Chemosphere 234 (2019) 81–88

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Pollution with trace elements and rare-earth metals in the lower course of Syr Darya River and Small Aral Sea, Kazakhstan

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HIGHLIGHTS

- Pollution of Syr Darya River (SDR) and Small Aral Sea (SAS) was studied.
- Waters of SDR exceeded WHO guideline values for Al, As, Cd, Pb and U.
- No pollution with Hg and Sb was detected.
- Concentrations of B, Ba, Cr, Cu, Ni and Se fall below WHO guideline levels.
- Increased levels of REEs, particularly Pr, Ce and Nd, were found in SDR and SAS.

ARTICLE INFO

Article history:
Received 2 May 2019
Received in revised form
19 May 2019
Accepted 5 June 2019
Available online 7 June 2019

Handling Editor: Patryk Oleszczuk

Keywords:
Aral Sea
Syr Darya
Toxic metals
Arsenic
Rare-earth elements
Kazakhstan

ABSTRACT

Over recent decades the Aral Sea has faced a major human-driven regression leading to environmental, economic and health impacts. Previous research has indicated that its region may be highly polluted yet there is little recent data to assess the scale or nature of the pollution. The present study investigated the concentration of elements for which the World Health Organization (WHO) has established guideline levels (Al, As, B, Ba, Cd, Cr, Cu, Ni, Pb, Sb) as well as 16 rare-earth elements (Ce, Eu, Er, Gd, La, Nd, Pr, Sc, Sm, Dy, Ho, Lu, Tb, Tm, Y, Yb) in the Small Aral Sea (SAS) and its inflow, the Syr Darya River (SDR). The latter displayed increased levels of Al (mean 851 $\mu g\,L^{-1}$), As (35.8 $\mu g\,L^{-1}$), Cd (2.8 $\mu g\,L^{-1}$), Pb (10.1 $\mu g\,L^{-1}$) and U (4.9 $\mu g\,L^{-1}$), exceeding the guideline limits at selected sites. In the SAS these limits were exceeded at certain locations in the case of As and U. The total mean concentration of REEs in the SDR and SAS amounted to 22.6 and 61.7 $\mu g\,L^{-1}$, respectively, with Pr, Ce and Nd constituting the greatest share. The concentrations of B, Ba Cr, Cu, Se and Ni were below the WHO guideline levels at all studied sites while Sb and Hg were always below detection limits. This research provides an updated status on the levels of contamination of the surface waters in the ecological disaster zone of the Aral Sea in Kazakhstan.

1. Introduction

In the last century, the Aral Sea, once the fourth largest lake on Earth, experienced an unprecedented human-driven regression initiated by decisions to divert its two feeding rivers, the Amu Darya and the Syr Darya, mainly for the irrigation of cotton and rice

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Abbreviations: ICP-OES, inductively coupled plasma optical emission spectrometer; LOD, limit of detection; REE, rare earth element; SAS, Small Aral Sea; SDR, Syr Darya River; WHO, World Health Organization.

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https://doi.org/10.1016/j.chemosphere.2019.06.036
0045-6535/

fields (Krivonogov et al., 2014). This resulted in a nearly 80% loss of the lake surface by the end of the 1990s, and various associated consequences including climate change, loss of biodiversity, cessation of fishery and economic crisis (Aladin and Potts, 1992; Khan et al., 2004; Lioubimtseva, 2014; Aladin et al., 2019; Kawabata et al., 2019). Under such regression three smaller basins, the Small Aral, the Eastern Large Aral, and the Western Large Aral, all characterized by high salinity, emerged (Izhitskiy et al., 2016). Over the years some measures to partially restore the Aral Sea have been undertaken; supported financially by the World Bank and resulting in 2005 in the construction of the Kokaral Dam that accumulated waters of Syr Darya River (SDR) in the northern part of the lake known as Small Aral Sea (SAS) (Micklin, 2014). Consequently, the water level in this water body had progressively increased, causing a simultaneous decrease in salinity, the reappearance of freshwater and brackish fish species, and the restoration of fishery (Ermakhanov et al., 2012; Plotnikov et al., 2016). However, at the same time water contributions from the Amu Darya River have nearly ceased, and the southern part of Aral Sea, once a massive water body, has now mostly vanished (Aladin et al. 2009, 2019).

Although some aspects of this ecological disaster have been partially mitigated, there is accumulating evidence that the population living in the region of the Aral Sea may face adverse health outcomes resulting not only from low socioeconomic status and limited medical care but possibly also from certain effects of desertification and water desiccation such as chemical loading and transport of organic pesticides and toxic elements with salt and dust aerosols, and deterioration of drinking water quality (Ataniyazova et al., 2001; Erdinger et al., 2003; Kadyrzhanov et al., 2005; Bosch et al., 2007; Dewan et al., 2015). As reported, populations inhabiting this region may be characterized by an increased risk of cognitive function impairment, anemia, miscarriage, preeclampsia and neonatal morbidity (Zetterstrom, 1999; Crighton et al., 2011; Igissinov et al., 2011; Mamyrbayev et al., 2016; Sakiev et al., 2017; Turdybekova et al., 2017).

