

Investigation of Heavy Metal Contamination in the Surface Sediments of Anzali Wetland in North of Iran

Shariati, S.¹, Pourbabaei, A. A.^{1*}, Alikhani, H. A.¹ and Rezaei, K. A.²

1. Department of Soil Science Engineering, University of Tehran, Karaj, Iran

2. Department of Food Science, Engineering, and Technology, University of Tehran, Karaj, Iran

Received: 05.04.2018

Accepted: 07.07.2018

ABSTRACT: Over the last few decades, Anzali wetland has been at risk of pollutants, especially from heavy metals. The present research analyzes some physical and chemical properties and heavy metals concentration in 27 points in nine stations of Anzali wetland. The samples of each station have been mixed, acidic digested, and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The mean concentrations of Fe, Mn, Pb, Zn, As, Cd, Cu, Hg, Ni, and Cr have been 50527.2, 1210, 23.3, 79.4, 8.8, 0.23, 32.1, 0.25, 31.6, and 31.5 mg/Kg, respectively. In addition, it can be seen that the concentrations of Cd (0.31 mg/Kg) and As (25.47 mg/Kg) in Hendekhale station, Hg (0.52 mg/Kg) in Pirbazar station, and Pb (52.69 mg/Kg) in Khazar villa station surpass world surface rock average. According to contamination factor (CF), in case of Mn and Pb, both Hendekhale, and Khazar Villa stations have been in considerable contamination level. The calculation of Pollution Load Index (PLI) shows that Hendekhale and Khazar Villa stations have had moderate pollution. The mCd index survey indicates that only in Hendekhale station, has heavy metals contamination been at a low degree level of contamination. According to PER index, mercury metal contamination in Hendekhale station faces medium risk. The calculated mean ERM quotient indicates the probability of heavy metals toxicity, equal to 21% in the examined stations.

Keywords: Caspian Sea, Contamination Factor, Pollution load index (PI), Toxic elements.

INTRODUCTION

Metals enter aqueous environments mostly through atmospheric phenomena, land erosion, and human activities such as domestic and industrial wastewater production not to mention mining operations (Rzetala, 2015). Sediments, which act as a sink for the storage and accumulation of metals, readily adsorb heavy metals (Karbassi et al., 2008; Vukovic et al., 2014). Measurement of heavy metals in the sediments is a suitable tool to determine pollution levels in aqueous ecosystems (Xiao

et al., 2013). Many researchers have conducted extensive research on sediment pollution via heavy metals because of the toxicity, stability, and non-degradability of these elements and their compounds in the environment and since heavy metals, even at low concentrations, pose a threat to aquatic organisms and human beings (Fu et al., 2014; Raju et al., 2012; Harikrishan et al., 2017). Unfortunately, the Anzali Lagoon is exposed to the serious danger posed by pollution from heavy metals in recent years, due to unsuitable management and excessive entry of contaminants, present in domestic, agricultural, and industrial wastewater

*Corresponding Author, Email: pourbabaei@ut.ac.ir

discharged into the lagoon (Zamani Harghalani et al., 2014; Ziarati et al., 2015). Khosheghbal et al. (2012) reported that the average concentration of Co, Cr, Cd, As, Cu, Zn, Pb, Ni, Mn, and Fe in the sediments of Anzali wetland was equal to 20.29, 98.72, 0.25, 12.49, 54.58, 109.83, 22.87, 68.22, 1540, and 49000 mg/kg, respectively. Jamshidi & Bostami (2016) reported that concentrations of arsenic, nickel, chromium, and copper in the sediments of the Anzali Lagoon were higher than the Sediment Quality Guidelines (SQGs). Stable and widely spread in aqueous ecosystems, these metals have a strong tendency to accumulate in the tissues of living organisms such as fishes, wetland plants, and birds (Alhashemi et al., 2011, 2012). Because of above-mentioned characteristics they may endanger the natural physiological processes of organisms, and may also enter the human food chain through biomagnification (Water Research Commission, 2014; Yilmaz et al., 2018). Results of the research by Salamat et al. (2016) showed that concentration of lead in tissues of pike (*Esox lucius*) in the Pirbazar and Anzali regions exceeded the permissible levels, established by World Health Organization (WHO). Khanipour et al. (2016) stated that accumulation levels of the heavy metals lead and zinc in the edible muscle tissues of Crucian carp (*Carassius auratus*) exceeded the standard permissible limits, set by Food and Drug Administration (FDA) and WHO. Considering Anzali wetland's registration as an international wetland in Ramsar Convention in 1975 along with its significance in different aspects of environment, fishing, and tourism, this study aims at investigating the concentration of heavy metals (iron, zinc, manganese, mercury, copper, arsenic, lead, nickel, cadmium, and chromium) in various parts of Anzali wetland, comparing it with other studies.

MATERIALS AND METHODS

Anzali wetland is located in the southwest

region of Caspian Sea in Guilan Province with an area of about 193 km². It is 24 m below the free water level, being located in the geographical range of 48°45' to 49°42' eastern longitude and 36°55' to 37°32' northern latitude. Eleven main rivers and 30 sub-rivers flow to the wetland after irrigation of farms and rice fields with runoff waters with 3600 square kilometers catchment area. Regarding the ecological importance of this ecosystem, more than 150 species and more than 1 million birds migrate to Anzali wetland throughout the winter. It is covered with reed bed, playing a key role for fish spawning and growth. In terms of tourism, more than two million people visit the lagoon every year and with regard to the environmental importance of the wetland, it can be said that due to the arrival of a large number of the province's rivers as well as wastewater to the wetland, it plays a vital role for refining the Caspian Sea and the living organisms of these ecosystems (Naderi et al., 2017; Zamani Harghalani et al., 2014, Khosheghbal et al., 2013). Sampling containers were rinsed with distilled water, got filled with HNO₃ 3%, and were allowed to stay still for 24 hours so that all metals would be removed. Sediment samples were taken from 9 stations, with each sample being consisted of three sub-samples, collected from the surrounding of each site (within 50×50 m², 1 kg each) (Fig.1). Surface sediments (0–10-cm) were randomly collected, using stainless steel Van Veen grab.

