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Assessment of metal pollution in the Anzali Wetland sediments using chemical partitioning method and pollution indices

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Abstract

Metal pollution in aquatic ecosystems is of immense importance. Under various environment circumstances, the metal contents of sediments can enter into the overlying water body leading to severe toxicity. This study aims to determine metal concentrations in sediments of Anzali International Wetland in Iran. Chemical partitioning method is used to determine the portion of anthropogenic pollution and the mobility potential of each metal. The intensity of metal pollution in sediments of the wetland is assessed using three reliable indices. The results of chemical partitioning reveal that cadmium bear the highest risk of being released into the aquatic environment and high amount of manganese in sulfide bond phase implies the initiation of redox state in aquatic environment of the Anzali Wetland. The results of chemical partitioning studies show that Pb, Cd, Mn and As have the highest anthropogenic portion. Cluster analysis also confirms the results of chemical partitioning and indicates that the mentioned metals can be originated from anthropogenic sources. Sediment pollution indices, including, $I_{\rm geo}$, $I_{\rm POLL}$, and m-ERM-Q reveal that metals are in the range of low to moderate pollution and also show that the highest metal pollution is in the eastern and central parts of the wetland. This can be ascribed to rivers which are the recipient of industrial, agricultural and municipal wastewaters and flow into these parts of the wetland.

Key words: pollution, environment, sediment, metal, geochemistry

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1 Introduction

Heavy metal pollution is one of the environment challenges emerged as a consequence of economic growth in many countries (Gao and Chen, 2012). They can accumulate in microorganisms, flora and fauna of aquatic habitats and find their way into human food chain leading to health problems (Sakar et al., 2011; Varol, 2011; Hosseini Alhashemi et al., 2012). Part of these particles are deposited and stabilized on sediments where they bound with different organic and inorganic matters due to low solubility of heavy metals, and in this way they are stored in sediments (Devesa-Rey et al., 2010; Karbassi et al., 2015). Heavy metals stabilized in sediments may return to water columns through chemical and biological processes (Yang et al., 2012). In case of alteration in environmental conditions (e.g., Eh, sediment redox potential), sediments can act as the source of heavy metals released into the aquatic environment (Chandra Sekhar et al., 2004; Zamani Hargalani et al., 2014). Sediments have a substantial effect in controlling the concentrations of heavy metals in the aquatic environments and are used as a monitoring tool in the risk assessment studies (Karbassi et al., 2008; Mashiatullah et al., 2013; Vaezi et al., 2015b). Sediment analysis is, therefore, a suitable method for examining metal pollution in a region (Varol, 2011). Determination of the total metal concentration in sediments alone does not provide us with an accurate estimation of environmental impacts. The reason is that metal speciation, seems to affect the bioavailability and the metal content accessible for biota (Chandra Sekhar et al., 2004). Moreover, application of total metal content for measuring the heavy metal toxicity in sediments may be controversial, because the extracted sediments with the same total metal content may have different bioavailabilities (Di Toro et al., 1990). It is widely accepted that the metals bonded with carbonates, sulfides and organic matters, have a stronger association with pollution and higher risk in bioavailability (Karbassi and Amirnezhad, 2004). Hence, the chemical partitioning methods have been developed and utilized to determine metal bonds and identify metal pollution in different sedimentation phases (Karbassi et al., 2005). During recent decades, various indices have been developed to assess the ecological risk or metal pollution intensity in sediments (Sakar et al., 2011; Yang et al., 2012; Vaezi et al., 2015a). Wetlands have been the recipients of considerable amount of anthropogenic pollutants, such as heavy metals, originated from industrial, agricultural and urban sources (Caeiro et al., 2005). The Anzali Wetland is a unique and valuable aquatic ecosystem, which has been under serious pressures in recent years. Urbanization and growth of population, industrialization, tourism and agricultural activit-

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ies are known as the main sources of heavy metals which enter the Anzali Wetland through rivers (Vesali Naseh et al., 2012; Jamshidi-Zanjani and Saeedi, 2013). Therefore, investigation of metal pollution in this wetland can be of great importance for the assessment of sediments quality in the region. In the present study, it is attempted to find out the metal contents (As, Cr, Cu, Co, Mn, Ni, V, Cd, Zn, Al, Fe, and Pb) and their association with various sedimentary phases in the Anzali Wetland. Cluster analysis was also applied to determine the correlation between metal and to find their origin in sediments of the Anzali Wetland. Also, the metals pollution intensity in the wetland sediments is assessed using three reliable indices. For the first time we adopted new classification of pollution intensity formulas to bring out environment conditions.

