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A STUDY OF POLLUTION IN SEDIMENTS FROM ANZALI WETLAND WITH GEO-ACCUMULATION INDEX AND ECOLOGICAL RISK ASSESSMENT

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Abstract

The Anzali Wetland, is located in south west of the Caspian Sea, is one of the most important aquatic ecosystems in Iran. In recent decades much domestic and industrial untreated wastewater has been deposited in the wetland. This study was done to obtain a preliminary assessment of heavy metals contamination in the wetland sediments. Tests were done to determine levels and distribution of the heavy metals Cd, Cr, Cu, Pb, and Zn in surface sediment of the wetland. Results showed that averages of metal concentrations (in µg/g) were: Cd: 1.46±0.66; Cr: 6.12 ±0.27; Cu 18.12±4.11; Pb: 17.97± 1.69 and Zn: 78.08 ± 7.08. Contamination status was evaluated on the Geo-accumulation Index for each of these metals and ecological risk assessment was determined accordingly. The Geo-accumulation Index determined that levels of metals were not in the range indicating contamination (except for Cd that showed a level of moderate contamination), and in terms regional variation, levels of contamination were evaluated in the following order: Shyjan > Hendekhale > Siyahkeshim > Abkenar. Ecological risk assessment showed that Cd was the only metal posing a potentially high risk to the environment and contributed 77.5% of the total potential ecological risk in the Anzali Wetland.

Key words: contamination, heavy metals, Geo-accumulation Index, potential ecological risk index

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1. Introduction

Today environmental pollution is currently a major problem. Among pollutants, heavy metals cause high level contamination of aquatic systems and this is a major cause for concern as these elements are non-biodegradable and have toxic effects to the aquatic life (Elias et al., 2012; Li et al., 2017; Yi et al., 2011). In the hydrological cycle, metals are mostly stored in sediments and very little in water (Iordache et al., 2016; Vesal Nasab et al., 2012). Inorganic pollutants enter water bodies originate from various sources but occurrence of heavy metals in environments is mainly as a result of industrial activity (Mdegela et al., 2009). Today one of major causes for concern is environmental pollution from urbanization and population increasing (Alemdaroglu et al., 2003; Sadiq, 1992). Industrial emissions and urban runoff are the most common sources of contamination of water resources (Gobeil et al., 2005; Ona et al., 2006;

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Zhu et al., 2011). Contaminated sediments are known to contribute to the degradation of water quality in wetlands (Toluna et al., 2001; Venugopal et al., 2009). Heavy metals contamination of wetland sediments can cause critical degradation to an aquatic ecosystem (Charkhabi et al., 2005). The sediments of an aquatic systems are potential sources for bioavailability of contaminants like heavy metals (Sun et al., 2012).

Sediments survey is an economically viable assessment procedure for catchment management and is increasingly being employed in the early phases of environmental assessment of aquatic ecosystems (Soares et al., 1999). Assessments of heavy metals contamination in the aquatic ecosystems are focusing on analysis of sediment rather than water (Herr and Gray, 1997; Soares et al., 1999). Sediment in wetland is as sinks of heavy metals and analysis of it is an effective way to evaluate the qualification of a wetland environment (Bretscho, 1991; Gray, 1996). Priju and Narayana (2007) analyzed heavy metals on sediments of Vembanad Lake in India. In this study, industrial effluents were important source of metal enrichment in the desired ecosystem. The other study, Ghazban and Zare (2010) analyzed heavy elements of sediment of Anzali wetland and compared it with the Caspian Sea and global sediments and stated that the concentrations of heavy metals in wetland sediments are higher than them. Ecological risk assessment is a technique for identifying and addressing risks in environment. It is important tool for ranking, assessing, reducing, and managing environmental risks (USEPA, 1989, 1996). Sediment contamination is the important indicator for the prediction of ecological risks in aquatic systems instance wetlands (Cevik et al. 2009). Polluted sediments affect aquatic organisms, endangering the health of both the aquatic organisms and humans consume aquatic organisms (Varol, 2011). Thus, ecological risk assessment is a serious step in water environment management.