Therefore, it is imperative to regularly monitor levels of soil, air and water pollution in the area of Aral Sea and identify its potential sources. Some previous research has already reported increased levels of radionuclides and selected toxic metals in the SDR (Friedrich, 2009) presumably due to the mining and tailings activities in the watershed, yet its water is used for irrigation of agricultural fields, including rice paddies (Kadyrzhanov et al., 2005; Friedrich, 2009). Considering that mining production is currently increasing in Kazakhstan (OECD, 2018) it is important to investigate the levels of certain contaminants in both the SDR and the SAS which is feed with its waters. To answer this call the present research investigated the concentrations of elements for which the guideline levels were established by World Health Organization (WHO, 2017) as well as the concentration of rare-earth elements which are emerging environmental contaminants (Mleczek et al., 2016; Poniedziałek et al., 2017; Gwenzi et al., 2018) but for which no maximum allowance levels in water have been proposed so far.

2. Material and methods

2.1. Study area

The present research was conducted along the lower section of the Syr Darya River (SDR), from Kyzylorda City (total inhabitants 295,800, density 120 inhabitants per km^2) Kyzylorda through Kazaly (municipality in the vicinity of the Syr Darya delta) to the Small Aral Sea (SAS). The study area is characterized by a dry continental climate. Mean air temperature in January in the meteorological station in Kazaly (Fig. 1) is −11.3 °C, and in July 26.0 °C. Total annual atmospheric precipitation usually reaches only 145 mm and air relative moisture approx. 60%. During winter, snow cover persists (for an average of 81 days), usually with a thickness of approximately 10 cm (Ryabtsev and Yeliseev, 2014). The SDR is the main and only river in the studied area. It originates in the Ferghana valley, at the confluence of the Naryn River and Karadarya River. The former stream flows out at a height of approximately 3750 m a.s.l. from glaciers, snow, and lakes in the Tien Shan Mountains. Outside the mountain area, the SDR flows through steppes and desert areas. Its length is 2218 km (including 1746 km in the territory of Kazakhstan), and its catchment area (according to the majority of sources) is approx. 442 thousand km^2 (Chen et al., 2017). Somewhat more than 30% of the catchment area belongs to Kazakhstan, and the remaining parts are located on territory belonging to Kyrgyzstan, Uzbekistan, and Tajikistan.

The SDR is characterized by nival-glacial-rain alimentation. In the upper part of the catchment area (above 1500 m a.s.l.), the highest water stages and discharges induced by snow and ice melting occur in April and May. A number of artificial reservoirs have been constructed in this part. In the lower part of the catchment, the primary factors shaping the hydrological regime of the SDR include: floods in early spring or at the beginning of summer, water infiltration in the floodplain, swamps or oxbow lakes, evaporation and transpiration. Along this section the river meanders between low banks. It features numerous arms and canals. Some of them are used for the irrigation of the Kyzyl-Kum desert.

In the second half of the 20th century the hydrological regime of the SDR underwent considerable transformations. They resulted from economic activity and involved: intensification of irrigation (up to 2 million hectares in total), water intake for irrigation and other production purposes (up to >23 km^3 per year), return of strongly polluted water to the SDR, as well as the construction of reservoirs, ponds, etc. From 1965 to 1995 due to the increased number of irrigated areas and water intake, drainage flow increased which resulted in worsening land and water quality (Golovanov et al., 2013). In addition to a drastic reduction of water resources, water pollution from irrigated agricultural areas became a major problem. The use of pesticides and insecticides is estimated at $(38–57) \times 10^3$ t and $(570–1140) \times 10^3$ t of mineral fertilisers (Taltakov, 2015). Water salinity in the delta of the SDR increased to 2.9 g L^{-1} (Murray-Rust et al., 2001). Due to hydrogeological conditions the SDR flows within an artesian basin represented by a complex multiple-layer fluid-flow system with an underground water system connected to the Aral Sea (Panichkin et al., 2017). The most intensive seepage occurs in the northern part of the SAS. The underground waters there are in oligocenic deposits and flooded upper-eocenic deposits. In addition, the region is rich in geothermal water (Kudysovitch et al., 2014). The occurrence of unfavourable anthropogenic transformations co-occurs with climatic changes, the effects of which also negatively affect the hydrology of the SDR (Bernauer, 2012).

2.2. Sampling

The sampling was carried out in April-May 2018 according to the guidelines of the Environmental Protection Agency (Surface Water Sampling 2013). Surface waters (20 cm below the water table) were collected at five sites located on the SDR between the Kyzylorda City (S1) and the Kokaral Dam (S5) discharge as well as six sites (A1-A6) located on the SAS (Fig. 1). The samples were transferred to propylene bottles, filtered through GF/C filters (Whatman, UK), acidified with HNO_3 (Sigma-Aldrich, Germany) for preservation, and deposited in 50-mL tubes at −20 °C. Three samples per each site were collected. The mean ± SD of water temperature and range of pH during collection was respectively 21.0 ± 0.8 °C and 7.4–8.1 in the SDR and 16.1 ± 2.3 °C and 7.0–8.6 in

Fig. 1. The studied area and location of sampling points along the Syr Darya River (S1–S5) and Small Aral Sea (A1-A6).

the SAS.