2 Materials and methods

2.1 *Study area*

The Anzali Wetland, with an area of about 193 km^2, is located in Guilan Province at the north of Iran. It lies between 37°22'–37°32'N, and 49°15'–49°36'E. Catchment of the wetland covers an area of about 3 610 km^2. The waterways to the Anzali Wetland can be divided into four sections of western (Abkenar), eastern (Shijan), central (Hendekhaleh) and south-western (Siahkeshim) (Jamshidi-Zanjani and Saeedi, 2013). The Anzali Wetland is the habitat of unique and invaluable fish species and other flora and fauna, which is internationally known as a route for bird migration and has been registered at Ramsar Site since 1975 (Vesali Naseh et al., 2012; Zamani Hargalani et al., 2014).

The Anzali Wetland is the main and largest fresh water coastal wetland in the southern part of the Caspian Sea, which is mainly fed by ten rivers with an average discharge of 76 m^3/s. Pir-Bazar, Pasikhan and Shijan are among the important rivers in the catchment area of the Anzali Wetland, which play an important role in the transfer of pollutants into the wetland (Jamshidi-Zanjani and Saeedi, 2013). The Pir-Bazar River originates from a forested basin and is formed from the merging of two rivers of Goharrud and Zarjoob. This river, after passing through Rasht City and receiving all kinds of municipal and industrial wastewater, enters the eastern part of the Anzali Wetland (Shijan) with a discharge rate of 9.42 m^3/s (Ayati, 2003). The Pasikhan River is one of the independent rivers of the Caspian Sea basin and belongs to the sub-basin of the Anzali Wetland. This river has two main branches, both originated from Latte Berahneh mountain slopes, which are 2 667 m high. These branches merge and form the Pasikhan River, and then in No-Khaleh region intersect with Shut-Chay River and enter the central part of the Anzali Wetland (Hendekhale) with a discharge rate of 22.8 m^3/s (JICA, 2004; Ayati, 2003). In Khomam City, the Khomamrud River intersects with Gurabjir branch, and form the Shijan River. This river, with an average discharge rate of 3.89 m^3/s enters the eastern part of the wetland (JICA, 2004; Ayati, 2003). These rivers are shown in Fig. 1. According to JICA studies, more than 40 percent of Gilan Province’s population live in the cities located in the catchment area of Anzali Wetland. Different industries such as steel, rubber, ceramic, textile and food industry located in the cities of Rasht, Anzali, Some’e Sara are among the various sources of pollution, and the wastewater of these industries flows into the rivers and finally enters the wetland (JICA, 2004). Farmlands occupy 935.25 km^2 of the catchment area of Anzali Wetland. Drains from chemical fertilizers and herbicides and fungicides used in these farmlands are important sources of pollution in the Anzali Wetland. Additionally, water penetration from the Caspian Sea through the shipping channels, and oil leaks from tourist and fishing motor boats are important sources of oil pollution in the Anzali Wetland (Zamani Hargalani et al., 2014; Khosheghbal et al., 2013).

2.2 *Sampling and chemical analysis*

In April 2014, surface sediment samples were collected from seven stations in the Anzali Wetland using Peterson grab

