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Comparative analysis and human health risk assessment of contamination with heavy metals of Central Asian rivers

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ABSTRACT

The study focuses on heavy metals contamination, drinking water quality, and associated health risks for adults and children by consuming water from Central Asian Rivers (Syr-Darya, Nura, and Ili Rivers). Water samples were collected from three rivers within the 2014–2019 period by the RMS "Kazhydromet" and analyzed for various physicochemical parameters. The study revealed that the concentrations of Fe, Cd, Cr (VI), Hg, Mn, and As significantly exceeded local and international drinking water standards in at least one water body. The lowest total water quality index (55.1%) was observed in the Nura River ("marginal water category"). Coal, soil, non-ferrous metals, and iron ore industries were found to be the major sources of heavy metals in the regions. Deterministic risk assessment revealed serious cancer risks (>1E−5) in rivers due to As and Cr (VI) exposure by oral and dermal contact for adults and children. Stochastic risk assessment confirmed high cancer risks (>1E−4) due to Cr (VI) contamination of the Syr-Darya River. The study results indicate the serious lifetime cancer risk to the residents due to the use of river water for drinking and household activities. Therefore, the study area urgently and continuously requires heavy metal removal, effective monitoring, and good quality drinking water supply.

1. Introduction

As a Central Asian country, the Republic of Kazakhstan suffers from water scarcity due to harsh natural conditions characterized by an arid or semi-arid climate. Since the level of precipitation is comparatively low, the country's water availability is usually determined by the lake and river runoff [1]. The water shortage in the country is further worsened by the active operation of agricultural and industrial sectors that intensively use surface and underground water resources [2]. The experts of the United Nations Development Programme (UNDP) predicted that the water supply to the capital city, Astana, may be significantly limited to 75.0 million m^3/year by 2030 due to an unmanageable increase in water consumption [3]. The drinking water supply of Uralsk City, one of the top 25 populated cities in the country with ~320,000 citizens, consists of the Ural River water by 60% [4]. In the summer of 2019, Uralsk residents from some city districts were left without access to drinking water [3]. It is obvious that in small villages, the drinking water supply issue is even worse, and distant rural regions of Kazakhstan have no access to clean and safe drinking water. As a result, their residents are using water from rivers and lakes for drinking and cooking. Citizens reported that their families and neighbors were used

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to drinking river water and continuously consumed it for cooking, showering, and cleaning purposes [5,6].

The industrial sector is an essential part of the economic growth of Kazakhstan and is the largest anthropogenic source of water pollution with heavy metals [7]. In Kazakhstan, industrial enterprises can be found along major rivers such as the Ural, Elek, Nura, and Ili Rivers [8]. It has already been investigated that several water basins in Kazakhstan were contaminated with pollutants from discharges of oil refining, mining, metallurgical, chemical industries, and municipal wastewater [10–12]. Yessenamanova et al. (2021) [13] reported that along the Ural River, the content of Cu metal exceeded the maximum allowable concentration (MAC) by 1.5–6.3 times. Rzymski et al. (2019) [14] detected that Al, Cd, Pb, As, and U concentrations exceeded World Health Organization (WHO) guidelines in the Syr-Darya River. The Sarusy River, located in the Karaganda region, was found to be polluted by petroleum products and phenols whose concentrations exceeded MAC by 18 and 6 times, respectively. High concentrations of Cu (≈ 20 MAC) and Zn (≈ 25.7 MAC) from metallurgic enterprises, coal mines, and thermal power stations were monitored in the Irtysh River [10].

Trace amounts of heavy metals such as As, Fe, Pb, Ni, Cd, Mn, and Cr are required for human metabolisms to maintain good health. However, in large amounts, these metals can disrupt the functioning of the brain, lungs, kidneys, liver, and other organs [15]. Long-term exposure to heavy metals can lead to the development of Parkinson's disease, muscular dystrophy, and Alzheimer's disease, while some metals can even cause cancer [16,17]. Citizens can be exposed to heavy metals when consuming contaminated water. More than 40% of Kazakhstani citizens (>3.6 million people) live in rural areas [2,18]. Assuming that most of them consume contaminated river water for drinking and domestic purposes, the question about the surface water's impact on residents' health can be seriously rising. Previous studies determined concentrations of various heavy metals from water and fish samples in large water bodies in Kazakhstan [19,20]. Few studies have been conducted to assess the human health risk of heavy metals through oral ingestion and dermal contact in a certain water body [21,22]. However, the local and international literature lacks information about the heavy metal pollution status of large rivers in Kazakhstan. Relevant publications provided the concentrations of detected metals but did not provide quantitative data on the carcinogenic and non-carcinogenic human health risks associated with metal contamination [10,13, 14]. Therefore, there is a need for a study containing the analysis of large Kazakhstani rivers in terms of metal pollution, water quality, and health risks in comparison to each other. It can be justified by the urgent problem of surface water contamination and inadequate water treatment in some areas of Kazakhstan [23]. The results of this study can be used as a basis for properly modifying the approach to water treatment, water remediation, and drinking water management at the state level. In addition, the study can contribute to global knowledge about the effect of surface water pollution with metals on locals' health. Since the study includes results for two transboundary rivers (Syr-Darya and Ili) which flow through Kazakhstan, Kyrgyzstan, and China, the study results can be useful for the whole Central Asian region.

The aims of this study are to investigate the status of metal contamination of three large rivers in Kazakhstan; to quantitatively assess residents' carcinogenic and non-carcinogenic health risks from consuming river water containing trace heavy metals and, thus, to fill in the gap in heavy metal pollution control studies of major water bodies in Central Asia.

The preliminary analysis of 8 large rivers in Kazakhstan (Syr-Darya, Ili, Ertis, Esil, Nura, Talas, Tobol, and Ural) demonstrated that