2.3. Elemental analysis

The concentration of total Hg was assessed using Cold Vapour Atomic Absorption Spectrometry with a Mercury MA-2 analyser (Nippon Instruments, Japan). The analysed sample underwent thermal decomposition after which the Hg was atomized and the vapours were amalgamated. The amalgam was heated to release the Hg atoms, determined by atomic absorption cold vapour at 253.7 nm. The limit of detection (LOD) was 0.1 μg L^{-1}.

Determination of the concentration of Al, As, B, Ba, Cd, Cr, Cu, Ni, Pb, Sb, Se and U as well as sixteen rare-earth elements: Ce, Eu, Er, Gd, La, Nd, Pr, Sc, Sm, Dy, Ho, Lu, Tb, Tm, Y, Yb was performed using the inductively coupled plasma optical emission spectrometer Agilent 5110 ICP-OES (Agilent, USA). A simultaneous axial and radial view of plasma was obtained by a vertical dual view using dichroic spectral combiner technology. The following common conditions were applied: radio frequency power 1.2 kW, nebulizer gas flow 0.7 L min^{-1}, auxiliary gas flow 1.0 L min^{-1}, plasma gas flow 12.0 L min^{-1}, charge-coupled device temperature −40 °C, viewing height for radial plasma observation 8 mm, accusation time 5 s, 3 replicates. ICP commercial analytical standards CM17 PrimAg Plus and KP7 PrimAg (Romil, England) were applied for the calibration. The detection limits for the elements determined were found at the level of 1 μg L^{-1}. The applied wavelengths were as follows: Al – 396.152 nm, As – 188.980 nm, B – 249.772 nm, Ba – 455.403 nm, Cd – 214.439 nm, Cr – 267.716 nm, Cu – 327.395 nm, Ni – 231.604 nm, Pb – 220.353 nm, Sb – 206.834 nm, Se – 196.026 nm, Ce – 446.021 nm, Dy – 400.045 nm, Er – 349.910 nm, Eu – 420.504 nm, Gd – 342.246 nm, Ho – 348.484 nm, La – 333.749 nm, Lu – 307.760 nm, Nd – 406.108 nm, Pr – 417.939 nm, Sc – 361.383 nm, Sm – 442.434 nm, Tb – 350.914 nm, Tm – 336.261 nm, Y – 361.104 nm and Yb – 328.937 nm.

