



Quality Evaluation and Study of Ecological Toxicity of Heavy Metals in Shadegan Wetland

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ABSTRACT

Wetlands hold a principal position in storing food for primary producers, so they are not able to bear the pressure. The slightest disturbance, hence, may harm wetlands and cause detrimental effects. The present study aims at monitoring heavy metals and evaluation of the sediment quality index of Shadegan wetland in Iran. Thus, a sampling of surface sediments of the wetland was performed at ten stations with three replications; after the preparation of samples with aqua regia, the concentrations of heavy metals were measured by atomic absorption spectroscopy. The quantification of sediment pollution using the contamination factor, contamination degree, pollution load index, ecological risk assessment index, and ecological toxicity of heavy metals in the region were all carried out. The results of Cf and Cd showed that the degree of zinc and copper contamination is low; however, the degree of lead contamination is moderate. Moreover, the obtained PLI was less than 1 indicating a lack of sediments contamination with heavy metals. The RI was less than 150 indicating a low risk of contamination. In addition, comparing the concentrations of elements with National Oceanic and Atmospheric Administration and Sediment Quality Guidelines showed slightly toxic and non-toxic sediments, respectively. Finally, based on a mixture of effect range median, all sediment samples are placed in the first category with less than 12% toxicity probability.

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1. Introduction

Aquatic ecosystems, as one of the main environmental features, are a key supplier of food and a roof over aquatic organism's head; on the other hand, they are also large sources for a wide range of pollutants. Since these ecosystems withstand a high capacity for development, they are subject to more serious risk due to the pollutants. Domestic and industrial sewage discharges, the growth in urbanization,

and industrial activities in coastal areas are severe threats to the safety of the coastal environment and aquatic ecosystems. Among

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the existing pollutants in the sewage, heavy metals can be mentioned, especially the ones that play important roles in society as the main raw materials for many industries. (Zhuang and Gao, 2014; Caerio, et l, 2005) Some, such as copper and zinc, play a vital role in the metabolism of the human body. However, in high concentrations, they turn into toxic substances. Being attributable to high persistence toxicity, solubility low absorption and accumulation in the bottom sediments, heavy metals cause contamination in aquatic environments. (Caerio, et al., 2005) The biological toxicity and bio-magnification in food chains have made the issue of heavy metals a significant global problem. (Förstner and Wittmann, 1983) the ways to clean up contaminated sediment are mostly costly, and in some cases impossible. Hence, the evaluation of sediment contamination in the aquatic environment, identifying sources of pollution, applying management policies, and processes to reduce a number of pollutants into the aquatic environment is more important than focusing on clearing techniques.

Many studies have been done in this regard, among which the one carried out by Zarezadeh and Rezai, (2014) can be mentioned through which they have investigated the heavy metals in the sediments bed of mangroves Khurgabrik in Jack Port involving Molar coefficient, the degree of reformed contamination, and ecological risk assessment index. Vaezi et all, (2014) have investigated Mollar environmental index, pollution load, ecological toxicity in sediments in Mosa Firth, Persian Gulf. Chai et al., (2016) explored heavy metal pollution in river sediments in Serbia by calculating the pollution load index and ecological risk assessment. Chai and et al. Sakan and Dordevic, (2015) examined the index of enrichment, molar and ecological risk assessment in Xiangjiang River sediments. In the present study, the types of sediment geochemical index have been determined. Moreover, the ecological risks have been assessed, and ecological toxicity of sediments with heavy metals, namely lead, zinc and copper have been analyzed. The results have been compared with the standards of NOAA and SQG, respectively.

2. Materials and Methods

2.1 Area of study

The Shadegan Wetland with an area of approximately 400,000 hectares in the range of coordinates 48 degrees 17 minutes and degrees 50 minutes east, 30 degrees 17 minutes 30

degrees and 58 minutes north is located in Khuzestan province, Iran, and has been recognized as an international wetland in the Ramsar Settlement in 1972. (Nasirian et al., 2015) (

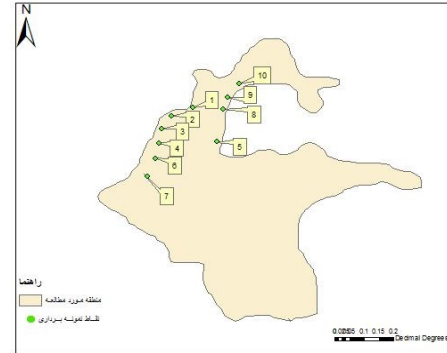


Figure 1).

