ORIGINAL ARTICLE



Potential ecological risk assessment, enrichment, geoaccumulation, and source identification of metals in the surface sediments of Choghakhor Wetland, Iran

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Received: 15 May 2016/Accepted: 24 May 2017/Published online: 5 June 2017 © Springer-Verlag Berlin Heidelberg 2017

Abstract This study reported the first comprehensive research on identification of metal concentrations (Fe, Mg, Mn, Pb, Cd, Cr) in order to provide baseline data for future studies, identify possible sources, determine degree of pollution, and identify potential ecological risks of metals in surface sediments from Iran's Choghakhor Wetland. The order of metal concentration was as follows: Fe > Mg > Mn > Pb > Cd > Cr, with mean concentrations of 6140.35, 1647.32, 289.03, 1.10, and 0.45 µg/g of dry weight, respectively. These results reveal that Choghakhor Wetland is not heavily polluted compared to other regions. The results of enrichment factor (EF) and geoaccumulation index (Igeo) showed that Fe, Pb, Mg, Cr, and Mn presented low levels of contamination and probably originated from natural sources. On the other hand, the results of EF and Igeo indices suggested that Cd concentrations in sediments of Choghakhor Wetland originated from anthropogenic sources. Based on the results of three sets of sediment quality guidelines, only Cd concentration in sediments of Choghakhor Wetland is a threat for aquatic organisms of Choghakhor Wetland. The results of multivariate analysis such as principal component analysis and cluster analysis showed that Fe-Mn, Cr-Mg, and Pb groups originated from natural sources, while Cd concentrations in sediments of Choghakhor Wetland originated from both natural and anthropogenic sources (mainly chemical

fertilizers). To our knowledge, this is the first study about metal concentrations in sediments of Choghakhor Wetland, and because of low levels of these metals, these concentrations can be considered background levels for future investigation.

Keywords Metals · Sediments · Enrichment factor · Geoaccumulation index · Multivariate statistical analyses · Choghakhor Wetland

Introduction

Contamination by metals has considerable importance because of its extreme toxicity to humans and biological systems (Benson et al. 2007). The contamination of aquatic ecosystems by metals is one of the most challenging pollution issues due to the toxicity, abundance, persistence, and, finally, bioaccumulation of metals (Fu et al. 2014). Sediments are the final destination of metals, because of adsorption, desorption, precipitation, diffusion, chemical reactions, biological activity, and a combination of these phenomena. Sediments are an important sink for metals, but when some physical disturbance occurs, or there is diagnosis, and/or there are changes in pH or redox potential, they can become a source of metal pollution, released into the overlying water column (Chatterjee et al. 2009). Moreover, it is widely known that metals are indestructible and can be retained in soils for a long time (Gao et al. 2013), as they cannot be chemically or biologically degraded. Sediments have been used as an important tool to assess the health status of aquatic ecosystems and provide a history of anthropogenic pollutant input (Zahra et al. 2014). Spatial surveys of metal concentrations in sediments are useful to assess pollution in the aquatic environment

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and to provide basic information for the judgment of environmental health risks (Hu et al. 2013). Without the baseline dataset, it is not possible to judge environmental health risks and apply a suitable environmental remediation program.

Like other creatures, aquatic organisms are vulnerable to pollution at both toxic and subtoxic concentrations. This weakens them and can result in decline or death of populations, by making them more vulnerable to disease, impaired fertility, and/or early death. Furthermore, certain aquatic creatures through their unique biological processes can amass trace metals far greater than those typically found in the organisms. Consequently, the risk extends beyond their lives and into upstream risk to the humans and animals that depend upon these protein resources (Kibera 2016).