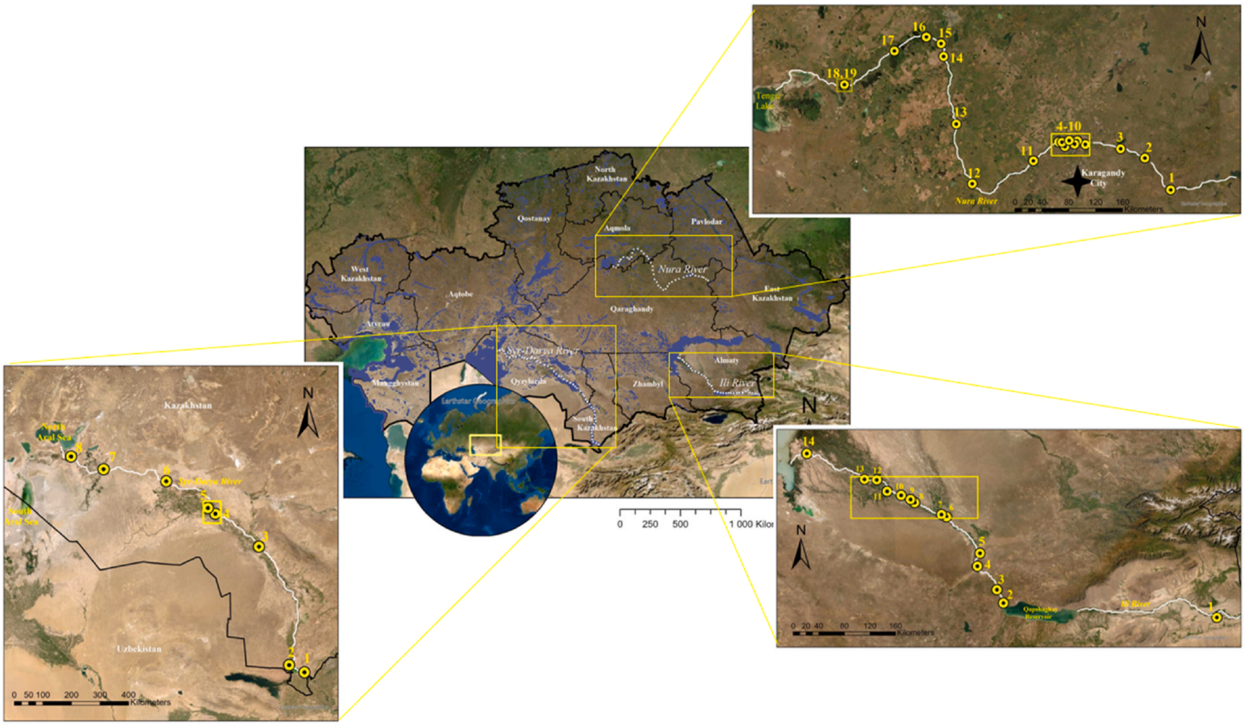

Fig. 1. The map of the study area with sampling points along the rivers.

Table 1
Geographical information about the Syr-Darya, Nura, and Ili rivers [24].

River	Longitude and Latitude	Length in KZ, (km)	Water Basin	Basin Area in KZ, (km^2)	Administrative Districts	Population in KZ, (million)
Syr-Darya	61.0947; 46.019	1627	Aral-Syr-Darya	345,000	South Kazakhstan and Kyzylorda	2.6
Nura	73.0126; 50.11769	978	Nura-Sarysu	139,700	Qaraghandy and Aqmola	1.0
Ili	75.4515; 45.05	815	Balkash-Alakol	353,000	Almaty	3.3

KZ – Kazakhstan.

the most concerning concentrations of heavy metals were present in three rivers (Syr-Darya, Nura, and Ili). As a result, these water bodies were chosen for this study for more detailed analysis and human health risk assessment. The study determined the water quality statuses of three rivers by season and assessed the content, distribution, and variation of eleven heavy metals (Fe, Hg, Cd, Pb, As, Cu, Zn, Cr, Ni, Co, and Mn) in rivers in comparison to governmental and international drinking water standards. Then carcinogenic and non-carcinogenic risks were calculated deterministically and stochastically for adults (>18 years old) and children (5–18 years old) for oral and dermal exposure routes assuming that river water was used for drinking, showering, washing, cooking, and other household purposes.

2. Methodology

2.1. Study area

The study area covers three rivers – Syr-Darya, Ili, and Nura Rivers (Fig. 1). The middle part of Fig. 1 illustrates the territory of Kazakhstan and three study rivers highlighted with yellow rectangles. The map extensions provide a closer view of each river with sampling points. The coordinates of each sampling point are provided in Tables S1–S3 in Supplementary Information (SI). As can be noted from Fig. 1, the chosen rivers do not intersect each other and flow through different administrative districts and, hence, represent different water basins. Geographical information about the studied rivers is provided in Table 1. More detailed geographical information about each river's region is provided in Text S1 in SI.

2.2. Sampling and detection

The concentrations of contaminants and environmental factors in the presented study area were measured by the Republican State Enterprise (RSE) "Kazhydromet" of the Ministry of Ecology, Geology, and Natural Resources of the Republic of Kazakhstan. According to Kazakhstan governmental sampling technical standards [25], the RSE "Kazhydromet" constantly collected surface water samples every month at different locations along each river in the period between 2014 and 2019 years. The detailed sampling sites along Syr-Darya, Nura, and Ili Rivers are demonstrated in Fig. S1, Fig. S2, and Fig. S3, respectively. Water samples were collected in 250 mL polymer containers prewashed with nitric acid. Surface water samples were taken at a depth range of 0.1–0.5 m and within the temperature range of 0–30.2 °C. From 8 sites along the Syr-Darya River, 724 water samples were collected. The largest number of samples (2437 samples) were taken from 14 sampling sites along the Ili River. And in the Nura River, 2011 water samples were collected from 19 sampling sites. All collected samples were delivered to the laboratory at a cooling temperature of 2–5 °C in amber bottles to minimize the effect of photolysis.

In the laboratory, the presence of metals (Fe, Hg, Cd, Pb, As, Cu, Zn, Cr, Ni, Co, and Mn) in water samples was analyzed, according to the governmental standard [26]. By this standard methodology, one part of the water samples was filtered through the 0.45 μm membrane filter, and the filtrates were preserved in nitric acid. These filtrates were further used to determine the elements' dissolved forms in water samples. Another part of the water samples was heated with an excess of nitric acid and hydrogen peroxide. Prepared solutions were filtered through the 12.5 cm filter paper and further directed to analyze the sample's mass fraction of all metal forms. Analytical identification and quantification of the heavy metals in the samples were performed by flameless atomic absorption spectrometry using an MGA-915/MGA-1000 spectrometer (Lumex instruments co., Russia).

After the laboratory analysis, the concentrations of metals (Fe, Hg, Cd, Pb, As, Cu, Zn, Cr (VI), Ni, Co, Mn), water parameters (pH, BOD5, DO, Oil), and concentrations of ions (SO_4^{2-}, NO_3^-, PO_4^{3-}) were stored as one dataset and used for further calculations in this study (RSE "Kazhydromet", 2019).

2.3. Data analysis and estimation

2.3.1. Treatment of left-censored data

The studied data was assumed to be left-censored, meaning that the concentrations of heavy metals reported as zeros are, in fact, below the limit of detection (LOD) of the analytical equipment used. The percentage of non-detects among 11 metals in three rivers is given in Table S4. 30% censoring was chosen as the maximum allowable censoring limit for the analysis of the data. The censored values were treated by the half substitution method in Matlab R2021a where non-detected concentrations were substituted with one-half of their respective detection limit (HDL) [27–29]. Limits of detection (LOD) for each respective metal were chosen as the lowest detected concentration of the corresponding metal among datasets from three rivers (Table S5). Detailed information about the outliers in the studied dataset, and the performance of the summary statistics and spatiotemporal variations is provided in the Supplementary Information (Text S2–Text S3).

2.3.2. Water quality indexing

To assess the suitability of Kazakhstan's water resources for humans and animals, the water quality in each river was ranked by the Canadian Council of Ministers of the Environment water quality index (CCME-WQI) for four seasons of the year [30]. One set of parameters was chosen for the rivers following the industrial segments located in different parts of Kazakhstan and their direct and indirect effect on selected water bodies. We chose Cd, Cr(VI), Hg, Mn, As, Oil, total iron, nitrates, sulfates, and phosphates as the primary contaminants of Kazakhstan's water resources and used them along with water parameters (pH, BOD5, and DO) for the calculation of CCME-WQI.