There are eleven major river systems entering the Anzali wetland. The Siahroud River is one of the most important external pollutant sources of Anzali wetland by entrancing high amounts of industrial, agricultural and urban pollution to it (Vesal Nasab et al., 2012). The Siahroud River passes the middle part of Rasht City, the most populated urban area in the northern part of Iran, agriculture and urban activities were the major pollutant sources. This study of the Anzali wetland was done to evaluate levels of trace elements in the sediment in order to determine an ecological risk assessment.

2. Material and methods

2.1. Study area

The Anzali wetland of Southwest Caspian Sea is a water lagoon with shallow impoundments and seasonal flooded meadows. It is important as a spawning and nursery ground for fish, and as a breeding, staging and wintering area for a wide variety of waterfowl. It was registered as a ‘Ramsar’ site in June 1975 in accordance with the Convention on Wetlands of International Importance (Taher-Shamsi and Bakhtiary, 2008). The wetland is located at the north of its watershed with the geographical location of 37º-23' to 37º-33' N and 49º-15' to 49º-38' E. The area of Anzali Wetland watershed is of 3610 km^2 (Vesal Nasab et al., 2012).

2.2. Analytical method

In this study surface sediment from twelve stations in Anzali wetland was collected using a Peterson grab sampler (three stations in every part) and were transported to the laboratory and air-dried at room temperature. Then sediment samples were powdered and passed through 160 µm sieve. The samples packed in pre-cleaned polythene bags and stored below −20°C prior to analysis. Samples were weighed placed into the digestion bombs with 1.5 mL of HNO_3 and 4.5 mL HCl and digested in a microwave digestion system. In this study used from APHA (2005) procedure for determining the concentrations of heavy metals. Then concentrations of heavy metals Cu, Pb, Cd, Zn and Cr were determined with a Shimadzu AA/680 atomic absorption spectrophotometer. Concentrations of metals were calculated on a dry weight basis and expressed as µg/g.

In this study there was used the index of Geo-accumulation, I_{geo} and index of pollution to quantify the degree of anthropogenic contamination of heavy metals in wetland sediments, this index was originally stated by Muller in 1969. Calculations are made with Eq. (1):

$$I_{geo} = \log_2 C_n / 1.5B_n \quad (1)$$

where C_n is the concentration of metal in the sediment and B_n is the geochemical background concentration or reference Factor 1.5 is used because of possible variation in background values for a given metal in an environment as well as very small anthropogenic influences.

Muller categorized I_{geo} into seven distinct classes (Buccolieri et al., 2006).

$I_{geo} \leq 0$, class 0, unpolluted; $0 < I_{geo} \leq 1$, class 1, from unpolluted to moderately polluted; $1 < I_{geo} \leq 2$, class 2, moderately polluted; $2 < I_{geo} \leq 3$, class 3, from moderately to strongly polluted; $3 < I_{geo} \leq 4$, class 4, strongly polluted; $4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted; and $I_{geo} > 5$, class 6, extremely polluted.

RI is ecological risk index of heavy metals in soil or sediment as originally proposed by Hakanson (1980). The potential ecological risk index presents a comprehensive evaluation of ecological risk to an environment from contamination by toxic metals. The calculating methods of *RI* are listed below (Eq. 2). He has defined potential risk levels of *RI* and *Er* for pollution evaluation in four categories (Table 1).

$$RI = \sum_{i=1}^{m} Er^i \tag{2}$$

$$E_r^i = T_r^i \cdot C_f^i \tag{2.1}$$

$$C_f^i = C_d^i / C_n^i \tag{2.2}$$

where E_r^i is the potential risk of an individual heavy metal; T_r^i is the toxic response factor for a given substance, and C_f^i is the contamination factor. The T_r^i values of heavy metals, that T_r^i of Cd, Cr, Cu, Pb, and Zn are 30, 2, 5, 5, and 1, respectively (Yi et al. 2011). Also C_d^i is the concentration of a metal in a sample; C_n^i is the reference value for the metal.

The background value of a compound is estimated from data presented in previous studies (Zamani, 2013). The following terms are used to describe contamination factors: $C_f^i < 1$, low contamination factor; $1 \leq C_f^i < 3$, moderate contamination factor; $3 \leq C_f^i < 6$, considerable contamination factor; and $C_f^i \geq 6$, very high contamination factor.

