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Contamination and ecological risk assessment of trace elements in sediments of the Anzali Wetland, Northern Iran

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ABSTRACT

In this paper, concentrations of some heavy metals in surficial sediments of the International Anzali Wetland were measured, this wetland is located in the northern part of Iran. Sediment pollution levels were examined and analyzed using reliable pollution indices including Pollution Load Index (PLI), Geoaccumulation Index (Igeo) and Enrichment Factor (CF), and finally it was revealed that heavy metal pollution ranged from low to moderate loads in the wetland. According to Sediment Quality Guidelines (SQGs) and Ecological Risk Index (ERI), it was concluded that As and Ni may have significant toxic impacts on aquatic organisms and also according to Effect Range Median (ERM), the toxicity probability of sediments in the Anzali wetland was estimated at 21%.

Key words: International Anzali Wetland, pollution level indices, risk assessment, sediment quality guidelines

HIGHLIGHTS

- Metal pollutions in aquatic ecosystems have raised worries worldwide.
- Anzali Wetland is one of the most important aquatic ecosystems in Iran and is threatened by different kinds of contaminants such as metals.
- Sediment pollution analysis is one of the proper approaches to investigate metal in the aquatic environments.
- Ecological risk assessment with this method has been done for the first time in Anzali.

1. INTRODUCTION

Extensive use of heavy metals in small- and large-scale industries, mines, and agricultural sectors has caused remarkable levels of heavy metal pollution in aquatic ecosystems (Gao & Chen 2012; Zare Khosheghbal *et al.* 2020). Existence, abundance and toxicity of heavy metal contaminants in the aquatic ecosystems raised concerns worldwide. Heavy metals can accumulate in the tissues of living organisms in the aquatic ecosystems and then enter the human food chains, imposing health risks on humans (Varol 2011; Esmaeilzadeh *et al.* 2016, 2019; Mohammadi *et al.* 2020). In the aquatic ecosystems, most of the contaminants, particularly heavy metals, can be easily absorbed by suspended particles. Some of these suspended particles would settle and stabilize on the sediments and bond with organic and inorganic materials due to the low solubility of heavy metals, and then be stored in the sediments (Devesa-Rey *et al.* 2010). This process is vital in controlling heavy metal concentrations in the aquatic ecosystems, then the sediments would be proper indicators in the pollution monitoring program for Environmental Risk Assessment and Management; therefore, sediment sample analysis is a suitable method to determine the heavy metal pollution in each aquatic ecosystem (Karbassi *et al.* 2008; Varol 2011). Different geochemical analyses and indicators are used to examine the sediment pollution loads. The use of geochemical indicators alone cannot provide a picture of contamination in an aquatic ecosystem due to biological activities and changes in physicochemical conditions that lead to release of metals from sediments and upstream watersheds. Therefore, it is necessary to examine the impacts of heavy metals on the aquatic organisms. In this paper, accurate and optimal monitoring methods to determine the severity of heavy metal pollution in the sediments are presented, using two groups of the geochemical index (Igeo) and Ecological Risk Index (ERI). The Anzali wetland has been considered an unparalleled and outstanding aquatic ecosystem in Iran but it has been threatened by various natural and human-induced stresses for a while. Urbanization and population growth, agricultural, industrial and tourism activities are the principal causes of heavy metals released directly or indirectly into the rivers and finally flow into the wetland (Jamshidi Zanjani & Saeedi 2013; Berenjkar *et al.* 2019). This research aimed at interpreting data obtained from sediment sampling, measurement of heavy metal contents and analysis of pollution levels in the wetland to explore the water quality in this site. For this purpose, the following steps have been done:

- Determination of heavy metals (As, Cr, Cu, Co, Mn, Ni, V, Cd, Zn, Fe, Pb) for analysis in the surface sediments of the Anzali wetland.
- Measurement of the heavy metals using reliable methods.
- Ecological Risk Assessment of the heavy metals using relevant indices and comparing them with the Sediment Quality Guideline (SQG).

2. METHODOLOGY

2.1. The study area

The Anzali wetland, with an approximate area of 193 square kilometers, is located in the northern part of Iran, Gilan province. The wetland is situated in the latitude of 37° 22′ to 37° 32′ and longitude of 49° 15′ to 49° 36′. The watershed area of the wetland is about 361,000 ha. Anzali wetland is the most important and largest freshwater wetland in the south coastal area of the Caspian Sea (JAICA 2004). The wetland is fed by 10 main inlet rivers with an average flow rate of 76 m^3/s. In terms of water inlets, the wetland can be divided into 4 parts including the west part; Abkenar, the east part; Shijan, the central part; Hende Khaleh, and the last one is the southwest part; the environmental protected area of Siahkesheem (Jamshidi-Zanjani & Saeedi 2013; Berenjkar *et al.* 2019). The wetland has been a habitat for various rare and valuable species of fish, fauna, and flora, also as a habitat for migratory birds during the overwintering period. The Anzali wetland has been listed as a Ramsar site since 1975 (Vesali Naseh *et al.* 2012; Zamani Hargalani *et al.* 2014).

2.2. Sampling and chemical analysis

Surface sediment sampling was conducted using the Peterson Sampler at seven stations in the wetland. The geographical locations of sampling stations are shown in Figure 1.