CCME-WQI was calculated based on the scope, frequency, and amplitude of the deviations of each parameter in the respective river from the government guidelines provided in Tables S7 and S8. The scope (F_1) illustrates the percentage of parameters that do not meet the guidelines for the total number of chosen parameters. The frequency (F_2) represents the percentage of individual samples (tests) that do not meet the guidelines. The amplitude (F_3) shows the numerical amount by which each failed test does not meet its standard value. The equations used for calculating F_1, F_2, and F_3 were retrieved from the CCME Water Quality Index User's Manual (2017) [30] and were provided in Table S9. The following Formula (1) was then used to calculate the water quality index for each river.

$$CCME - WQI = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732}\right) \tag{1}$$

As a result, water quality was characterized by one of five categories, depending on the value of CCME-WQI. They are "Excellent" (95–100), "Good" (80–94), "Fair" (65–79), "Marginal" (45–64), and "Poor" (0−44) categories.

2.3.3. Toxicity ranking

An incremental risk in the specific site depends on the present chemicals' toxicity, persistence, mobility, concentration, and distribution [31]. Primarily, the effect of concentration and toxicity of a chemical was considered in this study. Eleven heavy metals were detected in the surface waters of three rivers. It was assumed that some metals significantly correspond to the region's incremental carcinogenic and non-carcinogenic risks, while the effect of other metals was negligible. To justify the assumption, the toxicity ranking was performed for carcinogenic and non-carcinogenic metals. The toxicity score (*TS*) for noncarcinogens was calculated by the following Formula (2) from Ref. [31]:

$$TS = \frac{C_{max}}{RfD} \tag{2}$$

where C_{max} is the maximum detected concentration of heavy metal (mg/L); *RfD* is the reference dose of the respective metal (mg/kg·day). For carcinogens, the following Formula (3) was used [31]:

$$TS = SF \bullet C_{max} \tag{3}$$

where *SF* is the slope factor of carcinogenic heavy metal (kg· day/mg).

Detected metals were divided into carcinogenic and non-carcinogenic groups, depending on the availability of carcinogenic risk data. The first group includes As, Cr(VI), and Pb, while the second group consists of the remaining metals. The chemicals were ranked by their toxicity scores. Metals with the highest toxicity scores were chosen for further risk assessment. Reference doses and slope factors for oral and dermal exposure routes, which were used in the calculation of *TS* were provided in Tables S10 and S11.

2.3.4. Risk assessment

To assess the potential health risks caused by heavy metals, it was essential to estimate the doses of these metals to which locals are exposed at the exposure sites. Two exposure routes were considered, i.e., ingestion when using surface water for drinking and cooking purposes and dermal contact when using river waters for bathing and washing. The reference intake rate of metal through the ingestion route (I_o) was calculated by the following equation (4) [32]:

$$I_o = \frac{C_w \bullet IR \bullet EF \bullet ED}{BW \bullet AT} \tag{4}$$

where C_w is the metal concentration at the exposure site (mg/L); *IR* is the ingestion rate (L/day); *EF* is the exposure frequency (day/year); *ED* is the exposure duration (years); *BW* is the average body weight (kg); *AT* is the averaging time (day); The reference intake rate of metal through dermal contact (I_d) was calculated by the following equation (5) [32]:

$$I_d = \frac{C_w \bullet SSA \bullet k_p \bullet CF \bullet ET \bullet EF \bullet ED}{BW \bullet AT} \tag{5}$$

where *SSA* is the skin surface area (cm^2); k_p is the permeability coefficient specific for each metal (cm/h); *CF* is the respective conversion factor (L/cm^3); *ET* is the exposure time (h/event); Oral and dermal intakes are expressed in terms of mg/kg of body weight/day.

2.3.5. Risk assessment: carcinogenic risk

The carcinogenic risk caused by a specific heavy metal was estimated by Eq. (6) [32]:

$$Risk = I \bullet SF \tag{6}$$

Since two exposure routes and several metals were considered in this study, the total cancer risk caused by chosen metals through oral and dermal exposures was estimated using Eq. (7) [32]:

$$Risk = \sum_{i=1}^{n} \sum_{j=1}^{m} I \bullet SF \tag{7}$$

The threshold range for carcinogenic risk was taken as $10^{-6} - 10^{-4}$ [31].

2.3.6. Risk assessment: non-carcinogenic risk

Non-carcinogenic risk characterized by the hazard quotient (*HQ*) was estimated by Eq. (8) [32]:

$$HQ = I / RfD \tag{8}$$

The total non-carcinogenic risk caused by several metals through both exposure routes was characterized as the hazard index (*HI*) and estimated as the sum of obtained hazard quotients [32] as given in Eq. (9):

$$HI = \sum_{i=1}^{n} \sum_{j=1}^{m} HQ \tag{9}$$

The threshold value for non-carcinogenic risk was taken as 1.00 [31].

Deterministic risk assessment was calculated based on median, mean, maximum, and 95th percentile concentrations of heavy metals. Stochastic risk assessment was performed by the Monte Carlo simulation in the Matlab R2021a program with 10,000 random values of concentrations generated for the defined probability functions. Exposure parameters from Eqs. (4) and (5) for the deterministic and stochastic risk assessments were provided in Table S12 for both age groups.

3. Results and discussion

3.1. Summary statistics

It is important to note that Fe metal was detected at the highest concentrations in all three rivers compared to other metals. In the Syr-Darya River, the maximum concentration of Fe is 390 μg/L which is more than twice the maximum concentration of the river's top-2 abundant Cr (VI) metal (170 μg/L). The least abundant metal in the Syr-Darya River is Hg which was detected with a median concentration of 0.02 μg/L and a maximum concentration of 0.08 μg/L. The distribution of trace metals in the Syr-Darya River is wide. Coefficients of variance ranging from 28.5% for Cu to 99.0% for Co prove that point concentrations of heavy metals were extensively dispersed around the mean values. The mean concentrations of all metals in the Syr-Darya River, except Fe, are slightly higher than the median concentrations of the corresponding metals. This indicates that the distribution functions for these metals are positively skewed, while Fe metal's distribution function is negatively skewed. According to the quantitative results of the metals' concentrations, the main three contaminants in the Syr-Darya River are Fe, Cr (VI), and Mn.

The top 3 abundant metals detected in the Nura River are Fe, Mn, and Zn. The maximum concentration of Fe metal in the Nura River is 800 μg/L, the median is 96.7 μg/L, and the mean is 158.1 μg/L. Fe metal concentrations are extensively dispersed around the mean value with a coefficient of variation of 107% and a positive skewness. As was observed in the Syr-Darya River, the contaminant present at the lowest concentrations in the Nura River is Hg. Its maximum concentration in the river is 2.33 μg/L, and the median concentration is 0.03 μg/L. Point concentrations of Hg demonstrate the greatest dispersion around the mean value with the CV of 194%. Distribution curves of all heavy metals detected in the Nura River show positive skewness. This indicates that outliers of the distribution curve are on the right side, corresponding to the maximum concentrations of heavy metals.