To our knowledge, no study has reported on metallic pollution in the sediments of Choghakhor Wetland, located in Chaharmahal and Bakhtiari Province, southwestern Iran. To address this critical knowledge shortcoming, this study aimed to investigate the state of the metal contamination in surface sediments of this aquatic ecosystem using several indices, such as enrichment factor (EF), geoaccumulation index (Igeo), and sediment quality guidelines (SQGs), and a multivariate approach. In recent years, several indices have been used to assess metal contamination and its ecological risk (Hou et al. 2013). For better management of aquatic ecosystems, their contamination assessment should be easily communicated to local managers and decision makers. Environmental quality indicators and indices are powerful tools for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, or the public (Caeiro et al. 2005). In addition, to reveal possible sources of metals and determine relationships among metals, multivariate statistical approaches can be useful. In recent decades, Choghakhor Wetland has been affected by human activities such as dam construction, agricultural activities, livestock grazing, boating, fishing, and wastewater discharge from nearby villages. In this study, we report the first comprehensive research on identification of metal concentrations providing baseline data for future studies, identifying possible sources, determining degree of pollution, and categorizing potential ecological risks of metals in surface sediments from Choghakhor Wetland.

Materials and methods

Study area

Choghakhor Wetland is internationally known, located in Chaharmahal and Bakhtiari Province, located at latitude 31°55'N, longitude 50°54'E, encompassing 1687 ha (Fig. 1). This wetland is near Tang-e-Sayad and Sabz-koh Biosphere Reserves in southwestern Iran. The wetland was designated a Ramsar site in 2011. Choghakhor Wetland is considered one of the most important sites in Iran for the endemic Zagros pupfish (*Aphanius vladykovi*). It is important for flood control and ground water replenishment and is generally considered a reservoir for biodiversity (RSIS 2010). As mentioned above, in recent decades Choghakhor Wetland has been affected by human activities such as construction of a dam, agricultural activities, livestock grazing, boating, fishing, and discharging wastewater from encompassing villages.

Sample collection

Fifty-two surface sediment samples were collected from the top 6 cm of sediment with a polypropylene coring device measuring 3 m long with 5 cm internal diameter. Locations of sampling points were recorded using a Global Positioning System. Samples were placed in sterile plastic bags and then stored in a refrigerator prior to analysis. Because of the high density of aquatic plants in the central area of the wetland, it is virtually impossible to collect sediment samples from the center of the wetland. Samples were air-dried and sieved through a 2-mm sieve in order to remove stone and coarse debris and then passed through a 0.125-mm sieve.

Analytical methods

For all samples, 1 g of dried and homogenized sediment was carefully weighed and digested with HNO₃-HClO₄-HF mixture in Teflon tubes at a temperature of 160 °C for 6 h (Gao et al. 2013). The digestion solution was filtered and diluted with deionized water to 25 ml in a volumetric flask. All samples were kept at 4 °C prior to analysis (Massolo et al. 2012). Metal concentrations in solutions were analyzed using an atomic absorption spectrometer (PerkinElmer model A Analyst 400, MA, USA). All samples were analyzed in three replicates. Chinese geochemical standard reference sample GSD 9 (stream sediments) and Standard Reference Materials (SRMs) (SRM 2711 and SRM 2709, National Institute of Standards and Technology) have been used to estimate accuracy. The average recoveries of the standard reference materials were 125, 98.4, 97, and 93.9% for Cd, Pb, Mn, and Cr, respectively.

Assessment of metal contamination

Enrichment factor (EF)

EF is commonly used to determine and quantify the anthropogenic contribution of metals over natural inputs



Fig. 1 Map and sampling points of surface sediments in Choghakhor Wetland, Iran

(Li et al. 2013a; Sungur and Özcan 2014). To reduce the influence of the particle grain-sized effects on metal contamination, concentration data should be normalized by a conservative element (Wang et al. 2015). Mn was used as a reference element to calculate anthropogenic metal enrichments (Zahra et al. 2014). In addition, other metals such as Li, Cs, Sc, and Fe have been used as reference elements (Ruhong et al. 2010; Zahra et al. 2014). The enrichment factor can be calculated as follows:

$$EF = \frac{\left(\frac{C_{EE}}{C_{Mn}}\right)Sample}{\left(\frac{C_{EE}}{C_{Mn}}\right)Reference material}$$

In this equation, the numerator refers to the ratio of the concentration of a sample's examined element (C_{EE}) to the reference element (Mn). The denominator shows the ratio of the concentration of a reference material's examined element (C_{EE}) to the reference element (Mn) (Zahra et al. 2014). World average shale is one of the materials commonly used to provide reference elements. The regional reference elements for these metals are not available in the study area. Thus, the reference elements of heavy metals in the average shale obtained from Turekian and Wedepohl (1961) are used in this study. The EF value was interpreted as suggested by Wang et al. (2015), where EF < 2, minimal enrichment; EF = 2–5, moderate enrichment;

EF = 5-20, significant enrichment; EF = 20-40, very high enrichment; and EF > 40, extreme enrichment.