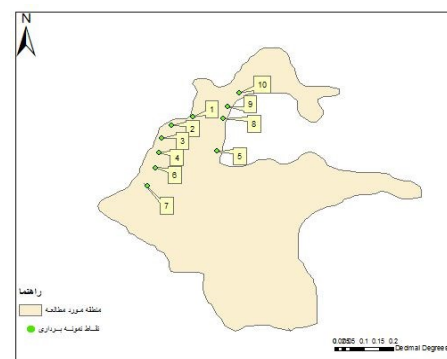
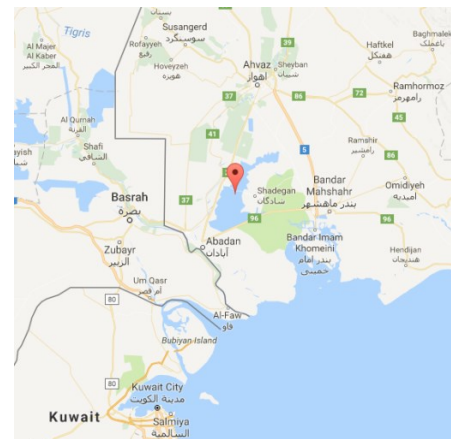


Figure 1. The location of the Shadegan wetland (left) [Source: Google map], and the locations of the sampling stations within the wetland (right).

2.2 Sampling and Preparing Samples

As per available access points, a sampling of surface sediments was carried in 10 stations with three replications and recording the geographic coordinates (

Table 1). For the purpose of preparation, the sediment samples were dried in an oven at a temperature of 105° C. Then, they were crushed in a stone mortar and screened by a 63-micron sieve. For the acid ingestion of sediments, Direct Aqua Regia was employed, following the ingestion; with the contribution of double distilled water in a 25 mL volumetric flask, the volume was delivered. (Yap et al., 2012) To ensure the accuracy of ingestion and elimination of errors due to sample preparation and to undo the effect of consumed materials on the concentration of metals in each of ingestion operations, a control sample was considered; at the end of atomic absorption ContrAA700analyticjena, the concentration of metals in the samples was read. Detection limit for Cu, Pb and Zn in flame method was 0.23, 0.88 and 0.25 microgram per gram, respectively.

Table 1. Geographical coordinates of the sampling stations within Shadegan wetland.

Land use	Geographical Coordinates		
Road & Entrance of the village	N 66.55 " 49' 30	74.1" E 48°33'	
Rural residential area	N 32.3 " 30°48'	34.25"E 48°32'	
Rural residential area	N 23.58 " 30°45'	18.57" E 48°31'	
Recreation area	N 85.48 " 30°43'	87.58"E 48°30'	
Recreation area	N 99.38 " 30°45'	83.11"E 48°35'	
Recreation area	N 12.5 " 30°42'	96.47" E 48°39'	
Place & Pleasure Pier refueling	N 87.0 " 30°41'	44.15"E 48°27'	
Agricultural area	N 16.26" 30°48'	70.36"E 48°38'	
Agricultural area with an area of low	N 16.22" 30°49'	33.24" E 48°40'	
Agricultural & Wastewater discharge	N 75.20" 30°50'	87.52"E 48°41'	

3. The Investigated Indices

Data geochemical description and choosing the sample ground play an important role in investigations. Many researchers have used the mean of cortical or frequency of data as a base. In the present study, to determine the extent of sediment contamination by heavy metals Shil Mean of Cu, Zn and Pb were 45, 95 and 20, respectively, which are presented by Turkian, and Wedephol, (1964) This index is a benchmark to measure pollution which is achieved by dividing the concentration of the elements to the same concentration of elements in the reference material (Shil average). it shows the amount of sediment contamination by heavy metals. The classification of Hakanson pollution index. (Hakanson, 1980) $C_f = M_x/M_b$ (Table 2).

Cf Value	Contamination factor level	Cd class	Degree of Contamination level
$C_f < 1$	Low	$cd < 6$	Low
$1 \leq C_f < 3$	Moderate	$6 \leq cd < 12$	Moderate
$3 \leq C_f < 6$	Considerable	$12 \leq cd < 24$	Considerable
$6 \leq C_f$	Very high	$24 \leq cd$	Very high

3.1 Cp Potential Pollution Index

Potential pollution index is obtained by dividing the maximum amount of each metal in the sediment on the average value of the same metal in the earth's surface and is calculated as follows:

$$C_p = \frac{(metal)_{sample\ Max}}{(metal)_{Background}}$$

where $C_p < 1$ indicates a low pollution, $1 \leq C_p < 3$ moderate pollution, and $3 \leq C_p$ severe pollution, Cd⁵ Pollution Degree Index. (Davault, and Rognerud, 2001)

Cf Value	Contamination factor level	Cd class	Degree of Contamination level
$C_f < 1$	Low	$cd < 6$	Low
$1 \leq C_f < 3$	Moderate	$6 \leq cd < 12$	Moderate
$3 \leq C_f < 6$	Considerable	$12 \leq cd < 24$	Considerable
$6 \leq C_f$	Very high	$24 \leq cd$	Very high

and Rognerud, 2001)

Total coefficients of pollutant contamination which are being studied show the overall degree of sediment contamination called Hakson pollution degree and is obtained from $C_d = \sum_{i=1}^n C_{f_i}$ (Table 2).

