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Spatiotemporal evaluation of water quality and risk assessment of heavy metals in the northern Caspian Sea bounded by Kazakhstan

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A R T I C L E I N F O

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A B S T R A C T

The water quality of the northern Caspian Sea has not been well-known, and its contamination can adversely affect the health of swimmers and seashore residents. The study sought to determine the contamination state of the Caspian Sea in Kazakhstan and quantify human health risks coming from the existing heavy metals concentration. The Caspian Sea was found to be "fairly to marginally" contaminated (24 < CCME-WQI < 64), with Cd influencing the index significantly. Concentrations of Cd and Pb increase over time (seasonal Kendall test, p-values = 2–4 %) in sites near oil fields and ports, suggesting the significant role of anthropogenic sources in causing diverse pollution events. Pb demonstrated the highest variability and number of outliers (4.3 % of all samples with coefficients of variation reaching up to 175 %). The principal component analysis further revealed that various discharges from oilfields and upstream transport could contribute to the contamination by heavy metals and their concentrations. Contamination is associated with up to 6 % cancer risk for adults. The long exposure duration of swimmers in water increases risks by up to 18 %, indicating the local population is at a higher risk. In conclusion, statistical tests and analysis indicate the presence of anthropogenic sources, and risk assessment reveals swimming can contribute to cancer risk.

1. Introduction

The Caspian Sea is the largest enclosed body of water in the world surrounded by Kazakhstan, Azerbaijan, the Russian Federation, Iran, and Turkmenistan. It covers approximately 390,000 km^2 and reaches up to 1025 m depth in the southern part and <15–20 m in the northern part (Kosarev, 2005). The enclosed water body has two major depressions in the middle and southern parts, affecting water circulation (Zyryanov, 2015). It is mainly fed and drained by the Volga (233 km^3/year) and the Ural rivers (6.6 km^3/year) (United Nations Economic Commission for Europe, 2011; Zyryanov, 2016) and precipitation. Evaporation averaged 6.72 cm/year during 1996–2015 and is estimated to increase (Chen et al., 2017). Apart from its geopolitical significance, the Caspian Sea area distinguishes itself by various natural resources, including bio-resources and hydrocarbons (Zonn, 2005). The abundant resources resulted in industrial developments near the Caspian Sea region, putting its environmental condition at risk. Previous studies from different regions in other countries reported that anthropogenic activities near the water body, such as fuel combustion, oil extraction, and refining, were linked with significant heavy metal waste discharges into the Sea regions (He et al., 2005; Kumar et al., 2019; Okogbue et al., 2017; Wagner and Boman, 2003). Heavy metals' toxic, persistent, and bioaccumulative nature has caused primary public concerns because they can adversely affect global ecosystems and human health (Armitage et al., 2007; Jaishankar et al., 2014). For example, Cd and Pb are biologically nonessential and classified as carcinogens (Brevik and Burgess, 2012; IARC, 2019). Long-term exposure to high Cd concentrations may result in kidney disease, cardiovascular disease, and arthritis, whereas Pb affects the nervous system, especially in young children (Santana et al., 2020; Sobhanardakani et al., 2018). Cr may cause liver and kidney diseases and nervous system disorders (Sobhanardakani, 2017). Therefore, it is crucial to know the contamination status of heavy metals in the Caspian Sea and their potential harmful impacts on humans.

Multiple studies indicated the presence of heavy metals in various parts of the water body. High As, Ni, Cr, and Cu concentrations in sediment were found in the southern Caspian Sea of Iran (Bastami et al.,

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2014). Pb concentrations were exceptionally high in southeastern part of the water body (Saeedi Saravi and Shokrzadeh, 2013). Hg sediment concentrations were high near Azerbaijan's coastline (De Mora et al., 2004), but sediment's ecological risks were reported at low levels (Ahmadov et al., 2020). Moreover, low concentrations of heavy metals in seafood were reported in the southern Caspian Sea (Dadar et al., 2017; Hosseini et al., 2013; Sobhanardakani et al., 2018), except for relatively high Hg concentration in the Zander fish (*Sander lucioperca*) from the southwestern part (Manavi and Mazumder, 2018). Algae near Iran's coastline contained excessive Pb, Cd, and Cr (Ebadi and Hisoriev, 2017). These studies provided valuable insights on concentration levels of heavy metals in the Caspian Sea but were focused only on the southern and western regions of the Caspian Sea. Kazakhstan's coastline is highly populated and industrialized, but its contamination and potential risks have been barely investigated. The area of the water object adjacent to two administrative regions of Kazakhstan – Mangystau and Atyrau – has around 1.37 million residents and 360,000–460,000 tourist inflow annually ("National statistical committee," 2019). Heavy metal contamination can adversely affect the human health of residents and tourists; therefore, exposure risks should be estimated. Given the transboundary nature of the Caspian Sea, contamination can affect even more people. Also, previous studies primarily report risks due to fish consumption but no other exposure pathways such as swimming, fishing, or boating. Swimming is particularly important because of tourist inflow.

The literature lacks evaluations of the environmental contaminations in the northern part of the water body and swimming scenario in risk assessment. This study aimed to fill these gaps and investigate the environmental contamination by heavy metals in the Caspian Sea of Kazakhstan side. In particular, the paper presented an overview of heavy

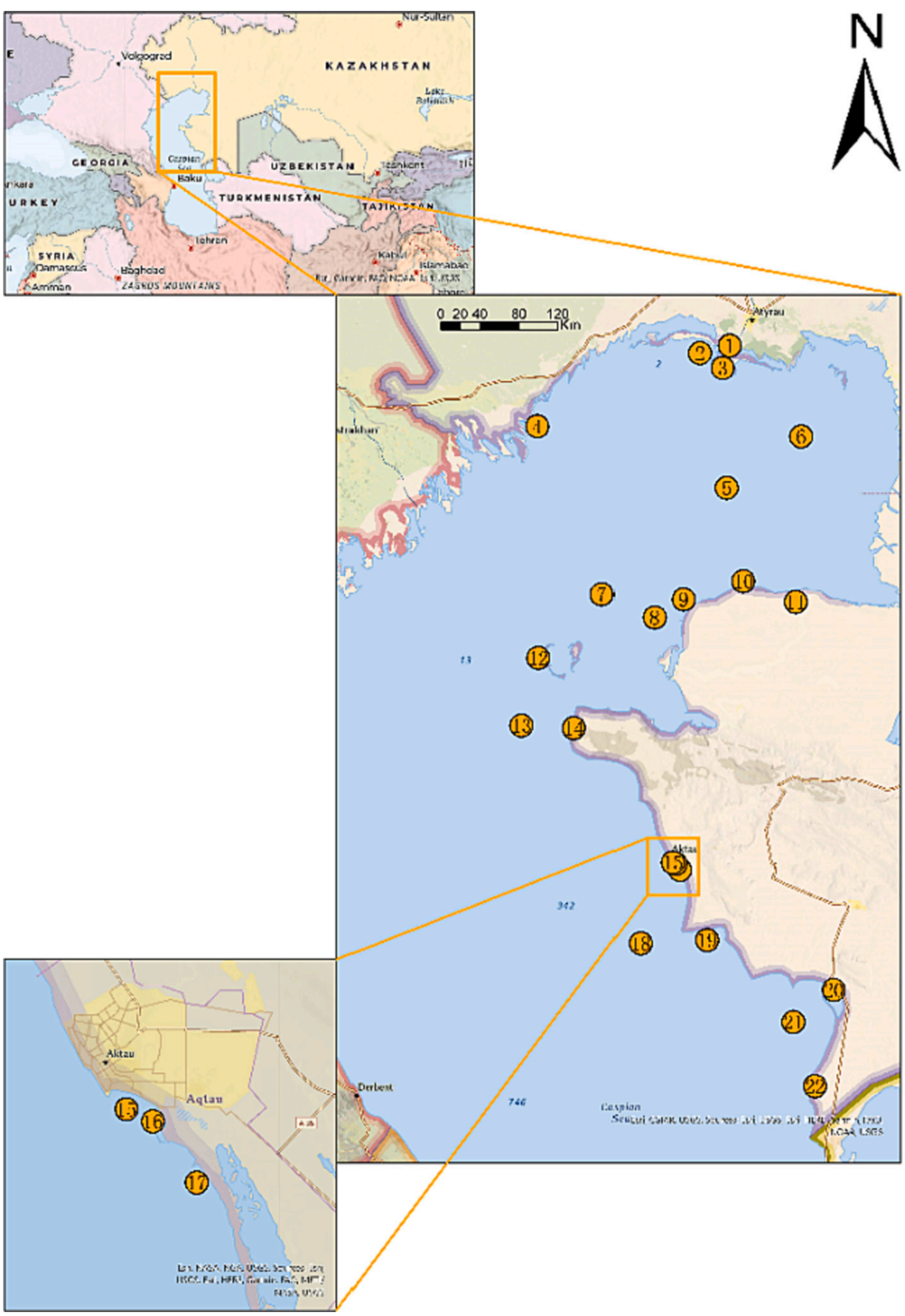

Fig. 1. Map of the studied area.

metal concentrations and statistical analysis during the 2014–2019 period and an evaluation of the impact of heavy metal contamination on the health of humans. Firstly, it summarizes the main trends of the contamination, i.e., mean, median, significant outliers, hypothesis testing (Kruskal-Wallis and seasonal Kendall test), and outliers for heavy metals of interest (Cd, Pb, and Cr(VI)). Next, the Canadian Council of Ministers of the Environment-water quality index (CCME-WQI) was used to assess the overall Seawater quality. This index is an overall estimate of how water quality differs from standards, considering many parameters in addition to heavy metals. Approximate source determination using principal component analysis is done to determine trends in data. Lastly, human health risks are calculated to determine the effect heavy metals have on people due to swimming in the area.

