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Evaluation of the heavy metal risk potential in salts extracted from the Shorbarik River

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ABSTRACT

Because heavy metals can build up within the bodies of living things, and because of chemical reactions, they can become poisonous and carcinogenic. Among other things, heavy metal-containing salts are one way these elements enter the body. In Khuzestan Province, Iran, the Shorbarik River is one of the most significant rivers from which salt is mined. In order to assess the health and quality of the salt taken from the Shorbarik River in accordance with national regulations, this study looked into the concentration of heavy metals (lead and cadmium) in these salts. The Shorbarik River was the study region, and the surface salts of the dried bed were sampled in four stages. After drying in an oven, they were injected with acid into an atomic absorption device. Due to the high concentration of cadmium in the region's salts, the risk of cancer from exposure to heavy metals through salt consumption is serious. Ecologically, the Shorbarik River's salt is generally low in lead contamination and considerably high in cadmium contamination, with high levels in the spring and summer. Therefore, it is recommended to consume refined salt.

1. Introduction

Over the past ten years, there has been a notable rise in human-made pollutants, e.g., heavy metals, entering aquatic ecosystems. This poses a substantial risk to aquatic life. Aquatic systems are, by nature, the end recipients of these metals and serve as a site for the sedimentation and accumulation of these elements [1]. Among surface flows, rivers are more effective at improving people's living standards than other resources due to their association with the growth and development of societies; in this regard, they are more at risk of pollution and quality degradation than other sources [2]. The Shorbarik River in the Haftkal region of Khuzestan Province is not exempt and is constantly

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exposed to various pollutants. Therefore, it is very important to assess the quality of its condition. In addition, the salinity of the water in this area is very high due to the presence of gypsum and marl layers of the Gachsaran Formation, sandstone and siltstone of the Aghajari Formation and Lehbari section in these areas, and gypsum and sulfate beds. This feature has led the locals to consume the salt that accumulates in the riverbed. It is common to extract salt from lakes in arid and semi-arid regions. Cheraghali et al. (2010) reported that the extraction of salt from salt lakes has a long history dating back to 6,000 B.C. Heavy metals are one of the main impurities in salt. Because of their toxicity, stability, and lack of biodegradability, heavy metals are one of the most significant and hazardous categories of contaminants [3]. Their effects on human health and the buildup of these metals in the environment have become a concerning issue in recent years [4]. The primary risk posed by these elements comes from their ability to spread through the food chain, build up within the bodies of living things, and undergo chemical reactions that can transform them into poisonous and cancer-causing compounds [5]. After entering the body, heavy metals accumulate in tissues like fat, muscles, bones, and joints. These deposits can lead to a variety of illnesses and consequences, including cancer, respiratory conditions, neurological disorders, and liver, kidney, and brain damage [6]. Consuming food tainted with heavy metals, such as cadmium, can lead to the development of Itai-Itai sickness, as well as the degeneration of the testicles and kidneys [7]. The central and peripheral neurological systems are affected by lead [8]. Additionally, the body's ability to absorb micronutrients can occasionally be hampered by the presence of heavy metals in salt [9]. Numerous research studies have calculated the concentration of heavy metals in refined and unprocessed salt due to the significance of this issue on a worldwide scale [10-14]. The Shorbarik River holds great significance for the residents of the surrounding villages due to its oil wealth and the presence of a stone crusher, a mine, and potential contaminants in the river and collected salts. As a result, it is crucial to understand its current state of health. The purpose of this study was to determine the lead and cadmium concentrations in the salts recovered from the Shorbarik River to assess their quality and healthfulness in relation to national criteria.

2. Materials and methods

The area studied is the Shorbarik River, which originates in the heights of the Sardeli Mountains around the Haftkel-Baghmalek road and is located 15 kilometers east of the city of Haftkel (Figure 1). This river is located in the east of Khuzestan Province with the geographical coordinates of 31° 35' 03'' north latitude and 49° 31' 48'' east longitude. To achieve the research objectives, four phases of sampling the surface salts of the dry riverbed (Figure 2) were carried out seasonally from winter 2021 to autumn 2022 along the course of the Shorbarik River.