In order to measure some physicochemical properties of the sediments, the sediment samples were initially air dried and then oven-dried at 105 C° for 8 h to a constant weight. Then, they were ground and passed through a 10-mesh sieve prior to analysis. The samples were baked in a muffle furnace at 550 C for 6 h and organic matter percentage was determined by measuring the weight loss (Jia et al., 2011). Electrical conductivity and pH were also measured in 1:1 water–sediment slurry via

EC- (JENWAY 4320) and pH-meter (UNICAM 9455) (Sparks, 1996). Percentage of clay was measured, using traditional hydrometer method (Gee & Bauder, 1986).

In order to measure heavy metals in the sediments (oven-dried and passed through a 10-mesh sieve) (Djordjevic et al., 2012; Pandey & Singh, 2017), acid digestion of sediment was performed. For this purpose, the mixture of HCl and HNO₃ with a ratio of 3:1 was added to one gram of the sediment. The samples were then digested in the two-acid mixture at 100°C on a hot plate for three hours. Once cooled down, the digested solution was filtrated and in order to remove contamination, 2 ml of 10% potassium solution was added to the filtered sample. Finally, heavy metal ions were analyzed by using coupled plasma mass spectrometry inductively (SPECTRO ARCOS) (Amini Ranjbar, 1998; Pandey &

Singh 2017). To determine the contamination level of the studied area, Contamination Factor (CF), Pollution Load Index (PLI), Geo-Accumulation Index (Igeo), Potential Ecological Risk (PER) index, and mean ERM quotient index were calculated in accordance with the total concentration of the elements.

Contamination Factor (CF): The contamination level of the sediments by heavy metals is described, using the pollution factor index. It is calculated with Formula 1, wherein C_m Sample is the concentration of the element in the sediment sample and C_m background is the average element concentration in the surface rocks, measured by Martin and May Beck (Martin & Meybeck, 1979).

$$CF = \frac{C_{m_{\text{metal}}}}{C_{m_{\text{background}}}} \quad (1)$$

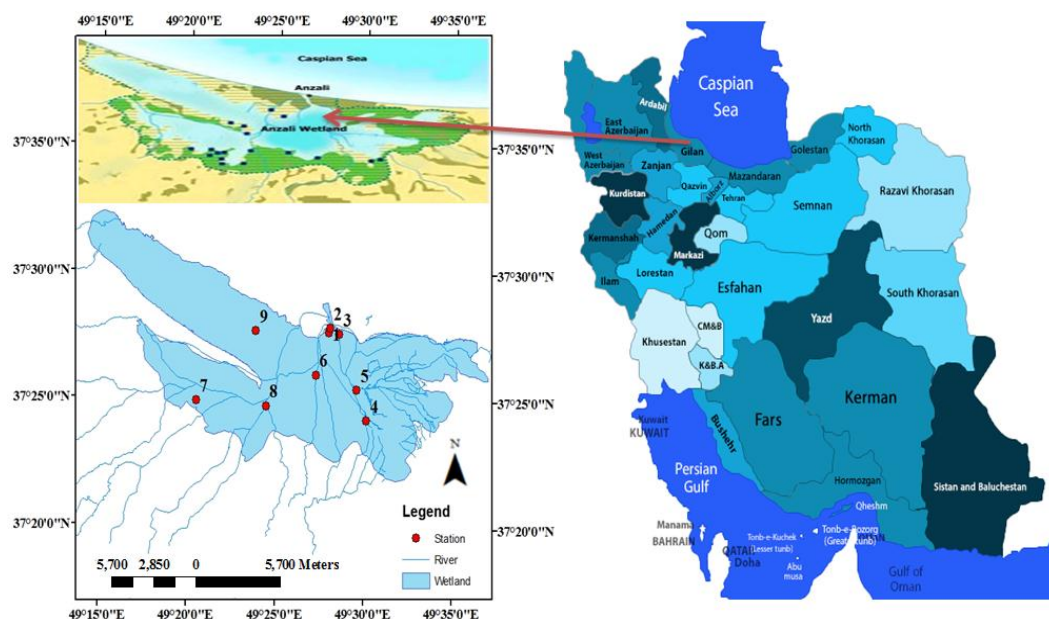


Fig. 1. Sampling stations in Anzali wetland

Table 1. Contamination Factor (CF) and Contamination level (Hakanson 1980)

Contamination Level	Grade	Contamination Factor (CF)
Low Contamination	I	$CF < 1$
Moderate Contamination	II	$1 \leq CF < 3$
Considerable Contamination	III	$3 \leq CF < 6$
Very High Contamination	IV	$CF > 6$

Pollution Load Index (PLI): This indicator is employed to show the contamination of every region and can show an estimate of the level of metal contamination. It can be calculated, using formula 2.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (2)$$

In which "n" and Cf are the number of measured metals and contamination factor, respectively (Tomlinson et al., 1980). PLI values vary from zero (non-contaminated) to 10 (very contaminated). Typically, values below 1 are suggestive of non-contamination, while those above 1 indicate contamination with heavy metals (Harikumar et al., 2009).

Contamination Degree Index (Cd): In 1980, Hakanson introduced another index called "Contamination Degree". In 2008, Abraham and Parker modified it to the mCd index based on the following relations:

$$Cd = \sum_{i=1}^8 C_f^i \quad (3)$$

where C_F is a factor of contamination and Cd is the total of C_F , calculated with Equation 1.

$$mCd = \frac{\sum_{i=1}^8 C_f^i}{n} \quad (4)$$

In which C_f stands for contamination factor and n is the number of analyzed parameters. The mCd allows studying a variety of heavy metals without any limitation.

Geo-accumulation Index (Igeo): This index was first introduced by Muller in 1979 (Muller, 1979). It is calculated to measure and determine the contamination of sediments by comparing the current concentrations of an element with its amount prior to industrialization in the sediments. It is defined based on the following formula (5).

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \quad (5)$$

where C_n is the heavy metal concentration in the sediment sample and B_n , the amount of the metal in the shale (in mg/Kg). The constant number of 1.5 was applied to minimize the effect of possible alterations in the field value, related to lithologic changes. Based on the results, obtained from the land accumulation index, seven categories of contamination can be detected, shown in the table below (Harikrishnan et al., 2017).