The sediment samples were stored in polyethylene bags and placed in iceboxes, then transported to the laboratory. To measure the heavy metal contents in the sediments, the samples were air-dried and sieved from mesh size 230 (that amounts to 63 μ). Afterward, the samples were powdered. The sediment samples were entirely analyzed using HNO3/HCl/H2O2 (EPA 1996). Heavy metals in the solutions were analyzed using Inductively Coupled Plasma (ICP varian735-OES radial). Data accuracy was controlled through double digestion and re-measurement. Blank samples were prepared and analyzed to reduce laboratory errors.

2.3. Sediment pollution analysis

In the recent decades, in order to analyze heavy metal contents in sediments and ecological risk assessment, various geochemical indices have been developed (Yang *et al.* 2012). The indices differ in terms of reference baselines. Many researchers have applied the average shale values or the average crustal abundance data as the baseline. However, many researchers believe that the best alternative for baseline reference is unpolluted sediments in the study area (Sakan *et al.* 2009; Varol 2011). In this research, for pollution level analysis in the sediments, reliable indices were used and elaborated more in the following.

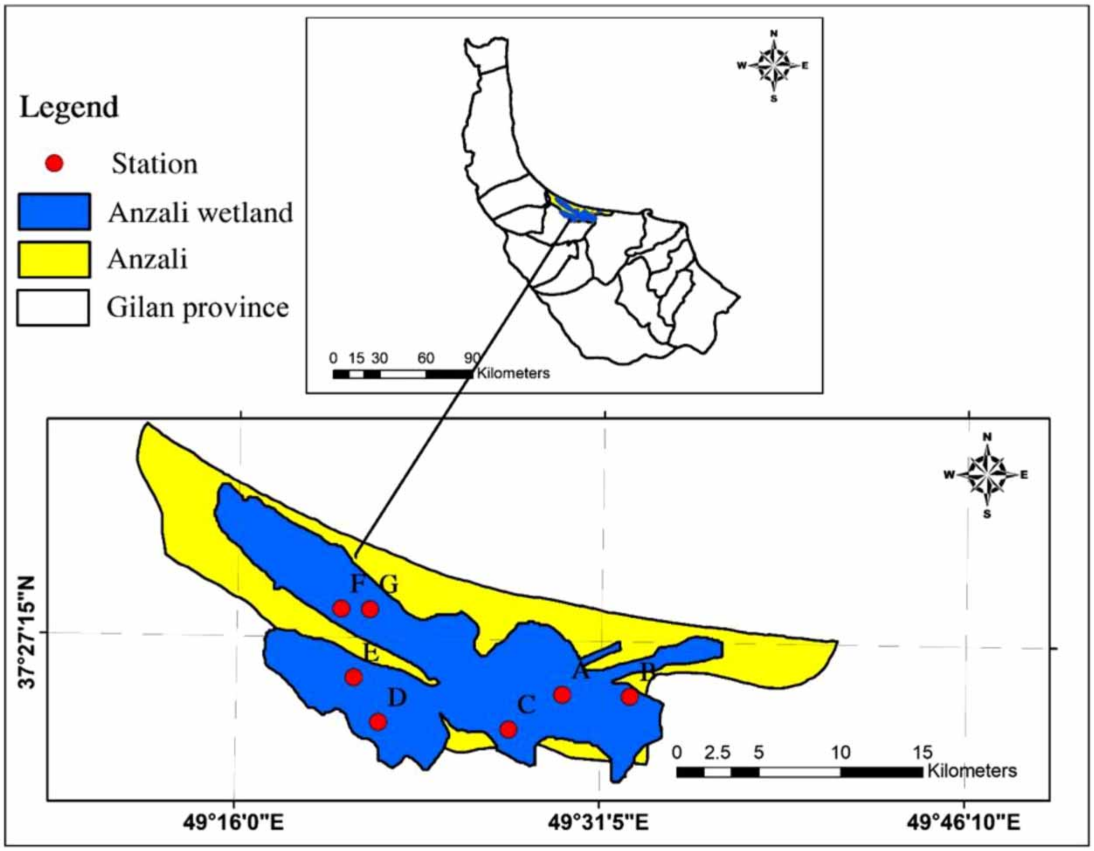

Figure 1 | Geographical locations of the sampling stations in the Anzali wetland.

2.3.1. Contamination factor index

For the first time, the Contamination Factor (CF) index was developed and introduced by Hakanson in 1980 (Hakanson 1980; Varol 2011). CF is calculated by the following formula:

$$\mathrm{CF} = \frac{C\ heavy\ metal}{C\ background}$$

CF is the ratio of the heavy metal concentration in the sediment samples to the background values for that metal (the metal concentration in uncontaminated sediments). Where CF < 1 indicates low pollution level, 1 > CF > 3 is a depiction of moderate pollution, 3 > CF > 6 is considerable pollution and CF < 6 is an indication of very high pollution.

2.3.2. Pollution load index

Pollution Load Index (PLI) is an empirical index that predicts the relative level of metal pollution in the area concerning all of the metals investigated in that area (Tomlinson *et al.* 1980; Banerjee & Gupta 2012). PLI is calculated using the following formula, where CF stands for the contamination factor and n is the total number of the heavy metals examined.

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots..CFn)^{\mathbf{1/n}}$$

PLI < 1 indicates that there is no pollution in the area, 1 > PLI < 2 is indication of moderate pollution, 2 > PLI < 3 is a high level of pollution and PLI > 3 shows that pollution is at the highest level.