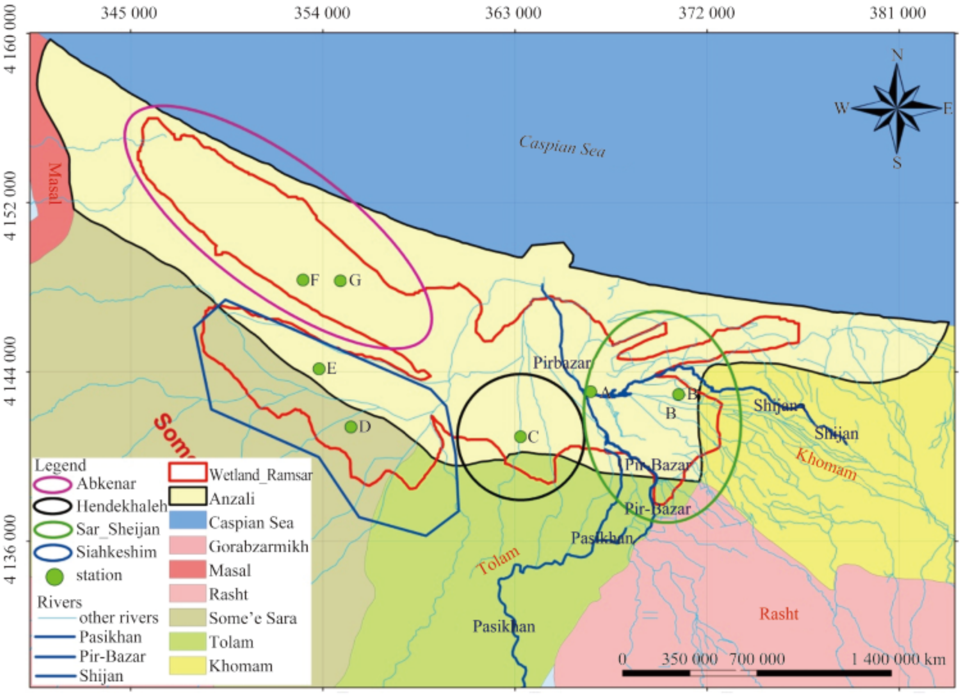

Fig. 1. Map of sediment sampling sites in the Anzali Wetland.

sampler. The sediments were collected from non vegatation areas. Figure 1 shows the location of sampling stations. Sediment samples were stored in polyethylene bags and transferred to the laboratory in an ice box. In order to determine the total metal contents, air dried sediment samples were passed through a mesh size less than 63 μm and subsequently powdered by an agate mortar and pestle. About 0.5 g of powdered sample was treated with 5 mL aqua regia in a TFM beaker at 125°C. Subsequently, 3 mL $HClO_4$ was added to the mixture and it was heated up again to reach the dryness state. The samples were cooled down at room temperature and subsequently passed through whatman filter No. 50. They were made up to volume in a 50 mL volumetric flask. Chemical partitioning studies were conducted in three sequential steps as follows (Chester and Hughes, 1967; Gibbs, 1973; Tessier et al., 1979; Environmental Protection Agency, 1996):

(1) Acetic acid with the volume ratio of 25%;

(2) Acetic acid with the volume ratio of 25%, 0.1 mol/L hydroxylamine hydrochloride;

(3) 30% H_2O_2 extraction with 1 mol/L of ammonium acetate.

In all the three steps, metal concentrations were determined by inductively coupled plasma (ICP-OES). Accuracy of the obtained data was re-checked through duplication of digestion and measurements. Blank samples were also prepared and applied in each step to minimize the laboratory errors. Analysis of the standard sediment sample (MESS-3), prepared to check the accuracy of the data obtained, revealed a laboratory error of less than ±5% (Table 1). The multivariable statistical program (MVSP) was used to assess the correlation amongst the studied parameters.

Table 1. Analytical results obtained from MESS-3 (mg/kg)

Metals	MESS-3	This study
Zn	159±8	152
V	243±10	234
Pb	21±0.7	20.8
Ni	46.9±2	45.6
Cr	105±4	107
As	21.1±1	20.6
Cd	0.24±0.01	0.23
Cu	33.9±1.6	33.3
Co	14.4±2	12.8
Mn	324±12	316
Fe%	4.34±0.11	4.27
Al%	8.59±2.3	7.84

2.3 *Assessment of sediment contamination*

Selection of background level plays a key role in interpretation of geochemical data. Average shale or average metal in the Earth's crust are frequently used by many researchers (Nasrabadi et al., 2010; Sekabria et al., 2010; Muñoz-Barbosa et al., 2012; Jamshidi-Zanjani and Saeedi, 2013). From textural and mineralogical points of view, the most appropriate option is to compare the concentration of contaminated and non-contaminated sediments in a region (Sakan et al., 2009; Varol, 2011). In this study, three different indices were used to assess the degree of metal contamination in sediments of the Anzali Wetland. The first index is geo-accumulation index (I_{geo}) (Müller, 1981) that determines the intensity of pollution in sediments based on total metal content. The second index reveals the intensity of pollution in sediments according to chemical partitioning method. This index is I_{POLL} (Karbassi et al., 2008). The third index, that ascertains the pollution considering all of the metals examined in each station. This index is mean ERM quotient (m-ERM-Q) (Gao and Chen, 2012).

