

Original Research

Ecological Assessment of Heavy metals in Sediments of the Farahabad Region (Iran)

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Abstract

The current study assessed trace metal contamination in sediments using different types of indices. Six heavy metals such as Cu, Zn, Mg, Fe, Mn, and Ca were investigated in the sediments of the Farah Abad region in Iran. The metals concentration was found in the range of 15, 16, 59, 770, 3.2, and 14.5 mg/kg for Cu, Zn, Mn, Fe, Mg, and Ca, respectively. The enrichment factor was lower than unity, indicating the absence of anthropogenic influence. The contamination factor and geo-accumulation indices for Cu, Zn, Mn, Mg, and Ca were <1 and <0 , respectively, indicating no pollution at all from the selected metals, whereas CF and I_{geo} values for Fe were significantly greater than 5, suggesting a high enrichment from anthropogenic sources. The potential ecological risk index for Cu and Zn showed a value of 2.376, indicating low ecological risk to the selected sites from the accumulation of trace metals.

Keywords: metal, ecological assessment, sediments, Farahabad Region, Iran

Introduction

The rate of rapid development in the coastal regions of the world have resulted in environmental pollution [1]. Increased concentrations of metals in aquatic ecosystems has now become a global problem [1-2]. Sediments act as a reservoir for metal accumulation, which poses a serious threat to adjacent ecosystems [3]. Metals released into aquatic ecosystems are adsorbed by suspended sediments and settle [4]. This results in a lower concentration of heavy metals in the water column and makes the surface sediments a reservoir for particulate-bound pollutants

[5]. Benthic fauna depend on bottom sediments as their habitat and food source [6]. The accumulated heavy metals in sediments are released into the water column by certain variables like redox potential, altering pH, mobilization of benthic biota, and sediment re-suspension [7]. Thus, particulate-bound metals are a source of contamination to aquatic ecosystems. Due to processes like bioaccumulation and bio-concentration, the effects of heavy metals may be detected on land through the food web [8].

Metals are toxic owing to their bio-magnification and non-biodegradability in the food chain [9]. Discharge of heavy metals from natural and anthropogenic sources ultimately may accumulate in sediments [5]. The biotas attached to sediments are at high risk to metal exposure,

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which ultimately makes its way into the food chain [5, 10]. Thus it is important to constantly monitor the enrichment pattern in order to evaluate the natural and anthropogenic sources of metal pollution [11].

Sediments can be used as an indicator to monitor pollution level of aquatic ecosystems [3, 12]. Extensive literature is available to estimate sediment contamination of aquatic ecosystems [13]. This includes sediment quality guidelines [14-15], enrichment factor (EF) [16], contamination factor (CF) and contamination degree (Cd) [17], modified degree of contamination (mCd) [16], pollution load index (PLI) [18], and contamination severity index and assessment of potential ecological risk [17].

The Farahabad region in northern Iran is a tourist hub. Its beaches attract a number of tourists every year. Owing to anthropogenic activities, it is necessary to monitor its pollution status. None of the study has yet been conducted to evaluate the metal pollution of the selected sites. Therefore, the aim of this study is to evaluate the concentration of selected metals in the study area and apply various indices to determine the potential ecological risk and degree of contamination.

Experimental

Study Area

The Farah Abad Region in Mazandaran Province is an important tourist site located in northern Iran. Figure 1 depicts the Farah Abad Region and points of sample collection.

Sample Collection

Surface sediments were collected from four sampling sites. The whole area was partitioned into four sampling stations. At each sampling site, four sediment samples

(5 cm of surface sediment) were taken in a covered area of 16 m² using a Peterson grab sampler. A composite sediment sample was made for each station using a plastic spoon. The sediment samples were placed in polyethylene bottles, temporarily stored in a cooler at less than 4°C, and then transported to a laboratory [19-20].

Chemical Treatment

For acid digestion, each sediment sample (1.0 g) was digested in an acid-cleaned vessel of Teflon that contained 5 ml of nitric acid (ultra-pure) and 2 ml conc. hydrofluoric acid (ultra-pure). For each batch of digestion a blank sample was prepared containing the same ratio of acids without sediment samples. The prepared digested sediment samples were then passed through Whatman No.1 filter paper and stored at 4°C for instrumental analysis [19, 21].