Table 2. Hakanson rankings on the basis of sediment CF contamination factor (Hakanson, 1980; Abraham & Parker 2008)

Degree of Contamination	Description
$Cd < 6$	Low degree of contamination
$6 < Cd < 12$	Moderate degree of contamination
$12 < Cd < 24$	Considerable degree of contamination
$Cd > 24$	The very high degree of contamination

Table 3. Classification of sediment according to mCd (Abraham & Parker 2008, Hafizur et al., 2012)

The modified degree of contamination (mCd)	Description
$mCd < 1.5$	Zero to the very low degree of contamination
$1.5 \leq mCd < 2$	Low degree of contamination
$2 \leq mCd < 4$	Moderate degree of contamination
$4 \leq mCd < 8$	High degree of contamination
$8 \leq mCd < 16$	The very high degree of contamination
$16 \leq mCd < 32$	The extremely high degree of contamination
$mCd \geq 32$	Ultra-high degree of contamination

Table 4. Mullers classification for geo-accumulation index (I_{geo})

Class	I_{geo} value	Sediment Quality
0	<0	Unpolluted
1	0-1	From unpolluted to moderately polluted
2	1-2	Moderately polluted
3	2-3	From moderately to strongly polluted
4	3-4	Strongly polluted
5	4-5	From strongly to extremely polluted
6	>6	Extremely polluted

Potential Ecological Risk (PER)

Index: The potential ecological risk index was introduced to evaluate the amount of metal contamination in sediments. The formulae, required to calculate this index, are given below (Hakanson, 1980).

$$E = TC \quad (6)$$

$$C = \frac{C_a}{C_b} \quad (7)$$

$$PER = \sum E = \sum TC \quad (8)$$

wherein, C represents the contamination factor of the examined element, C_a is the amount of that element in the samples, and C_b is the amount of elements in the reference. E is the PER factor of each element individually and T, the biological toxicity factor of any element with values as follows: Cu = Pb = 6, Zn = 1, As = 10, Cd = 30, Cr = 2, Ni = 6 and Hg = 40. (Hakanson, 1980). PER is a comprehensive ecological index of potential environmental risk, equivalent to the sum of E's.

Mean ERM quotient index: The Sediment Quality Guidelines (SQGs) appear to be an important tool for assessing pollution in marine and ocean sediments. Two sets of these SQGs, designed for marine

and ocean ecosystems, were used in this study to assess the environmental hazard of metals in the sediments (MacDonald et al., 1996; Long & MacDonald, 1998). They included (a) The effect range low (ERL)/effect range median (ERM) and (b) the threshold effect level (TEL)/probable effect level (PEL) values. The low range amounts (i.e., ERLs or TELs) are often concentrations lower than expected with adverse impacts on animals living in the site of sedimentation. In contrast, the ERM and PELs represent chemical concentrations, above which the adverse effects may occur (Long & MacDonald, 1998). Since the metals always occur in sediments as complex mixtures, the mean ERM quotient method was employed to determine the possible biological effect of combined metal groups by calculating mean quotients for a large range of contaminants, using the formula below (Carr et al., 1996; Gao & Chen, 2012):

$$\text{Mean ERM quotient} = \sum \left(\frac{C_x}{\text{ERM}_x} \right) / n \quad (9)$$

where C_x is the sediment concentration of component x; ERM_x , the ERM of x; and n, the number of components.

Table 5. Some physical and chemical properties of the sediment

Number	Station	Depth (m)	X	Y	pH	EC (ds/m)	Clay (%)	Organic Matter (%)
1	Jazire Beheshti	2.3	364228	4147087	7.9	1.32	11	6.04
2	Nahang Roga	4.0	364373	4147453	8.0	5.75	35	9.68
3	Sosar Roga	1.5	365124	4146981	8.2	1.62	39	7.96
4	Pirbazar	1.5	367358	4140698	7.8	1.85	15	6.30
5	Sheijan	2.0	366551	4142951	8.1	0.71	47	9.16
6	Sorkhankol	0.5	363143	4144043	8.1	1.25	33	9.35
7	Hendekhale	1.2	353142	4142246	8.2	2.16	49	13.90
8	Siahdarvishan	0.6	358972	4141820	8.2	0.97	21	4.13
9	Khazar Villa	0.5	358160	4147267	8.0	4.64	18	22.50