2.3.1 *Geo-accumulation index (I_{geo})*

Müller's (1981) geo-accumulation index is defined by Eq. (1) as

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right), \tag{1}$$

where C_n is measured metal concentration in the sample, B_n is metals concentration in shale, and 1.5 is correction factor used to incorporate the influence of lithospheric factors. Geo-accumulation index utilizes shale concentration as a reference for making comparison. Since shale concentration may geologically vary from one region to another, it cannot provide precise information (Hosseini Alhashemi et al., 2011; Ra et al., 2013).

Geo-accumulation index based on adopted new classification by Salehi et al. (2014) is as follows:

$I_{geo}<0.42$ =unpolluted,
$0.42<I_{geo}<1.42$=low polluted,
$1.42<I_{geo}<3.42$=moderate polluted,
$3.42<I_{geo}<4.42$=strongly polluted,
$I_{geo}>4.42$=extremely polluted.

2.3.2 *I_{POLL} index*

Through chemical partitioning steps, anthropogenic and lithogenic portions of each metal can be differentiated. Therefore, by calculating the chemical partitioning values, Muller equation can be modified or optimized to measure the intensity of metal pollution more precisely. I_{POLL} uses lithogenic portion in place of shale metal content (Karbassi et al., 2008).

$$I_{POLL} = \log_2\left(\frac{C_n}{B_n}\right), \tag{2}$$

where I_{POLL} is intensity of pollution, C_n is metal concentration in sediment, and B_n is lithogenic portion of metal in sediment/soil sample and it was computed by subtraction of the anthropogenic portion of metals from bulk concentration. Shale concentration has not a significant role in Eq. (2) and correction factor (1.5) for normalization would not be required. (Farsad et al., 2011; Zamani et al., 2014; Biati et al., 2014). Determination of pollution intensity is rendered according to the new Muller's classification (Salehi et al., 2014).

2.3.3 *Mean ERM quotient (m-ERM-Q)*

To evaluate adverse biological effects and conservation of the aquatic organisms inside or near the polluted sediments, the method of Sediment Quality Guidelines is applied. This method was developed by Long and Morgan for the National Oceanic and Atmospheric Administration's (NOAA) as informal tools in screening sediment. These guidelines are composed of Effect Range Guidelines derived from a database of sediment chemistry and toxicity bioassay information. Effect-range-low (ERL) represent of chemical concentrations below which adverse effects are rarely observed and effects-range-median (ERM) indicative of concentrations above which adverse effects may frequently occur (Long et al., 1995; Darvish Bastami et al., 2012; Jamshidi-Zanjani and Saeedi, 2013).

Heavy metals exist in sediments in the form of a complex mixture. The m-ERM-Q determines the probability of biological effects resulted from toxicity of components like heavy metals mixture in sediment. The m-ERM-Q is calculated by Eq. (3) (Long et al., 2000; Gao and Chen, 2012). The ERM values 270, 410, 370, 218, 51.6, 9.6, and 70 mg/kg have been specified for metals of Cu, Zn, Cr, Pb, Ni, Cd and As, respectively, in the sediment quality Guideline (Long et al., 1995).

$$\text{Mean } ERM \text{ quotient} = \sum \left(\frac{C_x}{ERM_x} \right) / n, \tag{3}$$

where C_x is concentration of metal in sediment, ERM_x is the amount determined for each metal by SQG, and n is number of studied metals. According to the studies on matching chemical substances with toxicity data for more than 1 000 sediment samples from estuaries of the United States, the following classifications were presented:

ERM-Q<0.1 implies 9% toxicity probability in sediment samples,

0.11<*ERM-Q*<0.5 implies 21% toxicity probability in sediment samples,

0.51<*ERM-Q*<1.5 implies 0.49% toxicity probability in sediment samples,

ERM-Q>1.5 implies 75% toxicity probability in sediment samples.