2. Methodology

2.1. Site description and data source

The map of the studied region is demonstrated in Fig. 1, with the corresponding geographical information provided in Table 1. Concentrations of target contaminants were measured at 22 sites in the northern and central parts of the Caspian Sea adjacent to Kazakhstan's coastline. The study area lies from 42° 33′ N to 46° 56′ N latitudes and from 49° 48′ E to 52° 40′ E longitudes. The number of samples varied from 39 to 340 at each site. The region has low annual precipitation levels ranging from 90 to 330 mm (UNEP/GRID-Arendal, 2006). The annual average temperature varied in the northern (8.5–10.5) and central (8.5–14 °C) parts of Kazakhstan's coastline (UNEP/GRID-Arendal, 2006). During the sampling, the water temperature ranges were 4.7–21.9 (spring), 12.5–30.9 (summer), 1.8–25.0 (fall), and 2.0–22.5 °C (winter), respectively (RSE "Kazhydromet," 2019).

Table 1
Sampling location information.

No	# of samples[a]	Sampling location	Latitude	Longitude
1	48	Ural river	46° 56′ N	51° 42.5′ E
2	272 (275 for Cr(VI))	Ural seaside	46° 53.2′ N	51° 26′ E
3	317 (324 for Cr(VI))	Islands of the Bay of Shalygi-Kulaly	46° 47.6′ N	51° 38.6′ E
4	90	Volga seaside	46° 25.6′ N	49° 56.8′ E
5	211 (210 for Pb)	Caspian (additional profile)	46° 2.8′ N	51° 40.8′ E
6	120	Tengiz field	46° 21.8′ N	52° 22′ E
7	45	Flooded wells area	45° 22′ N	50° 32.3′ E
8	39	Karazhanbas field	45° 13′ N	51° 1′ E
9	40	Arman field	45° 20′ N	51° 17′ E
10	40	Kalamkas	45° 27′ N	51° 50′ E
11	63	The water area of the dam on the coast of JSC "MMG"	45° 19′ N	52° 19′ E
12	45	Kulaly island region	44° 57.3′ N	49° 57.3′ E
13	68	Mangyshlak Chechen'	44° 31′ N	49° 48′ E
14	40	Coastal Fort Shevchenko	44° 30′ N	50° 17′ E
15	80	Aktau, port area	43° 37′ N	51° 11′ E
16	194	Special economic zone, Aktau	43° 36.5′ N	51° 12.5′ E
17	81	Aktau, recreation area	43° 34′ N	51° 15′ E
18	69	Peschany-Derbent	43° 4.7′ N	50° 53.3′ E
19	62	District port Kuryk	43° 6′ N	51° 30′ E
20	40	Fetisovo	42° 46′ N	52° 40′ E
21	69	Divichi-Kenderli	42° 33′ N	52° 17.7′ E
22	42	The border area of the Middle and southern Caspian sea (Adamtas lighthouse)	42° 7' N	52° 29.7′ E

[a] Same for all metals unless stated otherwise.

2.2. Reagents, sampling, and equipment

The Republican State Enterprise (RSE) "Kazhydromet" collected and processed the samples during the 2014–2019 period and measured ~52 physicochemical parameters. Contaminants of interest in this study were Cd, Pb, and Cr(VI), with additional parameters used for statistical analyses (Cu, Zn, Ni, Mn, total petroleum hydrocarbons (TPH), pH, dissolved oxygen (DO), suspended solids (SS), sulfate, nitrate, total iron, and chloride).

Reagents include ultrapure nitric acid of reagent grade, deionized water, and standard solutions. All standard solutions were of analytical grade and complied with Kazakhstan's state standard samples grade (GSO) (Kazakhstan Institute of Standardization and Metrology, 2013). Sampling was conducted in the pre-washed bottles at an assigned depth (0.2–5 m), following the State Standard of Kazakhstan (CT RK GOST P 51592-2003). Before the analysis, water samples were transferred to PTFE containers, stored in the dark at 2–5 °C, and filtered (0.45 μm). Nitric acid (2.5 mL) was added to each sample (50 mL), and then the sample was transferred to the oven for 2 h. The sample was then prepared by analysis by filtration (2 μm). An atomic absorption spectrometer with electrothermal atomization (MGA-915/1000, Lumex, Saint Petersburg, Russia) was used to measure Pb, Cd, Cu, Mn, Ni, and Zn (CT RK 2318-2013). Cr(VI) concentrations were determined by the diphenylcarbazide method (CT RK 2321-2015) using a fluorescence analyzer (Fluoraat-02-4M/02-5M, Lumex, Saint Petersburg, Russia). A short overview of measurement methods for the remaining parameters can be found in Table S1. Quality control measures included measuring triplicate samples and ensuring <6 % standard deviation in concentrations of the samples.

2.3. Statistical analysis

Before statistical analysis, data were treated with regard to missing values, outliers, and zeros. All missing values (11 records or < 1 % of the whole dataset) were removed from the data listwise in all analyses. Only abnormally high outliers were removed from the dataset (>50 × IQR) in all analyses. The Kaplan-Meier method (Kaplan and Meier, 1958) has been popularly used in estimating the distribution of incomplete observations for censored data. Therefore, the descriptive statistics obtained were based on the Kaplan-Meier estimate for data to account for non-detects in the data (Antweiler and Taylor, 2008). It was performed in R 4.0.5.

The Kruskal-Wallis (KW) nonparametric test was used to compare the mean ranks of metal concentrations among sites. It was selected because the data were primarily non-normal. The number of samples varied among sites and years, but a minimum sample size of 5 was ensured for all calculations. Non-detects were replaced with $\sqrt{2}/2$ times the detection limit for group comparison (Antweiler, 2015). Matlab R2018b was used for the test.

The seasonal Kendall test was applied to analyze the long-term heavy metal concentrations for trends. The null hypothesis is that there is no trend, and the alternative hypothesis is that there is a trend. Concentrations were plotted against time in Figs. S1–22, but the test determined the overall trend. The seasonal cycle was a source of variation in water quality data; therefore, the test took seasonality into account (Hirsch and Slack, 1984). The Durbin-Watson test was used to identify if serial dependence was significant enough to be considered (Matlab R2018b). Multiple data records within the same season and year were represented by a median as recommended in measurements inconsistent with the number of samples per season (Helsel and Hirsch, 1992). XLSTAT software was used for the test.

The CCME-WQI was calculated for each site to determine the water quality status. Twelve parameters (Pb, Cu, Zn, Cr(VI), Ni, THP, nitrates, sulfates, pH, DO, SS, and total iron) were chosen based on discharge type for CCME-WQI calculation. Water quality guidelines for these parameters are listed in Table S2. Equations for calculation were indicated in Table S3. This study also selected parameters associated with the oil and gas industry, smelters, and mining (CCME, 2017). The water quality of the samples can be categorized as excellent (95–100), good (80–94), fair (65–79), marginal (45–64), and poor (0–44).

Principal component analysis (PCA) was performed by extracting the eigenvalues and eigenvectors from the correlation matrix. Eigenvectors times the square root of eigenvalues equals the loading matrix, explaining the correlation between original variables and principal components (Olsen et al., 2012). Thus, PCA reduces data dimension and shows relationships between variables. Principal components can hint at possible sources of contamination. The top 5 % of concentrations were removed to reduce the effect of outliers. PCA was performed using Matlab R2018b with Varimax rotation.