3. Results and discussion

Average concentrations of Cu, Cd, Pb, Cr and Zn recorded in sediment samples from the Anzali Wetland are presented in Table 2. These clearly demonstrate that higher concentrations of heavy metals were analyzed at Sheyjan. Mean concentration of metals in the area from highest to lowest were recorded in the following pattern: Zn > Cu > Pb > Cr > Cd.

Results showed that there were the highest concentration of Zn in the Abkenar and Sheyjan (83.47, 83.41µg/g). The lowest average concentration of Cd (0.84µg/g) was recorded in Abkenar. The Abkenar is a forested terrain where the level of erosion and leaching is also negligible. As mentioned earlier, no major anthropogenic sources can be detected in this part.

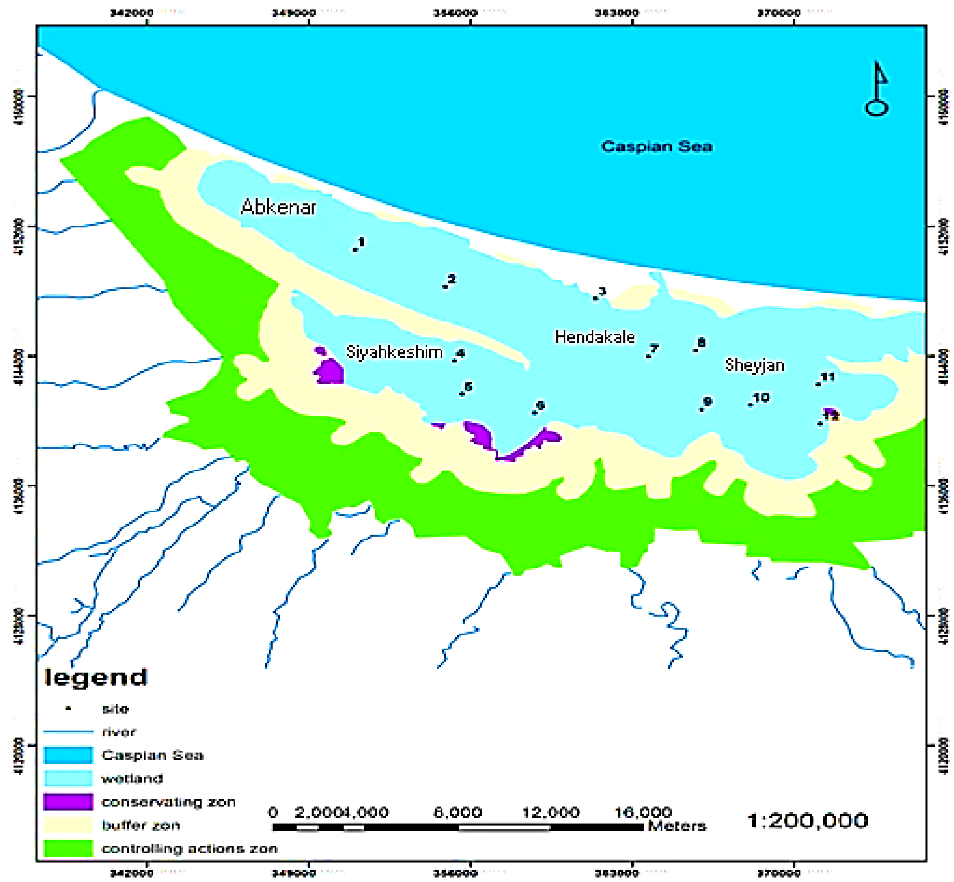

Fig. 1. The sampling sites in Anzali wetland

Table 1. Indices and Grades of potential environment

E_r^i	*Ecological risk of metals contamination*	*RI*	*Ecological risk of metals contamination*
$E_r^i < 40$	Low potential risk	RI < 150	Low risk
$40 \leq E_r^i < 80$	Moderate potential risk	150 ≤RI < 300	Moderate risk
$80 \leq E_r^i < 160$	High potential ecological risk	300≤ RI < 600	High ecological risk
$160 \leq E_r^i < 320$	Very High potential ecological risk	RI ≥ 600	Very High ecological risk