2.3.3. Muller Geo-accumulation Index (I_{geo})

The Muller geo-accumulation index (Igeo) is obtained using the following equation (Müller 1981);

$$Igeo = \log 2\left[\frac{\text{Cn}}{\text{Bn} \times 1.5}\right]$$

C_n is the measured concentrations of the heavy metal in the sediment samples, and B_n is the background content of that heavy metal in the shale, and 1.5 is the correction factor that has been considered in the formula due to the lithospheric effect. This index applies metal concentrations in shale as a baseline reference for comparison. I_{geo} is divided into six classes (Bhuiyan *et al.* 2010):

$0 < \text{Igeo} < 1$: unpolluted to moderately polluted, $1 < I_{geo} < 2$: moderately polluted, $2 < I_{geo} < 3$: moderately to strongly polluted, $3 < I_{geo} < 4$: strongly polluted, $4 < I_{geo} < 5$; strongly to extremely polluted, and $5 < I_{geo}$: extremely polluted.

2.3.4. Enrichment factor

Enrichment Factor (EF) is an appropriate parameter for determining heavy metal pollution resulting from anthropogenic activities. This factor is calculated through the following formula (Sakan *et al.* 2009);

$$EF = \frac{(\text{cn}/\text{Fe})\text{Sample}}{(\text{cn}/\text{Fe})\text{Background}}$$

where EF stands for Enrichment Factor, *(Cn/Fe) sample* is the ratio of each element concentration in the sample to Fe concentration in the sediment, and *(Cn/Fe) background* is the element concentration relative to Fe concentration, both in the Earth's crust. In this study, Fe was used for geochemical normalization because iron is associated with fine solid particles in the sediments, the other reason is that it has similar geochemical properties to many trace elements, and the last reason is that its natural concentration is uniform (Varol 2011).

The EF values are categorized according to the following classes (Sakan *et al.* 2009);

$EF < 1$: without enrichment, 1–3: low enrichment, 3–5: moderate enrichment, 5–10: considerable enrichment, 10–25: high enrichment, 25–50: very high enrichment, and $EF < 50$: extreme enrichment.

2.3.5. Sediment quality guidelines

SQGs prove useful for predicting the adverse biological impacts of heavy metals on organisms in or near the contaminated sediments (Long *et al.* 1995). These guidelines provide indicators and different effect ranges that are obtained from toxicity analysis, biological and chemical information from laboratory analysis and field investigations. The Effect Ranges in the SQGs include Effect Range Low (ERL) and Effect Range Median (ERM), which are presented by Wildlife Affairs and Marine Resources Affairs in EPA. ERL value is a concentration in which and lower ones, negative biological impacts are rarely observed and when concentrations exceed the ERM values, the adverse biological effects will increase. Two ranges of effects named Threshold Effects Level (TEL), and Probable Effects Levels (PEL) are provided in the Canadian Sediment Quality Guideline for protecting aquatic life and freshwaters. TEL is a threshold level, with lower values, rarely adverse impacts excepted on the organisms in the sediments and PEL is the probable level and more than that in which the probability of adverse impacts will increase. The effect levels and ranges by each element are shown in Table 1.

2.3.6. Mean ERM quotient index

In the nature, all heavy metals are always found as compounds and in complex with other metals. The mean ERM quotient (m-ERM-q) parameter determines the probability of biological effects regarding the caused by toxicity of combined toxicant groups in sediments.

$$\text{m} - \text{ERM} - \text{q} = \sum\left(\frac{Cx}{ERMx}\right)/n$$

where, C_X is the given concentration of a metal in a sediment sample, ERM stands for Effect Range Median that is defined in the SQG for each metal, and n is the total number of metals that are examined. Based on many previous studies regarding

Table 1 | Effect levels and ranges in SQG

Element	ERL	ERM	TEL	PEL
Cu	34	270	18.7	108
Zn	150	410	124	271
Cr	81	370	52.3	160
Pb	46.7	218	30.2	112
Ni	20.9	51.6	15.9	42.8
Cd	1.2	9.6	0.68	4.21
As	8.2	70	7.24	41.6

chemicals and their toxicity data obtained from more than 1,000 sediment samples in the estuaries of America, the following classification of toxicity probability has been developed;

In m-ERM-q < 0.1, 9% probability, in 0.11 < m-ERM-q < 0.5, 21% probability, in 0.51 < m-ERM-q < 1.549% probability, in m-ERM-q > 1.5, 76% probability (Long *et al.* 2009; Gao & Chen 2012).

2.3.7. Potential ecological risk (PER) index

In this study, the Potential Ecological Risk Index (PER) that was first introduced and developed by Hakanson has been used, which was first introduced by Hakanson (Hakanson 1980). This comprehensive method considers the composition level of toxicity, concentration, and ecological sensitivity of heavy metals (Jiang *et al.* 2014):

PER is calculated by the following formula:

$$C_f = Ci/C_0$$

$$E_i = T_i \times C_f$$

$$PER = \sum_{i=1}^{n} Ei$$

where C_i is the metal content in the sediment and C_0 is the background values. In this study, we used the background metal concentrations in the sediments sampled from the Anzali wetland, which were 3.9, 2.1, 140.2, 35.1, 135.5, 33.3, 104.4 ppm, for As, Cd, Cr, Cu, Ni, Pb, and Zn, respectively (Hargalani *et al.* 2014; Jamshidi & Darvish Bastami 2016). C_f is the contamination factor, T_i is the toxic-response factor for a given substance that accounts for the toxic requirement, and the sensitivity requirement ($C_d = 30$, $A_s = 10$, $C_u = P_b = 5$, $Cr = 2$ and $Zn = 1$), E_i is the monomial potential ecological risk factor, and PER is calculated through the sum of potential ecological risk factors of the heavy metals in the sediments. The scales of PER and E_i are given in Table 2 (Jiang *et al.* 2014). PER is the all-inclusive potential ecological index; that is, the sum of E_is. It outlines the sensitivity of the biological community to the toxic substances and demonstrates the potential environmental risk induced by the overall pollution.