2.4. Risk assessment

Environmental human health risk assessment was used to calculate non-carcinogenic and carcinogenic risks associated with Cd, Pb, and Cr (VI) in the Caspian Sea of Kazakhstan side. The recreational exposure scenario was considered, i.e., risks were estimated for people swimming in surface water. Exposure pathways used in the study were accidental swallowing during swimming and dermal contact (Schets et al., 2011). Eqs. (1) and (2) were used to calculate the daily intake via accidental swallowing and dermal constant, respectively. C_w is the target heavy metal concentration in the Caspian Sea water, IR is the accidental swallowing rate, EF and ED stand for exposure frequency and duration, respectively, BW is the average body weight, and AT is the average lifespan time. K_p is the permeability coefficient of the contaminant through the skin, SSA is the skin surface area exposed to water, t_{event} is the exposure duration (ED) in each activity. All exposure parameters depend on age, gender, and lifestyle and were selected to match Kazakhstan's characteristics where possible, as presented in Table S4. Dermal intake is an absorbed dose of the chemical, but oral ingestion intake is an administered dose.

$$I_{oral}\left[\frac{mg}{kg\times d}\right]=\frac{C_w\left[\frac{mg}{L}\right]\times IR\left[\frac{mL}{event}\right]\times\frac{1}{1000}\frac{[L]}{[mL]}\times EF\left[\frac{event}{y}\right]\times ED[y]}{BW[kg]\times AT[d]} \quad (1)$$

$$I_{dermal}\left[\frac{mg}{kg\times d}\right]=\frac{C_w\left[\frac{mg}{L}\right]\times K_p\left[\frac{cm}{h}\right]\times SSA[cm^2]\times\frac{1}{1000}\frac{[L]}{[cm^3]}\times t_{event}\left[\frac{h}{event}\right]\times EF\left[\frac{events}{y}\right]\times ED[y]}{BW[kg]\times AT[d]} \quad (2)$$

Based on the calculated daily intake, non-carcinogenic risk expressed as hazard index can be determined (Eq. (3)). Calculation of HI requires reference dose (RfD), a toxicological parameter representing the minimum dose that causes a particularly harmful effect. Carcinogenic risk is expressed as a probability (Eq. (4)). SF stands for carcinogenic slope factor, a toxicological parameter showing the probability of the toxic effect caused by the contaminants per unit intake for the whole lifetime (USEPA, 2010). Eqs. (5) and (6) adjust an administered dose to an absorbed dose to derive RfD and SF for dermal exposure. Toxicological chemical-specific parameters were listed in Table S5. Commonly accepted HI and cancer risk thresholds were 10^{-6} and 1, respectively (USEPA, 2010).

The stochastic risk assessment used numerous simulations to obtain empirical results on data probability distributions of risks. The Monte-Carlo method, a probabilistic risk assessment approach, was employed to perform the stochastic simulation. Matlab R2018b was used to run 10,000 simulations. The distributions of target contaminant concentrations were approximated using the kernel density function (normal distribution) to explain uncertainties in the concentrations. Kernel density estimation is a nonparametric method to find the probability density function of a random variable.

$$HI=\frac{I_{oral/dermal}\left[\frac{mg}{kg\times d}\right]}{RfD\left[\frac{mg}{kg\times d}\right]} \quad (3)$$

$$\text{Carcinogenic risk}=I\left[\frac{mg}{kg\times d}\right]\times SF\left[\frac{kg\times d}{mg}\right] \quad (4)$$

$$RfD_{dermal}\left[\frac{mg}{kg\times d}\right]=RfD_{oral}\left[\frac{mg}{kg\times d}\right]\times ABS_{GI} \quad (5)$$

$$SF_{dermal}\left[\frac{kg\times d}{mg}\right]=\frac{SF_{oral}\left[\frac{kg\times d}{mg}\right]}{ABS_{GI}} \quad (6)$$

3. Results and discussion

3.1. Descriptive statistical analysis of contamination and water quality index

3.1.1. Statistical summary for heavy metals

Table 2 summarizes statistical information of the dataset, including average (95 % CI), median, and standard deviation (SD)). Fig. 2 shows the boxplots of concentrations. The heavy metal concentrations of the sampling sites did not follow a normal distribution (Anderson-Darling test, p-value < 0.01), except for site #1 for Pb and site #15 for Cr(VI).

Cd concentrations were measured at 11 sites out of 22 (sites #1–7, 12, 13, 18, and 21). Overall median at all sites ($n = 1354$) was 0.003 mg/L. The range of heavy metal concentrations (expressed as Q1-Q3) was 0.002–0.005 mg/L. The highest median was observed at site #7 (0.006 mg/L), whereas the lowest was in sites #4 and 6 (0.002 mg/L). Site #7 was located near flooded wells, at the center of the water body. Flooded abandoned oil wells have been reported to leak methane, oil residues, and produced water (Townsend-Small and Hoschouer, 2021). The oil residues and produced water can disperse heavy metals and contaminate the water systems (Bakke et al., 2013).

The median of all Pb concentrations ($n = 2074$) was 0.004 mg/L. The Q1-Q3 range of Pb concentrations was 0.0022–0.0094 mg/L. Sites #7 and 12 showed the highest median (0.007 mg/L), whereas the lowest median (0.002 mg/L) was observed in sites #8, 10, 14, 16, 19, 20, and 22. Site #7 near flooded wells showed the highest median concentration, possibly due to the release of the impurities-containing produced water, as in the case with Cd. Site #12 was near Kulaly island at the center of the water body. The two sites were in proximity to each other and probably had similar sources of contamination: flooded wells and oil drilling.

The median of Cr(VI) concentrations ($n = 2085$) was 0.0063 mg/L. The Q1-Q3 range for Cr(VI) concentrations was 0.004–0.019 mg/L. Site #16 showed the highest median (0.01 mg/L) with unusual behavior. Most Cr(VI) concentrations (62 %) were centered around the value of 0.01 mg/L at site #16, resulting in 64 outliers (33 % of all samples at the

Table 2
Description of data (range of average 95 % CI, median, standard deviation (SD), coefficient of variance (CV%)) and MK test results (p-value)). Average, median, and SD values' unit is μg/L.

Site		Cd	Pb	Cr(VI)
1	Average	2.6–3.7	4.7–5.9	6.1–9.7
	Median	3	5	6
	SD (CV%)	1.92 (60.3)	2.13 (40.1)	6.44 (81.3)
	p-value	0.57	0.00	0.00
2	Average	2.6–3	4.3–5.3	5.6–6.7
	Median	3	4	5
	SD (CV%)	1.59 (56.89)	0.46 (9.5)	4.81 (77.8)
	p-value	0.39	0.00	0.01
3	Average	3.1–3.8	5.4–8	5.9–7
	Median	3	5	4
	SD (CV%)	3.16 (90.9)	11.82 (175.8)	5.04 (78.6)
	p-value	0.83	0.00	0.01
4	Average	2.1–2.6	2.5–3	2.9–3.5
	Median	2	3	3
	SD (CV%)	1.01 (43)	1.17 (42.8)	1.44 (44.6)
	p-value	0.84	0.30	0.54
5	Average	4.2–4.8	13.3–20	7.4–9.5
	Median	4	6	6
	SD (CV%)	2.22 (49.4)	25.09 (150.6)	7.63 (90.2)
	p-value	0.04	0.01	0.02
6	Average	2.7–3.4	5.2–6	7.4–9.7
	Median	2	5	7
	SD (CV%)	1.95 (63.2)	2.25 (39.9)	6.27 (73.6)
	p-value	0.19	0.00	0.00
7	Average	4.5–5.9	4.9–12.3	7.1–10.4
	Median	6	7	8
	SD (CV%)	2.42 (46.9)	12.53 (145.8)	5.65 (64.6)
	p-value	0.67	0.15	0.00
8	Average		2.2–3.1	7–10.4
	Median		2	7
	SD (CV%)		1.38 (52.7)	5.43 (62.2)
	p-value		0.17	0.00
9	Average		2.5–3.4	6.9–9.2
	Median		3	7.5
	SD (CV%)		1.41 (48.2)	3.79 (47)
	p-value		0.03	0.00
10	Average		2–3.1	7.1–9.9
	Median		2	8
	SD (CV%)		1.82 (71.3)	4.59 (53.8)
	p-value		1.00	0.00
11	Average		2.6–3.3	7.5–9.6
	Median		2.1	8
	SD (CV%)		1.34 (45.6)	4.35 (51)
	p-value		0.38	0.13
12	Average	4.3–5.8	6.3–17.2	6.8–10.4
	Median	5	7	7
	SD (CV%)	2.6 (51.3)	18.65 (159.3)	6.03 (70.2)
	p-value	1.00	0.15	0.00
13	Average	4.5–5.5	6.6–14.2	6.6–9.8
	Median	5	6.85	6
	SD (CV%)	2.12 (42.2)	15.96 (153.2)	6.74 (82.5)
	p-value	0.21	0.00	0.09
14	Average		1.9–3.7	6.7–8.8
	Median		2	7
	SD (CV%)		2.85 (102.6)	3.33 (43.1)
	p-value		0.33	0.00
15	Average		4.2–6.7	6.1–6.9
	Median		4.6	6.5
	SD (CV%)		5.56 (102.3)	1.91 (29.4)
	p-value		0.02	0.04
16	Average		2.6–3	9.5–10.6
	Median		2	10
	SD (CV%)		1.63 (58.4)	3.99 (39.6)
	p-value		0.02	0.00
17	Average		3.8–4.7	6.3–7
	Median		3.3	7
	SD (CV%)		2.02 (47.9)	1.75 (26.3)
	p-value		0.15	0.75
18	Average	3.5–4.4	7.9–17.4	8.1–11.1
	Median	4	6	8
	SD (CV%)	2.05 (52)	20.21 (159.6)	6.23 (64.9)
	p-value	0.03	0.03	0.00
19	Average		2.1–3.1	7.6–9.4
	Median		2	8
	SD (CV%)		2.03 (77.4)	3.72 (43.7)
	p-value		0.78	0.07
20	Average		1.9–3.1	6.7–9
	Median		2	8
	SD (CV%)		1.97 (78.4)	3.78 (48.4)
	p-value		0.94	0.00
21	Average	4.1–5.3	9.4–20.8	6.8–9.7
	Median	5	6	6
	SD (CV%)	2.42 (51.3)	24.06 (159.1)	6.23 (75.6)
	p-value	0.43	0.00	0.05
22	Average		1.9–2.8	8.6–11.9
	Median		2	8
	SD (CV%)		1.51 (63.7)	5.46 (53.2)
	p-value		0.19	0.13