3 Results and discussion

3.1 *Total metal content in the Anzali Wetland sediments*

Metal concentration in sediments of the Anzali Wetland and in mean crust along with mean world sediment and shale are presented in Table 2. The range of studied metals in sediments of the Anzali Wetland is 10.6–33.2 mg/kg for As, 48.4–62.2 mg/kg for Cu, 0.27–0.52 mg/kg for Cd, 19.2–24.5 mg/kg for Co, 66–107 mg/kg for Ni, 17.6–31 mg/kg for Pb, 107–132 mg/kg for V, 104–138.7 mg/kg for Zn, and 97–140 mg/kg for Cr.

High concentrations of As, Cu, Ni, Pb, Zn, V and Cr were observed in Hendekhaleh (Sta. C). This station is under oil pollution by cargo ships. Moreover, high amount of wastewater from Anzali City is discharged into the wetland. High concentration of Cu (62 mg/kg) in Abkenar (Sta. F), which is in the vicinity of a landfill (Khosheghbal et al., 2013), reveals the anthropogenic source of Cu pollution in the wetland sediments. The highest concentration, almost for all the studied metals, was found in the eastern part of the wetland, called Shijan (Stas A and B) where the mass of wastewater from Rasht and Khomam cities is discharged to. The main rivers of Shijan, Pirbazar and Pasikhan, which receive a massive wastewater, carry the pollutants from agriculture and industrial activities to the wetland (JICA, 2004). The lowest concentration of metals in sediment samples was found in Siahkeshim (Stas D and E) where there was no specific source of pollution. These sites are located in the southwest of Anzali Wetland, where is a part of protected area. In these sites, the anthropogenic activities are prohibited and this can be the main reason for lower concentration of metals in the area. The results indicated that the concentrations of metals (except V, Fe and Al) in different stations are higher than those in the mean world sediment. Comparing the values obtained in the study area with those in the mean crust and mean world sediment, it can be concluded that anthropogenic activities in the region have led to the contamination of sediments in the Anzali Wetland.

3.2 *Metal fractionation*

Measuring the total metal content is, undoubtedly, one of the fundamental methods for assessing the sediment quality; however, other methods are required to determine the mobility, bioavailability and toxicity of metals in the sediments. The characteristics of metals in the sediments depend not only on total concentration but also on their physiochemical characteristics (Gleyzes et al., 2002; Shrivastava and Banerjee, 2004). Metal fractionation method has been recommended to pave the way for gathering more precise information about the correlation between metals and sediments (Tessier et al., 1979). Portion of each metal, obtained in each stage of chemical fractionation, is presented in Fig. 2.

3.2.1 *Loosely bonded ions*

Concentration of metals in the first stage was influenced by the weakest metal bonds (loose bonds), and metals having this bond may easily be released following an aquatic misbalance (Padro et al., 1990). Most of the metals in this bond are strongly mobile and can pose high risks to the environment (Gao and Chen, 2012). Among the studied metals, Cd and Mn had the highest (over 20%) while V and Al had the lowest mobility in acid soluble phase. Cd had the highest mobility in loosely bonded ions phase as compared to other phases, showing its high potential for being a threat to aquatic organisms, especially the benthic

Table 2. Bulk concentration (mg/kg) of metals in sediments of the Anzali Wetland

Station	As	Cd	Co	Cr	Cu	Zn	V	Ni	Pb	Mn	Al/%	Fe/%	Ca/%
A	27	0.45	23	140	59	139	131	103	28	1 240	3.9	4.1	28.2
B	33	0.48	24	128	58	130	125	107	31	1 180	3.2	4.5	30.3
C	23	0.52	24	131	48	123	132	101	27	1 860	2.8	4.3	11.6
D	12	0.29	21	101	51	106	110	66	18	1 123	2.05	4.1	9.2
E	11	0.33	19	97	49	104	107	72	18	1 000	2.1	4.2	12.3
F	18	0.27	20	121	62	120	123	80	24	1 263	3.4	4.6	22.1
G	15	0.33	22	107	55	116	124	93	20	1 230	2.9	4.5	20.8
Min	11	0.27	19	97	48	104	107	66	18	1 000	2.05	4.1	9.2
Max	33	0.52	24	140	62	139	132	107	31	1 860	3.9	4.6	30.3
Mean	20	0.38	22	118	54	120	122	89	24	1 270	2.9	4.3	19.2
Crust1)	5	0.2	20	100	50	75	130	80	14	950	8.2	4.1	4.1
Mean world sediment1)	–	–	14	70	33	95	130	52	19	–	7.2	4.1	6.6
Shale value1)	13	0.3	19	90	45	95	130	68	20	850	8.1	4.7	2.2

Note: 1) Bowen (1979).