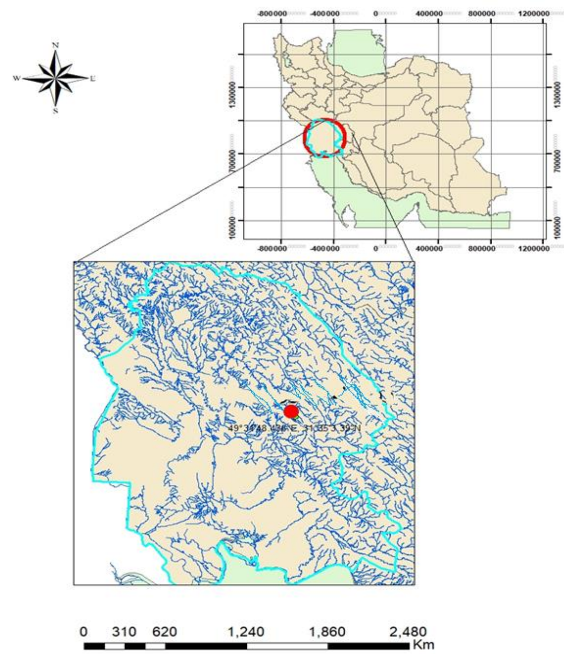

Fig. 1. Geographical location of the study area.

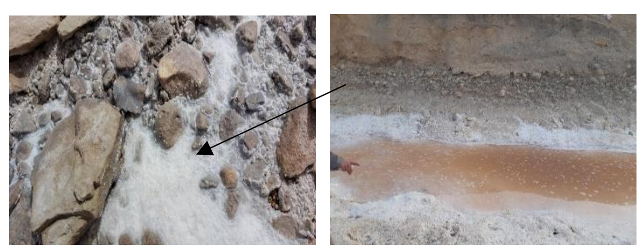

Fig. 2. Salt sediments in the study area.

The samples were put in specialized sampling bags and transported on ice to the Khuzestan University of Agricultural Sciences and Natural Resources lab. The salt samples were dried for 24 hours in a laboratory setting in an oven set to 105°C.

Subsequently, the dried samples were put through a 200-mesh screen to remove any contaminants. One gram of the dried sample was put into digestion tubes to prepare salt samples for determining the quantity of heavy metals (lead and cadmium). Then, 10 milliliters of a 3:1 mixture of 65% nitric acid and 67% perchloric acid were added. First, the PTFE tubes were heated on a hot plate for an hour at 40°C. Then, the temperature was gradually raised to 140°C for three hours. The samples were removed from the machine and filtered using Whatman #42 filter paper and a polyethylene funnel after being acid-digested and allowed to cool. After using distilled water to wash the filter's contents, a balloon was used to raise each solution's volume to 25 milliliters. To avoid volume decline, the samples were put into polyethylene bottles with lids and sample code labels and kept in a refrigerator at 4°C. Since the storage time should not be long, the samples were injected into an atomic absorption device as quickly as possible after digestion, and the cadmium and lead concentrations contained therein were calculated [11]. Every sample was tested three times, and the average was noted to guarantee the test's correctness. Additionally, a technique of raising the standard and percentage of metal recovery was employed to guarantee the precision of the test and analysis procedure to measure the metals in the samples and establish their accurate amount. Each of the analyzed samples in this investigation received 10 milliliters of the reference solution containing lead and cadmium metals at a concentration of one microgram per gram. It should be mentioned that two samples of each metal were made in the same manner and under identical circumstances, but only one of them received the addition of the standard solution. Then, the concentration of each individual metal was determined separately (by extrapolation of the relevant calibrations), and the recovery percentage of the metals was calculated using the following formula.

$$R = 100\ (A2 - A1)/\ As \qquad (1)$$

where R: percent recovery, A1: sample concentration in micrograms/grams without a standard,

A2: The micrograms per gram concentration of the sample bearing the standard, and As: standard solution concentration in µg/g.

The method used to determine the metals has sufficient reliability based on the recovery rates of various metals (97 ± 102). Under the presumption that the data were normal, parametric tests were used to undertake statistical analysis of the data using SPSS 26 software.