site). Site #16 is located at Aktau seaport. The lowest median was found at site #4 (0.03 mg/L).

To further analyze contamination, extreme outlier events were analyzed. Extreme outliers were detected based on the 3 × IQR criterion. For Cd, two extreme outliers were detected: 0.05 mg/L at site #3 in May 2017 (the maximum observed concentration of Cd) and 0.011 mg/L at site #1 in July 2014. These sites were located in the Ural river basin, near Atyrau city. The Ural River has been a well-known anthropogenic source of contamination of the Caspian Sea (JICA, 2007). Elevated total Cr and Pb concentrations were encountered in the river (Tulemisova et al., 2021), but no record of extremely high Cd concentration was found. However, considering the industrial facilities located upstream (oil refinery, metallurgy, oil wells, and woodworking factories) (Yessenamanova et al., 2021), occasional releases of Cd could possibly occur. For Pb, 90 outliers were observed in 82 % of all sites (summary in Table S6). Most outliers (33 out of 90) occurred at site #5 in 2014 (0.05–0.09 mg/L). Sites #3, 18, and 21 also included many outlier measurements (9, 7, and 9 out of 90, respectively) ranging from 0.056 to 0.09 mg/L. The maximum Pb concentration of 0.09 mg/L was observed at sites #7 and 12 (September 2014 for both sites) and 13 (August 2014). Remarkably, 2014 had the highest number of outliers (66 out of 90), followed by 2017 (18 out of 90), suggesting probable extreme events affecting the water quality of the water body. For Cr(VI), most outliers (64 out of 73) were observed at site #16. Nine more outliers were observed: 0.08 mg/L at site #5 (May 2014), 0.03 mg/L at site #8 (August 2018), 0.03 and 0.02 mg/L (6 measurements) at site #22 (March and October 2014–2016).

Overall, concentrations of heavy metals varied significantly. The KW test revealed a statistically significant difference among the target concentrations ($p < 0.01$) for Cd ($df = 10$), Pb ($df = 21$), and Cr(VI) ($df = 21$) (Fig. 2). This test's result suggests significant differences in concentrations among sites. Concentrations can vary due to different factors such as industrial activities on the site, horizontal transport, and precipitation. The highest medians were observed at sites near industrial areas, suggesting a link between site and heavy metals concentrations. Outliers could indicate pollution events, but they can also indicate natural events or measurement errors. There were not many outlier concentrations for Cd. For Cr(VI), outliers were mostly observed at one site only (#16), whereas Pb outlier events were detected all over the water body and at all years. These trends require further study to understand natural or anthropogenic sources of extreme events causing outliers.

3.1.2. *Water quality index*

Analyzing only heavy metals is not enough to describe the overall contamination of the water body. CCME water quality index was used to determine contamination status (Fig. 3). All indices fell into either "fair" or "marginal" water quality (59.3–74.8). The lowest WQI (59.3) was

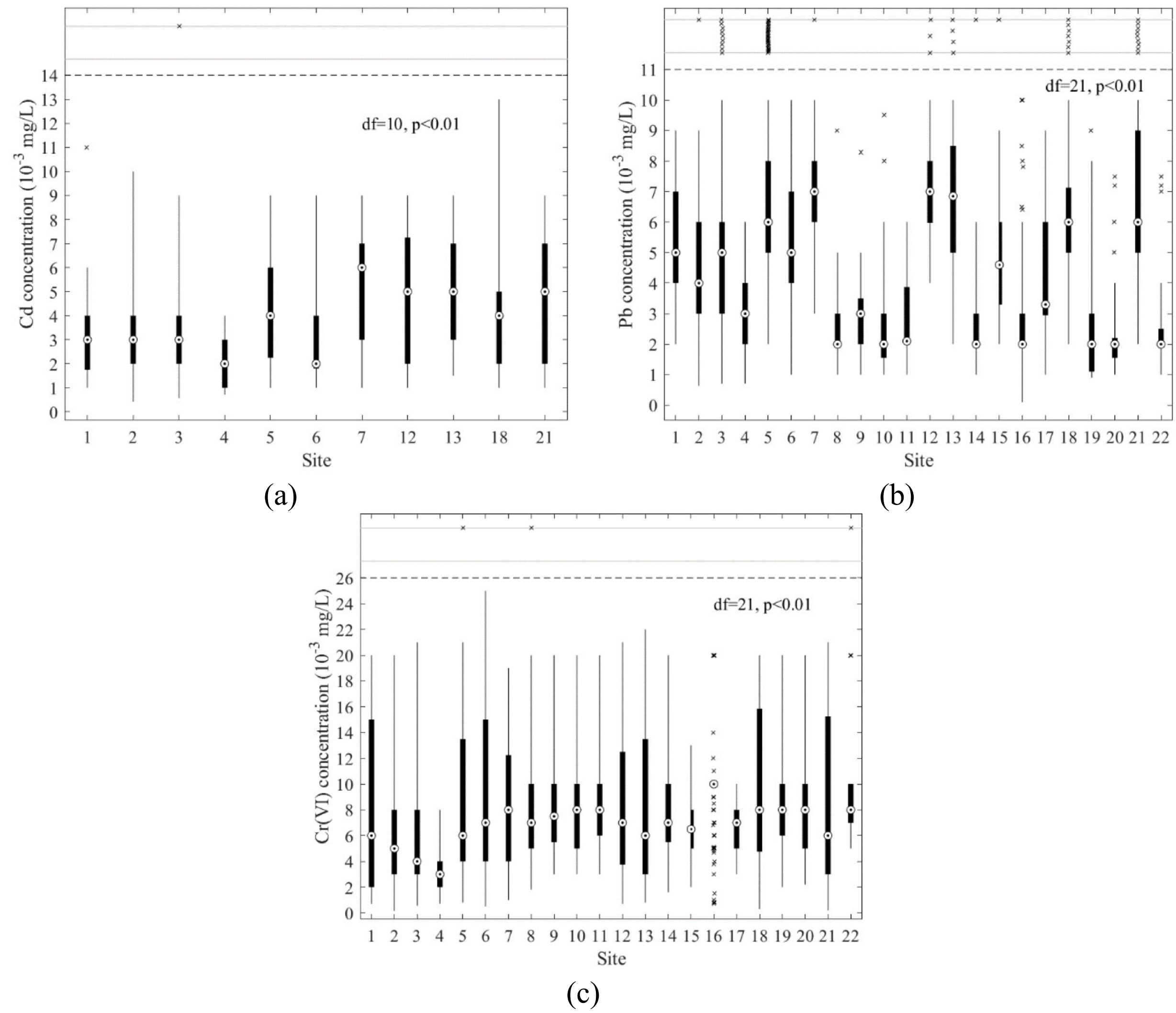

Fig. 2. Variations of (a) Cd, (b) Pb, and (c) Cr(VI) concentrations by Kruskal-Wallis test at sampling sites.