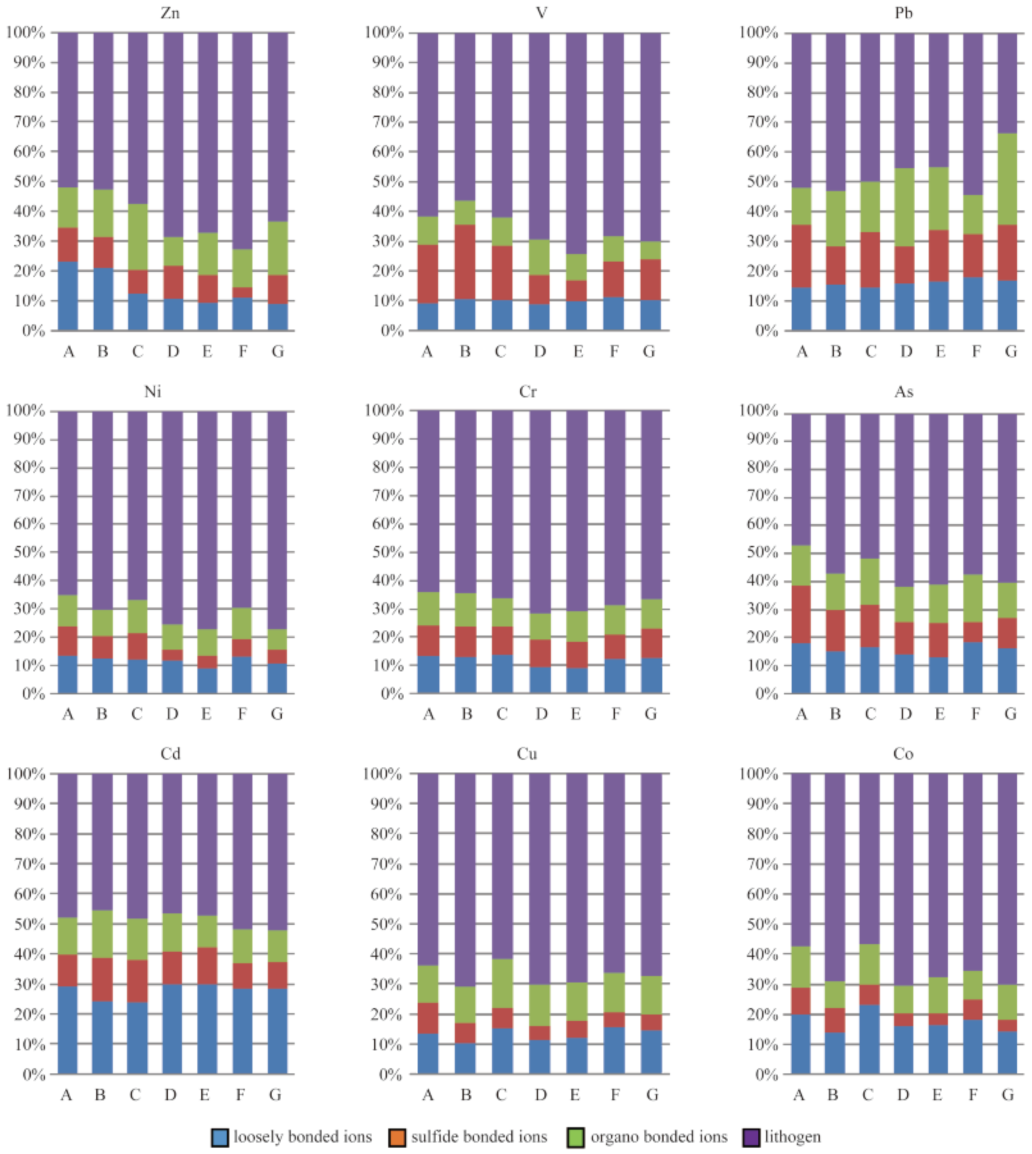

Fig. 2. Chemical partitioning of metals in sediments of the Anzali Wetland.

ones. Results show the higher mobility for Cd in the central and eastern parts of the wetland. This is known to be attributed to the typically anthropogenic nature of Cd and its release into the environment through the industrial wastewaters. Order of the mean concentration of metals in loose bonds phase in the Anzali Wetland is Cd(26%)>Mn(23%)>Co(18%)>AS & Pb(16%)>Zn(15%)>Cu(14%)>Ni & Fe(12%)>Cr(11%)>V(10%)>Al(8%).