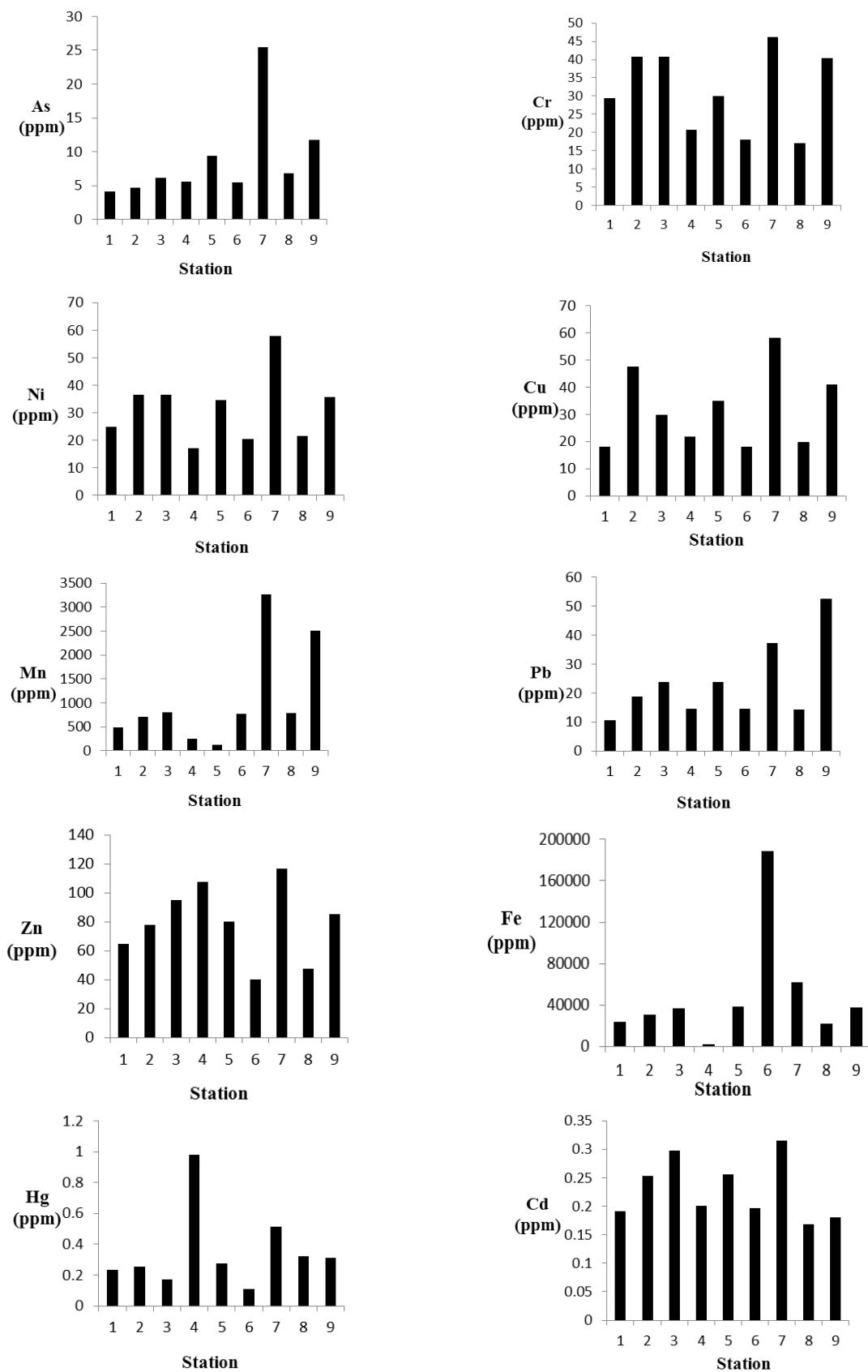


Fig. 2. Heavy metal distribution in different locations' sediments

As shown in Fig. 3, the amounts of arsenic, chromium, nickel, copper, manganese, zinc, and cadmium were the highest in HendeKhaleh station. In case of lead, iron, and mercury, Khazar Villa, Sorkhankol and Pirbazar stations had the highest values, respectively.

Results from heavy metals' measurement showed that the average concentrations of iron, manganese, and lead had been higher than the average element concentration in the world surface rocks (Martin & Meybeck, 1979). Also, the average concentrations of iron, manganese, lead, zinc, cadmium, and arsenic were higher than the average concentrations of elements in the earth's crust (Esmaeilzadeh et al., 2016).

Table 6 compares the mean concentration of heavy metals in this study with those of other studies in Iran and the world. As seen in Table 6, the amount of iron in the Sorkhankol station was higher than all conducted studies. Zinc values, obtained, were higher than the studies by Harikrishnan et al. (2017) in Tamil Nadu, India; Pandey & Singh (2017) in Ganga, China; Pejman et al. (2017) in North West Persian Gulf, Iran; Karbassi & Pazoki (2015) in Shavoor River, Iran; and Moore et al. (2015) in Gowatr Bay, Iran. The mean concentration of manganese in this research stood higher than all other studies, except the one by Esmaeilzadeh et al. (2016) in Anzali wetland. Nickel concentration was lower than other

amounts, reported in Anzali wetland, but was higher than the studies by Harikrishnan et al. (2017) in Tamil Nadu, India; Pandey & Singh (2017) in Ganga, China; and Karbassi & Pazoki (2015) in Shavoor River, Iran. In case of lead, the values obtained in this study had been higher than the lead concentrations, found in the studies by Khosravi et al. (2011), Naseh et al. (2012), Jamshidi & bastami. (2016), Khosheghbal et al. (2013), and Alizade et al. (2018), all conducted in Anzali Wetland, Iran, as well as the ones by Harikrishnan et al. (2017) in Tamil Nadu, India; Moore et al. (2015) in Gowatr Bay, Iran; and Taghinia et al. (2011) in Kabini River, India. For Cu, the values obtained were higher than the findings of Alizade et al. (2018) in Anzali wetland, Iran; Karbassi & Pazoki (2015) in Shavoor River, Iran; Moore et al. (2015) in Gowatr Bay, Iran; Vaezi et al. (2015) in Persian Gulf, Iran; Pandey & Singh (2017) in Ganga, China; and Niu et al (2015) in Taihu Lake, China. Obtained Cadmium values were higher than the researches, conducted by Khosravi et al. (2011), Naseh et al (2012), and Khosheghbal et al. (2013). all in Anzali wetland, along with the one by Fu et al. (2013) in Taihu Lake, China. In case of Arsenic, the values obtained in this study was only higher than the concentrations in Harikrishnan et al. (2017), whose research had been conducted in Tamil Nadu, India.

Table 6. The concentration of heavy metals in sediment samples and their comparison with the average concentration of the elements in surface rocks, earth crust, and different standard values

Metal	Minimum	Maximum	Mean	World surface rock average ¹	Mean Earth's crust ²	WHO ³	USEPA ³	CCME ³
Fe	16270.00	188812	50527.23	35900.0	41000.0	-	30	-
Cr	17.15	46.14	31.48	71.0	100.0	25	25	37.3
Mn	245.00	3261.00	1210.44	750.0	950.0	-	30	-
Pb	10.66	52.69	23.36	16.0	14.0	-	40	35
Zn	40.07	116.93	79.37	127.0	75.0	123	110	123
Cu	17.96	58.10	32.10	32.0	50.0	25	16	35.7
Cd	0.17	0.31	0.23	0.2	0.2	0.6	0.6	0.6
Ni	17.13	57.93	31.66	49.0	80.0	20	16	-
As	4.16	25.47	8.81	13.0	5.0	-	-	-
Hg	0.09	0.52	0.25	0.4	-	-	-	-

Table 7. Concentrations of heavy metals in the Anzali wetland sediments (in mg/Kg) in comparison with other local and world river sediment studies