Instrumentation

Samples of sediment were then quantified by atomic absorption spectrophotometry for the selected six metals, including manganese (Mn), copper (Cu), magnesium (Mg), zinc (Zn), iron (Fe), and calcium (Ca). For accuracy the calibration line method was employed by maintaining optimum analytical conditions (Kimbrough and Lauenstein 2007). All the standard solutions and reagents were of analytical grade with a high degree of purity (>99.99%). The accuracy of the method was maintained by comparing with the standard reference material (MESS-3) [22].

Assessing Sediment Contamination

For determining the contaminants at any site, it should be compared to any other pre-anthropogenic reference site. The comparative proportion would show the degree of contamination. A number of methods have been developed



Fig. 1. Sampling points of Farah Abad region sediment.

to monitor the heavy metal pollution by comparing it to reference values [17]. As there is no pre-industrial data of the study area, the average shale-certified values [16] were used as background values [22]. The enrichment factor, Geoaccumulation index, contamination factor, and modified degree of contamination all were based on comparison of a local reference site with respect to the average shale values [16, 23].

Enrichment Factor (EF)

To monitor the anthropogenic impact on sediments, a common approach called enrichment factor is commonly used to compare the contaminated site with the background reference site [23]. The advantage of enrichment factor is its normalization factor. This factor normalizes the value of measured heavy metals with respect to the benchmark or reference values. This can be done by multiplying both values to those of Fe or Al. Various studies have reported different elements for normalization factor. This study used Fe as a normalization factor owing to its constraint properties of anthropogenic addition to sediments and its high natural concentration [16]. The enrichment factor can be calculated as follows:

$$EF = \frac{M_x \times Fe_b}{M_b \times Fe_x} \tag{1}$$

...where EF is the enrichment factor, and M_x and Fe_x are the contaminated sample concentrations of sediment and normalization element, respectively. M_b and Fe_b are the reference site values for sediments and normalization element, respectively.

Pollution Load Index (PLI)

The pollution load index was suggested by the Irish Estuarine Research Group and mainly was used for heavy metal contamination by a number of studies [18]. The pollution load index requires the contamination factors that can be derived by comparing the level of contaminated sediments to the reference value. The sum of contamination factors for various metals was used to find out the pollution index of each polluted site. This index helps to categorize the polluted sites into various contaminated zones and then can be compared. The pollution index can be described as the nth root of various contamination factors [18]. The equation is as follows:

$$PLI = \sqrt[n]{C_f^1 \times C_f^2 \times C_f^3 \times \dots \times C_f^n} \tag{2}$$

$$C_f^n = \frac{C_s^i}{C_n^i} \tag{3}$$

...where PLI is pollution load index and C_f^n is the contamination factor. C_s^i is heavy metal concentration

in contaminated sediments and C_n^i is heavy metal concentration of reference site.

Geoaccumulation Index (I_{geo})

Based on some studies, we used a common method for determining sediment quality (Table 1). Although it is also based on polluted site to that of reference site, this model also shows us numerical values to designate the quality of sediments. The Müller equation uses factor 1.5 to normalize the variation of natural geochemical differences between the reference and potential site of contamination [24]:

$$I_{geo} = \text{Log}_2 \frac{C_n}{1.5B_n} \tag{4}$$

...where C_n is the element concentration in sediments while B_n is the benchmark value or reference value.

Modified Degree of Contamination (mCd)

For ecological risk assessment, Hakanson proposed an ecological risk index model. As a requirement value for that model, Hakanson also proposed a proportionate called degree of contamination [17]. The degree of contamination is only limited to seven metals for their contamination. One cannot add additional elements for their degree of contamination. Thus, there was a need to design a model that entails all the metals. Abraham (2005) modified and generalized the Hakanson model called modified degree of contamination. This index takes the sum of all contamination factors and divides it by the total number of pollutants. The mean values of modified degree of contamination were divided into seven classes based on degree of contamination [16]. The modified equation is as follows:

$$mCd = \frac{\sum_i^n C_f^i}{n} \tag{5}$$

...where n stands for total number of elements analyzed and C_f^i stands for contamination factor (Table 2).

Table 1. Geoaccumulation Index.

Igeo value	Igeo class	Level of contamination
>5	6	Extremely contaminated
4-5	5	Strongly to extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately to strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
0	0	Uncontaminated

Table 2. Modified degree of contamination.