The lowest average concentration of metals (except Zn) was recorded at the station of Abkenar and the highest level of concentrations was recorded in Sheyjan. In this survey the sediments of Sheyjan is the most polluted of the investigated area, where extremely runoff and urban sewage are discharged (Fig. 2.). The Provincial Sediment Quality Guidelines and New York Sediment Criteria for metals divide ISQG-Low level of concentrations according to low range effect and ISQG-High level of concentrations high range effect. ISQG-Low level indicates that a sediment contaminant does not have an adverse effect on aquatic organisms in the sediment. ISQG-High level indicates that a contaminant certainly does have an adverse effect on organisms. Also, levels of sediment contamination between ISOG-Low and ISQG-High show that contaminants have probably had adverse effects. According to this comparison, levels of Zn, Pb and Cr were below the ISQG-Low level and concentrations of Cd, and Cu exceeded ISQG-Low levels that place the level of contamination between ISOG-Low and ISQG-High (Table 3).

The degree of pollution in a sediment sample can be assessed by determination of indices such as the Geo-accumulation Index I_{geo}. Evaluations of the I_{geo} index for heavy metal concentrations in sediment ranged from -5.66 to 2.39. Based on the Muller Scale, the sediment samples taken from all sampling stations were partially determined at the unpolluted rate for Cr (-5.66/-04.07) and Pb (-1.36/-0.79), Cu (-2.25/-1.56), Zn (-1.06/-0.78) all areas determined Cd (0.26/2.39) levels at moderately to strongly polluted rates in Sheyjan and moderately polluted rates for other areas (Fig. 3).

Table 2. Concentrations of heavy metals (μg/g) in Anzali wetland sediments

Site	*Stations*	*Cr*	*Pb*	*Cd*	*Zn*	*Cu*
Abkenar	1	3.80	13.24	0.77	76.87	16.98
	2	3.84	13.35	0.81	78.22	18.26
	3	3.83	13.18	0.75	77.46	17.75
	4	3.48	6.86	0.91	89.87	10.68
	5	3.65	6.98	0.94	90.12	11.01
	6	3.52	6.78	0.88	88.46	10.75
	mean±SD	3.68±0.16	10.06±3.49	0.84±0.07	83.47±6.59	14.23±3.77
	Min	3.48	6.78	0.77	76.87	10.68
	Max	3.84	13.35	0.94	90.12	18.26
Siyahkeshim	1	7.10	14.15	1.31	75.78	19.24
	2	7.11	14.10	1.43	75.95	19.71
	3	7.14	14.12	1.33	75.69	19.45
	4	6.73	10.65	0.81	77.85	11.65
	5	6.76	10.83	0.83	78.26	12.31
	6	6.64	10.46	0.83	77.48	11.88
	mean±SD	6.91±0.22	12.38±1.90	1.08±0.29	76.83±1.15	15.08±4.12
	Min	6.64	10.46	0.81	75.69	11.88
	Max	7.14	14.15	1.43	78.26	19.71
Hendekhale	1	5.10	15.25	1.84	67.62	22.92
	2	5.14	15.32	1.88	68.1	23.06
	3	4.95	15.20	1.79	67.25	22.65
	4	4.79	8.65	1.34	69.48	15.22
	5	4.84	8.82	1.38	70.18	15.42
	6	4.75	8.59	1.25	68.65	14.96
	mean±SD	4.92±0.16	11.05±3.59	1.58±0.28	68.51±1.12	19.03±4.20
	Min	4.75	8.59	1.25	67.25	14.95
	Max	5.10	15.32	1.88	70.18	23.06
Sheyjan	1	9.22	15.93	1.84	86.62	24.91
	2	9.28	15.95	1.88	86.68	24.93
	3	9.24	15.90	1.86	86.53	24.86
	4	8.97	12.50	2.84	79.98	22.24
	5	9.04	12.63	2.88	80.45	22.38
	6	8.94	12.21	2.79	80.24	21.98
	mean±SD	9.11±0.14	14.18±1.38	2.35±0.53	83.41±3.50	23.55±1.48
	Min	8.94	12.21	1.84	79.98	21.98
	Max	9.28	15.95	2.79	86.68	24.93
Wetland	Mean	6.12	12.14	1.46	78.08	17.97