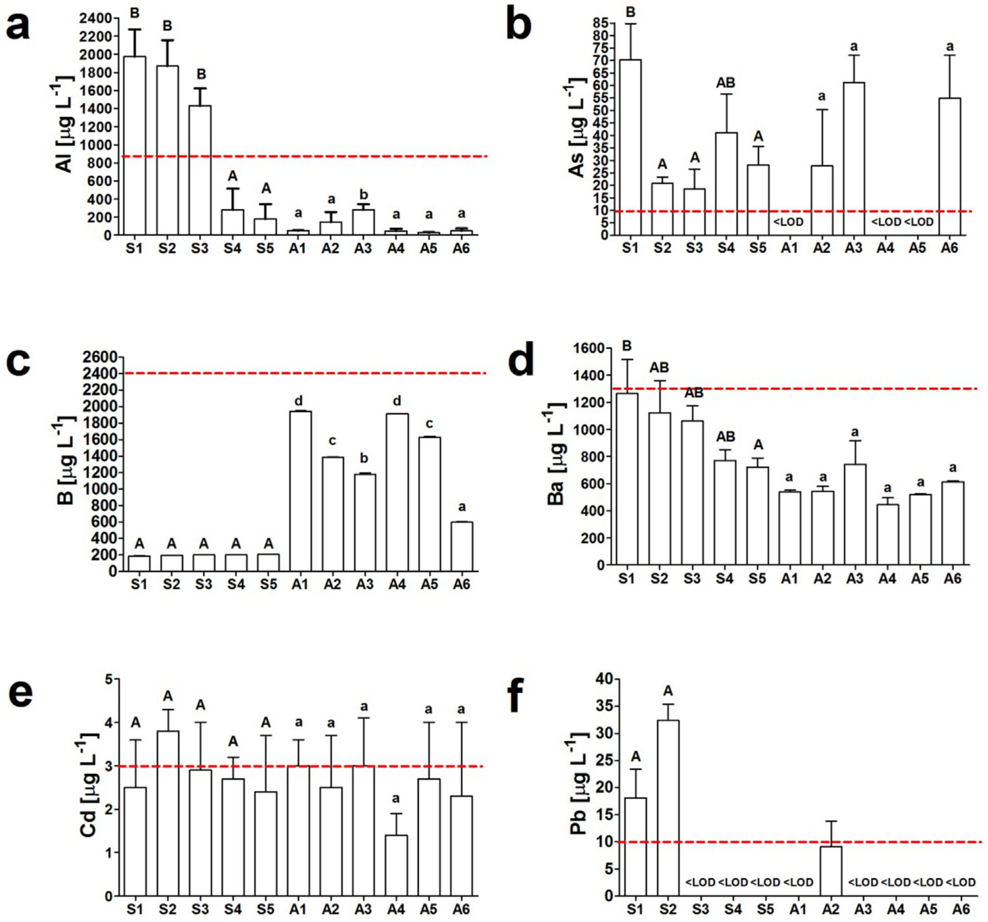

Fig. 2. The mean ± SD concentrations of Al (a), As (b), B (c), Ba (d), Cd (e) and Pb (f) in the Syr Darya River (SDR; S1–S5) and Small Aral Sea (SAS; A1-A6). Different superscripts given in upper case letters denote a significant differences between SDR sites while lowercase letters denote a significant differences between SAS sites, according to post-hoc Tukey's HDS test (MANOVA). The red dotted line indicates the WHO guideline level for drinking water.

2.4. Statistical analyses and calculations

The results were analysed using STATISTICA 13.1 software (StatSoft, USA). The differences in the concentration of elements between particular sampling sites were analysed with ANOVA and post-hoc Tukey's HSD test while the difference between SAS and SDR were compared with a *t*-test. In all analyses, $p < 0.05$ was considered as statistically significant.

Determined concentrations of analysed elements were compared to guideline levels set for drinking water established by the WHO. The following values were used: As – 10 μg L^{-1}; B – 2400 μg L^{-1}; Ba – 1300 μg L^{-1}; Cd – 3 μg L^{-1}; Cr – 50 μg L^{-1}; Cu – 2000 μg L^{-1}; Hg – 6 μg L^{-1}; Ni – 50 μg L^{-1}; Pb – 10 μg L^{-1}; Sb – 20 μg L^{-1}; Se – 40 μg L^{-1}; U – 3 μg L^{-1} (WHO, 2017). In the case of Al no exact guideline value was established, although the WHO states that a health-based value of 900 μg L^{-1} could be derived, and this level was used to confront the determined Al concentration (WHO, 2017). No recommendations for concentration of specific REEs or their total concentration have so far been proposed.

3. Results

3.1. Aluminum

Compared to the SAS, the SDR waters were characterized by Al levels higher by an order of magnitude (mean ± SD 1147.4 ± 862.6 *vs* 98.8 ± 98.1 μg L^{-1}; p < 0.01). The provisional WHO safety level of Al for drinking water was exceeded at 3/5 (60%) sites of the SDR. The highest values, exceeding WHO limits on average by over two-fold, were found at S1 (Kyzylorda City) and then gradually decreased along the course of the river (Fig. 2).

3.2. Antimony, barium and boron

Total Sb concentration was below LOD at all studied sites in the SDR and SAS. Ba was detected at all SDR and SAS sites. In the former the highest mean concentration, constituting 97.3% of the WHO guideline value, was noted at S1 (Kyzylorda City) and decreased along the river course. The SDR levels of Ba were significantly higher compared to those noted in the SAS (mean ± SD 988.6 ± 233.3 *vs* 567.0 ± 102.0 μg L^{-1}; p < 0.05). In the latter, the highest concentrations were observed at A3. Compared to the SDR, significantly higher B concentrations were observed in the SAS (1316.5 ± 448.3 *vs* 196.4 ± 8.0 μg L^{-1}; p < 0.01), although in both environments its levels displayed low variation and were below the WHO guideline (Fig. 2).

3.3. Arsenic

As was detected at all studied SDR sites at a mean ± SD level of 35.8 ± 21.2. The highest concentration was found at S1 (Kyzylorda City), although no trend related to the river course could be seen.