(mCd) values	Contamination Level
mCd<1.5	Nil to very low degree of contamination
1.5≤mCd<2	Low degree of contamination
2≤mCd<4	Moderate degree of contamination
4≤mCd<8	High degree of contamination
8≤mCd<16	Very high degree of contamination
16≤mCd<32	Extremely high degree of contamination
mCd≥32	Ultra high degree of contamination

Potential Ecological Risk Index

The ecological risk index was designed by Hakanson [17]. The risk index is to find out the risk associated to the ecological health owing to the entrance of pollutants that will ultimately make its way into the food chain. The concentration of metals in contaminated sites were compared to the average shale values to find out the contamination factor by the following equation.

$$C_f = \frac{C_{0-1}}{C_n} \tag{6}$$

The sum of contamination factors were used to find out the degree of contamination by using the following equation:

$$E_r^i = T_r^i \times C_f^i \tag{7}$$

The ecological risk factor E_r^i was calculated by multiplying toxic risk factor already given by Hakanson to the contamination factor. The toxic risk factor of heavy metals is shown in Table 3.

The equation for risk factor was determined as follows:

$$E_r^i = T_r^i \times C_f^i \tag{8}$$

The sum of risk factor values was used to determine the potential ecological risk index based on the following equation:

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i \tag{9}$$

...where E_r^i stands for potential ecological risk factor, T_r^i

Table 3. Toxic risk factor for heavy metals developed by Hakanson.

Heavy Metals	T_r^i
Cu	5
Zn	1

Table 4. RI classification (Hakanson 1980).

RI values	Risk intensity
<150	Low ecological risk
150≤RI<300	Moderate ecological risk
300≤RI<600	Considerable ecological risk
<600	Very high ecological risk

stands for toxic response factor of heavy metal I, and C_f^i stands for contamination of heavy metal .

Potential ecological risk index (RI) is classified into four different classes shown in Table 4:

Results and Discussion

Table 5 shows heavy metals concentrations in four sites. The summarized values, average concentrations, and average shale or background values were also delineated in the table. The highest concentration (779 mg/kg) of Fe was detected at site 4 and the highest concentration of Mn (59 mg/kg) was detected at site 1. The concentration for Cu was in the range of 13 to 15 mg/kg and Zn ranged 15 to 16 mg/kg. The values of Fe were in the range 762 to 779 mg/kg and Mg concentration from 2.9 to 3.8 mg/kg, while the concentrations of Ca were 14.5-19 mg/kg.

The selected heavy metals concentration in the four sites showed little variation in concentration because the whole area is uniformly influenced by anthropogenic activities. The one-way ANNOVA results showed that the data was non-significant. The concentration of selected metals from sites 1 to 4 were used to derive the enrichment factor, geo-accumulation index, pollution load index, modified degree of contamination, and potential ecological risk in order to assess sediment contamination. Average shale values of heavy metals were used as background reference values taken from uncontaminated sites, and their use helps to evaluate heavy metal enrichment whether from natural or anthropogenic sources.

Heavy metals at all sites showed enrichment factor (EF) values <1, suggesting that the heavy metals were not significantly enriched from human activities and the selected sites were unpolluted from Cu, Mn, Zn, Fe, Mg, and Ca. The contamination factor values were also calculated. The contamination factor (CF) values of the heavy metals were also all <1 except for Fe, which showed a contamination factor value of 214.136, demonstrating that the contamination of Fe may be influenced by human activity. CF values of Cu, Zn, Mn, Mg, and Ca suggested low contamination or no contamination at all.

Human exposure to heavy metals is a concern for public health that has attracted the attention of researchers and health experts all over the world [25]. The multiple industrial, domestic, agricultural, medical, and technological applications have led to wide distribution

Table 5. Concentrations of heavy metals and average shale values.

Sampling Stations	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Ca (mg/kg)
S1	15	16	59	770	3.2	14.5
S2	14	16	56	764	3.4	15.8
S3	13	16	57	762	3.8	16.00
S4	15	15	58	779	2.9	19.00
Average shale value ^a	32	129	720	3.59	21.1	53.6

^aChakravarty and Patgiri 2009

Table 6. Calculated geoaccumulation index.

Sample location	Cu	Zn	Mn	Fe	Mg	Ca
S1	-1.680	-3.591	-4.184	7.159	-3.308	-2.473
S2	-1.775	-3.591	-4.265	7.148	-3.224	-2.351
S3	-1.884	-3.591	-4.238	7.145	-3.059	-2.329
S4	-1.680	-3.680	-4.211	7.175	-3.556	-2.065

Table 7. A) Enrichment factor, B) contamination factor, and pollution load index (PLI).