3. Non carcinogenic risk assessment

Generally, there are two categories of harmful effects that heavy metals can have on the human body: carcinogenic and non-carcinogenic effects [15]. The ratio of the intended pollutant concentration to the oral reference value (RfD) is known as the Hazard Ratio (THQ) or Hazard Potential, and it is used to assess the non-carcinogenic effect of heavy metals. A person is unlikely to experience considerable lifetime risk if their THQ score is less than one [15].

$$THQ = EDI/RfD \qquad (2)$$

The daily oral exposure of a pollutant during an individual's lifetime (without considerable danger) is known as the RfD oral reference value. This value is calculated using the EPA's tables and is expressed in mg/kg body weight per day. The following formula is used to compute the EDI, which is the daily intake of heavy metals from food, water, and soil per kilogram of body weight per day (mgr kg^{-1} day^{-1}) [16].

$$EDI = (IR \times C \times ED \times EF \times CF)/(BW \times AT) \qquad (3)$$

In this context, EF is the frequency of consumption per year (days/years), ED is the length of the consumption period (years), BW is body weight (kg), CF is the conversion factor that is equal to 10. -6 kg/mg, C is the pollutant concentration in the food (mg/kg), and AT is the product of ED in the number of days of the year (years). The connection below determines the overall risk or cumulative risk estimate for diseases other than cancer:

$$HI = \Sigma THQ \qquad (4)$$

This study looked at two age groups: adults (18–54 years old) and children (under 7 years old) [16]. The frequency of EF consumption is determined by counting the number of days in a year (365 in this case) that the desired material (salt) is consumed.

The period of consumption in this study was four years for children and 30 years for adults. Adults and children were thought to weigh 70 and 17 kg, respectively.

4. Carcinogenic risk assessment

The USEPA's suggested method of calculating the carcinogenic risk (CR) of lead and copper is to multiply its slope factor by the quantity of lead and copper exposure resulting from salt consumption [15]:

$$CRi = SF_i \times EDI_i \qquad CR = \Sigma CR_i \tag{5}$$

where CRi is the carcinogenic rate per lifetime and SFi is the oral carcinogenic slope factor from the integrated risk information system database (0.0085 and 15 mg/kg/d for Pb and Cd, respectively) [17]. The range of 10–6 to 10–4 is the permissible lifetime CR limit [18–19]. An individual's cancer progression would be greater than 1 in 100,000 if the number was greater than 10–5 [20].

5. Ecological risk assessment

5.1. Contamination Factor (CF) and Pollution Load Index (PLI)

The concentration of each metal in the salt divided by the background or baseline value yields the CF ratio.

$$CF_i = (C_i / B_i) \tag{6}$$

where Ci and Bi stand for the metal I background value and measured concentration, respectively. CFi is a heavy metal contamination factor found in salt. Background levels of Cd are 0.3 mg/kg and Pb are 20 mg/kg, respectively [21]. On a scale from 0 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, and 6 = very strong), the levels of contamination can be categorized according to their intensities [22]. PLI has been shown to evaluate the total amount of heavy metals (Eq. 7) [23]. The research region's sediment quality was assessed using PLI in a rapid and easy manner [24].

$$PLI = (CF_1 \times CF_2 \times \cdots \times CF_n)^{1/n} \tag{7}$$

where n is the number of metals (n = 2 in this study) index provides a simple, comparative means for assessing the level of heavy metal pollution. PLI = 0: perfect quality, PLI < 1: No pollution; PLI > 1: Polluted.

6. Results and discussion

Figure 3 illustrates the average concentration of heavy metals in the salt of the Shorbarik River at various periods of the year. It is evident that the lead, with an average of 1.79 ± 1.48, is higher in different seasons than the average of the cadmium (0.18 ± 0.06). A comparison of the lead and cadmium concentrations revealed a significant difference (P<0.05) in the concentrations of these two elements. Seasonal variations in lead concentration in the investigated area were also found to be statistically significant (P<0.05). This element was found in the highest concentrations during the summer and in the lowest concentrations during the winter. Seasonal variations in the amount of cadmium were found to be statistically significant (P<0.05). According to Tukey's post-test, the amount of cadmium was in the same group in the spring, summer, and autumn, even though the maximum amount was recorded in the summer and the lowest in the winter. The average concentration of heavy metals (lead and cadmium) in the Shorbarik River's salt was 1.79 and 0.18, respectively. The lead concentration was higher than the permissible amount (lead and cadmium were 1 and 0.2 μg/g, respectively) recommended by the Iranian table salt standard 1195 ISIIR, while the cadmium concentration was slightly lower.