Table 2 | Potential ecological risk value and criteria

E_i	Ecological risk criteria for heavy metal	PER	Ecological risk criteria of environment
E_i <30	Low risk	PER < 100	Low risk
30 < E_i <50	Moderate risk	100 < PER < 150	Moderate risk
50 < E_i < 100	Considerable risk	150 < PER < 200	Considerable risk
100 < E_i < 150	Very high risk	200 < PER < 300	Very high risk
E_i >150	Disastrous risk	PER >300	Disastrous risk

3. RESULTS AND DISCUSSION

3.1. Total concentrations of heavy metals in the Anzali Wetland

The concentrations of various elements in the sediments sampled from the Anzali Wetland, average crustal abundance, global average concentrations, and average shale values are presented in Table 3. In Hende Khaleh, station C, high concentrations of various metals like As, Cu, Ni, Pb, Zn, V, and Cr were found. This location is polluted by oil and vessels coated by Cu- and Cr-based paints. Furthermore, a substantial volume of urban wastewater from Anzali city might be responsible for the high concentrations of the mentioned metals in this area. Cu, in the sediments sampled from station F, situated in the Abkenar area, was found at high concentration of 62 ppm, which may be due to the vicinity of a landfill (Zare Khosheghbal *et al.* 2013). The highest concentrations of heavy metals, almost for all of the examined metals, were found in the eastern part of the wetland, stations B and A. This part of the wetland is extremely influenced by wastewater released from Rash city, especially raw wastewater, and also its main rivers, receiving a large volume of wastewater flow into this part of the wetland (Ayati 2003; JICA 2004). In general, the lowest concentrations of metals in the sediment samples were observed in the Siahkesheem, environmental protected area (stations D and E), where there are no main sources of pollution. This area is located in the southwestern part of the Anzali wetland, which is designated an environmental protected area under management of DoE and all human activities are prohibited in this area. This issue may be one of the main reasons for the low metal concentrations in the mentioned area. In all of the stations, the average of metal contents except for V and Fe were more than global average concentrations and average shale values. Comparisons between the amounts of these elements in the samples and average crustal abundance and their global average concentrations indicate that anthropogenic pollution has led to the sediments being contaminated with heavy metals in the study area.

3.2. Pollution load index in sediment analysis

The measured indices of CF and PLI are provided in Table 4. The most CF values of CF were observed in the eastern and central parts of the wetland, in at stations A, B, and C stations. And the lowest values were found in the southwestern part of the wetland, stations D and E in the Siahkesheem Siah Keshim area. In all of the stations, contamination factors for of metals, including Co, Cr, Cu, Mn, and Zn, were measured at the level of $1 > CF > 3$, which reflects moderate pollution in the area. The most value of CF was related to As, at the level of 2.55. Based on several previous types of researches, using fertilizers and fungicides in rice farms and agricultural lands is the main origin of many heavy metals, especially, As in the Anzali Wetland (Zare Khosheghbal *et al.* 2013). In At stations D and E, the Siahkesheem Siah Keshim Aarea, the CFs of As and Pb were lower than 1, which showsexplained low pollution in that area, whereas based on this index in at the other stations, pollution of As and Pb were estimated at a moderate level. According to the CF index, V has a low pollution level in at all of the the stations (other than stations A and C), while Ni (except for station D) and Cd (except for stations D

Table 3 | The measured concentrations of heavy metals in the sediment sampled from the Anzali wetland

Station	As	Cd	Cr	Cu	Zn	V	Ni	Pb	Mn	Fe %
A	27	0.45	140	59	139	131	103	28	1,240	4.1
B	33	0.48	128	58	130	125	107	31	1,180	4.5
C	23	0.52	131	48	123	132	101	27	1,860	4.3
D	12	0.29	101	51	106	110	66	18	1,123	4.1
E	11	0.33	97	49	104	107	72	18	1,000	4.2
F	18	0.27	121	62	120	123	80	24	1,263	4.6
G	15	0.33	107	55	116	124	93	20	1,230	4.5
Minimum	11	0.27	97	48	104	107	66	18	1,000	4.1
Maximum	33	0.52	140	62	139	132	107	31	1,860	4.6
Mean	20	0.38	118	55	120	122	89	24	1,270	4.3
Average crustal abundance	5	0.2	100	50	75	130	80	14	950	4.1
Global average	–	–	70	33	95	130	52	19	–	4.1
Average shale values	13	0.3	90	45	95	130	68	20	850	4.7

Table 4 | The CF and PLI values of the sediments from the sampling stations in the Anzali wetland