3.2.2 *Sulfide bonded ions*

This phase is known as redox phase. Under redox conditions metals that are present in oxide forms can gradually be reduced in to the overlying water. Metal bonds to iron/manganese oxide fraction are unstable and turn into solution under reducing conditions (Sharmine et al., 2010). The mean concentration of metals in sulfide bonds in sediments of the Anzali Wetland follows the order: Mn(18%)>Pb(17%)>V(15%)>As(14%)>Cd(12%)>Zn & Cr(9%)>Ni(7%)>Cu & Co(6%)>Fe(5%)>Al(3%).

In this phase, the largest share belongs to manganese ranging 17.4%–17.8%, and the lowest belongs to aluminum ranging of 4.3%–5.2% in different stations. Higher concentrations of Mn, Cd, Pb, Zn, Cr and Ni in sulfide bonds can be attributed to their adsorption by iron and manganese colloids (Purushothaman and Chakrapani, 2007). High concentration of manganese and presence of iron in this phase signifies the start of transition from oxidation state to reduction state (Karbassi, 1996).

3.2.3 *Organo bonded ions*

Metal bonds with organics stem from interaction of metals with organic materials in sediments. Decomposition of organic materials under oxidation condition leads to release of metals into the overlying waters (Purushothaman and Chakrapani, 2007).

Organic materials and sulfides are key factors and play an important role in mobility and bioavailability of metals (Wang et al., 2010). The impact of organic matters on toxicity of heavy metals has been a controversial issue; For example, it has been suggested that combination of cadmium and organic matter in daily meals results in higher cadmium toxicity for nematodes (Wang et al., 2010; Höss et al., 2001). Among the studied metals, lead with a mean value of 19% has the highest organic bond, while manganese with a mean value of 5% has the lowest affinity towards organic bonds. The mean percentage of metals present in organic bonds can be ordered as Pb(19%)>Zn & As(15%)>Cd & Cu(13%)>Co(11%)>Ni & Cr(10%)>V(9%)>Al(7%)>Fe(6%)>Mn(5%).

3.2.4 *Resistant and within lattice bonded ions (lithogenic portion)*

Metals in this phase have a much lesser toxicity to aquatic organisms as they are chemically stable and biologically inactive (Wang et al., 2010). The concentration of heavy metals in these bonds is mainly controlled by mineralogy and weathering; they do not become solution in laboratory conditions and are considered to be at background level (Sharmin et al., 2010). The sum of metal contents in these two bonds is considered as lithogenic portion. Since the high amounts of heavy metals in loose, sulfide and organic bonds stem from anthropogenic sources, it can be concluded that the total amount of metals in these three stages minus 10% of the total metal content is representative of the anthropogenic portion (Karbassi et al., 2008; Farsad et al., 2011). Pb (50%) and Cd (46.6%) have the highest mean concentration in anthropogenic bonds. However, in comparison to metal contents of the Earth's crust or shale, the bulk metal concentration of the wetland sediments shows slightly higher amounts of Pb and Cd. Almost in all stations, Cd and Pb have the anthropogenic portions of over 40%. Other metals have the highest anthropogenic portion in Stas A and C (eastern and central parts of the wetland) and the lowest anthropogenic portion in Stas D and E (south-west of the wetland). Therefore, comparison of metal concentrations with mean crust, world sediment and shale, may not provide useful information. Order of the mean percentage of metals concentration in the Anzali Wetland sediment for anthropogenic part is Pb (52%)>Cd (51%)>Mn (46%)>As (45%)>Zn (39%)>Co (35%)>V (34%)>Cu (33%)>Cr (30%)>Ni (29%)>Fe (23%)>Al (18%).

3.3 *Indices of sediment contamination*

The results of Geoaccumulation index (I_{geo}) and I_{POLL} are presented in Table 3.

Based on the defined classification, As in Stas A and B, and Mn in Sta. C, are in low pollution range ($0.42<I_{geo}<1.42$), but for other metals have $I_{geo}<0.42$ in the studied stations, and based on this index are non-pollution. Results from the mean geo-accumulation index reveal the following trend Cd>Mn>As>Cr>Ni>Zn>Cu >Co>Pb>V.