Geoaccumulation index (I_{geo})

Geoaccumulation index is another index commonly used to calculate the metal contamination levels (Müller 1979). The equation used for the calculation of I_{geo} is expressed as follows:

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5B_n}$$

where C_n is the examined element in the sediment for heavy metal n, B_n is the examined reference for the metal n, and the factor 1.5 is used because of possible variations of the background data due to lithological variations (Ghrefat et al. 2011). In the present study, global average shale data from Turekian and Wedepohl (1961) were used as examined reference to calculate I_{geo} . This index defines seven classes with respect to sediment quality: unpolluted ($I_{geo} \leq 0$); unpolluted to moderately polluted ($0 < I_{geo} - \leq 1$); moderately polluted ($1 < I_{geo} \leq 2$); moderately to strongly polluted ($2 < I_{geo} \leq 3$); strongly polluted ($3 < I_{geo} \leq 4$); strongly to extremely polluted ($4 < I_{geo} - \leq 5$); and extremely polluted ($I_{geo} > 5$) (Müller 1981; Li et al. 2013a).

Sediment quality guidelines (SQGs)

To evaluate ecological risk of heavy metals in sediments, three sets of sediment quality guidelines were performed as follows. (1) The effect range low (ERL) and effect range median (ERM) were carried out. (2) Next, the threshold effect level (TEL) and probable effect level (PEL) values were implemented. ERL and ERM are defined as the levels below which adverse biological effects are unexpected. In contrast, ERM and PEL represent chemical concentrations above which adverse biological effects are expected to happen (Xiao et al. 2011; Li et al. 2013b). (3) Finally, the lowest effect level (LEL) and severe effect level (SEL), defined below, were determined. As expected, at LEL, there was no effect on the majority of sediment-dwelling organisms. Above that level, however, namely at SEL, serious adverse effects on the majority of sedimentdwelling organisms are expected (MOE 1993).

Multivariate statistical methods

Multivariate techniques, such as principal component analysis (PCA) and cluster analysis (CA), are commonly performed to identify possible source of heavy metals from natural or anthropogenic inputs (Bai et al. 2011; Hu et al. 2013; Li et al. 2013b; Fu et al. 2014; Wang et al. 2014, 2015). Statistical analyses were performed using SPSS 17.0 and MINITAB 17.0 software packages. Before performing PCA, Kaiser–Meyer–Olkin (KMO) and Bartlett's tests were applied to assess the suitability of the data for testing (Fu et al. 2014). In addition, normality of data was checked before running tests. All data were reported as $\mu g/g$ of dry weight (dw).

Results and discussion

Metal concentrations in sediments

Table 1 shows descriptive statistics of Cr, Pb, Cd, Mn, Fe, and Mg in surface sediments of Choghakhor Wetland. The order of metal concentrations was as follows: Fe > Mg > Mn > Pb > Cd > Cr with mean concentrations of 6140.35, 1647.32, 289.03, 1.10, and 0.45 µg/g dw, respectively. Fe, Mg, and Mn are among the most abundant metals in the Earth's crust (Yaroshevsky 2006), and the order of these metals in this study is in adherence to their amounts in the Earth's crust. The sequence of metal concentrations in this study is similar to previous studies, which showed high levels of Fe, Mg, and Mn compared to other examined metals(An and Kampbell 2003; Arain et al. 2008; Ennouri et al. 2010). In addition, Fe and Mn had the highest spatial variability, with a coefficient of variation of 0.68 and 0.39, respectively. The comparison of metal concentrations with other regions is presented in Table 2.