Rivers and wetlands	As	Cd	Cu	Pb	Zn	Cr	Ni	Mn	Fe	Reference
Anzali wetland	8.8	0.23	32.1	23.3	79.3	31.4	31.6	1210.4	50527.2	This study
Anzali wetland	-	-	31	20	86	95	53	19300	38600	Alizade et al. (2018)
Tamil Nadu, India	5.3	-	-	11.1	39.7	80.0	24.8	-	-	Harikrishnan et al. (2017)
Ganga, China	-	1.7	29.8	26.7	67.8	69.9	26.7	372	319 88.6	Pandey and Singh (2017)
North West Persian Gulf	-	0.8	32.1	48.3	62.5	89	112.1	-	-	Pejman et al (2017)
Anzali wetland	11.0	0.55	39.3	11.9	88.0	102.0	43.2	-	43200	Jamshidi and bastami (2016)
Anzali wetland	20	0.38	55	24	129	118	89	1270	43200	Esmacilzadeh et al. (2016)
Gowatr Bay, Iran	-	-	25	17	62	54	84	616	29700	Moore et al. (2015)
Shavoor River, Iran	-	-	31	-	57.2	-	44.9	495.1	23300	Karbassi and Pazoki (2015)
Persian Gulf	10.5	-	22	-	93	43	62	351	-	Vaezi et al. (2015)
Taihu Lake, China	-	0.74	28.2	29.8	79.7	72.1	34.3	-	-	Niu et al. (2015)
Anzali wetland	12.4	0.25	54.5	22.8	109.8	72.9	68.2	1540	49000	Khosheghbal et al. (2013)
Taihu Lake, China	-	0.14	34.1	33.5	105.5	68.0	36.2	-	-	Fu et al. 2013
Anzali wetland	24.6	0.2	126.7	28.6	120.9	126.7	80.0	23870	23870	Naseh et al (2012)
Yangtze, China	-	1.0	60.0	49.2	230.4	108.0	41.9	-	-	Wang et al. (2011)
Kabini River, India	-	-	110.5	11.6	87.9	254.5	91.1	115.6	1597.7	Taghinia et al. (2011)
Anzali wetland	-	0.15	44.4	0.0	186.9	-	-	-	-	Khosravi et al. (2011)

Table 8 lists the values of contamination factor for each element and the pollution load index of each station. Regarding the contamination factor of the iron element,

stations 3, 5, 7, and 9 had moderate and station 6 had a significant degree of pollution. In case of chromium and zinc, according to the values obtained for the

pollution factor, the contamination level of these elements was low. As for lead, stations 2, 3, 5, and 7 were moderately polluted, but station 9 was significantly contaminated. In case of manganese, stations 3, 5, 6, and 8 experienced low pollution levels, while stations 7 and 9 were at a significant level of pollution. As for arsenic, nickel, and mercury, station 7 (Hendekhaleh) also had a moderate level of pollution. In case of copper, stations 2, 5, 7, and 9 had a moderate pollution level. And as for cadmium, stations 2, 3, 4, 5, and 6 had a moderate level of pollution. The values of Cd (Table 7) showed that stations 2, 3, 5, and 6 were at the moderate level of pollution, while stations 7 and 9 were at a significant one. In addition, the comparison with the mCd index indicated that station 7 was at a low pollution level. Also, the results of measurement of pollution load index (PLI) showed that two stations of Hendekhaleh and Khazar Villa had a pollution load index over 1. According to the values of this index (less than 1 = no pollution, between 1 and 2 = moderate pollution, between 2 and 3 = high pollution, and more than 4 = extremely heavy pollution) (Chakravarty & Patgiri, 2009; Seshan et al., 2010), these two regions had a moderate level pollution to heavy metals (Harikumar et al., 2009).

PLI results of Hendekhaleh, concerning contamination with heavy metals, are consistent with those of Khosheghbal et al.

(2013). This can also be attributed to the higher percentage of clay in this area than other parts and the highest amount of organic matter after station 9. The researchers argued that fine sediments with relatively high area to volume ratio, organic carbon, and higher ionic absorption affinity were effective in absorbing metals (McCave, 1984; Horowitz & Elrick 1987). The higher pollution rate of the Hendekhaleh and Khazar Villa stations, compared with the eastern parts, can be attributed to higher percentage of organic matter and electrical conductivity in this station than the rest of the areas. The researchers indicated that there was a high correlation between the amount of organic matter in the sediment and the electrical conductivity of sediment with heavy metals, and due to high complexation capacity with metals, the organic matter was the main source of heavy metal deposits in the sediments (Coquery & Welbourn 1995; Bai et al., 2012; Bastami et al., 2015). Another reason can be the proximity of this area to urban areas, especially Khazar Villa town.

Results of Igeo index showed that most of the stations stood at zero values and the contamination level of heavy metals in many stations was in an unpolluted level, although in few stations, the level of contamination was in the range of unpolluted to moderately polluted, according to table 4.

Table 8. Contamination factor values, pollution load index, and modified degree of contamination for sediment samples of Anzali wetland

Station	Hg	Cu	Ni	Cd	As	Cr	Mn	Pb	Zn	Fe	PLI	Cd	mCd
1	0.58	0.56	0.50	0.96	0.32	0.41	0.65	0.66	0.50	0.65	0.55	5.83	0.58
2	0.63	1.48	0.74	1.26	0.35	0.57	0.94	1.16	0.61	0.85	0.79	8.64	0.86
3	0.43	0.93	0.74	1.49	0.47	0.57	1.06	1.48	0.74	1.01	0.82	8.95	0.89
4	0.24	0.67	0.34	1.00	0.42	0.29	0.32	0.91	0.84	0.45	0.49	5.53	0.55
5	0.69	1.09	0.70	1.28	0.71	0.42	1.74	1.48	0.63	1.06	0.90	9.84	0.98
6	0.27	0.56	0.41	0.98	0.41	0.25	1.02	0.91	0.31	5.25	0.63	10.42	1.04
7	1.29	1.81	1.18	1.57	1.95	0.64	4.34	2.32	0.92	1.71	1.56	17.78	1.77
8	0.80	0.622	0.43	0.84	0.52	0.24	1.05	0.88	0.37	0.60	0.57	6.39	0.63
9	0.77	1.27	0.72	0.90	0.90	0.56	3.35	3.29	0.66	1.05	1.10	13.52	1.35

As seen in Table 9, the highest PER rates were related to two elements of cadmium and mercury, while the lowest PER rate was related to two elements of zinc and chromium. According to the classification (Hakanson, 1980), the PER rates in the sediments by metals are divided into the following categories: Low risk: $E < 40$; $PER < 150$, Medium risk: $40 \leq E < 80$; $150 \leq PER < 300$, Significant risk: $80 \leq E < 160$; $300 \leq PER < 600$, High risk: $160 \leq E < 320$; $PER \geq 600$, and Very high risk: $E \geq 320$. According to what was mentioned above, the ecological risk factor (E) rate for all metals was individually less than 40 and the PER index value was less than 150 in different regions. Therefore, in terms of ecological risk, the concentration of heavy metals was at low risk. These results are consistent with those

of Jamshidi & Bastami's research (2016).