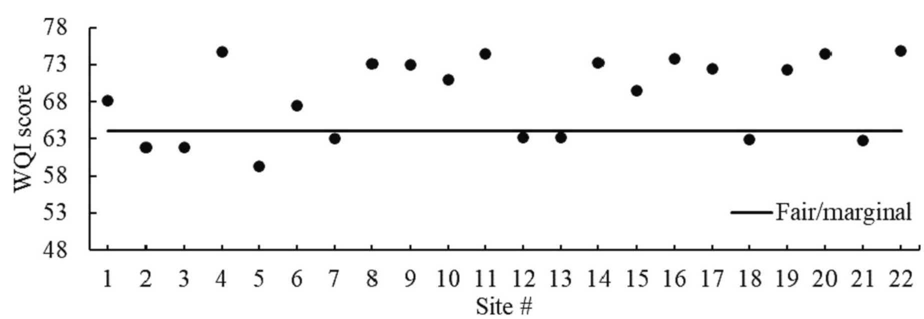

Fig. 3. CCME-WQI indices of all sampling sites.

observed at site #5, indicating the poorest water quality. In addition to site #5, water quality at sites #2, 3, 7, 12, 13, 18, and 21 (8 out of 22) was classified as "marginal" (<64). The rest of the sites (#1, 4, 5, 6, 8–11, 14–17, 19, 20, 22) were categorized as having "fair" water quality (>64), with sites #4 and 22 showing the highest index of 74.8. Sites with lower water quality are mainly located near the Ural River basin and in open waters. This suggests that (1) surface water guidelines were exceeded in these areas more frequently, (2) more water quality parameters failed to meet guideline criteria, and (3) the magnitude by which guideline is not fulfilled is higher (CCME, 2017). Variable inputs through rivers or discharges to open seas and climatic conditions could affect the quality.

Cd was omitted from the analysis to avoid inconsistency as it was measured only in 11 out of 22 sites to provide a common ground for comparing the sites. However, by including Cd in the CCME-WQI analysis can decrease by a certain amount (3.9–6.7) where Cd measurement was available. Including Cd and other water quality measurements (As, Hg, or organic contaminants) in all sites would better understand the current status of Caspian Sea water quality.

3.2. Seasonal Kendall test

While previous sections capture environmental status at a particular period (2014–2019), the time-related trend is not known. The p-value of the seasonal Kendall test (Table 2) shows if a remarkable trend was observed, and the sign convention of τ in the Kendall test indicates whether the trend is increasing or decreasing. For Cd, sites #5 ($\tau = 0.45$) and 18 ($\tau = 0.52$) with an increasing trend ($p < 0.05$) indicate continuous contamination by Cd or natural processes contributing to the contamination despite low Cd concentrations in 2014–2019. Both sites were located near oil extraction sites: Kashagan (site #5) and Nursultan (site #18). Heavy metals could be present in the crude oil as impurities (Osuji and Onojake, 2004) and could be further accumulated through the release of produced water or oil spills. No trend was observed for other sites.

Temporal variation analysis of Pb by seasonal Kendall test demonstrated no remarkable trend in half of the sites ($p > 0.05$). Out of the remaining 11 sites ($p < 0.05$), nine sites showed a decreasing trend ($\tau = -0.53$ to -0.87). Sites #9 and 16 demonstrated an increasing concentration between 2014 and 2019. Although medians were low in the sites, a rising contamination level could suggest the presence of contamination source. Site #9, located in the Arman oil field, could accumulate Pb at the site. Site #16 was a special economic zone in Aktau city situated in the port. Seaport activities could release high concentrations of heavy metals into surrounding water and sediment environments (Jahan and Strezov, 2018). For example, ballast water in ships was a significant Pb, Cd, Ni, and Cu source in the Persian Gulf area (Tolian et al., 2020). It can be loaded in polluted areas and discharged into coastal waters, contributing to severe heavy metal contamination. Additional sources such as industrial wastewater and storage and transportation of hazardous chemicals may lead to high Pb concentrations (Jahan and Strezov, 2017).

For Cr(VI), there was a trend at most sites, except #4, 11, 17, and 21. Further evaluation of τ vale revealed a decreasing trend ($-1 < \tau < -0.45$) at all sites, which might be attributed to a rapid Cr(VI) reduction to stable Cr(III) by readily available reducing agents such as sulfur or reduced organic matter species. Oxidation of Cr(III) to Cr(VI), however, is not favorable in the contaminated natural reducing environment (Tumolo et al., 2020).

3.3. Source determination

3.3.1. Coefficient of variation

The coefficient of variation (CV) is a relative measure of the spread of the datasets (Table 2). To further investigate variability, histograms were drawn for each site (Figs. S23–S27). CVs for Cd, Pb, and Cr(VI) varied between 42.2–90.9 %, 9.5–175 %, and 26.3–90.2 %, respectively. Cd and Cr(VI) are CV values were <100 %, indicating low variability among the concentrations (Mamat et al., 2014). Pb concentrations show the highest variability among all heavy metal concentrations. Sites #3, 5, 7, 12–15, 18, and 21 showed higher CVs than 100 %, indicating high variability. The highest variation (CV) of all target contaminants was observed in sites #3 (Ural river basin) and 5 (oil field). Low CV indicates a natural origin of heavy metals (Yongming et al., 2006), suggesting that Pb contamination is more likely to have an anthropogenic origin.

Table 3
PCA results.

	1	2	3	4	5
Pb	−0.16	0.01	0.19	0.89	0.12
Cr(VI)	0.35	0.77	−0.17	0.19	0.01
Cu	0.28	0.40	0.31	0.54	−0.31
Zn	0.25	0.40	0.63	0.33	−0.15
Ni	−0.05	0.89	0.08	−0.04	−0.14
Mn	0.74	0.39	0.04	0.03	0.34
TPH	−0.10	−0.12	0.90	0.16	0.13
NO_3^-	−0.71	−0.12	0.03	0.21	0.32
SS	−0.18	−0.12	0.06	0.03	0.91
SO_4^{2-}	0.74	−0.08	0.37	0.15	−0.14
Cl^-	0.77	0.11	−0.42	−0.06	−0.27
Eigenvalues	3.43	2.33	1.28	1.06	0.68

3.3.2. Principal component analysis

PCA was conducted with data from all sampling sites during the measurement period to find the approximate sources of heavy metals (Table 3). Kaiser-Meyer-Olkin's measure of sampling adequacy was >0.7 (0.73), and Bartlett's test of sphericity (p-value) was 0, which indicates that the dataset was suitable for PCA (Ustaoğlu and Tepe, 2019). The percentage of total variance for each component did not vary significantly (1.8–31.2 %). Five components were extracted to achieve 70 % of each parameter's variance explained by the components. Loadings higher than 0.4 or lower than −0.4 were considered significant.

Component 1, accounting for the largest variance (31.2 %), showed high loadings associated with Mn, sulfate, and chloride ions (0.74–0.77). A significant negative correlation was observed between these variables and nitrates (−0.71). Nitrate is a primary indicator of biological pollution, possibly from agricultural or municipal water runoff. The negative nitrate loading further supports the anthropogenic sources of component 1. Table S7 demonstrates the median concentrations of water parameters used in PCA by years at eight representative sites with a specific application (oil fields, river basins, or seaports). High concentrations of Mn, sulfate, and chloride ions occurred simultaneously at Karazhanbas and Arman oilfields in 2014, 2015, and 2016, and at seaport Kuryk in 2016. However, some oil fields (Tengiz area) did not show high concentrations of these parameters, suggesting different types of discharges at oil fields. Possible sources of contamination in oil fields include produced water containing metal impurities and sometimes high salinity contributing to chloride content (Bakke et al., 2013). Moreover, some oil reservoirs in the Caspian Sea contain a high hydrogen sulfide content (North Caspian Operating Company N.V. (NCOC), 2016). The geogenic characteristic of the site could also contribute to increased concentrations.