The same observations mentioned above can be made for the contamination of the Ili River. Fe metal is the most abundant

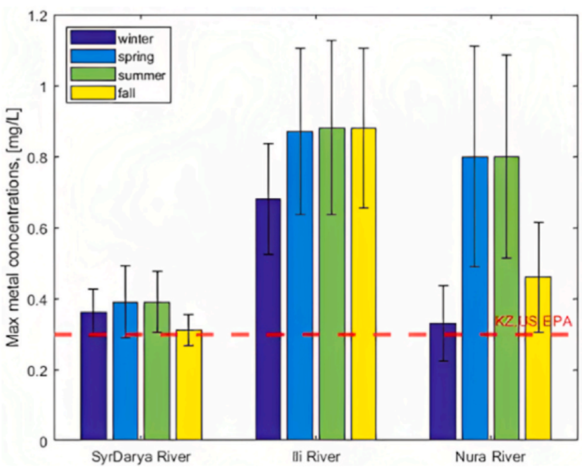

Fig. 2. Seasonal variations of Fe in three rivers.

contaminant in the river detected at a maximum concentration of 880 μg/L and a mean concentration of 170.6 μg/L. Distribution curves for the presented heavy metals have positive skewness and demonstrate a high degree of concentration dispersion with the CV up to 142%. Since Hg was absent in the analysis for the Ili River due to the numerous non-detects (55.6%), the least abundant contaminants in the river were Cr (VI) and Ni at mean detected concentrations of 0.91 μg/L and 0.81 μg/L, respectively.

As observed for all three rivers, metals are highly dispersed around their mean values. This can be explained by the effect of spatial variation of metals since the contaminants were analyzed in several sampling sites along the lengths of rivers. Both anthropogenic and natural factors such as the proximity of industrial enterprises, degree of agricultural activity and runoff intensity, may affect the spatial variation of heavy metals. Previous research works demonstrated a correlation between industrial activity, sediment particle size, pH, and TOC on the metal accumulation in surface sediments and soil samples [33,34]. Therefore, the distance between sampling points is assumed to be the major reason for the statistical variation of detected heavy metals in three rivers.

3.2. Seasonal and temporal variations

Contaminants discussed above whose maximum concentrations significantly exceeded governmental and international drinking water standards were presented for seasonal variations in Figs. 2–7. The red dashed lines demonstrate the maximum allowable concentrations for heavy metals, according to Kazakhstan's (KZ), United States Environmental Protection Agency (US EPA) and WHO standards, as noted in the figures.

Fig. 2 presents seasonal variations of Fe in the Syr-Darya, Ili and Nura Rivers. Maximum concentrations of Fe in the Syr-Darya River that exceeded Kazakhstan's and US EPA limits (0.3 mg/L) were detected in four seasons. The highest concentrations were found in the spring and summer seasons. Among 502 samples checked for Fe content in the Syr-Darya River, 1.39% exceeded relevant regulations. Maximum concentrations of Fe in the Ili River were higher than Kazakhstan's and US EPA regulations by 1.03–2.9 times in four seasons. 17.7% of checked samples were registered with unacceptable Fe concentrations. In the Nura River, among 482 water samples checked for Fe content, 19.5% exceeded Kazakhstan's and US EPA standards. The magnitude of heavy metal concentrations varied in the range of 1.03–2.67 MAC. The lowest concentration of Fe was registered in winter in three rivers. Therefore, Fe content in the rivers is affected by seasons due to the difference in rain frequency, intensity, and flood season duration [35].

The seasonal distribution of Cd was analyzed in the Syr-Darya River (Fig. 3). The maximum concentration of Cd in the river exceeded KZ regulation in all seasons, and only winter samples exceeded WHO limitations. Among 58 samples from the Syr-Darya River checked for Cd content, 41.4% of them showed concentrations higher than MAC set by Kazakhstan (1.1–3.5 times MAC). Unlike for Fe metal, opposite correlation was observed between Cd content and season: the highest concentration of Cd was observed in winter.

The variation of Cr (VI) in the Syr-Darya and Ili Rivers is depicted in Fig. 4. US EPA set MAC for Cr (VI) as 0.1 mg/L, while Kazakhstan and WHO set this threshold value as 0.05 mg/L. The highest concentration of Cr (VI) in the Syr-Darya River was observed in spring. 4.5% of 493 samples from the Syr-Darya River had Cr (VI) content which exceeded Kazakhstan's MAC in all seasons by 1.2–3.4 times. Concentrations of Cr (VI) registered in the Ili River were within the acceptable range.

Fig. 5 illustrates seasonal concentrations of Hg detected in the Syr-Darya and Nura Rivers. No unacceptable concentrations of Hg were observed during the winter in the Nura River. However, water samples in other seasons contained high concentrations of Hg, exceeding the concentration limits. Nevertheless, the percentage of these unacceptable values was low (0.85%) compared to the content of Fe in the Nura River. The content of Hg in the Syr-Darya River did not exceed KZ and US EPA standards and was much lower, compared to the Nura River.

Fig. 6 presents the maximum concentrations of Mn in three water bodies. It is clear, that the content of Mn varies significantly

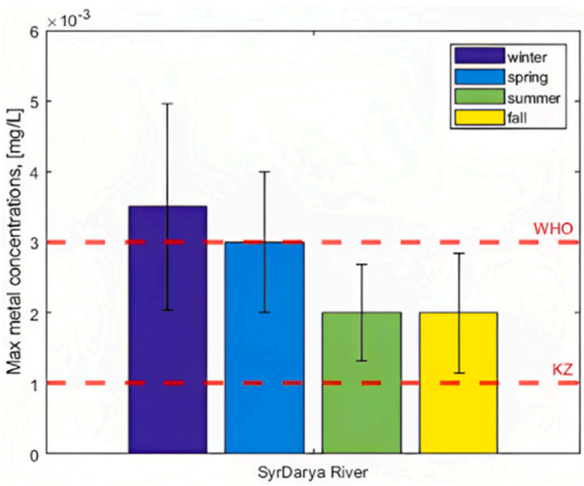

Fig. 3. Seasonal variations of Cd in the Syr-Darya River.

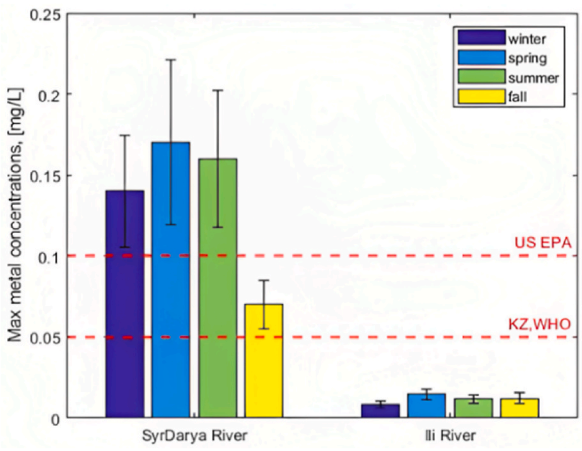

Fig. 4. Seasonal variations of Cr (VI) in the Syr-Darya and Ili Rivers.