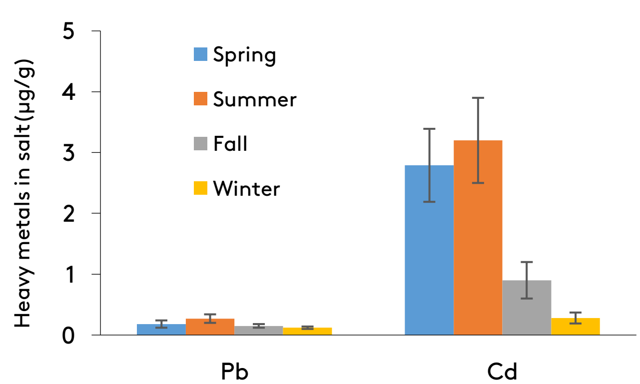

Fig. 3. Comparison of lead and cadmium concentration in different seasons.

The total amount of heavy metals ingested from the salt of the Shorbarik River

Equation 2 was used to determine the total amount of heavy metal ingested by adults and children from the Shorbarik River salt. The results are displayed in Table 1. The amount of absorbed metal was then computed by multiplying the result by the body weight. ISIRI, Codex, and FDA standards were utilized to compare the levels of heavy metals entering the body with reference values (Table 2).

Table 1. The amount of metal that entered the bodies of adults and children (mg/day) due to the consumption of salt from the Shorbarik River.

Metal / Age groupe	Cadmium	Lead
Adult	0.001	0.0098
Child	0.0003	0.0027

Table 2. Permitted amounts of heavy metals in different standards (reported by [16])

Metal / Recommendatio	Cadmium	Lead
UL (mg/day)	0.064	-
RfD (mg/kg day)	0.001	0.004
ISIRI 1195 (mg/kg)	0.2	1
ISIRI12968 (mg/kg Bw)	0.001	0.004
Codex (mg/kg)	0.5	2

A joint committee of experts (JECFA) of the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (JECFA) established a reference value known as the temporary tolerable daily intake (PTDI); it estimates the safe daily intake of pollutants such as heavy metals in milligrams per kilogram of body weight. The overall exposure to the targeted pollutant from food and non-food sources was calculated and used as a primary health index. This exposure was then multiplied by body weight to obtain the tolerated daily intake for each individual (PTDIp). The amount of salt consumed was calculated using a report from [25], which gives the amount consumed in several parts of the country. In the current research, the average reported values, i.e., 11 grams per day, were considered. The Ministry of Health reported that 50% of the salt consumed enters the body through food. Therefore, the amount of salt consumed directly by adults in this research was 5.5 grams per day. There is no written report regarding the amount of salt consumed by children in Iran, but the recommended permissible amount for children (World Health Organization report) by the Community Nutrition Improvement Office, Deputy Health Ministry's (Ministry of Health and Medical Education) is three grams per day, which was considered for children in this research [26]. The amount of Pb and Cd from the Shorbarik River that entered the bodies of children and adults was lower than the allowed amount.

The potential danger of heavy elements

The risk potential values for lead and cadmium metals present in the salt samples of the Shorbarik River were calculated using Equation 2. The results showed that among the investigated metals, the highest risk potential value (for the average samples) was obtained for Pb, which was equal to 2.46 and 0.67 for adults and children, respectively; the lowest risk potential value (for the average samples) for Cd was 0.99 and 0.27 for adults and children, respectively. The risk potential values for lead and cadmium in the salt samples for adults and children were less than one, which showed that the risk caused by the examined metals was within an acceptable range. The important point in this section is that if the amount of salt consumed changes, the THQ values will also change.