Table 3. Concentrations of heavy metals obtained in this study with sediment quality guidelines (μg/g)

Cr	***Cd***	***Cu***	***Pb***	***Zn***	***Subjects***
6.12	1.46	18.12	17.97	78.08	***Present study***
26	0.6	16	32	120	***New York sediment criteria lowest effects range***
110	9	110	110	270	***sever effects range***
26	0.6	16	31	120	***Sediment quality criteria lowest effects range (ISQG-low)***
110	10	110	250	220	***high effects range (ISQG-high)***

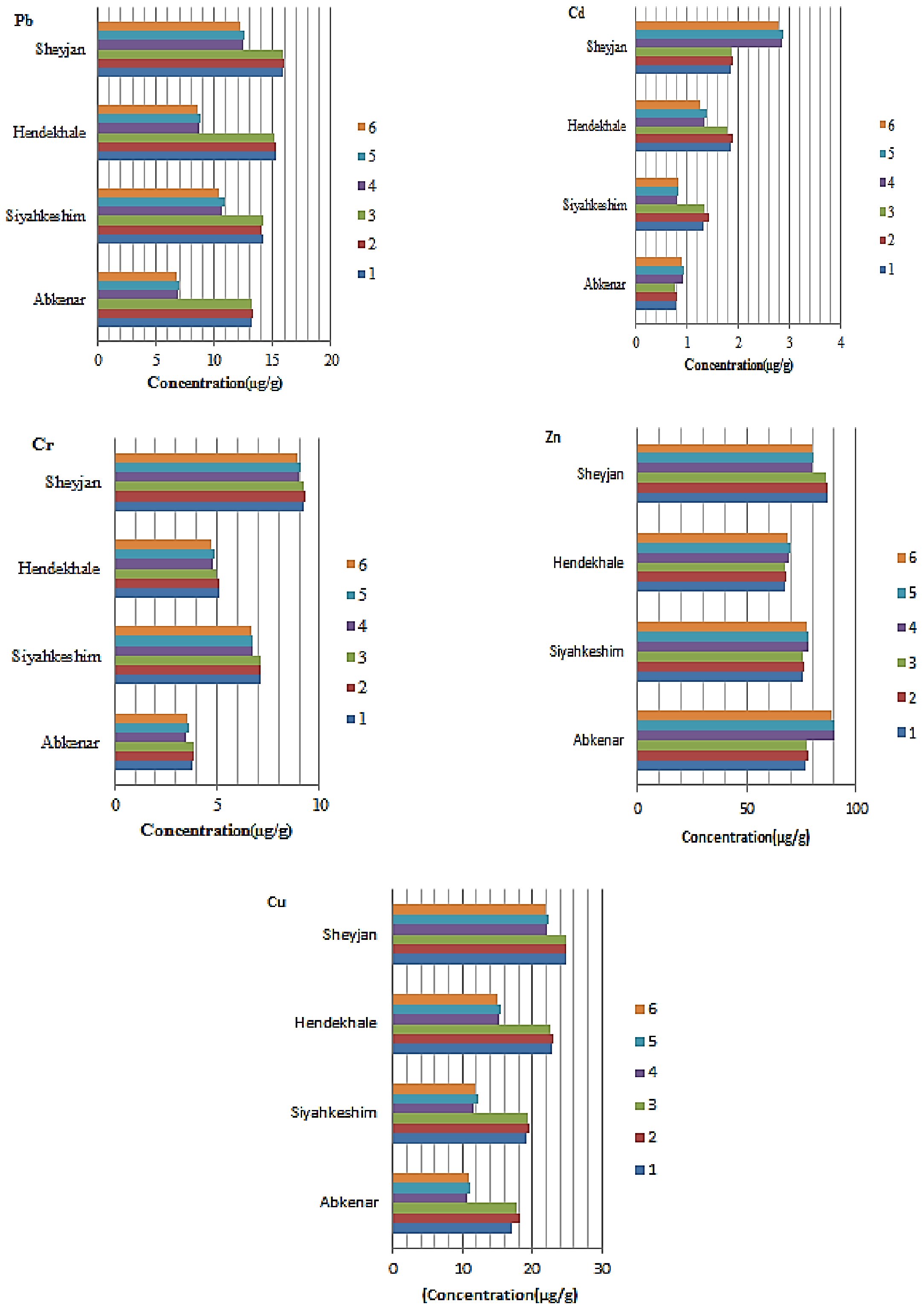

Fig. 2. Spatial variation of sediment concentration metals in sampling stations along the Anzali wetland