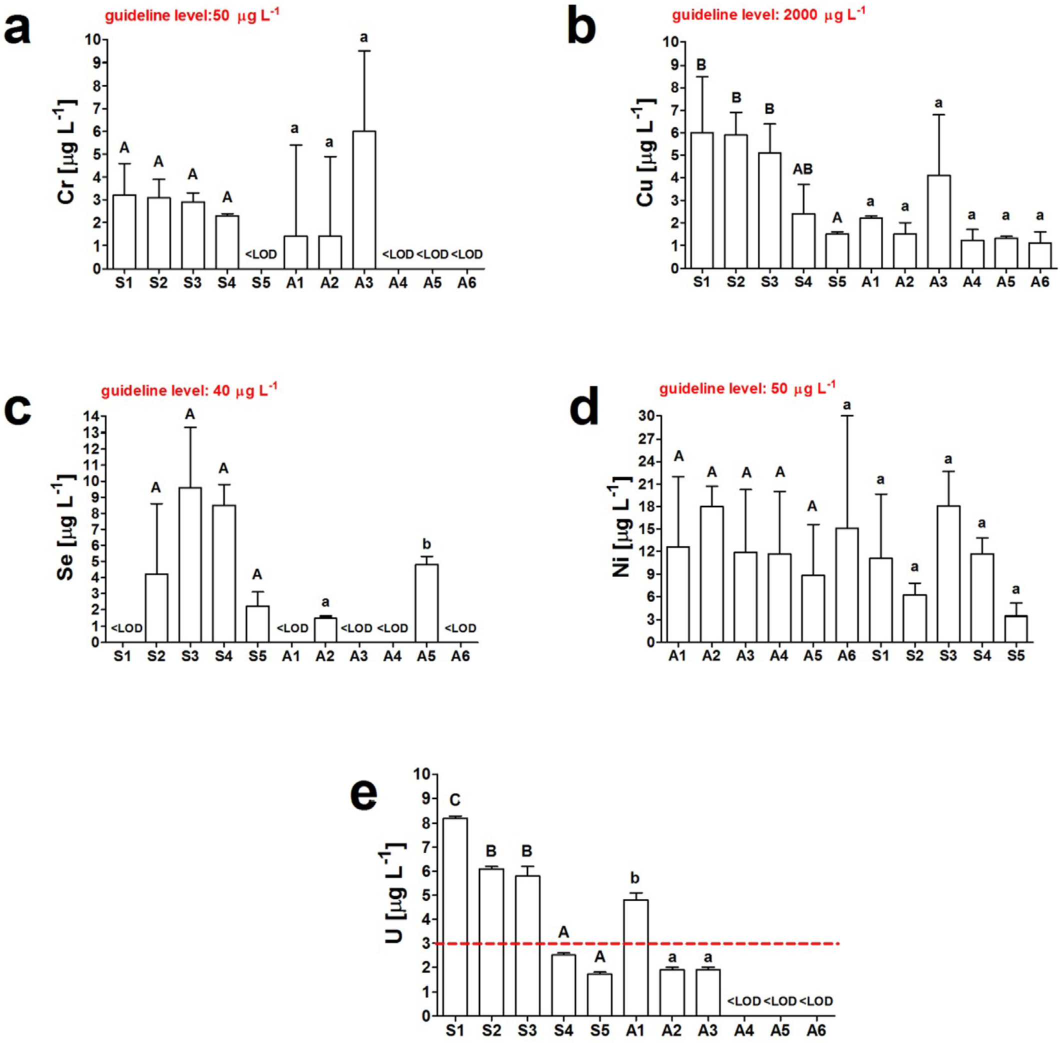

Fig. 3. The mean ± SD concentrations of Cr (a), Cu (b), Se (c), Ni (d) and U (e) in the Syr Darya River (SDR; S1–S5) and Small Aral Sea (SAS; A1-A6).). Different superscripts given in upper case letters denote a significant differences between SDR sites while lowercase letters denote a significant differences between SAS sites, according to post-hoc Tukey's HDS test (MANOVA). The red dotted line indicates the WHO guideline level for drinking water.

Nevertheless, the observed As levels were in the range of 186–703% of the WHO guideline level. In the SAS, As concentrations were identified above detection limits at only three sites A2, A3 and A6 and exceeded the guideline value by 279, 612 and 548%, respectively (Fig. 2).

3.4. Cadmium, lead and mercury

Cd was detected at all the studied sites at similar concentrations in the SDR and SAS (mean ± SD 2.8 ± 0.6 *vs* $2.5 \pm 0.6\,\mu g\,L^{-1}$; $p > 0.05$) and constituted 76.7–126.7% and 46.7–100% of the WHO guideline level, respectively (Fig. 2). Pb in the SAS was detected only at one site (A2), slightly below the WHO guideline level. In the SDR, two sites S1 and S2 displayed detectable concentrations of this metal, exceeding by nearly 2-fold and over 3-fold the guideline limit, respectively (Fig. 3). Total Hg concentration was below LOD at all studied sites.

3.5. Chromium, copper and selenium

All SDR sites except S5 displayed detectable levels of Cr, ranging from 2.3 to $3.2\,\mu g\,L^{-1}$. In the SAS, Cr was identified only at A1, A2 and A3 with the latter revealing the highest concentration of $6.0 \pm 3.5\,\mu g\,L^{-1}$ (Fig. 3). Compared to the SAS, higher levels of Cu were noted in the SDR (mean ± SD 1.9 ± 1.2 *vs* $4.2 \pm 2.1\,\mu g\,L^{-1}$; $p < 0.05$) in which it displayed the highest concentrations at S5 (Kyzylorda City) and a gradual decrease along the river course. In the SAS, the highest Cu concentrations were noted at A3 (Fig. 3). Se in the SDR was identified at S2–S5 in the 2.2–$9.6\,\mu g\,L^{-1}$ range while in the SAS it was only detected at A2 and A5 at a mean concentration of 1.5 and $4.8\,\mu g\,L^{-1}$, respectively (Fig. 3). In the case of all studied sites detectable levels were much below WHO guideline values for Cr, Cu and Se.