Metal concentrations in sediments of Choghakhor Wetland were lower than those reported from Shadegan Wetland of Iran (Alhashemi et al. 2012). In addition, the mean concentration of Cd in sediments of Choghakhor Wetland was higher than the mean concentration of Cd from Iran's Anzali Wetland, but the mean concentration of Pb from Choghakhor Wetland was significantly lower than the mean reported from Anzali Wetland (Zamani-Ahmadmahmoodi et al. 2013). Overall, as shown in Table 2, metal concentrations in sediments of Choghakhor Wetland were lower than those reported from other bodies of water, except in some cases the mean concentration of Cd, Fe, and Mn in sediments of Choghakhor Wetland was higher than reported elsewhere. These results reveal that Choghakhor Wetland is not heavily polluted compared to other regions.

Contamination assessment of metals, using EF and I_{geo}

Enrichment degree of metals was calculated using enrichment factor. The EF values for investigated metals were as following order: 4.94-16.98 (mean = 10.13) for Cd; 0.03-2.62 (mean = 0.43) for Fe; 0.09-5.16 (mean = 0.42) for Pb; 0.14-1.02 (mean = 0.37) for Mg; and 0.01-0.04

Table 1 Metal concentrations (µg/g dw) in sediments of Choghakhor Wetland and comparison with different standard quality guidelines

	Fe	Mg	Mn	Pb	Cd	Cr
Mean \pm standard error	6140.35 ± 586	1647.32 ± 20	289.03 ± 16	1.82 ± 03	1.10 ± 0.05	0.45 ± 0
Range	171–14,297	1274–1954	101–578	1.32-2.46	0.54-1.84	0.32-0.57
CV	0.68	0.08	0.39	0.12	0.3	0.11
TEL	-	-	-	35	0.596	37.3
ERL	-	-	-	35	5	80
PEL	-	-	-	91.3	3.53	90
ERM	-	-	-	110	9	145
LEL	20,000	-	460	31	0.6	26
SEL	40,000	-	1100	250	10	110

Table 2 Comparison of metal concentration in sediments of Choghakhor Wetland with other aquatic ecosystems

References	Fe	Mg	Mn	Pb	Cd	Cr	Study site
This study	6140.35	1647	289	1.82	1.10	0.45	Choghakhor Wetland, Iran
Ennouri et al. (2010)	33,631	11,813	234	54.13	0.27	-	Gulf of Tunis
Nemr et al. (2006)	2239	-	115.54	70.44	9.92	25.6	Suez Gulf, Egypt
Katip et al. (2012)	27,664.2	-	781.94	33.37	5.03	131.6	Lake Uluabat, Turkey
Chaudhary et al. (2013)	2942	2939	105	-	-	53	Korangi Creek, Pakistan
Harikumar and Jisha (2010)	-	-	127.8	43.46	0.2	1.71	Kottuli Wetland, India
Alhashemi et al. (2012)	-	-	310	14.22	4.66	12.36	Shadegan Wetland, Iran
Zamani-Ahmadmahmoodi et al. (2013)	-	-	-	34.95	0.024	-	Anzali Wetland, Iran
Gao et al. (2013)	-	-	-	30.72	0.67	81.33	Baiyangdian Lake, China
Ruhong et al. (2010)				25.17	0.31	54.97	Tangxi River Estuary, China
Li et al. (2013b)				60.99	4.65	88.29	Dongting Lake, China

(mean = 0.02) for Cr, yielding a sequence of Cd > Fe > Pb > Mg > Cr. The results show that the EF values of Fe, Pb, Mg, and Cr were less than 2. According to the EF levels suggested by Wang et al. (2015), EF levels less than 2 exhibit minimal enrichments, and likely are of natural origin in the study area. However, Cd had higher EF value compared to the other metals and showed significant enrichment, suggesting possible anthropogenic sources in the study area.

The I_{geo} values of surface sediments from Choghakhor Wetland were negative values, with the mean of -3.9, -3.9, -3.7, -8.2, and -2.2 for Fe, Pb, Mg, Cr, and Mn, respectively. The negative I_{geo} values are the results of relatively low levels of contamination by metals (Zamani-Ahmadmahmoodi et al. 2013). According to scale proposed by Müller (1979), the I_{geo} values for Fe, Pb, Mg, Cr, and Mn fell in the first class, unpolluted ($I_{geo} \le 0$). These findings confirmed the results of EF for Fe, Pb, Mg, and Cr, which presented minimal enrichments and showed low levels of contaminations for the metals. In contrast, for Cd the mean I_{geo} value was 1.23, positioning Cd in the third class, moderately polluted ($1 < I_{geo} \le 2$). This result was similar to the result of EF for Cd, in that Cd had significant enrichment and probably had anthropogenic sources in the study area.