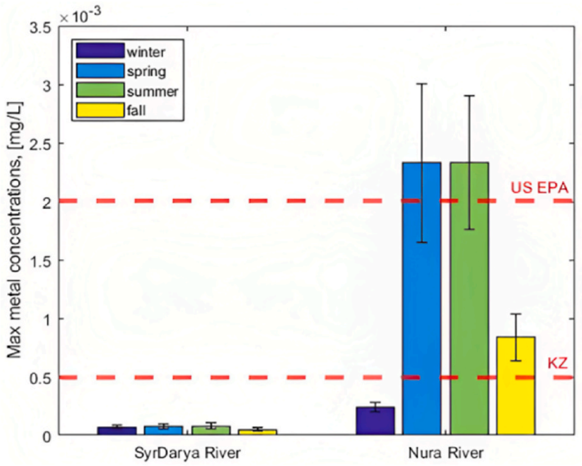

Fig. 5. Seasonal variations of Hg in the Syr-Darya and Nura Rivers.

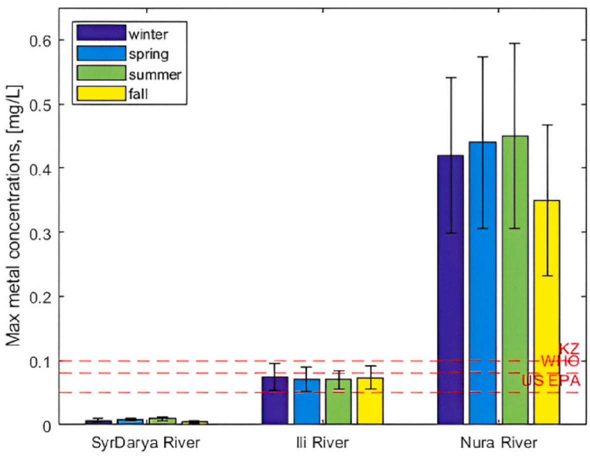

Fig. 6. Seasonal variations of Mn in three rivers.

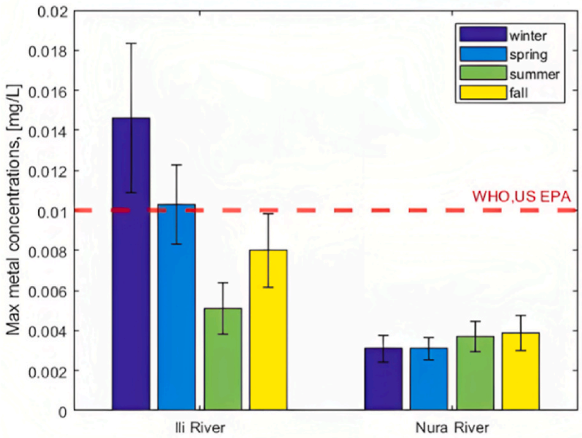

Fig. 7. Seasonal variations of As in the Ili and Nura River.

across rivers. This can be explained by the spatial variation of metals. In total, 64.4% of water samples from the Nura River contained Mn concentrations higher than US EPA regulation, 39.3% were above the WHO limit, and 31.7% were above Kazakhstan's standard. These concentrations varied by 1.02–9.2 MAC in accordance with US EPA regulations. Maximum concentrations of Mn in the Ili River were above the US EPA regulation, exceeding it by 1.02–1.5 times in 1.24% of all samples.

The variations of As metal are depicted in Fig. 7. This metal did not exceed WHO and US EPA standards in the Nura River in the whole study period. In the Ili River, concentrations of As metal in winter and spring samples exceeded the WHO and US EPA guidelines.

The preliminary analysis of eight large rivers from all water bodies in Kazakhstan revealed that Fe is present in all rivers at concentrations that exceed domestic and international regulations. The maximum concentration of Fe in the Ertis River was 0.71 mg/L, 1.18 mg/L in the Esil River, 0.32 mg/L in the Talas River, 2.62 mg/L in the Tobol River, and 0.5 mg/L in the Ural River. Hence, it is reasonable to state that Fe is the most dominant metal contaminant in Kazakhstan's water basins.

Temporal variations of heavy metals in 2014–2019 are presented in Figs. S4, S5, and S6 in the SI. Concentrations of Fe and Cr (VI) in the Syr-Darya River showed decreasing trends, and Hg in the Nura River did the same trend too. The Hg concentration significantly dropped within 6 years from 0.00233 mg/L exceeding Kazakhstan regulation by 4.66 times to 0.00016 mg/L, 3 times lower than MAC set by Kazakhstan's government. The resulting trend could be caused by the intensive work of the "Nura River Cleanup Project" whose primary aim was to clean the River from Hg contamination [36].

3.3. Sources of contamination

The principal component analysis (PCA) was performed to identify the possible sources of heavy metal contamination that could affect the studied rivers. Tables S13–S15 summarize the PCA results of matrix components, where significant loadings higher than 0.4 were highlighted in bold. According to Table S13, the PC1 in the Nura River (Table S13) is strongly and positively loaded with Ni (0.812), SO_4^{2-} (0.711), Al (0.609), Cl^- (0.588), and Mg^{2+} (0.579) and is moderately and positively influenced by Co (0.439) and Be (0.403). This indicates that the contaminant sources can come from both natural and anthropogenic origins. Sulfate ions (SO_4^{2-}) in the Nura River water could originate from the operation of coal and soil industries, while Cl^- ions could result from the hydrochloric acid gas emissions during industrial activities [37]. Mining and processing of non-ferrous metals, iron ore, and hard coal prevail in the region of the Nura River [38]. Various metallurgical enterprises, including the largest "Temirtau Electrometallurgical Plant", "Karaganda Metallurgical Plant," limited liability partnership (LLP) "Corporation Kazakhmys", LLP "Orken", and LLP "Altyntau Kokshetau" may increase the content of heavy metals, including Fe, Ni, Al, Co, and Be in the Nura River due to constant waste discharge [38,39].

PC1 of the Syr-Darya River explains about 57% of the total variance and demonstrates a strong correlation among Cd (0.784), Pb (0.752), Co (0.624), and Mn (0.498) (Table S14). These values are negatively correlated with water pH (−0.548). In this region, mining activity could significantly increase the content of Mn [40], while photographic and engraving processes, as well as waste discharge containing batteries, paints, pigments and photoconductors could increase the content of Cd in the Syr-Darya River [41]. Pb metal could be seriously increased due to emissions from the automobile exhausts, and burning of coal. The agricultural sector which is dominant in the Aral-Syr-Darya water basin could be another reason for the Pb metal accumulation in surface water due to the application of fertilizers and pesticides containing Pb [41,42].

PCA performed for the Ili River (Table S15) illustrates that Component 1 accounted for 40.5% of the total variance and was positively influenced by Cu (0.576), Cd (0.568), Mn (0.450), Zn (0.426), and Ni (0.415). The content of these metals in the Balkhash-Ili water basin could be significantly affected by the operation of the "Balkhash Mining and Metallurgical Plant" that discharges industrial waste annually into the water basins [3].