3.6. Nickel

Ni was detected at all sites in the SDR and SAS at a mean ± SD concentration of 10.1 ± 5.7 and $13.0 \pm 3.2\,\mu g\,L^{-1}$, respectively ($p > 0.05$). In the former, no trend related to the river course was observed with the lowest and highest Ni concentrations found at S1 (Kyzylorda City) and S3, respectively (Fig. 3). In all cases, the observed concentrations were much below the WHO guideline level.

Table 1
The mean ± SD concentration (μg L^{-1}) of rare-earth elements in the Syr Darya River (SDR; S1–S5) and Small Aral Sea (SAS; A1-A5).

	Light REEs						Heavy REEs				
	La	Ce	Gd	Nd	Pr	Sc	Er	Tb	Tm	Y	ΣREEs
A1	<LOD	2.2 ± 1.4^{a}	<LOD	7.9 ± 1.3^{a}	42.6 ± 0.8^{d}	1.9 ± 0.2	1.1 ± 0.2	1.8 ± 0.2^{a}	1.7 ± 0.2^{a}	<LOD	59.2
A2		3.2 ± 2.2^{a}		9.1 ± 0.7^{a}	55.4 ± 3.5^{b}	<LOD	<LOD	1.6 ± 0.6^{a}	2.3 ± 0.1^{a}		71.6
A3	3.7 ± 0.1	8.6 ± 3.1^{b}	2.3 ± 0.4	10.5 ± 1.8^{a}	40.1 ± 5.8^{cd}			1.5 ± 0.6^{a}	1.9 ± 0.2^{a}	1.9 ± 0.1	65.2
A4	<LOD	2.1 ± 0.5^{a}	<LOD	9.1 ± 0.6^{a}	62.7 ± 2.0^{b}			<LOD	<LOD	<LOD	73.9
A5		2.6 ± 1.2^{a}		8.7 ± 1.1^{a}	56.6 ± 4.9^{b}			1.3 ± 0.3	2.2 ± 0.7		71.4
A6		1.3 ± 0.6^{a}		8.8 ± 0.6^{a}	18.7 ± 1.9^{a}			<LOD	<LOD		28.8
S1		1.0 ± 0.2^{A}		6.6 ± 0.9^{A}	11.2 ± 2.2^{B}			1.2 ± 0.4^{A}			20.0
S2		1.2 ± 0.5^{A}	1.3 ± 0.5^{A}	7.0 ± 0.3^{A}	4.6 ± 0.6^{A}			<LOD		1.0 ± 0.2^{A}	15.1
S3	1.4 ± 0.3^{A}	2.8 ± 0.6^{AB}	<LOD	7.2 ± 1.9^{A}	10.3 ± 1.0^{B}			1.3 ± 0.2^{A}		<LOD	23.0
S4	2.0 ± 0.1^{A}	3.3 ± 1.9^{B}	1.0 ± 0.2^{A}	7.5 ± 2.2^{A}	9.3 ± 1.6^{B}			2.1 ± 0.4^{A}		1.5 ± 0.2^{A}	26.8
S5	2.1 ± 0.2^{A}	4.8 ± 2.8^{B}	1.6 ± 0.2^{A}	9.2 ± 1.3^{B}	10.6 ± 3.4^{B}			<LOD		<LOD	28.3

LOD-detection limit; Eu, Sm, Dy, Ho, Lu and Yb were <LOD at all studied sites). Different superscripts given in upper case letters denote a significant differences between SDR sites while lowercase letters denote a significant differences between SAS sites, according to post-hoc Tukey's HDS test (MANOVA).

3.7. Uranium

U was identified at all studied sites in the SDR, and its concentrations gradually decreased along the river course. The WHO guideline level was exceeded at 3/5 (60%) of sites, and over 2.5-fold at S1 (Kyzylorda City). In the SAS, U concentrations exceeded detection limits at 3/6 of sites (50%), and exceeded the guideline value only at A1 (Fig. 3).

3.8. Rare-earth elements

The results of REE concentrations at the studied sites are summarized in Table 2. From sixteen investigated elements, six – Dy, Eu, Ho, Lu, Sm and Yb – were below limits of detection at all sites of the SDR and SAS, while Er, La, Sc, Tb, Tm and Y were detected only sporadically. Pr followed by Nd and Ce were the most abundant REEs and were identified at all sampling points. Compared to the SDR, waters of the SAS displayed three-fold higher concentrations of total REEs (mean ± SD 22.6 ± 5.3 *vs* 61.7 ± 17.0 μg L^{-1}; $p < 0.001$) (Table 1).