As shown in Table 10, the maximum concentrations of Cu and Pb were greater than ERL_a . However, the mean concentration of these elements was lower than the ERL_a standard. The mean and maximum concentrations of Zn, Cr, and Cd were also lower than the ERL_a . In case of Ni, As, and Hg, both the mean and maximum concentrations of these elements were higher than ERL_a and $ISQG_c$.

As seen in Fig. 3, all calculated Mean ERM's quotients were below 0.5, occurring within the range of 0.1 to 0.38. According to the classification, the probability of toxicity was 21%. Jamshidi et al., (2016) (from Anzali wetland) also obtained the Mean ERM quotient within the range of 0.15 to 0.34.

Table 9. Potential ecological risk (PER) index and E values

Station	Hg	Cu	Ni	Cd	As	Cr	Pb	Zn	PER
1	23.4	2.82	3.05	28.80	3.20	0.83	3.33	0.51	65.94
2	25.5	7.42	4.46	37.95	3.57	1.15	5.84	0.61	86.59
3	17.4	4.65	4.46	44.70	4.70	1.15	7.43	0.75	85.24
4	9.8	3.39	2.10	30.15	4.27	0.58	4.56	0.85	55.70
5	27.6	5.47	4.24	38.40	7.18	0.84	7.43	0.63	91.80
6	10.9	2.81	2.49	29.55	4.19	0.51	4.58	0.31	55.34
7	51.6	9.08	7.09	47.25	19.59	1.30	11.62	0.92	148.46
8	32.1	3.11	2.63	25.35	5.23	0.48	4.44	0.37	73.71
9	31	6.39	4.37	27.00	9.06	1.13	16.46	0.67	96.10
Average	25.5	5.01	4.33	34.35	6.77	0.88	7.29	0.62	-

Table 10. Comparison between heavy metal concentration in Anzali wetland and sediment quality guidelines from NOAA (Long et al., 1995) and Environment Canada (ISQG, 1995)

SQGs	Heavy metals							
	As (ppm)	Cd(ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb(ppm)	Hg (ppm)	Zn (ppm)
ERLa	8.20	1.20	81.0	34.0	20.90	46.70	0.15	150.00
ERMb	70.00	9.60	370.0	270.0	51.60	218.00	0.71	410.00
ISQGc	7.24	0.68	52.3	18.7	15.90	30.20	0.13	124.00
PEL	41.60	4.21	160.0	108.0	42.80	112.00	0.70	271.00
This study	8.81 (4.16-25.47)	0.23 (0.16-0.315)	31.5 (17.15-46.14)	32.1 (17.96-58.10)	31.66 (17.13-57.93)	23.36 (10.66-52.69)	0.25 (0.098-0.516)	79.37 (40.07-116.93)

a ERL = Effect range low (NOAA).

b ERM = Effect range medium (NOAA).

c ISQG= Interim sediment quality guideline (Environment Canada).

d PEL = Probable effects level (Environment Canada).

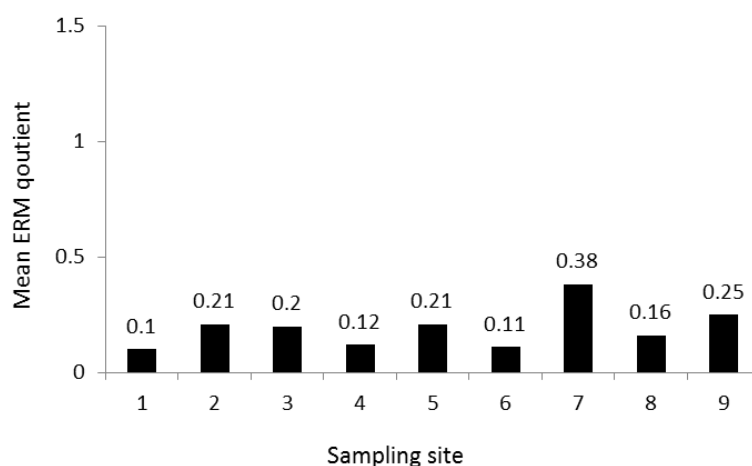


Fig. 3. Mean ERM quotient in the sediment samples of Anzali wetland

CONCLUSION

Results of this study provide valuable information about metal heavy pollution and physical characteristics of sediment from different sampling stations of Anzali wetland. The order of the mean concentrations of examined heavy metals was: $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cr} > \text{As} > \text{Hg} > \text{Cd}$. Geoaccumulation Index (Igeo), contamination factor (CF), Pollution load index (PLI), modified Contamination degree Index (mCd), Potential Ecological Risk (PER) Index, and Mean ERM quotient index were successfully used for assessment of contamination. According to Igeo: the sediments quality was in unpolluted to moderately polluted condition for Fe, Cd, Pb, As, Mn, and Cu while according to contamination factor (Cf): Pb, Fe, and Mn were responsible for considerable contamination and Cd, Ni, Cu, Hg, and As, for moderate contamination. According to PLI index and modified Contamination degree Index (mCd), Stations 7 (Hendekhaleh) and 9 (Khazar Villa) were polluted with heavy metals. The result of Potential Ecological Risk (PER) Index showed that cadmium and mercury had the highest PER index rates but in comparison with PER index categories, the concentration of these heavy metals was at low risk. According to the sediment quality guidelines,

both the mean and maximum concentrations of nickel, Arsenic, and Mercury elements were higher than ERLa and ISQGC. Finally, the result of Mean ERM quotient index showed that the probability of toxicity in Anzali wetland was 21%.

Acknowledgment

This work was supported by the Iran National Science Foundation (INSF) under Grant 96001920.

REFERENCES

- Abraham, G.M.S. and Parker, R.J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ. Monit. Assess.*, 136: 227–238.
- Alhashemi, A.S., Karbassi, A.R., Kiabi, B.H., Monavari, S.M., Nabavi, S.M. and Sekhavatjou, M.S. (2011). Bioaccumulation of trace elements in trophic levels of wetland plants and waterfowl birds. *Biol. Trace. Elem. Res.*, 142(3):500-16.
- Alhashemi, H.A., Sekhavatjou, M.S., Hassanzadeh Kiabi, B. and Karbassi, A.R. (2012). Bioaccumulation of trace elements in water, sediment, and six fish species from a freshwater wetland, Iran. *Microchemical Journal.*, 104: 1-6.
- Alizadeh Ketek Lahijani, H., Naderi Beni, A. and Tavakoli, V. (2018). Heavy metals in coastal sediments of South Caspian Sea: natural or anthropogenic source?. *Caspian J. Environ. Sci.*, 16 (1): 47-63.