Ecological risk assessment based on SQGs

Metal concentrations in surface sediments of Choghakhor Wetland were evaluated with respect to sediment quality guidelines for metals in freshwater ecosystems proposed by MacDonald et al. (2000) and sediment quality guideline developed by the Ministry of Environment and Energy, Ontario, Canada (MOE 1993). The results of these comparisons are tabulated in Table 1. For Mg, Mn, Pb, and Cr, all measured values were below the values recommended for the occurrence of adverse biological effects, namely either ERL, TEL, or LEL; or ERM, PEL, or SEL. In contrast, the mean value of Cd was higher than TEL or LEL and lower than the values proposed for ERL, ERM, PEL, and SEL. These results indicated that the values of Fe, Mg, Mn, Pb, Cd, and Cr were lower than levels above which adverse biological effects are expected to occur and above which serious adverse effects on the majority of sediment-dwelling organisms are expected. Furthermore, with the exception Cd, almost all of the values of Fe, Mg, Mn, Pb, and Cr were lower than levels below which adverse biological effects are not expected to happen and below which no effects on the majority of sedimentdwelling organisms are expected. These findings indicated that only Cd concentration in sediments of Choghakhor Wetland is a threat for aquatic organisms of Choghakhor Wetland, and remediation programs should be designed to decrease the Cd concentration in sediments.

Source identification

In the present study, multivariate techniques such as PCA and CA have been used to identify possible sources of metals. The results of Kaiser–Meyer–Olkin (KMO = 0.61) and Bartlett's tests (P < 0.05) confirmed the adequacy of the data set for PCA. The results of PCA appear in Table 3 and Fig. 2. The results of PCA show three principal components (PCs) explained 58.59% of the total variance in the original dataset. The rotated component matrix revealed that Cd, Fe, and Mn, associated with the first principal component, explained 37.59% of total variance with positive loading on Cd, Mn, and Fe. Mg and Cr, which had high strong positive and negative correlation with the second component, explained 21% of total variance. Pb was associated with the third component, explaining 15.42% of 74.01 of total variance (Table 3). Additionally, a loading plot was used to depict the results of PCA (Fig. 2). The lines that go in the same direction and are close to one another indicate how the variables may be grouped. The loading plot showed that Fe, Mn, and Cd had high positive association with the first component, while Mg and Cr had high strong positive and negative correlation with the

Metals	Componen	t	
	PC1	PC2	PC3
Cr	-0.382	-0.697	-0.171
Pb	0.063	-0.028	0.930
Cd	0.692	0.214	0.401
Mn	0.781	0.042	-0.177
Fe	0.836	-0.192	0.251
Mg	-0.265	0.831	-0.147
Initial eigenvalues	2.25	1.26	0.92
% of variance explained	37.59	21.00	15.42
% of cumulative	37.59	58.59	74.01

Bold values are significant at > 0.6



Fig. 2 Principal component analysis loading plot of the studied metals in surface sediments from Choghakhor Wetland