Sample Location	Cu		Zn		Mn		Fe		Mg		Ca		PLI
	A	B	A	B	A	B	A	B	A	B	A	B	
S1	0.002	0.469	0.0005	0.124	0.0003	0.081	0	214.484	0.0007	0.151	0.001	0.270	0.598
S2	0.002	0.437	0.0005	0.124	0.0003	0.077	0	212.813	0.0008	0.161	0.001	0.295	0.589
S3	0.001	0.406	0.0005	0.124	0.0003	0.079	0	212.256	0.0009	0.180	0.002	0.298	0.597
S4	0.002	0.469	0.0005	0.116	0.0003	0.080	0	216.991	0.0009	0.137	0.004	0.354	0.598
Average	0.0055	0.445	0.0005	0.151	0.0003	0.0792	0	214.136	0.0008	0.157	0.002	0.304	0.595

of metals in the environment, raising concerns over their potential effects on human health and the environment [26]. Their toxicity depends on several factors, including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals [27, 28]. All pollution load index (PLI) values are <1, which suggests that all sites were less polluted and that there is no concern of ecological risk from the selected metals.

The calculated values of geo-accumulation are shown in Table 7. Igeo values confirmed contamination and enrichment factors. The values for Cu, Zn, Mn, Mg, and Ca were <0, declaring their concentration uncontaminated, whereas Fe showed an extremely polluted level with Igeo value of >5, which suggests that the sites are highly polluted by Fe. Along with this, the modified degree of contamination values are also in agreement with pollution load index. The mCd values for Cu and Zn are 0.596. This value is <1.5 and comes in a class of nil or very low degree of contamination.

It is a well-established fact that heavy metals can be transferred from the topsoil to the other components of the environment like groundwater or crops, and may enter into the food chain through irrigation practices. Metals can cause serious health risks to consumers by intake of the contaminated food crops if these metals exceed the permissible limits [29-30]. The potential ecological risk index (RI) is calculated only for Cu and Zn because toxic risk factors of the Hakanson model are only for these two metals among the selected metals. The RI index value for these two metals was 2.376. This value declared that there is low ecological risk from these two metals.

The spatial-temporal changing characteristics and potential ecological risk combined with local policies and industrial status were analyzed. The metal contamination was studied by sediment quality guidelines (SQGs), potential ecological risk index (PERI), and geo-accumulation index (I_{geo}) of metals (Hg, Cr, Cd, As, Pb, and Cu) in the sediments of the

Xiaoqing River in Jinan [31]. The assessment suggested that Hg presented the highest levels of I_{geo} and was the largest contributor to RI, while Cd was the second contributor. This finding indicated that Hg and Cd had a strong effect on potential ecological risk. But it needs long-term effective management measures and a strengthened source control. The suggestions of targeted management have been proposed [31]. Similarly Fang et al., [32] argued that analyzed metals of sediment and aquatic organisms can provide important information on the environmental contamination and potential impact of aquatic food consumption. Thus, the concentrations of Cu, Pb, Zn, Cr, Cd, As, and Hg in sediments and fish from Chaohu Lake were analyzed with inductively coupled plasma mass spectrometry and atomic fluorescence spectrometry. The ecological risk evaluation showed that the metals in sediments posed low to medium risk. The health risk assessment suggested that the consumption of fish from Chaohu Lake is currently safe with respect to the metals. A study by Zhang et al. [33] suggested that Cd was the most prominent metal in the exchangeable and carbonate-included fraction. Cd posed the greatest potential ecological risk.

Finally, there are also many algal communities such as *Cladophora glomerata* L. in this region that can have interrelated with water and sediment qualities. The sensitivity of algal species renders them good biological indicators of water pollution. It has been pointed out that algal communities possessed many attributes as biological indicators of spatial and temporal environmental changes. Algal parameters, especially the community structural and functional variables that have been used in biological monitoring programs have been reviewed by Ebadi and Hisoriev [34].

Conclusions

The current study showed that various sites of the Farah Abad region received no or less input of heavy metals, except that Fe showed a high contamination factor and geo-accumulation index indicated high anthropogenic inputs of metals. This has also been confirmed by modified degree of contamination. The potential ecological risk index for Cu and Zn indicated that the selected sites were at low ecological risk for the accumulation of trace metals.

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