Table 2. Different contamination factor (Cf) and factor(Cd), (Hakanson, 1980)

3.2 Pollution Load Index (PLI)

Tomlinson, pollution load index, has been the n-th root pollution load factor at one station from all the elements and is determined as $I = \sqrt[n]{C_{f_1} \times \dots \times C_{f_n}}$. If $1 > PLI$, it indicates a low concentration of heavy metals and the lack of pollution; $PLI = 0$ indicates the proximity of metal concentration to the background concentration, and $PLI > 1$ indicates contaminated sediment. (Varol, 2001)

3.3 Ecological Risk Assessment Index (RI)

For assessment of ecological risk index deposits in the aquatic environment, Hakansvn, (1980) presented $RI = \sum_{i=1}^m E_r$ with $E_r = T_r * C_f$ where E_r is potential ecological risk for each element and RI

is potential ecological risk of the total metals (cumulative). Hakanson's theory, (1980), T_r , is defined as the ratio of toxicity in this equation, for Pb, Zn and Cu is 5, 1, and 5, respectively (Table 3).

Table 3. Risk index levels and their effects.

Risk index	Ecological risk criteria of environment
RI<150	Low
150≤R< 300	Moderate
300≤R<600	Considerable
600≤R	Very high

3.4 Estimation of Ecotoxicology

Diverse amounts of pollutants affect the exposed organisms in different ways. In this regard, in some countries standards for pollutants have been proposed, among which America Standard Quality Sediment NOAA and Canada Guidelines quality sediments SQGS are the best-knowns, and the most widely used ones. The primary purpose of these standards is protecting the fish from the negative impact of organic and inorganic pollutants in sediments, grading and prioritizing contaminated areas for further investigation, and estimating the location of sediment pollution. Two sets of instructions that are commonly used include: Effect Range Low (ERL), Effect Range-Median (ERM), Probable Effect Level (PEL), and Threshold Effect Level (TEL). While the effect range low (ERL or TEL) shows the concentration below which there is no possibility of harmful effects, the major impact range (ERM or PEL) refers to the higher concentrations above which harmful effects and side effects of pollutants are likely to be observed. (MacDonald et al,2000; NOAA,2009) (Table 4).

Table 4. Sediment Quality Guidelines (US and Canada) based on standard values.

Reference	Cu	Zn	Pb	Index	Standard
NOAA,2009	34	150	47	ERL	NOAA
	270	410	218	ERM	
Smith et al,1996	70.35	123	35	TEL	SQGS
	197	315	30.91	PEL	

To obtain more realistic amounts of sediment toxicity effects in living organisms, the probable effective limit coefficient (PELQ) and the average effective limit coefficient (ERMQ) are calculated according to the following equations:

$$PELQ = \frac{\sum_{i=1}^n \frac{Mi}{PELi}}{n} \quad \text{and} \quad ERMQ = \frac{\sum_{i=1}^n \frac{Mi}{ERMi}}{n}$$

Here M_i is concentrations in sediment i , PEL_i and ERM_i : The possible effective concentration and average effective concentrations in sediment i , respectively. The variable n is the number of investigated metals in each instance. Correspondingly, the factors associated with the quantity of sediments are reported in Table 5. To calculate the amount of toxicity resulting from the mixture of a group of toxic elements, SQGS is calculated as follows (ERM: mid- effective range, C_i : concentration, N : the number of elements):

$$m - ERM - Q = \sum_{i=1}^n \frac{C_i / ERM_i}{n}$$

Table 5. The relationship between sediment toxicity value of ERMQ and PELQ and chance of sediment toxicity classification based on ERM. (Hwang et al ,2008)

Sediment toxicity	ERMQ	PELQ	m-ERM-Q	Possibility of toxicity
non toxic	>0.1	>1.0	>0.1	12%
slightly toxic	0.1-0.5	0.1-1.5	0.5-0.11	30%
moderately toxic	0.5-1.5	1.5-2.3	1/5-0.51	40%
heavily toxic	<1.5	<2.3	<1/5	74%

4. Results

The results of the concentration of zinc, copper and lead in surface sediment samples of Shadegan wetland (in micrograms per gram dry weight) are shown in the Figure 2. The potential contamination index (C_p) values of Pb, Zn and Cu are 1.209, 0.483 and 0.316, respectively.