	Contamination Factor (CF)									
Station	**As**	**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**PLI**
A	2.08	1.50	1.55	1.30	1.45	1.51	1.41	1	1.46	1.42
B	2.55	1.60	1.42	1.28	1.28	1.57	1.55	0.96	1.36	1.45
C	1.78	1.73	1.45	1.07	2.18	1.48	1.35	1.01	1.29	1.42
D	0.95	0.96	1.12	1.14	1.32	0.96	0.88	0.84	1.12	1.02
E	0.81	1.10	1.07	1.09	1.17	1.05	0.91	0.82	1.09	1.03
F	1.35	0.90	1.34	1.38	1.48	1.18	1.18	0.95	1.26	1.19
G	1.16	1.10	1.18	1.22	1.44	1.36	1	0.95	1.22	1.17
Mean	1.25	0.93	1.30	1.47	1.21	1.30	1.16	1.27	1.29	1.24
Minimum	0.81	0.90	1.07	1.07	1.17	0.96	0.88	0.82	1.09	1.02
Maximum	2.55	1.73	1.55	1.38	2.18	1.57	1.55	1.01	1.46	1.45

and F) have moderate pollution in all of the the stations.The trend of average CF of different metals was as B > C > A > F > G > D > E. As tabulated in Table 4, the pollution load indices ranged from 1.02 to 1.45. At all of the stations, PLIs were measured at the range of $1 < PLI < 2$, according to the average PLI that amounts to 1.24 in the wetland, pollution level was moderate. PLI indices in the Anzali wetland followed the trend of B > A = C > F > G > E > D.

Table 5 demonstrates the I_{geo} and EF values for the examined heavy metals in the sediment samples. Obtained I_{geo} values for each element at all of the stations were at the range of $0 < I_{geo} < 1$, that means based on the I_{geo}, the stations and study area were not polluted with heavy metals, and categorized unpolluted. Among all 10 examined heavy metals, the most values of I_{geo} were related to As, Cd, Cr, and Ni from stations B, C, A, and B, respectively. Overall, the I_{geo} values at different stations followed the trend of B > A > C > D = E = F = G.

Some researchers maintain that the EF index ranged from 0.05 to 1.5, indicates that heavy metals in sediments are originated entirely from the earth's crust or their presence in the sediments is due to natural processes, whereas the EF index greater than 1.5 indicates the presence of an anthropogenic source of heavy metals in the nature (Zhang & Jinglu 2013).

Based on the EF index, the sediments are polluted with As more than all of the other examined heavy metals in the Anzali wetland, and it was measured at 3.48. This value of As was true for all of the stations except for station G, Cd at all of the stations except for station F, Mn at station C, Zn at stations A, B, and C, and Pb at stations A, B, C, and F exceeded 1.5.

These results indicated that anthropogenic activities in the region have led to an increase in metal concentrations in these stations.

The most levels of EF were in the two stations A and B. It should be noted that the polluted Pirbazar river flows into these parts of the wetland. This river receives industrial wastewater and agricultural drainage from the watershed and can be one of the main causes for the high pollution in that area.

Based on the classification of this index, Mn, Zn, Pb, and Cd were in the range of $1 < EF < 3$ in all of the stations, which means these elements accumulated in low amounts. All of the alternative metals were at the level of unpolluted or low pollution levels in all of the stations. The average EF index for all of the metals in the examined stations followed the trend of A > B > C > F > D > E > G.

Comparison of the metal pollution indices in the sediments of the Anzali wetland and other wetlands is presented in Table 6.

3.3. Ecological risk assessment indices

Heavy metals maintain in sediments, and owing to complicated coupled situation of environmental alterations and human interventions, these may release into water columns, so besides adverse impacts on the benthic organisms, these may impose threats on all of the aquatic organisms in the water columns. Some metals are biologically considered essential elements in living organisms, but when these metal concentrations exceed thresholds, it will impact biota adversely. the heavy metals in the sediments may accumulate in the tissues of aquatic organisms and lead to detrimental impacts on the

Table 5 | I_{geo} and EF indices in the sampling stations of the Anzali wetland

Station	AS		Cd		Cr		CU	
	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF
A	0.44	5.4	0	2.7	0.09	1.14	−0.19	**1.18**
B	0.73	6.09	0.08	2.6	−0.08	1.17	−0.22	**1.05**
C	0.23	4.4	0.19	3.02	−0.04	1.25	−0.47	**0.93**
D	−0.64	2.4	−0.62	1.7	−0.41	0.96	−0.38	**1.03**
E	−0.85	2.08	−0.43	1.96	−0.47	0.95	−0.11	**0.96**
F	−0.14	3.1	−0.7	1.25	−0.16	1.08	−0.11	**1.11**
G	−0.36	0.91	−0.43	1.79	−0.32	0.97	−0.91	**1.01**
Mean	−0.08	3.48	−0.02	2.14	−0.19	1.11	−0.34	**1.03**
Minimum	−0.85	0.91	−0.7	1.25	−0.47	0.95	−0.91	**0.93**
Maximum	0.73	6.09	0.19	3.02	0.09	1.25	−0.11	**1.18**