The I_{geo} values for all metals (except Cd) at all the sampling sites were negative. The values for Cd in the sediments exhibited class 2 moderately polluted in Hendekale, Siyahkeshim and Abkenar, Cd evaluation in the Sheyjan area was determined as class 3, which determines a pollution level of moderate to strong. Results shown in Fig. 3 demonstrate that all sampled areas may face the probability of trace Cd metal contamination. A small percentage of the samples are included in classes 2 and 3. The maximum value was recorded for Cd Sheyjan. This index determines that in general terms, the Anzali wetland is ranked in the range of moderately polluted to strongly pollute in terms of Cd. The Industrial activities, plastic and batteries may be the main sources of this metal.

Risk index analysis ranked stations according levels of ecological risk to biological communities in the Anzali Wetland. It was found that the risk indices of heavy metals were ranked in the order shown in Table 3.

Contamination factor (s) for sediment samples were compared in terms of levels of individual metals with respective background concentrations, and evaluations showed moderate contamination of sediment samples with Zn at Abkenar and Siyahkeshim, Cd at Siyahkeshim and Hendekhale and considerable contamination of sediments with Pb was recorded at Siyahkeshim and Hendekhale and Cd at Sheyjan. Values for C^i_f were between low and moderate for Cu and Cr recorded in all areas. In this study, average monomial risk factors were ranked in the following order Cd(49.70)> Pb(12.85)> Cu(3.32)> Zn(1.08)> Cr(0.06). The maximum ecological risk of Cd in the study area was 53.40. Also, levels of other metals were below 40, indicating that these metals posed low-level risk to the environment.

Finally, RI was calculated as the sum of the risk factors (Table 4), it shows that Cd contributed most the total ecological risk in Anzali Wetland in the all stations that this result matches the I_{geo} result in this study but not for all of the elements. Furthermore, Zn accumulations were higher than those of Cu and Pb but its ecological risk was lower due to its having low level toxicity. Thus the I_{geo} method is mostly applicable to accumulation levels of individual metals without regard to the factor of toxicity.

Regarding the E^r_i value, there is low level risk for most elements in sediment samples of the Anzali Wetland, Cd exhibited a moderate level of risk for the sediment in Shyjan (70.50) and in Hendekhale (47.4), and this does indicate that Cd in general terms is a relatively harmful environmental contaminant. The Ecological Risk Index could be used to describe both ecological risk caused by a single pollutant and an overall risk or contamination factor for a variety of pollutants (Hakanson, 1980). The contribution of heavy metals to overall ecological risk was demonstrated in Fig. 4.