second component, respectively; and Pb was associated with both components. The occurrence of Fe and Mn in the same PC might be due to strong association with the geochemical matrix between the two elements (Jonathan et al. 2010). In addition, a lithogenic control over the distribution of Fe and Mn has been reported by some authors (Han et al. 2006; Mico et al. 2006; Bai et al. 2011). Mico et al. (2006) stated that Fe and Mn are well known to be geogenic. Thus, these findings suggested that Fe and Mn concentrations in sediments of Choghakhor Wetland have a natural source and probably originated from parent rock materials. On the other hand, Cd is located in the same group with Fe and Mn. Cd is specifically adsorbed by crystalline and amorphous oxides of Al, Fe, and Mn (Rodriguez et al. 2006). The results of EF and I_{geo} indices suggested that Cd concentrations in sediments of Choghakhor Wetland originated from anthropogenic sources. Cd concentrations in sediments can result from use of phosphate fertilizers and other chemical fertilizers (Sundaray et al. 2011; Zahra et al. 2014; Wang et al. 2015). Therefore, Cd occurring with Fe and Mn in the first principal component suggests that most likely Cd concentrations in sediments in Choghakhor Wetland had both natural and anthropogenic sources in the study area. In the present study, agricultural activities are concentrated south of Choghakhor Wetland, and because of the tendency of agricultural lands to slope toward the wetland, runoff originating from agricultural lands can be easily released into the wetland. The second component consists of Cr and Mg and explained 21% of total variance with negative loadings on Cr and Mg. Chromium pollution is commonly attributed to industrial activities such as mining, tanneries, electroplating, paint facilities, and other chemical facilities (Silva Filho et al. 2010; Davutluoglu et al. 2011; Qadir et al. 2013; Ali et al. 2015). The mean concentration of Cr in sediments of Choghakhor Wetland was considerably lower than those reported elsewhere and lower than the average shale of this metal (Cr = 90), reported by Turekian and Wedepohl (1961). In addition, there are no chromium industries around Choghakhor Wetland. Furthermore, the mean concentration of Mg (1674 μ g/g dw) in sediments of Choghakhor Wetland is lower than other published data (Table 2) and the average shale of this metal (15,000 µg/g dw) (Turekian and Wedepohl 1961). Anthropogenic sources of magnesium include fertilizers and liming (Reimann and Caritat 1998). However, because of the low level of Mg in sediments of Choghakhor Wetland, the source of this metal is related to parent rock materials. Consequently, these findings suggest no clear influences from anthropogenic activities over the distribution of Cr and Mg in the study area. Cluster analysis was also applied to identify metal groups. Ward's method was used as a linkage method and correlation as a distance measure. Usually, CA is coupled with PCA to check the analytical results and to group individual parameters and variables (Wang et al. 2014; Li et al. 2013b). Dendrogram showed three main groups of metals: (1) Cr-Mg, (2) Pb, and (3) Cd-Fe-Mn (Fig. 3). The results of CA were in a good agreement with PCA. Similar to the results of PCA, Pb is positioned in the separate group and probably originated from natural sources because of its very low background level in Choghakhor Wetland (Table 1). In two other groups, Cr-Mg and Cd-Fe-Mn, clustering of metals was similar to the results of PCA, and a similar interpretation can be reached about possible sources of metals.

Conclusion

Implementation of multivariate analyses, such as PCA and CA, and indices, such as EF, I_{geo} , and SQGs, was useful to explore possible sources of heavy metals in Choghakhor Wetland. The results of the present study revealed that Choghakhor Wetland is not heavily polluted compared to



Fig. 3 Dendrogram of the metal concentrations in surface sediments from Choghakhor Wetland

other wetlands. Overall, the results of the present study demonstrate that with the exception of Cd concentrations in the sediments of Choghakhor Wetland, other metals present no concern in the study area. Regardless, regular biomonitoring programs should be designed and implemented to control inputting pollution sources, such as agriculture and wastewater runoffs. For many people around Choghakhor Wetland, their most important jobs are in fishing. Since the demand for fish consumption is increasing, as are agricultural and industrial activities, monitoring of metals in fish species in terms of environment and human health is essential. Based on the results of the present study, we assume that because the level of metals in sediment is low, the levels of metals in aquatic organisms such as fish are low; however, more analyses should be performed to confirm this hypothesis. To our knowledge, this is the first study about metal concentrations in the sediments of Choghakhor Wetland, and because of the low levels of these metals, these concentrations can be considered as background levels for future investigation. To date, little information has been developed about the examination of heavy metals in biota of Choghakhor Wetland. Rahimi and Raissy (2009) investigated the level of lead and cadmium in some fish species caught in Choghakhor Wetland. They found that the mean level of lead was lower than threshold limit recommended by the European Union, but the mean level of cadmium was higher than that acceptable to the European Union. Overall, information is lacking about the level of other important metals in Choghakhor Wetland, such as mercury, arsenic, and copper, which are important to ecotoxicology and should be investigated in future studies.

Acknowledgements This research was funded by Shahrekord University, Iran.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Research involving human participants and/or animals For this type of study, formal consent is not required. All procedures performed in studies involving animals were in accordance with the ethical standards of the institution or practice at which the studies were conducted.

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