3.4. Water quality

Fig. 8 illustrates the water quality index values (CCE-WQI) calculated for each season separately and the whole period (total) in three rivers. Horizontal lines present border lines between the water quality categories. Three categories of drinking water are shown in Fig. 8: “Good”, “Fair”, and “Marginal”.

The lowest total CCE-WQI (55.1%) was observed in the Nura River which represents the Nura-Sarusy water basin in Central Kazakhstan. The quality of water in the River can be classified as “Marginal” which is described by frequent impairment of water quality. Seasonal water quality indexes for the river fell within the “Fair” water category described by occasional impairment. 10 out of 14 environmental parameters in the Nura River exceeded governmental guidelines. BOD_5 exceeded the governmental guideline of 3 mg of O_2 per dm^3 in 11% of analyzed samples. Cd, Cr (VI), Hg, and Mn metals showed concentrations higher than their MAC. As was explained in part 3.3, the greatest threat to the water quality in the Nura River can be posed by enterprises such as “ArcelorMittal Temirtau” JSC company located in Temirtau and Karaganda cities which process coal, iron, and copper ores and produce iron, steel, and ferroalloys [38].

Higher water quality values were observed in the Syr-Darya and Ili Rivers, of which CCE-WQI indexes are 68.8% and 81.6%, respectively. Both Rivers flow through the regions where livestock and crop production predominate [38]. The difference among the Rivers’ CCE-WQI demonstrated that the water quality varied significantly by their geographical locations and industrial activity type, being the worst in areas with the extensive operation of industrial enterprises.

3.5. Toxicity ranking

Quantitative content of the metal alone is not a fully descriptive value. Some metals may be present in large amounts in water but may not be highly dangerous due to their low toxicity. Therefore, chosen heavy metals were further assessed in terms of their toxicological properties. Table 3 contains the calculated toxicity scores of carcinogenic heavy metals in three rivers expressed in percentage and their local ranking expressed in roman numbers in parentheses.

As a carcinogenic heavy metal, Pb does not contribute significantly to the total toxicity in three rivers. As can be seen in Table 3, the toxicity score of Pb in the Syr-Darya River is much lower than 0.05% for both oral and dermal exposure routes. This can be explained by the fact that the content of Pb was quantitatively lower than the content of other carcinogenic metals in the water bodies. In the Syr-Darya River, the peak Pb concentration was 0.0023 mg/L, while As and Cr (VI) metals’ concentrations were 0.0032 mg/L and 0.17 mg/L, respectively (see Table 2). Another explanation for the low toxicity score of Pb is that its oral and dermal cancer slope factors are comparatively low ($SF_o = SF_d = 0.0085$) compared to those of As and Cr ($SF_o(As) = 1.5$ and $SF_o(Cr(VI)) = 0.5$) (see Table S10). Since both the maximum concentration value and the slope factor of a heavy metal are directly proportional to its toxicity score, Pb could barely influence the total toxicity level of three rivers, while As and Cr (VI) contributed to the total toxicity by 99.9%. Hence, As and Cr (VI) were further checked for carcinogenic and non-carcinogenic human health risks.

Table 4 shows the calculated toxicity scores of non-carcinogenic heavy metals in three Rivers and their local ranking numbers.

It is interesting to note from Table 4 that Cd contributed to the toxicity level of the Syr-Darya River through dermal contact and oral ingestion. However, in the Nura and Ili Rivers, Cd was represented by non-detects in many samples, i.e., higher than 30% (see Table S4) and, hence, was excluded from the analysis. The contribution of Cu and Zn to all rivers by both exposure routes is minimal, no more than 1.09%. This is because reference doses of Cu and Zn are not as low as those of other metals (see Table S11). According to Eq. (2) from part 2.3, the low reference dose of a substance provides a higher toxicity score. Since Cu and Zn have relatively high reference doses, these two heavy metals possess relatively low toxicity scores. As defined by US EPA, reference doses are estimates of daily exposure to a toxic chemical that is likely to be without serious health risks [43]. Therefore, the lower reference dose illustrates that the

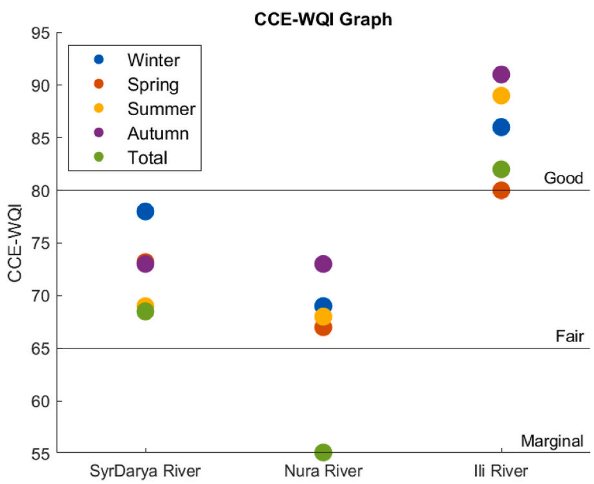

Fig. 8. Water quality indices in the rivers.

Table 2
Summary statistics for concentrations of heavy metals (μg/L) in the Syr-Darya, Nura and Ili Rivers.

Metal	Range of average	Median	Mean	Max	SD (CV%)	Range of average	Median	Mean	Max	SD (CV%)	Range of average	Median	Mean	Max	SD (CV%)
	Syr-Darya River					Nura River					Ili River				
Fe	10.00–229.5	120	113.6	390	74.0 (65.1)	4.2000–480.00	96.7	158.1	800	168 (107)	10.00–540.0	120	170.6	880	170 (99.5)
Hg	0.010–0.070	0.02	0.029	0.08	0.02 (59.6)	0.0003–0.2305	0.03	0.064	2.33	0.13 (194)	–	–	–	–	–
Cd	0.001–2.830	0.7	1.005	3.5	0.96 (95.2)	–	–	–	–	–	–	–	–	–	–
Pb	0.005–2.100	0.9	0.985	2.3	0.71 (72.5)	–	–	–	–	–	–	–	–	–	–
As	0.700–3.005	1.6	1.652	3.2	0.73 (44.4)	0.6000–3.1000	1.5	1.65	3.9	0.73 (44.3)	0.005–2.748	1.2	1.291	14.6	1.21 (93.9)
Cu	1.000–3.000	2	2.307	4	0.66 (28.5)	0.9000–6.5000	2.7	3.031	15	1.82 (60.0)	0.700–4.243	1.6	2.008	26.1	2.16 (107)
Zn	1.100–8.405	3.6	4.097	11.3	2.21 (54.0)	5.4000–34.000	17	18.11	99.2	9.81 (54.1)	0.734–6.236	1.9	2.568	19.9	2.45 (95.6)
Cr6+	1.560–50.00	10	18.66	170	20.1 (108)	–	–	–	–	–	0.060–5.760	0.91	1.628	14.7	2.02 (124)
Ni	1.085–5.750	2.45	3.029	7.9	1.63 (53.8)	–	–	–	–	–	0.079–3.600	0.81	1.223	26.4	1.74 (142)
Co	0.005–5.815	1.1	1.912	7.6	1.89 (99.0)	0.3000–2.3750	0.8	1.029	5.9	0.89 (86.9)	–	–	–	–	–
Mn	0.900–7.305	3.45	3.603	9.9	2.11 (58.5)	4.5000–280.00	67	98.8	460	87.4 (88.5)	2.020–28.85	8.8	11.11	75.2	9.64 (86.8)

Table 3
Toxicity scores (TS) in % and ranking numbers (RN) of carcinogenic heavy metals.