4. Discussion

A number of previous studies have investigated selected aspects of environmental pollution within the region of the Aral Sea, particularly as regards its potential effects on human health (Crighton et al., 2011). The present research conducted on the SDR and SAS assessed the concentrations of all of those elements for which the WHO has set drinking water guideline levels as well as REEs whose levels are still relatively rarely determined in surface waters and for which no guidelines have been established as yet. Considering the multi-dimensional development of Kazakhstan, particularly ongoing industrial and mining investments, as well as plans for further restoration of the SAS (OECD, 2018; Aladin et al., 2019), this study represents a valuable reference point for any future monitoring of contamination of surface waters occurring in this region and potential actions to mitigate it.

One of the worrisome findings of the present study was an increased As level at all studied SDR sites and selected ones in the SAS. In all cases, its levels exceeded the guideline established by the WHO at 10 μg L^{-1} (WHO, 2017). Previous studies have clearly shown that As levels in rice originating from the paddy fields used for rice cultivation which are located on the banks of the SDR in Kyzylorda Province are above maximum allowance levels (0.2 mg kg^{-1}) proposed by the WHO and the Food and Agriculture Organization of the United Nations (WHO/FAO, 2012). As suggested, this may arise from the discharge of industrial and domestic sewage from city areas (Tattibayeva et al., 2016). Arsenic compounds are fairly soluble in water and mobile over a wide range of redox conditions and under pH 6.5–8.5, which is typical for ground- and surface waters (Smedley and Kinniburgh, 2002). The present study indicates that the problem of As-contamination is persistent in the Kyzylorda/Aral area and requires further monitoring and measures undertaken to decrease potential human exposures. As shown, children living in the area of the SAS revealed detectable urinary levels of As of mean concentration 5.4 μg L^{-1} (Erdinger et al., 2003). One should, however, note that the toxicity of As largely depends on its species with inorganic forms, arsenate As(V) and arsenite As(III), displaying the greatest health concern followed by methylated and organic As compounds (Jain and Ali, 2000).

Another important observation of the present study included the increased Al concentration detected in the SDR, which was by one order of magnitude higher than in the SAS, as well as in rivers in which naturally elevated Al concentrations (usually up to 100–300 μg L^{-1}) occur (Guibaud and Gauthier, 2003). This may reflect a general pollution of Al in the SDR watershed, as previous studies have revealed higher levels of this element in the hair of children inhabiting areas close to Kyzylorda City compared to those living in close proximity to the SAS (Chiba et al., 2004).

There is a steady increase in mining of bauxite and other Al-containing ores in Kazakhstan, and it can be hypothesized that these are likely to be the main sources of Al-contamination in the SDR. Nevertheless, it should be borne in mind that the toxicity of this element depends on a number of other parameters, with pH being the single most important one – under acidic pH the toxicity to aquatic biota is greatly increased (Gensemer and Playle, 1999; Gensemer et al., 2018). The studied waters were in turn neutral-slightly alkalic, and under such conditions the formation of colloidal Al hydroxides reducing aquatic toxicity can be expected (Gensemer and Playle, 1999).

Cd was detected at all studied sites but displayed concentrations exceeding the WHO guideline level (3.0 μg L^{-1}) only at one site in the SDR. One should note, however, that it reached ≥2.5 μg L^{-1} in the case of 80 and 67% of sites at the SDR and SAS, respectively. Previous studies have indicated that the inhabitants of the Aral Sea face increased rates of renal tubular dysfunction which can be one of the clinical manifestations of Cd toxicity (Kaneko et al., 2003). However, the hair analysis conducted among those living near the Aral Sea did not reveal increased Cd levels (Chiba et al., 2004), although hair Cd levels may not always be well associated with the general body burden of this element (Rzymski et al., 2015). Nevertheless, considering that Cd is classified by the International Agency on Cancer Research (IARC) as a Group 1 carcinogen, its relatively high concentrations in the SDR and SAS justify the implementation of additional measures to ensure thatits levels within the Aral Sea region are minimized. This is particularly important given the fact that neoplasms such as esophageal cancer, carcinoma of lung, stomach cancer, and breast cancer were reported to be most frequent leading cancers in the Aral-Syr Darya ecological area of Kazakhstan (Igissinov et al., 2011), while Cd exposure has been linked to an increased risk of all of these malignancies (Hartwig, 2013).

The greatly increased concentrations of U in SDR and SAS waters reported previously in a 2002–2006 survey (16 and 36–61 $\mu g\,L^{-1}$, respectively) which likely resulted from mining and ore processing activities in Kazakhstan (Kadyrzhanov et al., 2005; Bosch et al., 2007; Friedrich, 2009) were not confirmed in the present study – as shown its levels always remained below 10 $\mu g\,L^{-1}$ in the SDR and 5 $\mu g\,L^{-1}$ in the SAS. However, particularly in the SDR in which U concentrations appeared to decrease gradually along the course of the river with the highest noted close to Kyzylorda City, the levels were mostly above the proposed WHO guideline for drinking water of 3 $\mu g\,L^{-1}$ (WHO, 2017). While it is plausible that U contamination in the area has decreased within recent decades (e.g. due to an increase in water level), it still appears to be an environmental concern and requires future monitoring.

