$H, $^{137}$Cs, $^{241}$Am, $^{90}$Sr, $^{239+240}$Pu) radionuclides in the Irtysh River water were determined. The research was carried out at the sites of greatest anthropogenic influence: at the confluence of the Shagan River into the Irtysh River and in the area of Ust-Kamenogorsk city. According to the obtained data, no anomalous values of the radionuclides content have been established: their content is below the detection limit, or numerical values are fixed lower than the intervention level. Except for the site of the confluence of the Shagan River into the Irtysh River. The presence of the $^{3}$H radionuclide was fixed here, which almost constantly inputs the various components of the Irtysh ecosystem with the Shagan River water, even in winter. Radionuclide $^{3}$H is the most mobile radionuclide, so it can be an indicator of radionuclide contamination in this site of the Irtysh River.

According to the results of chemical analysis, it was found that the Irtysh River water is neutral in terms of pH, fresh in terms of salinity, soft in terms of hardness. The exception was the site of the confluence of the Shagan River into the Irtysh River, where the $Cl^{-}$ content and the hardness degree exceed the Hygienic Standards established in the Republic of Kazakhstan. As a result of determining the concentrations of heavy metals and microcomponents (a total of 16 elements were determined) at only one site on the right bank of the Irtysh River in Ust-Kamenogorsk city, the Fe content is 2 times higher than the MPC, according to the Hygienic Standards of the RK. Despite the fact that only one element recorded an excess of the MPC, and given that in this site the Ulba River flows into the Irtysh River, the water of which, according to its quality class, belongs to the category of polluted waters,[25], constant control of this site is necessary.

Based on the research results, it follows that the Irtysh River requires constant monitoring of its radioecological condition, since the river is transboundary and has important strategic significance for Central Asian region.

## Abbreviations

| | |
|---|---|
| C | Concentration |
| CWPI | Complex Water Pollution Index |
| DL | Detection Limit |
| IAEA | International Atomic Energy Agency |
| IL | Intervention Level |
| LMWL | Local Meteoric Water Line |
| MPC | Maximum Permissible Concentrations |
| STS | Semipalatinsk Test Site |
| RK | The Republic of Kazakhstan |

## Data availability

The article data cannot be provided due to legal confidentiality requirements.

## Author contributions

Almira Aidarkhanova: methodology, formal analysis, investigation, visualization, writing – original draft, writing – review & editing. Natalya Larionova: methodology, validation, writing – review & editing. Azhar Tashekova: conceptualization, writing – original draft. Madina Dyussembayeva: conceptualization, methodology, writing – review & editing, project administration. Ainur Mamyrbayeva: validation, writing – review & editing. Lyubov Timonova: formal analysis, investigation. Yerbol Shakenov: formal analysis, investigation. Assiya Mulikova: formal analysis, investigation. Assan Aidarkhanov: conceptualization, writing – review & editing, supervision.

## Conflicts of interest

There are no conflicts of interest to declare.

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