Heavy metals have high loadings on components 2 and 4. Component 2 constituted 21.2 % of the variance with corresponding higher Cr (VI), Cu, Zn, Ni, and Mn concentrations (0.40–0.89). Ni and Cr(VI) have the highest loadings on component 2 and are observed in excessive amounts at river basins and oilfields. The component most likely represents oil fields because of negative loading on nitrate and SS, which are characteristic to the Ural river basin. Kuryk seaport also had high Ni and Cr concentrations (VI) in 2014. Notably, Pb was not correlated with other heavy metals, except for Cu. Component 4 could explain 9.7 % of the data associated with Pb (0.89) and Cu (0.54), i.e.,. High Pb and Cu concentrations occur in the Ural river basin and Tengiz oilfield region.

Heavy metals are common industrial pollutants and can originate from multiple sources. A potential source could be produced water (Azetsu-Scott et al., 2007), especially for Ni and Cr(VI) because their concentrations are high in all oil fields. In addition to the oil industry, ports have also been exposed to increased Fe, Zn, Cu, Co, Pb, Mn, and Cd concentration levels, as reported by an Australian seaport study (Jahan and Strezov, 2017). Seaports could also be used for oil transportation with possible accidental spills and leaks. The third possible reason could be the Ural river input. Lastly, the deposition of industrial emissions could affect the Seawater quality. For example, high contents of toxic heavy metals have been observed in the dust near steel manufacturing plants and coal-burning power plants (Dai et al., 2015).

Zn (0.63) and TPH (0.90) showed strong loadings on component 3 (11.6 % variance), whereas chloride ions demonstrated a negative loading (−0.42). High Zn and TPH concentrations and low chloride concentrations were observed at sites in the northern part of the studies area (Ural river basin (#1, 2, 3) and Tengiz field area (#6)). Ural river basin contamination is likely to be associated with upper stream contamination. Transport of these chemicals could contribute to the Tengiz field area. However, accidental oil spills could also contribute to high hydrocarbon concentrations. The information about oil spills is not available to the public, but satellite imaging revealed the hydrocarbon contamination at Kashagan oilfield (near sites #5 and 6) (Mityagina et al., 2019).

Component 5, covering 6.2 % of the data, was positively correlated with SS (0.91). SS is the highest in the Ural river basin region and near the Tengiz oilfield. This could be attributed to mixed inputs of industrial and municipal wastewater discharges, transport of chemicals, agricultural runoff, and disturbance events causing re-suspension of sediments.

Overall, contamination of the Caspian Sea is complex and is most likely caused by multiple sources. The study viewed contamination from the perspectives of three main sources (upstream transport, oilfields, and seaports) based on available information. However, even one source can produce different discharges. For example, oilfields and their discharges are different, as demonstrated by components 2 and 4. Component 1 (Mn, sulfates, chlorides) is likely to be associated with Karazhanbas and Arman oilfield area, whereas parameters related to components 2 and 4 (heavy metals) are high in the Tengiz oil field. Seaports show various trends in different years and have high concentrations of chemicals associated with component 1, component 2, and component 4 (Mn, sulfates, chlorides, and heavy metals). This result suggests the complex nature of contamination in seaports, and further controlled studies are needed to investigate it. Upstream transport-related sites near the Ural river basin also show high concentrations of chemicals and can be linked to almost all components. Moreover, it is important to note that there could be more sources (dust, hydrodynamics, agricultural discharge) contributing to the contamination and the interpretation of principal components can change based on available information. Another important point to consider is time. PCA was used to evaluate the general state of the contamination regardless of time, assuming that trends are consistent. However, Table S7 shows that most of the high concentrations used in PCA interpretation happened in 2014, suggesting some extreme event happened in 2014.

3.4. Human health risk assessment

Stochastic risk assessment was used for the risk calculation to account for uncertainties in exposure parameters, geography, and precipitation. Target concentrations from all sites were used to obtain model distributions to calculate overall risks in the Caspian Sea. Fig. S28 demonstrates the histograms of concentrations and fitted curves by kernel density estimates to ensure the goodness of fit. Table S8 shows the results of the probabilistic assessment. Non-carcinogenic risks were very low (<1) in all cases, both average and 95th-percentile values. Average carcinogenic risks for all ages are lower ($1–3 \times 10^{-7}$) than the corresponding threshold. However, the 95th-percentile risk (worst case scenario) for adults comprised 1.2×10^{-6}. The distributions of contaminants were heavily right-skewed; therefore, the large number of low concentrations lowered the risks.

The dominant contaminant was Cr(VI), and the dominant pathway was dermal contact for all ages and sites. Risks in all pathways associated with Pb were very low ($<10^{-9}$) and negligible. For Cr(VI), oral pathway-related risk constituted only 1–5 % of the dermal contact-related risk. This can happen due to the high slope factor of the dermal contact exposure pathway for Cr(VI) (20 $(mg/kg/d)^{-1}$). Dermal contact slope factors were based on the assumption that percutaneous absorption occurred upon contact with water. Thus, the dermal contact examined in this study was not connected to the direct toxicity of contaminants on the skin but rather to their toxicity absorbed through the skin and entering the circulatory system (USEPA, 2004). Once in-vivo, the slope factor needs to be adjusted for the absorbed chemicals. In oral exposure, intake was calculated as an administered dose to which a human was exposed and not absorbed. However, in the case of dermal absorption, the intake equation accounts for the absorption, not exposure. Therefore, the slope factor and the reference dose for the administered dose should be adjusted using Eqs. (5) and (6). The adjustment resulted in a high slope factor for Cr(VI), significantly contributing to the risk. There were several assumptions embedded in the calculated dermal slope factor. For example, the slope factor was adjusted with gastrointestinal absorption value, which did not necessarily reflect the absorption characteristics of the skin. Moreover, all absorption experiments to derive Kp and ABSGI were not derived from human health studies. Finally, a chemical was assumed to stay in its original form inside the body. In reality, other unknown metabolic by-products could be generated during the absorption through the organ and/or skin (USEPA, 2010), which could significantly overestimate the dose-response curve. Thus, dermal exposure was found to be significant in the Caspian Sea. As for oral exposure, Cr(VI) also resulted in higher risk but within the risk threshold.

The effect of exposure parameters on risk values was significant. Adults' HQ values were higher than children's due mainly to body weight differences, while in carcinogenic risk assessment, adults' risks were higher due to longer ED. Children's ED was averaged through the lifetime resulting in a low ED/AT ratio compared to adults. Since no studies examined swimming preferences in Kazakhstan, adults' ED with high variance was assumed to be 30 years as recommended by USEPA (USEPA, 2010). For residents near the Caspian Sea, it could be 60–70 years, who might swim very frequently. In such cases, adults' worst-case scenario and average case cancer risks could increase to 2.8×10^{-6} and 7.0×10^{-7}, respectively. Children's ED was taken over six years (8–14 years old). However, if we assumed a more extended period of 18 years, we could obtain relatively high-risk estimates, i.e., 1.7×10^{-6} and 4.3×10^{-7} as 95th-percentile and average cancer risks, respectively. To conclude, risks barely exceeded the threshold values except for worst-case scenarios with prolonged ED and 95th-percentile concentrations.

The empirical cumulative distribution function was plotted in Fig. 4 to show the randomness of stochastic risks calculated based on random numbers derived from kernel estimates and distributions indicated in Fig. S28. The probability of exceeding the HQ threshold (1) was 0 for all cases. At the same time, it was higher in cancer risks, i.e., the probability of exceeding the cancer risk threshold (10^{-6}) was 6 and 1.5 % for adults and children, respectively. The cancer risk rose to 18 and 10 % in case of the prolonged ED (70 and 18 years for adults and children). The results indicate that a moderate portion of the population could experience adverse health effects from heavy metals exposure in the Caspian Sea.

This study first investigated human health risks from heavy metals in the Casian Sea during swimming; therefore, no research results on a similar topic can be compared. Results could overestimate the risks for Pb and Cd because total concentrations of these metals were used in calculations. Studies mainly conducted risk assessments for the Caspian Sea, focusing on diverse fish consumption. Sobhanardakani et al. and Solgi et al. studied the caviar of Persian sturgeon, *Cyprinus carpio*, and *Chelon aurata* fishes in the Southern Caspian Sea (Iran coastline) and conducted a non-carcinogenic risk assessment of heavy metals. All HQ values were lower than 1, indicating that the Caspian fishes were safe for consumption (Sobhanardakani et al., 2018; Solgi et al., 2019). Further in-depth investigations are required to draw a complete picture of the contamination of the Caspian Sea regions with heavy metals and their effect on human health through food, air, and soil (sediment) in addition to the water.