As shown, the concentrations of Hg remained below detection limits in both the SDR and SAS. Potential water contamination with this element in the surface waters may arise from smelters, production of gold and cement, waste disposal and combustion processes at coal-firing power plants and the use of certain organic compounds in agriculture. The background levels are usually with the ppt range but may be increased to several $\mu g\,L^{-1}$ due to certain human activities. It is known that some rivers in Kazakhstan have a long history of receiving highly Hg-polluted untreated effluents, e.g. from acetaldehyde workshops (Heaven et al., 2000). There is no documented history of such pollution in the SDR, although some concerns have been previously expressed due to the use of organic Hg-based compounds as fungicides for seed preservation (Zetterstrom, 1999). The present study indicates that there is no risk of exposure to Hg via water of the SDR and SAS, and in line with this, a human biomonitoring study conducted by Erdinger et al. (2003) did not find any evidence of increased urinary and blood levels of Hg in children living in the Aralsk region.

Although some differences between studied sites were noted, the concentration of Cr, Cu, Ni and Se always remained much below the guideline levels set by the WHO indicating no significant pollution with these elements in the SDR and SAS. Higher levels of Ba were noted in the SDR while the SAS revealed higher B concentrations. This may be due to their geochemical background and/or from industrial use (Ba), and use as fertilizers (B) (Nable et al., 1997; Kravchenko et al., 2014). Additionally, B can enter the SAS via geothermal ducts (Parks and Edwards, 2005). However, one should note that at all sites Ba and B were still in the range of WHO recommendations.

The concentration of Sb in surface fresh and saline waters is usually up to 5 $\mu g\,L^{-1}$ (Filella et al., 2002; Niedzielski, 2006). As reported by Kulmatov (1988), the dominant dissolved form of this element in the area of the Aral Sea is $Sb(OH)_6$. The main source of increased Sb levels is mining and inflows of acid mine drainage (He et al., 2012). According to the present study there is no indication that mining of Sb in Kazakhstan, which has decreased over the years (Safirova, 2017), affects its levels in the SDR and SAS.

To the best of our knowledge, prior to the present study there is no data regarding REE levels in the region of the SAS. The only investigations in this regard were conducted in the area of the Amu Darya and the Large Aral Sea (before and after desiccation), and demonstrated uniform patterns of REEs in sediments collected from both ecosystems with Ce, Nd, La and Pr being the most abundant (Baturin et al., 2015). One should note that Kazakhstan is emerging as an REE-mining region and within the next several years is expected to increase its share in the global market. Therefore, it is of high importance to assess whether these operations are resulting in increased REE concentrations in the surface waters as can often be seen (Rzymski et al., 2017). As demonstrated in the present study, the total levels of REEs were two-fold higher in the SAS than in the SDR. This cannot be explained by differences in pH as REE availability is usually increased in an acidic environment (Astrom and Corin, 2003), while both the SDR and SAS displayed neutral to slightly alkaline pH. This may potentially indicate the presence of other than riverine sources of these elements. The most abundant REEs included Pr, Nd and Ce which can originate from the production of alloys, ceramics and coloured glass (Pagano et al., 2015). The data concerning the toxicity of REEs is based predominantly on animal studies and preliminary observations of occupational human exposures with no comprehensive observation on the effects of long-term exposure (Pagano et al., 2015). As reported using experimental models, Pr can induce liver dysfunction (Oga et al., 1986), exposure to Nd can induce cytotoxicity and genetic damage (Jha and Singh, 1995; Huang et al., 2011) while Ce can exhibit pro-inflammatory activities (Aalapati et al., 2014), although it is unknown whether these elements pose any threat in the concentrations found in SDR and SAS waters.

It should be highlighted that while the concentrations of elements reported for the SDR and SAS in the present study may serve as a reference point in future research on the contamination of the Aral region, the content of metals and metalloids in water can be subject to seasonal variations and that a full assessment of contamination would require analyses of their content in sediment and biota samples (Rzymski et al., 2014). To the best of our knowledge, no such studies have been conducted so far. Nevertheless, the findings of the present study indicate that additional measures to mitigate contamination in the lower course of the SDR and in the SAS are justified.

5. Conclusion

The present study provides updated data on pollution of the SAS and its feeding river, the SDR. The levels of B, Cr, Cu, Ni and Se in the studied waters all fell below WHO guideline values for drinking water. However, the SDR has been shown to be reveal increased levels of Al, As, Pb with concentrations decreasing systematically along its course. The U concentrations in the SDR as well as the SAS were also increased, although generally its levels were lower than previously reported in the literature. Relatively high levels of REEs, particularly Pr, Nd and Ce, were found in the studied waters with greater concentrations observed in the SAS. Considering that the ecological disaster zone of the Aral Sea in Kazakhstan and the SAS itself will likely undergo further restoration works, the data of the present study may not only serve as a reference point on its status of pollution but also as an indicator in potential actions to mitigate it.

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