River	Exposure route	As	Cr(VI)	Pb
Syr-Darya	Oral	≈5.3 (II)	≈94.6 (I)	⋘0.05 (III)
	Dermal	≈0.1 (II)	≈99.9 (I)	⋘0.05 (III)
Nura	Oral	100 (I)	–	–
	Dermal	100 (I)	–	–
Ili	Oral	≈75 (I)	≈25 (II)	–
	Dermal	≈7.3 (II)	≈92.7 (I)	–

Table 4
TS in % and RN of non-carcinogenic heavy metals.

	Syr-Darya River		Nura River		Ili River	
Metal	Oral	Dermal	Oral	Dermal	Oral	Dermal
Fe	<1	–	1.67 (V)	–	2.1 (V)	–
Hg	<1	<1	21.3 (III)	3.7 (II)	–	–
Cd	6.9 (IV)	5.74 (II)	–	–	–	–
Cu	<1	<<1	<1	<1	1.09 (VI)	<1
Zn	<<1	<<1	<1	<1	<1	<1
Ni	<1	<1	–	–	2.2 (IV)	9.2 (IV)
Co	24.9 (II)	–	28.8 (I)	–	–	–
Mn	<1	<1	28.1 (II)	93.5 (I)	5.22 (III)	21.8 (II)
As	10.5 (III)	<1	19.1 (IV)	2.67 (III)	81.14 (I)	14.3 (III)
Cr (VI)	55.7 (I)	92.9 (I)	–	–	8.14 (II)	54.5 (I)
Pb	<1	<1	–	–	–	–

heavy metal could be more toxic and dangerous for human health, which is valid for Hg, Cd, As, and Cr (VI). Due to the high toxicity of the heavy metals, As and Cr (VI) contribute significantly to the non-carcinogenic toxicity score of the chosen river.

3.6. Deterministic human health risk assessment

The deterministic human health risk assessment was performed for maximum, median, mean, and 95th percentile concentrations of As and Cr (VI) in three rivers. Risk at maximum concentrations represents the worst-case scenario, implying that an average citizen is constantly exposed to the highest concentrations of heavy metals throughout their life by oral and dermal exposure routes. It is evident that the risk of cancer occurrence is at the highest level under these conditions. However, it is crucial to understand that these conditions are unreal. This is because the determined maximum concentrations rarely occur in real life, and citizens are not likely to be exposed to heavy metals at these concentrations all the time. The worst-case scenario can be used to draw the upper limit for the highest possible risk of cancer development due to exposure to heavy metals.

Carcinogenic risks estimated by the deterministic approach at maximum, mean, and 95th percentile concentrations of carcinogenic heavy metals are presented in Table S16. Table 5 summarizes the results for cancer risks for adults and children due to oral and dermal exposures to surface water containing As and Cr (VI) metals.

According to Table 5, both heavy metals (As and Cr (VI)) in the three rivers can cause serious cancer risks to adults and children by oral exposure route preferably. This exposure route explains that locals use surface water containing As and Cr (VI) for drinking and cooking. It also includes accidental water swallowing during bathing and showering. It can be seen that calculated risks are primarily within the concerning threshold range from 1E-06 to 1E-04, pointing to high risks of cancer development under the considered scenario. "Cum.R" illustrates the cumulative risk of cancer development due to both oral and dermal exposures to both heavy metals simultaneously. The highest cumulative risk (1.72E−04) was observed for adults in the Syr-Darya River. Both As and Cr (VI) contributed almost equally to the cancer risks in the Syr-Darya and Ili Rivers. In the Nura River, only As was considered in the risk

Table 5
Cancer risks estimated by the deterministic approach at median concentrations of heavy metals.

		Adults			Children		
River	Metal	Oral	Dermal	Sum	Oral	Dermal	Sum
Syr-Darya	As	3.83E−05	3.40E−07	3.87E−05	9.33E−06	1.61E−07	9.49E−06
	Cr(VI)	7.99E−05	5.37E−05	1.34E−04	1.94E−05	2.55E−05	4.49E−05
	Cum.R			**1.72E−04**			**5.44E−05**
Ili	As	2.88E−05	2.55E−07	2.90E−05	7.00E−06	1.21E−07	7.12E−06
	Cr(VI)	7.23E−06	4.86E−06	1.21E−05	1.76E−06	2.30E−06	4.06E−06
	Cum.R			**4.11E−05**			**1.12E−05**
Nura	As	3.59E−05	3.18E−07	**3.63E−05**	8.75E−06	1.51E−07	**8.90E−06**

assessment due to the dataset treatment. However, even with only one heavy metal as a contributor, Nura River's results do not differ significantly from other rivers and present serious cancer risks (>1E−05).

The deterministic human health risk assessment was performed for maximum, median, mean, and 95th percentile concentrations of non-carcinogenic metals in three rivers. Non-carcinogenic risks estimated at maximum, mean, and 95th percentile concentrations of non-carcinogenic heavy metals are presented in Table S17. Non-carcinogenic cumulative risks, expressed in terms of the hazardous index (HI) being greater than the threshold value of 1.0, occur at maximum concentrations of heavy metals in three rivers (Table S17). Due to oral exposure, Cr (VI) in the Syr-Darya River can cause the highest non-carcinogenic risk to adults and children. At maximum concentrations of Cr (VI) alone, we could have high HQ values, i.e., 1.16 for adults and 1.60 for children. In the Ili River, As metal made the most outstanding contribution by oral exposure, which leads to HQ of 1.0 for adults and 1.05 for children. The contribution of other heavy metals (Cd, Co, Mn, and Hg) in the rivers was also significant since, at maximum concentrations, they could have HQ values in the range of 0.1–0.6, which significantly increased the total HI value.

Non-carcinogenic risks calculated at median concentrations of heavy metals are presented in Table 6. It is evident that no HI values were higher than the threshold value of 1.0 in any river. Considering the more realistic exposure scenario with median concentrations of heavy metals, no serious non-carcinogenic risks occurred to locals via oral ingestion and dermal contact. However, alarming results of HI at maximum and 95th percentile concentrations should be considered by Kazakhstan's government when choosing suitable technological options and decisions for further cleanup and remediation of water resources contaminated with heavy metals.

3.7. Stochastic human health risk assessment

The stochastic approach was used to calculate carcinogenic and non-carcinogenic risks due to exposure to chosen heavy metals and to validate the results of the deterministic approach. The stochastic risk assessment is more reliable since it calculates risks not at point estimates as in the deterministic case but using random numbers that fit the probability density function of the heavy metal concentration distribution in the chosen river. Fig. S7 provides an example of how the Matlab code fits the given concentrations of metals in the Ili River with the distribution function. The probability functions match the given distributions of heavy metal concentrations well and are expected to provide reasonable results.