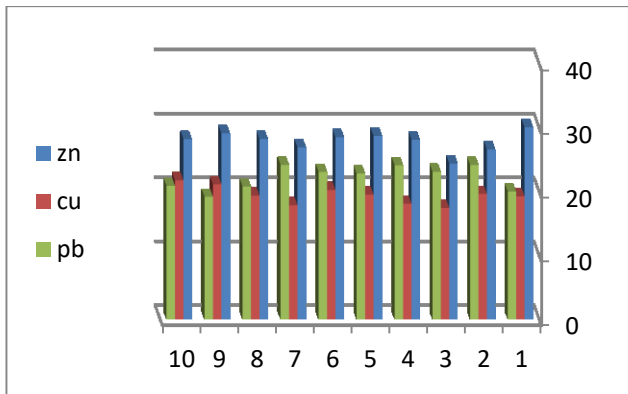


Figure 2. Average concentration of Zn, Cu and Pb in surface sediment Shadegan wetland (µg/g).

results are presented in Table 6. Ecological toxicity calculation results PELQ and ERMQ were 0.86 and 0.70, respectively, which are indicative of low toxicity and non-toxic sediments of the area in comparison to the studied elements. The results of the calculation of sediment contamination based on the of the ERM and the ERL indices are indicating that, in all the samples, concentrations of Pb, Cu and Zn are less than effective limit (<ERL). The calculated results of all the stations show that m-ERM-Q for the sediment samples exhibit 12% probability to contain toxicity probability.

In order to determine the extent of contamination in the area Cf, Cd, mCd, PLI, RI and m-ERM- Q indices were calculated. The

Table 6. The results of heavy metal pollution in sediments of the Shadegan wetland.

Cd	MCd	10	9	8	7	6	5	4	3	2	1	St.No
11.08	1.11	1.04	0.96	1.04	1.20	1.15	1.14	1.20	1.15	1.20	1.00	Pb
4.28	0.43	0.48	0.47	0.43	0.39	0.45	0.43	0.402	0.38	0.43	0.42	Cu
2.90	0.29	0.29	0.35	0.29	0.28	0.30	0.30	0.29	0.25	0.28	0.31	Zn
-	-	0.52	0.55	0.51	0.51	0.54	0.53	0.52	0.47	0.52	0.51	PLI
-	-	7.89	7.46	7.64	8.23	8.30	8.15	8.44	7.90	8.43	7.41	RI
-	-	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.07	0.08	0.08	m-ERM-Q

5. Discussion and Conclusion

Investigating the mean concentrations of heavy metals in wetland sediments indicates that Zn> Pb> Cu. The mean concentration of Zn and Cu compared to the permissible concentration of these metals in a global average is lower, and the mean of lead is higher than the average global of the Earth's crust. The cause of this can be the contamination of the sediments to these metals resulting from the discharge of industrial sewage at the sampling stations which is in line with the findings of Hatefi et al, (2016) and Mohammad Saleh et al, (2012) The Cp index results for 1<Pb<3 indicate that the average contamination in Shadegan wetland is in accordance with the results of Chandramohan studies. (Chandramohan, 2016) In this regard, Zn and Cu content is less than 1 which indicates their low pollution in the place.

As it was mentioned in the results section, the pollution index coefficient results (Cf) was less than 1 in all stations for copper and zinc. Hence, they are places in the first category with a low degree of contamination. The results of a lead pollutant index factor were those of average pollution in all stations except for the ninth station; this may be due to the practical usage of this station, which is a small agricultural area. The results are in line with the findings of Mohammad Saleh et al, (2012) and Hatefi et al,(2016) Moreover, based on the results

obtained from pollution index factor (Cd), Zn and Cu are ranked first as the two low pollution factors; the Cd factor of lead holds the second rank and has an average pollution factor, a finding which is consistent with the reports of Gholam Dokht Bandari et al,(2015) The obtained mCd index for Zn, Cu, and Pb revealed that all these metal elements are of very low pollution factors; the findings on Zn are similar to those of Zarezadeh and Rezaei,(2014) the results of Cu and Pb are in line with numbers of Gholam Dokht Bandari and Rezaie,(2015) studies. The index rate of PLI of all the stations was less than 1 which is indicative of pollution-free nature of the sediments there; this is consistent with the results found by Chandramohan et al, (2016) and Mohammad Saleh et al, (2012). The ecological risk index shows that, in all stations, the numerical results were less than 150 and that the stations exhibited low ecological risks; this was in harmony with Zarezadeh and Rezaei, (2000). Compared with the existing standards of the U.S. and Canada, the results of the present study are representative of low- or non-toxic nature of the sediments for the living organisms in all the stations with low-toxic ratios. Lastly, according to the results of the sediments assessment indices, the prominent role of the destructions of heavy metals in threatening wildlife and the involvement of both human and natural factors on the distribution and concentration of heavy

metals, as well as maintaining the balance of ecosystems, reviewing and monitoring the quality of the sediments are among the most important environmental considerations. It is paramount to identify the adverse effects of the pollutants on the environment as prerequisite for a proper management.

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