- Amini Ranjbar, G.H. (1996). Heavy metal concentration in surficial sediments from Anzali wetland, Iran. *Water. Air. Soil. Poll.*, 104:305-312.
- Bai, J., Xiao, R., Zhang, K. and Haifeng, G. (2012). Arsenic and heavy metal pollution in wetland soils from tidal freshwater and saltmarshes before and after the flow-sediment regulation regime in the Yellow River Delta, China. *J. Hydrol.*, 450-451: 244-253.
- Bastami, K.D., Neyestani, M.R., Shemirani, F., Soltani, F., Haghparast, S. and Akbari, A. (2015). Heavy metal pollution assessment in relation to sediment properties in the coastal sediments of the southern Caspian Sea. *Mar. Pollut. Bull.*, 92: 237-243.
- Carr, R.S., Long, E.R., Windom, H.L., Chapman, D.C., Thursby, G., Sloane, G.M. and Wolfe, D.A. (1996). Sediment quality assessment studies of Tampa Bay, Florida. *Environ. Toxicol. Chem.*, 15: 1218-1231.
- CCME. (1999). Canadian Water Quality Guidelines for Protection of Aquatic Life," Technical Report, Canadian Environmental Quality Guidelines, Canadian Water Quality Index 1.0.
- Coquery, M. and Welbourn, P.M. (1995). The relationship between metal concentration and organic matter in sediment and metal concentration in the aquatic macrophyte, *Eriocaulon septangulare*. *Water Res.*, 29 (9): 2094-2102.
- Djordjevic, L., Zivkovic, N., Zivkovic, L. and Djordjevic, A. (2012). Assessment of Heavy Metals Pollution in Sediments of the Korbevacka River in Southeastern Serbia. *Soil. Sediment. Contam.*, 21:889-900.
- Esmailzadeh, M., Karbassi, A. and Faramarz, M. (2016). Heavy metals in sediments and their bioaccumulation in *Phragmites australis* in the Anzali wetland of Iran. *Chin. J. Oceanol. Limn.*, 34 (4): 810-820.
- Fu, J., Zhao, C., Luo, Y., Liu, C., Kyzas, G.Z., Luo, Y., Zhao, D., An, S. and Zhu, H. (2014). Heavy metals in surface sediments of the Jialu River, China: Their relations to environmental factors. *J. Hazard. Mater.*, 270: 102-109.
- Gao, X. and Chen, C.T.A. (2012). Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Res.*, 46: 1901-1911.
- Gee, G.W. and BAUDER, J.W. (1986). Particle size analysis. In A. Klute, ed. *Methods of soil analysis*, Part 1. 2nd ed. Agronomy No. 9. Am. Soc. Agron., Madison, WI.
- Hafizur Rahman, S., Khanam, D., Mehedi Adyel, T., Shahidul Islam, M., Aminul Ahsan, M. and Ahedul Akbor, M. (2012). Assessment of heavy metal contamination of agricultural soil around Dhaka Export Processing Zone (DEPZ) (Bangladesh): Implication of Seasonal Variation and Indices. *Appl Sci.*, 2(3): 584-601.
- Hakanson, L. (1980). An Ecological Risk Index for Aquatic Pollution Control a Sedimentological Approaches. *Water Res.*, 14 (8): 975-1001.
- Harikumar, P.S., Nasir, Y.P. and Mujeebu Rahman, M.P. (2009). Distribution of heavy metals in the core sediments of a tropical wetland system. *Int. J. Environ. Sci. Te.*, 6(2):225-232.
- Harikrishnan, N., Ravisankar, R., Suresh Gandhi, M., Kanagasabapathy, K.V., Prasad, M.V.R. and Satapathy, K.K. (2017). Heavy metal assessment in sediments of east coast of Tamil Nadu using energy dispersive X-ray fluorescence spectroscopy. *Radiation Protection and Environment.*, 40 (1):21-26.
- Horowitz, A.J. and Elrick, K.A. (1987). The relation of stream sediment surface area, grain size and composition to trace element chemistry. *Appl Geochem.*, 2: 437-451
- ISQG. (1995). Interim Sediment Quality Guidelines. Environment Canada, Ottawa, 9.
- Jamshidi, S. and Bastami, K.D. (2016). Metal contamination and its ecological risk assessment in the surface sediments of Anzali wetland, Caspian Sea. *Mar. Pollut. Bull.*, 113:559-565.
- Jia, H., Sun, Y., Liu, X., Yang, M., Wang, D., Qi, H., Shen, L., Sverko, E.d., Reiner, E. and Yi-Fan, L. (2011). Concentration and bioaccumulation of dechlorane compounds in coastal environment of Northern China. *Environ. Sci. Technol.*, 45(7): 2613-2618.
- Karbassi, A., Monavari, S.M., Bidhendi, G.R.N. and Nematpour, K. (2008). Metal pollution assessment of sediment and water in the Shur River. *Environ. Monit. Assess.*, 147:107-116.
- Karbassi, A. and Pazoki, M. (2015). Environmental Qualitative assessment of rivers sediments. *Global J. Environ. Sci. Manage.*, 1 (2): 109-116.
- Khanipour, A.A., Ahmadi, M., Seifzadeh, M., Zareh gashti, G.H. and Zolfinezhad, K. (2016). Evaluation of Bioaccumulation of heavy metals (cadmium, lead and zinc) in edible muscle tissue of crucian carp (*Carassius auratus*) from international wetland of Anzali. *J.F.S.T.*, 13(54): 155-163. (In Persian).
- Khosheghbal, M.Z., Charkhabi, A.H., Sharifi, F. and Ghazban, F. (2013) An investigation of sediment pollution in Anzali wetland. *Pol. J. Environ. Stud.*, 22(1): 283-288.