Station	Mn		Ni		Pb		V		Zn	
	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF
A	−0.04	1.45	0.01	1.28	−0.85	2.02	−0.55	1	−0.04	**1.84**
B	−0.11	1.26	0.05	1.21	0.04	2.02	−0.62	0.87	−0.01	**1.58**
C	−0.51	2.08	−0.01	1.20	−0.14	1.80	−0.55	0.96	−0.2	**1.57**
D	−0.17	1.32	−0.62	0.82	−0.75	1.25	−0.8	0.84	−0.41	**1.42**
E	−0.34	1.14	−0.49	0.87	−0.68	1.27	−0.85	0.80	−0.45	**1.36**
F	−0.01	1.32	−0.34	0.89	−0.32	1.51	−0.64	0.84	−0.24	**1.43**
G	−0.05	1.31	−0.13	1.04	−0.57	1.30	−0.64	0.87	−0.29	**1.41**
Mean	−0.03	1.41	−0.21	1.05	−0.46	1.60	−0.66	0.88	−0.23	**1.51**
Minimum	−0.34	1.14	−0.62	0.82	−0.85	1.25	−0.85	0.87	−0.45	**1.36**
Maximum	0.51	2.08	0.05	1.28	0.04	2.02	−0.55	1	−0.01	**1.84**

Table 6 | Heavy metal indices in the sediments of Anzali wetland and some other wetlands

LOCATION	Index	As	Cd	Cr	Cu	Mn	Ni	Pb	v	Zn	
Anzali Wetland (This study)	**Igeo**	−0.08	−0.02	−0.19	−0.34	−0.03	−0.62	−0.85	−0.85	−0.45	
	EF	3.48	2.14	1.11	1.03	1.41	0.82	1.25	0.87	1.36	
	CF	1.25	0.93	1.30	1.47	1.21	1.30	1.16	1.27	1.29	
	PLI	–	–	–	–	–	–	–	–	–	1.24
Bamdezh wetland (Iran)	**Igeo**	–	–	–	–	–	–	–	–		
Vaezi *et al.* (2014)	**EF**	0.32	52.25	–	–	–	1.38	1.22	–	0.72	
	CF	0.29	47.36	–	–	–	1.28	1.09	–	0.66	
	PLI	–	–	–	–	–	–	–	–	–	1.37
Western Caspian Sea	**Igeo**	−0.21	−0.75	−2.466	−1.89	−1.48	−2.40	−1.00	−2.13	−1.64	
Ahmadov *et al.* (2020)	**EF**	4.22	2.77	0.81	1.19	1.64	0.84	2.25	1.011	1.42	
	CF	1.33	0.89	0.29	0.42	0.53	0.300	0.75	0.35	0.50	
	PLI	–	–	–	–	–	–	–	–	–	0.449
Tigris River (Turkey)	**Igeo**	0.14	0.48	−0.25	0.21	−0.27	0.33	1.33	–	0.60	
Varol (2011)	**EF**	1.72	2.08	1.28	5.66	1.27	1.90	3.78	–	2.50	
	CF	1.78	2.14	1.32	6.16	1.31	1.97	3.90	–	2.60	
	PLI	–	–	–	–	–	–	–	–	–	1.88
Karachi Coast (Pakistan)	**Igeo**	–	–	−0.62	–	−1.30	−1.58	−0.15	−1.37	1.14	
Mashiatullah *et al.* (2013)	**EF**	–	–	2.84	–	1.8	1.68	1.50	1.20	3.72	
	CF	–	–	–	–	–	–	–	–	–	
	PLI	–	–	–	–	–	–	–	–	–	1.05

human health through entering and gradually accumulating in the food chains (Ra *et al.* 2013). Therefore, it is vital to be aware of the sediment contamination risks to aquatic life. In this regard, the Ecological risk assessment indices provide us with applicable knowledge to a great extent. The calculated E values are shown in Table 7. Potential Ecological Risk (PER) indices were calculated 8.03, 24.92, 27.54, 11.77, 356.41, 38.14, and 54.42 for Zn, Pb, Ni, Cr, As, Cd, and Cu, respectively (Figure 2). As and Zn were the highest and lowest single risk factors, respectively. The average ecological risk of E value for all of the metals in the most surface sediments was <40, indicating a moderate risk to the local ecosystem.

According to the results of monomial potential ecological risk indices (E_r^i), Arsenic imposed a moderate ecological risk at stations A, C, and F and a considerable ecological risk at station B. Also, Zinc, Lead, Nickel, Chromium, Cadmium, and Copper imposed a low ecological risk at all of the stations, when the peak concentrations were recorded for Arsenic in station B. The potential ecological risk indices for monomial regulators indicated that the intensity of the five heavy metals sorted as; As > Cu > Cd > Ni > Pb > Cr > Zn, respectively.

As is a metalloid element widespread in the aquatic environment arising from natural and anthropogenic processes. It is an important and ubiquitous environmental contaminant imposing toxic risk on humans and public health worldwide (Kumari *et al.* 2017). In an aquatic ecosystem, a high level of As concentration, more than its permitted limit, would impact various

Table 7 | Potential ecological risk factor (Ei) and (PER) of the sediments in the Anzali wetland

	Zn	**Pb**	**Ni**	**Cr**	**As**	**Cd**	**Cu**
Sampling sites	**Monomial heavy metal potential ecological risk indices (E)**						
A	1.33	4.20	4.56	2.00	69.23	6.43	**8.40**
B	1.25	4.65	4.74	1.83	84.62	6.86	**8.26**
C	1.18	4.05	4.74	1.87	58.97	7.43	**6.84**
D	1.02	2.70	2.92	1.44	30.77	4.14	**7.26**
E	1.00	2.70	3.19	1.38	28.21	4.71	**6.98**
F	1.15	3.60	3.54	1.73	46.15	3.86	**8.83**
G	1.11	3.00	4.12	1.53	38.46	4.71	**7.83**
Minimum	1.00	2.70	2.92	1.38	28.21	3.86	**6.84**
Maximum	1.33	4.65	4.74	2.00	84.62	7.43	**8.83**
Average	1.15	3.56	3.93	1.68	50.92	5.45	**7.77**
PER	8.03	24.92	27.54	11.77	356.41	38.14	**54.42**

Notes: E is the monomial and PER is the potential ecological risk indices of multinomial heavy metal.