4. Conclusion

Water samples (~1000-2000) were collected between 2014 and 2019 in various parts of the Caspian Sea near the coastline of Kazakhstan, and their heavy metal (Cd, Pb, and Cr(VI)) concentrations were measured. This study summarized statistics of target heavy metal concentrations in the Caspian Sea and its water quality index analysis. The main conclusion is that the water in the studied area can be classified as “marginal” to “fair” on a large scale, based on CCME-WQI calculation. However, there are still alarming findings near oil-producing and seaport sites (#8, 16, 18, and 19), where Cd and Pb

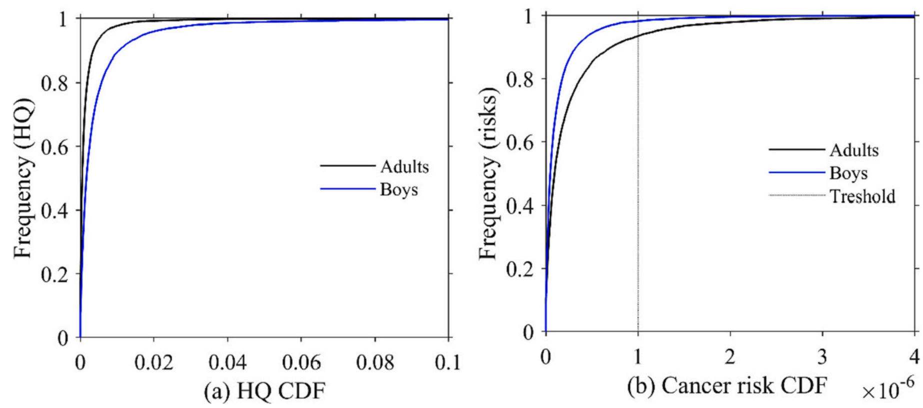

Fig. 4. The cumulative distribution function of risks.

concentrations increased during 2014–2019. Sampling sites near oil extraction sites, seaports, and the Ural river basin deserve a greater focus of attention for further thorough monitoring. Out of heavy metals studies, Pb needs to be investigated more because it has extreme outliers in most sites. Another important conclusion is that risk assessment showed a less significant impact of heavy metal contamination in the Caspian Sea of Kazakhstan's side on the population's health unless there was an extreme event with prolonged exposure. The study would help fill a gap in knowledge on the contamination of the Caspian Sea since no significant studies on the contamination of the Kazakhstan coastline have been conducted. Another environmental implication includes the consideration of swimming pathway and the associated risks. Results could be useful for policy-making regarding recreational waters. The results indicate a need for further monitoring and evaluation of the water body considering the following points: adding new contaminants and exposure pathways, investigating sediments and transport of metals, and studying the bioavailability of heavy metals.

CRediT authorship contribution statement

Elmira Ramazanova: investigation, methodology, writing original draft, visualization.

Yingkar Bahetnur: investigation, preliminary data analysis.

Kadisha Yessenbayeva: investigation, preliminary data analysis.

Seung Hwan Lee: data analysis, methodology, reviewing the manuscript.

Woojin Lee: supervision, conceptualization, writing and reviewing the manuscript, funding acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2022.113879.

References

Ahmadov, M., Humbatov, F., Mammadzada, S., Balayev, V., Ibadov, N., Ibrahimov, Q., 2020. Assessment of heavy metal pollution in coastal sediments of the western Caspian Sea. Environ. Monit. Assess. 192 https://doi.org/10.1007/s10661-020-08401-3.

Antweiler, R.C., 2015. Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets. II. Group comparisons. Environ. Sci. Technol 49, 13439–13446. https://doi.org/10.1021/acs.est.5b02385.

Antweiler, R.C., Taylor, H.E., 2008. Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets: I. Summary statistics. Environ. Sci. Technol. 42, 3732–3738. https://doi.org/10.1021/es071301c.

Armitage, P.D., Bowes, M.J., Vincent, H.M., 2007. Long-term changes in macroinvertebrate communities of a heavy metal polluted stream: the river nent (Cumbria, UK) after 28 years. River Res. Appl. 23, 997–1015. https://doi.org/10.1002/rra.1022.

Azetsu-Scott, K., Yeats, P., Wohlgeschaffen, G., Dalziel, J., Niven, S., Lee, K., 2007. Precipitation of heavy metals in produced water: influence on contaminant transport and toxicity. Mar. Environ. Res. 63, 146–167. https://doi.org/10.1016/j.marenvres.2006.08.001.

Bakke, T., Klungsøyr, J., Sanni, S., 2013. Environmental impacts of produced water and drilling waste discharges from the norwegian offshore petroleum industry. Mar. Environ. Res. 92, 154–169. https://doi.org/10.1016/j.marenvres.2013.09.012.

Bastami, K.D., Bagheri, H., Kheirabadi, V., Zaferani, G.G., Teymori, M.B., Hamzehpoor, A., Soltani, F., Haghparast, S., Harami, S.R.M., Ghorghani, N.F., Ganji, S., 2014. Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. Mar. Pollut. Bull. 81, 262–267. https://doi.org/10.1016/j.marpolbul.2014.01.029.

Brevik, E.C., Burgess, L.C., 2012. Soils Human Health, 1st ed. Taylor & Francis.

CCME, 2017. CCME Water Quality Index user's manual 2017 Update [WWW Document]. URL. Can. Water Qual. Guidel. Prot. Aquat. Life. http://www.ccme.ca/files/Resources/calculators/WQIUser'sManual(en).pdf.

Chen, J.L., Pekker, T., Wilson, C.R., Tapley, B.D., Kostianoy, A.G., Cretaux, J.F., Safarov, E.S., 2017. Long-term Caspian Sea level change. Geophys. Res. Lett. 44, 6993–7001. https://doi.org/10.1002/2017GL073958.

Dadar, M., Adel, M., Nasrollahzadeh Saravi, H., Fakhri, Y., 2017. Trace element concentration and its risk assessment in common kilka (Clupeonella cultriventris caspia bordin, 1904) from southern basin of Caspian Sea. Toxin Rev. 36, 222–227. https://doi.org/10.1080/15569543.2016.1274762.

Dai, Q.-L., Bi, X.-H., Wu, J.-H., Zhang, Y.-F., Wang, J., Xu, H., Yao, L., Jiao, L., Feng, Y.-C., 2015. Characterization and source identification of heavy metals in ambient PM10 and PM2.5 in an integrated iron and steel industry zone compared with a background site. Aerosol Air Qual. Res. 15, 875–887. https://doi.org/10.4209/AAQR.2014.09.0226.

De Mora, S., Sheikholeslami, M.R., Wyse, E., Azemard, S., Cassi, R., 2004. An assessment of metal contamination in coastal sediments of the Caspian Sea. Mar. Pollut. Bull. 48, 61–77. https://doi.org/10.1016/S0025-326X(03)00285-6.

Ebadi, A.G., Hisoriev, H., 2017. In: The Prevalence of Heavy Metals in Cladophora glomerata L. from Farahabad Region of Caspian Sea – Iran, 99, pp. 883–891. https://doi.org/10.1080/02772248.2017.1323894 doi:10.1080/02772248.2017.1323894.

He, Z.L., Yang, X.E., Stoffella, P.J., 2005. Trace elements in agroecosystems and impacts on the environment. J. Trace Elem. Med. Biol. https://doi.org/10.1016/j.jtemb.2005.02.010.

Helsel, D.R., Hirsch, R.M., 1992. Statistical Methods in Water Resources. https://doi.org/10.2307/1269385. Statistical methods in water resources.