Risk index

The risk value for the salt samples of the Shorbarik River was calculated using Equation 4. The results showed that the HI rate for adults was 3.45 and 0.94 for children. According to the EPA classification range (Table 3), children are in the risk level 2 group of low chronic risk, which shows the adverse effects of non-cancerous diseases due to the consumption of heavy elements caused by consuming salt from the Shorbarik River. Based on the EPA classification range and the HI rate for adults, they are in the risk level group 3, moderate chronic risk. Therefore, there are effects of non-cancerous diseases for adults due to the consumption of heavy elements caused by consuming Shorbarik River salt. Also, the value of HI will change with a change in the amount of salt consumed; therefore, one of the reasons for the lower risk index in children can be the less consumption of river salt and the less time of exposure to pollutants present in the salt. According to Figure 4, the CR mean of Pb in adults and children was 8.3*10-5 and 2.3*10-5, respectively. Additionally, the CR mean of Cd in adults and children was 15*10-3 and 4*10-3, respectively (Figure 4). As can be observed, the permissible range for CR of Cd in adults and children, is greater than permissible range for CR of Pb. Therefore, there is very little chance of developing cancer from consuming Pb-contaminated salt, but there is a significant danger of developing cancer from consuming Cd-contaminated salt. In general, the CR of salt consumption was found to be 4*10-3 for children and 15*10-3 for adults. Therefore, there is a significant risk of cancer from heavy metal exposure from salt use. The acceptable lifetime CR limit is between 10^{-6} and 10^{-4} [18-19]. An individual's cancer progression would be greater than 1 in 100,000 if the number was greater than 10–5 [20]. According to a non-carcinogenic health risk study, Mostafaii et al. (2022) found that all consumers (adults and children) were in the safe range (TTHQ<1) [27]. However, consumers who use salt that contains As (CR > 10–4) are at risk for cancer. Therefore, it is essential to regularly and thoroughly inspect the salt sediment of the Aran and Bidgol Lake for As entering sources. Two carcinogenic metals that might obstruct DNA synthesis and repair include lead and cadmium [28–29]. Heavy metal toxicity and carcinogenicity are dosage dependent. According to Gorini et al. (2014), high-dose exposure generated severe reactions in both humans and animals, increasing DNA damage and neuropsychiatric problems [30].

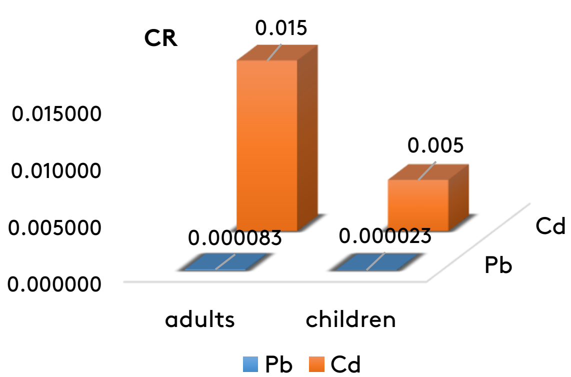

Fig. 4. CR level of lead and cadmium in adults and children.

Contamination Factor (CF) and Pollution Load Index (PLI)

The CF values of the metals displayed in Table 4 can be arranged in the following order: The ranges for Pb were 0.006 to 0.014 (mean 0.009), and those for Cd were 0.93 to 10.67 (mean 5.98). The CF mean indicated that the river's salt had minimal levels of Pb pollution. Considerable contamination was suggested by the Cd CF mean. Compared to the winter, the summer CF value was greater. In an urban river in Bangladesh, Islam et al. (2015) [31] and Ali et al. [32-33] discovered findings that were comparable. The study found that the primary sources of the increased metal levels found in the surface sediment were air deposition, municipal runoffs, industrial effluents, and home wastewater drainage [34]. The results of the current investigation and those of a study done in the Meghna River by Hassan et al. (2015) [35] were the same.

Table 4. Contamination factor (CF) in the salt of the Shorbarik River.