Table 7 presents the results obtained by the stochastic risk assessment. Significant carcinogenic risks were observed in the Syr-Darya and Ili Rivers. In the Syr-Darya River, Cr (VI) caused the highest risk (>1E−05) to adults and children, even at mean concentrations. Risks found stochastically for the Nura River do not cross the threshold of 1E−06, giving fewer chances of cancer development in this case. In the Ili River, the major contributor to cancer was also Cr (VI), causing risks to adults and children at mean concentrations (>1E−06). According to Table 7, seriously high HI values were not observed. However, the concerning value of HI of 0.9724 was found for children at 95th percentile concentrations of As and Cr (VI). Since the Syr-Darya and Ili rivers are located in the region with a prevailing agricultural sector, the major source of As metal to the rivers could be fertilizers, pesticides, and animal feeding operations releasing arsenic to the environment in high concentrations [15]. The main sources of Cr (VI) could be industrial effluents, wastewater, and chemical products such as dyes, paints, inks, and polymers containing chromate pigments [44].

Figs. S8–S10 in the SI illustrate cumulative distribution functions (CDF) of HQ and cancer risks calculated stochastically and generated by the Matlab code for three rivers. It is interesting to note that a different X-axis scale is given for each river due to the different risk levels presented in each water body. Some of them fell within the threshold range from 1E−05 to 1E−04, while others were even higher than the threshold value of 1E−04, as in the case of the Syr-Darya River (Fig. S8).

4. Conclusion

This study was focused on the analysis of the content of eleven heavy metals in the Syr-Darya, Nura, and Ili Rivers. Seasonal and temporal variations of metals, and water quality indices of water bodies were presented qualitatively in graphs. Human health risk assessment was performed deterministically and stochastically to present quantitatively carcinogenic and non-carcinogenic risks on locals due to oral and dermal exposure to heavy metals with high toxicity scores.

The lowest water quality was found in the Nura River ("Marginal" category). This river's water could be significantly impaired by the operation of mining, metallurgical, and chemical enterprises located in Karaganda and Temirtay cities. Fe metal was found to be the dominant contaminant in three rivers. The concentration of Fe exceeded Kazakhstan's and US EPA drinking water guidelines in all analyzed water bodies. However, Fe metal did not significantly contribute to carcinogenic and non-carcinogenic risks due to its low toxicity. Hg metal was determined to be the least abundant heavy metal in the rivers. As and Cr (VI) were the major contributors to the development of cancer and non-cancer diseases in locals living near the Syr-Darya, Nura, and Ili Rivers and using surface water for drinking and household purposes. Stochastic risk assessment showed that Cr (VI) in the Syr-Darya River at mean concentrations caused the highest carcinogenic risk (1.03E−04) to adults. Non-carcinogenic risks by the heavy metals in the rivers were lower than the threshold value of 1.0. Both industrial and agricultural activities in the investigated regions contributed to the increase of heavy metal concentrations in the water bodies of Kazakhstan.

This is the first study of comparative risk assessment of contamination of the Syr-Darya, Nura, and Ili Rivers in Kazakhstan. The study could be improved by adding the number of sampling locations and physiochemical factors in the investigation process and further risk assessment. It is also important to further analyze the spatial variation of heavy metals among the sampling sites in each river individually to understand the influence of various factors such as the proximity of industrial enterprises, degree of agricultural activity and runoff intensity on the content of metals. Actual Kazakhstan-specific parameters (i.e., averaging time, exposure frequency, body weight, etc.) should be established to minimize the uncertainties in the risk assessment process. The use of up-to-date information

Table 6
Non-carcinogenic risks estimated by the deterministic approach at median concentrations of heavy metals.

		Adults			Children		
River	Metal	Oral	Dermal	HQ sum	Oral	Derma	HQ sum
Syr-Darya	Cd	0.03	0.00	0.03	0.03	0.01	0.04
	Co	0.08	–	0.08	0.08	–	0.08
	As	0.11	–	0.11	0.11	–	0.11
	Cr(VI)	0.07	0.05	0.11	0.07	0.09	0.17
	HI			**0.33**			**0.40**
Nura	Fe	0.00	–	0.00	0.00	–	0.00
	Hg	0.00	0.00	0.00	0.00	0.00	0.00
	Co	0.05	–	0.05	0.06	–	0.06
	Mn	0.06	0.01	0.07	0.06	0.02	0.08
	As	0.10	0.00	0.10	0.11	0.00	0.11
	HI			**0.23**			**0.26**
Ili	Fe	0.00	–	0.00	0.00	–	0.00
	Cu	0.00	–	0.00	0.00	–	0.00
	Ni	0.00	0.00	0.00	0.00	0.00	0.00
	Mn	0.01	0.00	0.01	0.01	0.00	0.01
	As	0.08	0.00	0.08	0.09	0.00	0.09
	Cr(VI)	0.01	0.00	0.01	0.01	0.01	0.02
	HI			**0.11**			**0.12**

Table 7
Carcinogenic and non-carcinogenic risks estimated by the stochastic approach at mean and 95th percentile concentrations of heavy metals.

		Mean		95th percentile	
River	Parameter	Adults	Children	Adults	Children
Syr-Darya	Risk (As)	3.96E−07	2.90E−07	7.72E−07	7.94E−07
	Risk (Cr(VI))	1.03E−04	6.82E−05	2.74E−04	2.43E−04
	HI	0.0974	0.2859	0.2433	0.9724
Nura	Risk (As)	3.97E−07	8.28E−07	7.62E−07	8.09E−07
	Risk (Cr(VI))	–	–	–	–
	HI	0.0197	0.2437	0.0545	0.2003
Ili	Risk (As)	3.16E−07	1.01E−07	7.15E−07	6.87E−07
	Risk (Cr(VI))	9.16E−06	7.82E−06	3.30E−05	2.51E−05
	HI	0.0109	0.0343	0.0312	0.117

on water parameters and the concentrations of heavy metals in the rivers is essential for monitoring the current status of water pollution and its reduction. The results of the study emphasize that the contamination status of Kazakhstan's rivers with heavy metals is severe and life-threatening, requiring immediate remedial actions from the government, including continuous monitoring of the heavy metals in the water bodies and solid adequate long-term planning for the contaminated water cleanup.

Author contribution statement

Karina Turdiyeva: 2. Performed the experiments; 3. Analyzed and interpreted the data; 5. Wrote the paper.

Woojin Lee: 1. Conceived and designed the experiments; 3. Analyzed and interpreted the data; 4. Contributed reagents, materials, analysis tools, or data; 5. Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e17112.

Glossary

CCME-WQI	Canadian Council of Ministers of the Environment Water Quality Index
CDF	Cumulative distribution functions
CV	Coefficient of variance
HDL	Half of Detection Limit
LLP	Limited liability partnership
LOD	Limit of Detection
MAC	Maximum allowable concentration
PCA	Principal component analysis
RN	Ranking numbers
RSE	Republican State Enterprise
SI	Supplementary Information
TOC	Total organic carbon
TS	Toxicity Score
UNDP	United Nations Development Programme
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

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