Hirsch, R., Slack, J., 1984. A nonparametric trend test for seasonal data with serial dependence. Water Resour. Res. 20, 727–732.
Hosseini, S.M., Mirghaffari, N., Sufiani, N.M., Hosseini, S.V., Ghasemi, A.F., 2013. Risk assessment of the total mercury in Golden gray mullet (Liza aurata) from Caspian Sea. Int. J. Aquat. Biol. 1, 258–265.
IARC, 2019. Agents classified by the IARC monographs, volumes 1–125 [WWW document]. URL. https://monographs.iarc.fr/list-of-classifications/.
Jahan, S., Strezov, V., 2018. Comparison of pollution indices for the assessment of heavy metals in the sediments of seaports of NSW, Australia. Mar. Pollut. Bull. 128, 295–306. https://doi.org/10.1016/j.marpolbul.2018.01.036.
Jahan, S., Strezov, V., 2017. Water quality assessment of australian ports using water quality evaluation indices. PLoS One 12, 1–16. https://doi.org/10.1371/journal.pone.0189284.
Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N., 2014. Toxicity, mechanism and health effects of some heavy metals. Interdiscip. Toxicol. 7, 60–72. https://doi.org/10.2478/intox-2014-0009.
JICA, 2007. The Study on Capacity Development on Pollution Prevention and Control in the Petroleum Industry in the Caspian Sea and its Coastal Areas in the Republic of Kazakhstan.
Kaplan, E.L., Meier, P., 1958. Nonparametric estimation from incomplete observations. J. Am. Stat. Assoc. 53, 457. https://doi.org/10.2307/2281868.
Kazakhstan Institute of Standardization and Metrology, 2013. KR CT 2318-2013. Water. Determination of Elements Using Atomic Absorption Spectrometry With Electrothermal Atomization.
Kosarev, A.N., 2005. Physico-geographical conditions of the Caspian Sea. In: The Caspian Sea Environment. Springer, Berlin, Heidelberg, pp. 5–31. https://doi.org/10.1007/698_5_002.
Kumar, V., Parihar, R.D., Sharma, A., Bakshi, P., Singh Sidhu, G.P., Bali, A.S., Karaouzas, I., Bhardwaj, R., Thukral, A.K., Gyasi-Agyei, Y., Rodrigo-Comino, J., 2019. Global evaluation of heavy metal content in surface water bodies: a meta-analysis using heavy metal pollution indices and multivariate statistical analyses. Chemosphere. https://doi.org/10.1016/j.chemosphere.2019.124364.
Mamat, Z., Yimit, H., Ji, R.Z.A., Eziz, M., 2014. Source identification and hazardous risk delineation of heavy metal contamination in yanqi basin, Northwest China. Sci. Total Environ. 493, 1098–1111. https://doi.org/10.1016/j.scitotenv.2014.03.087.
Manavi, P.N., Mazumder, A., 2018. Potential risk of mercury to human health in three species of fish from the southern Caspian Sea. Mar. Pollut. Bull. 130, 1–5. https://doi.org/10.1016/j.marpolbul.2018.03.004.
Mityagina, M.I., Lavrova, O.Y., Kostianoy, A.G., 2019. Pattern of the Caspian Cea surface oil pollution revealed by satellite data. Ecol. Montenegrina 25, 91–105. https://doi.org/10.37828/em.2019.25.9.
National statistical committee, 2019 National statistical committee, 2019.
North Caspian Operating Company N.V. (NCOC), 2016. Sustainability Report.
Okogbue, C.O., Oyesanya, O.U., Anyiam, O.A., Omonona, V.O., 2017. Assessment of pollution from produced water discharges in seawater and sediments in offshore, Niger Delta. Environ. Earth Sci. 76 https://doi.org/10.1007/s12665-017-6682-x.
Olsen, R.L., Chappell, R.W., Loftis, J.C., 2012. Water quality sample collection, data treatment and results presentation for principal components analysis - literature review and Illinois River watershed case study. Water Res. 46, 3110–3122. https://doi.org/10.1016/j.watres.2012.03.028.
Osuji, L.C., Onojake, C.M., 2004. Trace heavy metals associated with crude oil: a case study of ebocha-8 oil-spill-polluted site in Niger Delta, Nigeria. Chem. Biodivers. 1, 1708–1715. https://doi.org/10.1002/CBDV.200490129.
RSE "Kazhydromet", 2019. Informational Bulletin on the State of the Environment in the Republic of Kazakhstan. https://doi.org/10.1017/CBO9781107415324.004.
Saeedi Saravi, S.S., Shokrzadeh, M., 2013. Heavy metals contamination in water and three species of most consumed fish sampled from Caspian Sea, 2011. Environ. Monit. Assess. 185, 10333–10337. https://doi.org/10.1007/s10661-013-3335-8.
Santana, C.S., Montalvan, D.M., Olivares, A., Silva, V.H.C., Luzardo, F.H.M., Velasco, F. G., De Jesus, R.M., 2020. Assessment of water resources pollution associated with mining activity in a semi-arid region. J. Environ. Manag. 273, 111148 https://doi.org/10.1016/j.jenvman.2020.111148.
Schets, F.M., Schijven, J.F., de Roda Husman, A.M., 2011. Exposure assessment for swimmers in bathing waters and swimming pools. Water Res. 45, 2392–2400. https://doi.org/10.1016/j.watres.2011.01.025.
Sobhanardakani, S., 2017. Potential health risk assessment of heavy metals via consumption of caviar of persian sturgeon. Mar. Pollut. Bull. 123, 34–38. https://doi.org/10.1016/j.marpolbul.2017.09.033.
Sobhanardakani, S., Tayebi, L., Hosseini, S.V., 2018. Health risk assessment of arsenic and heavy metals (Cd, cu co, pb, and Sn) through consumption of caviar of Acipenser persicus from southern Caspian Sea. Environ. Sci. Pollut. Res. 25, 2664–2671. https://doi.org/10.1007/s11356-017-0705-8.
Solgi, E., Alipour, H., Majnooni, F., 2019. Investigation of the concentration of metals in two economically important fish species from the Caspian Sea and assessment of potential risk to human health. Ocean Sci. J. 54, 503–514. https://doi.org/10.1007/s12601-019-0024-8.
Tolian, R., Makhsoosi, A.H., Bushehri, P.K., 2020. Investigation of heavy metals in the ballast water of ship tanks after and before the implementation of the ballast water convention: Bushehr Port, Persian Gulf. Mar. Pollut. Bull. 157, 111378 https://doi.org/10.1016/J.MARPOLBUL.2020.111378.
Townsend-Small, A., Hoschouer, J., 2021. Direct measurements from shut-in and other abandoned wells in the Permian Basin of Texas indicate some wells are a major source of methane emissions and produced water. Environ. Res. Lett. 16, 054081 https://doi.org/10.1088/1748-9326/ABF06F.
Tulemisova, G., Amangosova, A., Abdinov, R., Kabdrakhimova, C., Dzhanzakova, B., 2021. Ecological monitoring of the water bodies of the Ural-Caspian basin (Экологический Мониторинг водоеМов Урало-Каспийского бассейна). Cent. Asian J. Water Res. 7, 37–49. https://doi.org/10.29258/cajwr/2021-r1.v7-1/37-49.rus.
Tumolo, M., Ancona, V., Paola, D.De, Losacco, D., Campanale, C., Massarelli, C., Uricchio, V.F., 2020. Chromium pollution in european water, sources, health risk, and remediation strategies: an overview. Int. J. Environ. Res. Public Health 17, 1–25. https://doi.org/10.3390/IJERPH17155438.
UNEP, GRID-Arendal, 2006. Vital Caspian Graphics Challenges Beyond Caviar. UNEP/GRID-Arendal, Birkeland.
United Nations Economic Commission for Europe, 2011. Second Assessment of Transboundary Rivers, Lakes and Groundwaters: Chapter 4 Drainage Basin of the Caspian Sea. New York and Geneva.
USEPA, 2010. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part A), EPA/540/1-89/002 (Annotated). Washington, D.C. 20450 doi:EPA/540/1-89/002.
USEPA, 2004. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) EPA/540/R/99/005. Washington, DC.
Ustaoğlu, F., Tepe, Y., 2019. Water quality and sediment contamination assessment of pazarsuyu stream, Turkey using multivariate statistical methods and pollution indicators. Int. Soil Water Conserv. Res. 7, 47–56. https://doi.org/10.1016/j.iswcr.2018.09.001.
Wagner, A., Boman, J., 2003. Biomonitoring of trace elements in muscle and liver tissue of freshwater fish. Spectrochim. Acta B At. Spectrosc. 2215–2226. https://doi.org/10.1016/j.sab.2003.05.003.
Yessenamanova, M.S., Kulzhanova, G., Tlepbergenova, A.E., Yessenamanova, Z.S., Batyrbayeva, G., 2021. Environmental monitoring of water quality in the interstate Ural river. J. Phys. Conf. Ser. 32007. https://doi.org/10.1088/1742-6596/1889/3/032007.
Yongming, H., Peixuan, D., Junji, C., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci. Total Environ. 355, 176–186. https://doi.org/10.1016/j.scitotenv.2005.02.026.
Zonn, I.S., 2005. Environmental issues of the Caspian. Casp. Sea Environ. 5, 223–242. https://doi.org/10.1007/698_5_012.
Zyryanov, V.N., 2016. Hydrodynamic basis of formation of large-scale water circulation in the Caspian Sea: 2. Numerical calculations. Water Resour. 43, 292–305. https://doi.org/10.1134/S0097807816020184.
Zyryanov, V.N., 2015. Hydrodynamic basis of formation of large-scale water circulation in the Caspian Sea: 1. Asymptotic theory. Water Resour. 42, 776–787. https://doi.org/10.1134/S0097807815060111.