Season / Metal	Spring	Summer	Fall	Winter
Lead	0.006	0.008	0.014	0.009
Cadmium	0.93	3.00	10.67	9.30

The general public can obtain information regarding sediment quality from the PLI. Additionally, it gives decision-makers vital information on the level of pollution in the study area [36]. Figure 5 shows the metal pollution load index (PLI) values for salts. According to the figure, the examined location is completely contaminated if the PLI score is more than one. The PLI values for the sampling seasons were between 0.98 and 2.20 (mean 1.68), suggesting that the river was contaminated (PLI > 1). The PLI in the winter was less than one and greater than unity in the spring, summer, and fall because of the influence of various industrial and municipal activities in these areas.

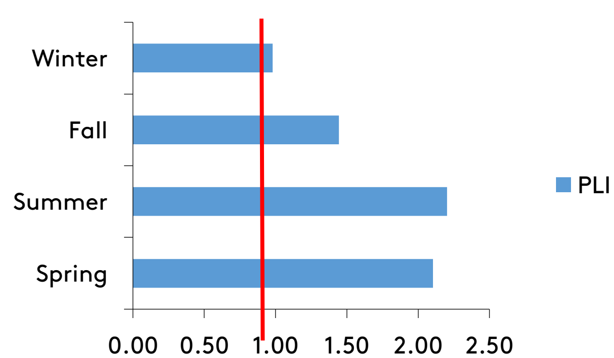

Fig. 5. PLI value in different seasons.

Conclusions

Overall, the study's findings demonstrated notable seasonal variations in the concentrations of lead and cadmium. These elements had the greatest concentrations during the summer and the lowest during the winter. The organic and suspended materials in the water were among the variables influencing the concentration of heavy metals in the bed. Water turbulence and mixing increased during the winter months as a result of rain, wind, and water currents. When sea turbulence and the weight of suspended sediments increased, the metals were more readily absorbed from the water by the suspended particles. In the summer, when the region faced a decrease in rainfall and incoming runoff and water currents, the organic and suspended matter content of metals settled in the seabed, and the concentration of heavy metals accumulated in the suspended matter and organic matter of the bed sediment reached its maximum. Compared to the winter season, it showed a significant increase. In other words, it could be said that the cause of these changes was related to heavy rains in the winter. These rains caused turbulence in the river current, and some of the river bottom sediments and heavy metals were washed away by the water flow. But with the end of the precipitation period and the beginning of the heat period, with an increase in the amount of evaporation, the concentration of these metals increased in the sediment. In fact, the concentration of elements reached its highest level in the summer with the decrease in river discharge, the beginning of the agricultural season, and the increase in evaporation. The cold (rainy) season was higher, which was consistent with the fact that heavy rains in the cold season caused the dilution and mobility of heavy metals in the sediments and water environment. The average concentration of lead and cadmium in the salt of the Shorbarik River showed that the amount of lead was higher than the permissible amount recommended by the Iranian table salt standard 1195 ISIIR, and the amount of cadmium was slightly lower. The results of the calculation of the total amount of Pb and Cd introduced into the bodies of the children and adults from consuming salt from the Shorbarik River was less than the allowed amount. The risk potential values for the lead and cadmium in the salt samples of the Shorbarik River for adults and children were less than one, indicating that the risk caused by the examined metals was within the acceptable range.

An important point in this section is that if the amount of salt consumed changes, the THQ values will also change. The risk value for the samples of salt from the Shorbarik River for children showed that the adverse effects of non-cancerous diseases due to the consumption of heavy elements caused by consuming salt from the Shorbarik River were low. It was in the medium chronic risk group for adults. This article found that there were effects of non-cancerous diseases for adults due to ingesting heavy elements found in the salt from the Shorbarik River. Also, the value of HI will change with a change in the amount of salt consumed. Therefore, one of the reasons for the lower risk index in children compared to adults could be that they consumed less salt from this river and had less exposure to the pollutants present in the river's salt. But the CR of salt consumption showed that the risk of cancer due to exposure to heavy metals through consuming the salt was serious, which was caused by the high concentration of cadmium in the salts of the region. Ecologically, based on the average CF, the salts were in the range of low contamination for lead and considerable contamination for cadmium. In the spring and summer, cadmium levels were in the very high pollution range. In general, the salts were in the polluted range according to the PLI index. Therefore, it is recommended to use refined salt rather than salt from the Shorbarik River.

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