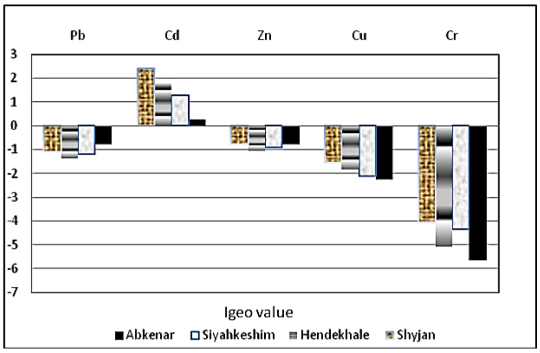

Fig. 3. I_{geo} value for Anzali wetland sediment

Table 4. Potential risk of heavy metals of Anzali Wetland sediments

RI value	R_i	E^r_i					C^i_f					***Station***
		Pb	**Cd**	**Zn**	**Cu**	**Cr**	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	
Low	22.41	1.90	16.80	1.17	2.50	0.04	0.38	0.56	1.71	0.50	0.02	**Abkenar**
Low	61.25	2.45	53.40	1.23	4.10	0.08	0.49	1.78	1.23	0.82	0.04	**Siyahkeshim**
Low	108.05	24.90	78.90	0.96	3.25	0.04	4.98	2.63	0.96	0.65	0.02	**Hendekhale**
Low	127.16	22.15	100.50	0.97	3.45	0.10	4.43	3.35	0.97	0.69	0.05	**Shyjan**
Low	79.72	12.85	49.70	1.08	3.32	0.06	2.57	2.08	1.21	0.66	0.03	**Average value**
	22.41	1.9	53.40	0.96	2.5	0.04	0.38	0.56	0.96	0.5	0.02	**Min**
	127.16	24.9	78.9	1.23	4.1	0.1	4.98	3.35	1.71	0.82	0.05	**Max**

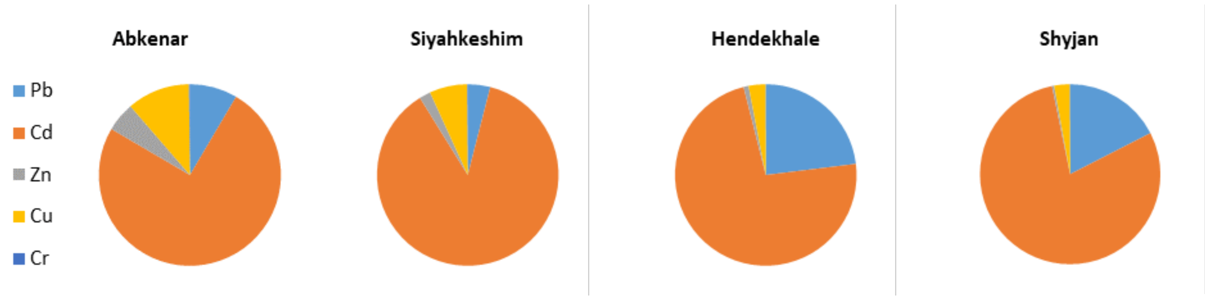

Fig. 4. Contribution of different heavy metals to ecological risk in different parts of Anzali wetland

Risk index values are categorized in the following order; Sheyjan (127.16)> Hendekhale (108.05) > Siyahkeshim (61.25) > Abkenar (22.41). All of the stations showed low-level risk to the local ecosystem. The evaluation of ecological risk from heavy metals contamination was evaluated as low. The ecological risk to regions such as Sheyjan and Hendekhale was evaluated as higher than that of other parts, therefore these areas should be under constant control of the inflow of pollutants, especially discharge of various pollutants to goharroud and zargoub rivers in Rasht city that After connecting, they enter the eastern part of the lagoon with the name of Siahroud river.

4. Conclusions

In this study, the main objective was to evaluate the contamination of heavy metals (Cr, Cd, Zn, Cu and Pb) in sediments of Anzali wetland. The metals were analyzed by total elemental analysis in the sediments of different parts of the lagoon.

Contamination assessment according to evaluation on the Geoaccumulation Index showed that levels of metals in samples were evaluated as uncontaminated (expect Cd that had moderate contamination), and levels of contamination in the different areas were in the following order: Sheyjan > Hendekhale > Siyahkeshim > Abkenar. The results of ecological risk assessment showed that Cd was the only metal posing a high potential ecological risk to the environment in Sheyjan site. The studied showed pollution sources there were more in the eastern part of wetland.

One of the factors is self-purification effect of wetland to reduce the amount of heavy metals that able to avoid causing environmental pollution of wetlands and wetland purification filter; however, their power is limited. Anzali wetland acted as a sediment trap, it prevents the pollutants entering to the Caspian Sea. Lack of proper management of the activities of the inhabitants of Anzali wetland watershed (in drainage of industrial waste to rivers leading to the lagoon, the increasing erosion of agricultural pollutants of the pond) have been made in metals to Anzali wetland especially on the east side.

The main act is to prevent the discharge of wastewater to rivers entering instants Pirbazar, Siyahroud Rivers. Since the pollution of metals isn't clear in Anzali wetland but due to importance of ecological value of this wetland there is need for persistent monitoring of pollution levels and studying risk of them to aquatic ecological system.

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