- Khosravi, M., Bahramifarm N. and Ghasempour, M. (2011). Survey of Heavy Metals (Cd, Pb, Hg, Zn and Cu) Contamination in Sediment of Three Sites Anzali Wetland. Iranian Journal of Health and Environment., 4 (2): 223-232. (In Persian).
- Jia, H., Sun, Y., Liu, X., Yang, M., Wang, D., Qi, H., Shen, L., Sverko, E.d., Reiner, E. and Yi-Fan, L. (2011). Concentration and bioaccumulation of dechlorane compounds in coastal environment of Northern China. Environ. Sci. Technol., 45(7): 2613–2618.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag., 19: 18–97.
- Long, E.R. and MacDonald, D.D. (1998). Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. Hum. Ecol. Risk. Assess., 4 (5): 1019–1039.
- McCave, I.N. (1984). Size spectra and aggregation of suspended particles in the deep ocean. Deep-Sea. Res., 31: 329–352.
- MacDonald, D.D., Carr, R.S., Calder, F.D., Long, E.R. and Ingersoll, C.G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology., 5: 253–278.
- Martin, J.M. and Meybeck, M. (1979). Elemental Mass-Balance of Material Carried by Major World Rivers. Mar. Chem., 7 (3):178-206.
- Moore, F., Nematollahi, M.J. and Keshavarzi, B. (2015). Heavy metals fractionation in surface sediments of Gowatr bay-Iran. Environ. Monit. Assess., 187: 4117.
- Muller, G. (1979). Heavy metals in the sediment of the Rhine-Changes seity. Umsch. Wiss. Tech., 79:778-783.
- Muller, G. (1981). The heavy metal pollution of the sediments of Neckars and its tributary A stocktaking. Chem. Zeit., 105:157-164.
- Niu, Y., Jiao, W., Yu, H., Niu, Y., Pang, Y., Xu, X. and Guo, X. (2015). Spatial Evaluation of Heavy Metals Concentrations in the Surface Sediment of Taihu Lake. Int. J. Environ. Res. Public. Health., 12(12): 15028-15039.
- Pakzad, H. R., Pasandi, M., Romiani, A. and Kamali, M. (2014). Distribution of Ni, Cr, Sr, Cu, and Zn in the FineGrained Sediments of Anzali Wetland. Environmental Sciences., 12(2):19-30. (In Persian).
- Pandey, J. and Singh, R. (2017), Heavy metals in sediments of Ganga River: up- and downstream urban influences. Applied Water Science, 7(4):1669–1678.
- Pejman, A.H., Nabi Bidhendi, G.R., Ardestani, M., Saeedi, M. and Baghvand, A. (2017). Fractionation of heavy metals in sediments and assessment of their availability risk: A case study in the northwestern of Persian Gulf. Mar. Pollut. Bull., 114(2):881-887.
- Pourkhabbaz, AR., Pourkhabbaz, HR., Khazaei, T., Behraves, S. and Ebrahimpour, M. (2011). Assessment of heavy metal accumulation in Anzali wetland, Iran, using a submerged aquatic plant, Ceratophyllum demersum. Afr. J. Aquat. Sci., 36 (3): 261–265.
- Rzetala, M. (2015). Assessment of toxic metal contamination of bottom sediments in water bodies in urban areas. Soil. Sediment. Contam., 24(1):49–63.
- Raju, K.V., Somashekar, R. and Prakash, K. (2012) Heavy Metal Status of Sediment in River Cauvery, Karnataka. Environ. Monit. Assess., 184 (1): 361-373.
- Salamat, N., Movahedinia, A.A., Deylami, E.E. and Mohammadi, Y. (2015). Pike (Esox Lucius) Bio-indicator of heavy metal pollution in Anzali wetland. Water. Qual. Expo. Health., 7:251-254.
- Sparks, D.L. (1996). Method of Soil Analysis. Part3. Chemical Methods (p. 1390). American Society of Agronomy.
- Taghinia Hejabi, A., Basavarajappa, H.T., Karbassi, A.R. and Monavari, S.M. (2011). Heavy metal pollution in water and sediments in the Kabini River, Karnataka, India. Environ. Monit. Assess., 182:1–13.
- Vaezi, A.R., Karbassi A. R. and Fakhraee, M. (2015). Assessing the trace metal pollution in the sediments of Mahshahr Bay, Persian Gulf, via a novel pollution index. Environ. Monit. Assess., 187: 613.
- Vesali Naseh, M.R., Karbassi, A.R., Ghazaban, F. and Baghvand, A. (2012). Relationship between Heavy Metal Concentration in Water and Sediments in Anzali Wetland, Iran. Journal of Health System Research, 8(1):114-123. (In Persian).
- Vukovic, D., Stankovic, S., Vukovic, Z. and Ksenija, J.K. (2014). Transport and storage of heavy metals in the Sava River Basin in Serbia. J. Serb. Chem. Soc., 79 (3): 379–387.
- Wang, Y., Yangm Z., Shenm Z., Tangm Z., Nium J. and Gao, F. (2011). Assessment of heavy metals in sediments from a typical catchment of the Yangtze River, China. Environ. Monit. Assess., 172(1–4):407–417.

Water Research Commission. (2014). Water and the environment. Water Wheel, 13: 8–14.

WHO (2004) Guidelines for Drinking Water Quality. 3rd Edition (p.515). World Health Organization.

USEPA. (1999). US Environmental Protection Agency: screening level ecological risk assessment protocol for hazardous waste combustion facilities. Appendix E: toxicity reference values, p 3.

Xiao, R., Bai, J.H., Huang, L.B., Zhang, H.G., Cui, B.S. and Liu, X.H. (2013). Distribution and pollution, toxicity and risk assessment of heavy metals in sediments from urban and rural rivers of the Pearl River delta in southern China. *Ecotoxicology*, 22 (10): 1564-1575.

Yilmaz, A.B., Yanar, A. and Alkan, E.N. (2018). Review of Heavy Metal Accumulation in Aquatic Environment of Northern East Mediterranean Sea Part II: Some Non-Essential Metals. *Pollution*, 4(1): 143-181.

Ziarati, P., Asgarpanah, J. and MirMohammad Makki, F. (2015). Phytoremediation of Heavy Metal Contaminated Water Using Potential Caspian Sea Wetland Plant: *Nymphaeaceae*. *Biosciences Biotechnology Research Asia*, 12(3): 2467-2473.

Zamani Hargalani, F., Karbassi, A., Monavari, S.M. and Abroomand Azar, P. (2014). A novel pollution index based on the bioavailability of elements: a study on Anzali wetland bed sediments. *Environ. Monit. Assess.*, 186 (4): 2329–2348.



Pollution is licensed under a "[Creative Commons Attribution 4.0 International \(CC-BY 4.0\)](https://creativecommons.org/licenses/by/4.0/)"