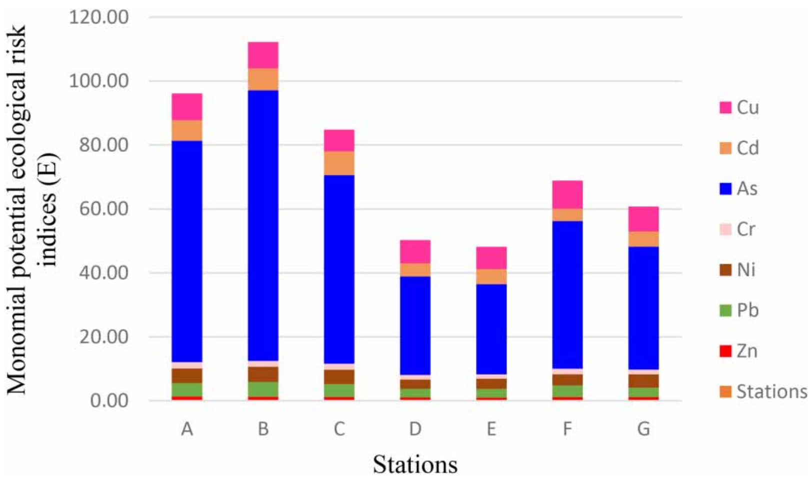

Figure 2 | Potential ecological risk assessment of selected heavy metals of the surface sediments in the Anzali Wetland.

physiological systems and processes such as growth, proliferation, ion regulation, smoltification, gene expression, immune function, enzyme activities, and histopathology of biota (Datta *et al.* 2009) As-contaminated fish consumption could result in As susceptibility in humans and lead to unpropitious health effects. As could elicit a series of molecular events implicated in oxidative stress, iron homeostasis, lipid metabolism disorder, and carcinogenic. (Kar *et al.* 2011; Kumari *et al.* 2017) SQGs are vital indices for ecological risk assessment in the aquatic ecosystem (Long *et al.* 1995).

In this paper, the TEL, PEL, ERL, and ERM ranges were applied to determine the toxicity level of contaminants in the sediment samples. In Figure 3, the results obtained from a comparison between heavy metal contents in the sediment samples with the values in SQG are demonstrated. As, Cr, and Cu metals, measured in samples from all of the stations, were higher than the TEL and ERL values and lower than the ERM and PEL values. Therefore, it can be concluded that these metals have the potential to impose a threat on the organisms in the wetland. Since the toxicity of these metals is between the two effect levels, these may be of moderate toxicity in the aquatic ecosystem and do not dominantly and permanently impact biota. In all

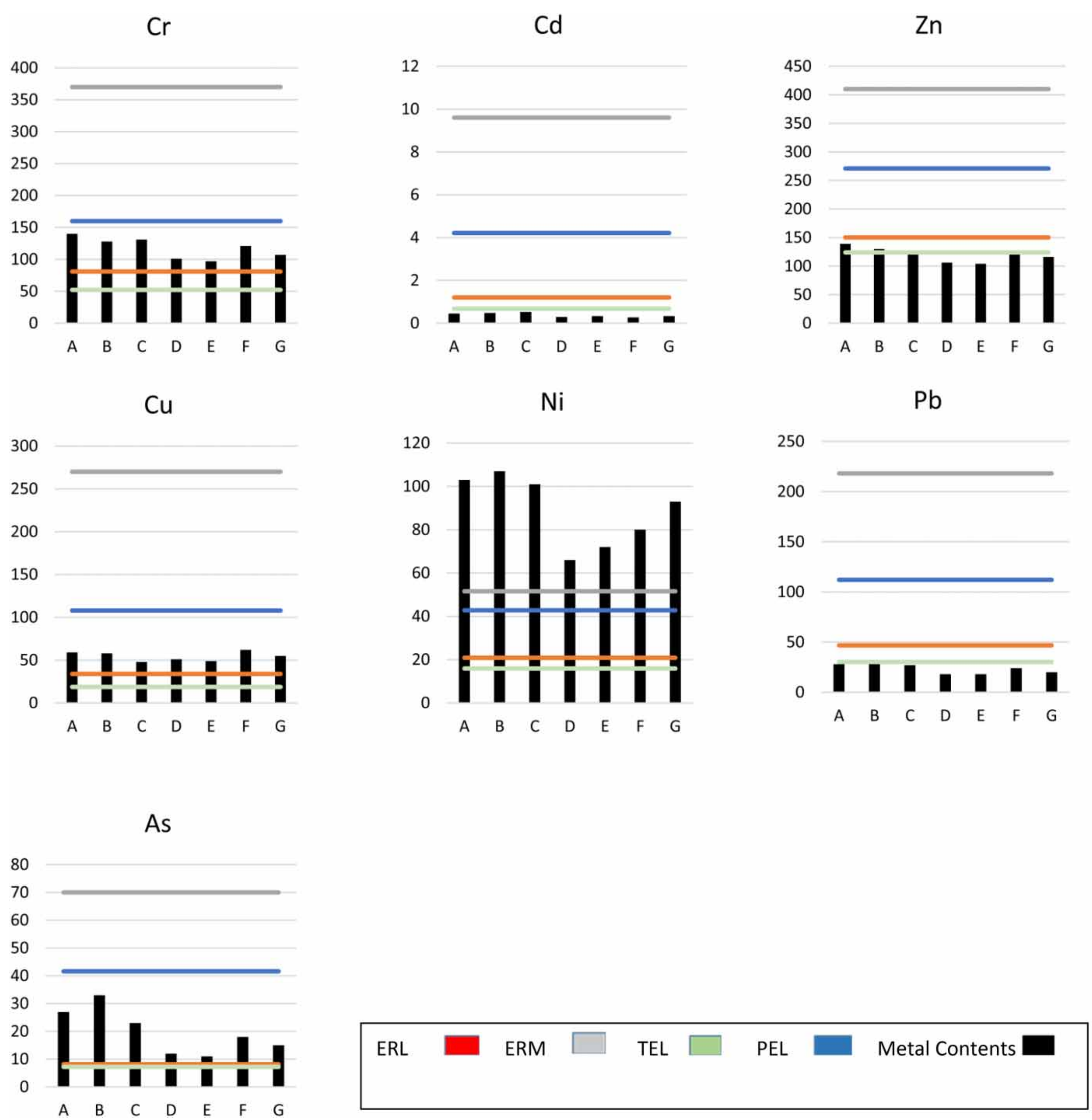

Figure 3 | Comparison between sediment quality guidelines (SQGs) and the heavy metal concentrations in the study area.

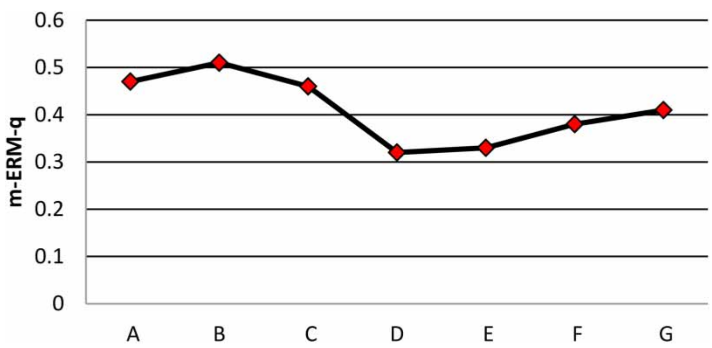

Figure 4 | The m-ERM-q values in the surface sediments of the Anzali wetland.

of the stations, Pb and Cd were at a lower level than all of the effect levels. Therefore, it can be concluded that these metals do not have harmful biological effects on the living organisms in the aquatic environment. In stations A and B, and also in 28% of the samples, Zn was slightly higher than the effect threshold (TEL), but in the other stations, it was lower than all of the effect ranges. In 100% of the samples, the Ni values were much higher than the four effect ranges of ERL, ERM, TEL, and PEL, and based on the results this metal imposes many adverse effects on living organisms in the study area. Nickel is discharged into an aquatic ecosystem by industrial activity such as the production, processing, and recycling of various Ni products, including stainless steel, electroplating, pigments, and ceramics. It seems that one of the main causes for the presence of Ni in the Anzali wetland is the Caspian Sea's oil pollution and wastewater release from the plating and chemical industries. Ni can be deposited in the sediment by such processes as precipitation, complexation and adsorption on clay particles. It is easily accumulated in the biota, particularly in the phytoplankton or other aquatic plants and fishes, Ni causes respiratory disorder, and kidney lesions in fish and other aquatic organisms, then enters as a risk factor in the human food chain. Several toxic effects of Ni on human health are recognized, including allergies, carcinogenesis, and cardiovascular and renal disorders (Nriagu & Pacyna 1988; Cempel & Nikel 2006; Palermo *et al.* 2015). Using m-ERM-q, the toxicity of combined toxicant groups in the sediment samples was analyzed and evaluated. In Figure 4, the m-ERM-q values obtained from different stations on the site are presented. The m-ERM-q values in the sediments were in the range of 0.32–051; that is to say, 10 combined toxicant groups had the probability of toxicity at 21%. This index was estimated for all of the stations and it indicated the trend of B > A > C > G > F > E > D.

4. CONCLUSION

In this paper, the geochemical and ecological indices were used simultaneously to monitor the sediments contaminated with some heavy metals in the Anzali wetland in Iran. Based on the estimated indices, the highest values of heavy metal concentrations were observed in the eastern and central parts of the wetland. The average concentrations of the total heavy metals followed the trend of Fe > Mn > V > Zn > Cr > Ni > Cu > Pb > As > Cd. Based on a comparison between heavy metal concentrations with the Sediment Quality Guideline, all of the heavy metals except for Ni were in the permissible ranges. Also, the PER index showed that As exceeded the permissible limits. According to these results, Ni and As are the most dangerous contaminants for the biota in the wetland, but the total toxicity of all of the metals in the sediment samples based on the m-ERM-q index was estimated at 21%, so the total toxicity was not significant. According to the finding of this research, discharge of raw wastewater must be prevented to avoid direct and indirect detrimental impacts on the aquatic ecosystems in the study area; the use of pesticides and fertilizers in agricultural activities should be limited. In general, for effective conservation of the wetland, it is needed to develop a management plan restricting pollution discharges into the aquatic ecosystems and the wetland watershed.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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