The amount of I_{geo} in different stations follows the order: Station B>Station A>Station C>Station D=Station E=Station F=Station G

The I_{POLL} index for As, Pb, Cd, and Mn in all the studied stations, Cr in all the stations (except for D and E), Zn in all stations (except for F and D), Co and Cu in Stas A, C and F, nickel in Stas A and C and V in Stas A, B and C are $0.42<I_{geo}<142$, which based on the related classification had the low pollution range. Results from the mean I_{POLL} index reveal the following trend: Pb>Cd>Mn>As>Zn>Cr>V>Co>Cu>Ni.

The overall order of I_{POLL} in studied stations is Station A>Station C<Station B<Station G<Station F<Station D<Station E.

The difference between the results for these two indices is because of the difference in background level. Geo-accumulation index is one of the oldest indexes for determining the intensity of pollution, in which the concentration of shale is used as the background level (Zamani Hargelani et al., 2014). The geology of various regions is different, and the concentration of shale is not the same in various regions. Given the flaws in the geo-accumulation index, this formula was modified by Karbassi, so that in the new formula, instead of using the concentration of shale, lithogenic portion of the metal that is determined by chemical partitioning method, is used. Therefore, it seems that the results obtained based on this index are more accurate (Karbassi et al., 2008; Ra et al., 2013; Zamani Hargelani et al., 2013). Generally,

Table 3. Geoaccumulation index (I_{geo}) and Pollution index (I_{POLL}) of metals in the Anzali Wetland sediments

Station	As		Cd		Co		Cr		Cu	
	I_{geo}	I_{POLL}	I_{geo}	I_{POLL}	I_{geo}	I_{POLL}	I_{geo}	I_{POLL}	I_{geo}	I_{POLL}
A	0.44	0.95	0	0.96	–0.29	0.66	0.09	0.49	–0.19	0.5
B	0.73	0.67	0.08	1	–0.29	0.17	–0.08	0.48	–0.22	0.35
C	0.23	0.81	0.19	0.94	–0.22	0.7	–0.04	0.45	–0.47	0.55
D	–0.64	0.54	–0.62	0.95	–0.43	0.36	–0.41	0.33	–0.38	0.22
E	–0.85	0.57	–0.43	0.9	–0.55	0.42	–0.47	0.35	–0.11	0.37
F	–0.14	0.66	–0.7	0.85	–0.47	0.47	–0.16	0.4	–0.11	0.45
G	–0.36	0.59	–0.43	0.79	–0.34	0.37	–0.32	0.44	–0.91	0.42
Mean	–0.08	0.68	–0.02	0.92	–0.36	0.45	–0.19	0.48	–0.34	0.4
Min	–0.85	0.54	–0.7	0.79	–0.55	0.17	–0.47	0.33	–0.91	0.22
Max	0.73	0.95	0.19	1	–0.22	0.7	0.09	0.49	–0.11	0.55

Station	Mn		Ni		Pb		V		Zn	
	I_{geo}	I_{POLL}	I_{geo}	I_{POLL}	I_{geo}	I_{POLL}	I_{POLL}	I_{geo}	I_{geo}	I_{POLL}
A	–0.04	1.21	0.01	0.47	–0.85	0.79	0.55	–0.55	–0.04	0.8
B	–0.11	0.86	0.05	0.36	0.04	0.76	0.68	–0.62	–0.01	0.78
C	0.51	0.66	–0.01	0.43	–0.14	0.85	0.68	–0.55	–0.2	0.66
D	–0.17	0.57	–0.62	0.26	–0.75	1.14	0.37	–0.8	–0.41	0.4
E	–0.34	0.52	–0.49	0.22	–0.68	1.01	0.29	–0.85	–0.45	0.43
F	–0.01	0.62	–0.34	0.37	–0.32	0.74	0.4	–0.64	–0.24	0.31
G	–0.05	0.92	–0.13	0.22	–0.57	1.43	0.36	–0.64	–0.29	0.49
Mean	–0.03	0.76	–0.21	0.33	–0.46	0.96	0.47	–0.66	–0.23	0.55
Min	–0.034	0.52	–0.62	0.22	–0.85	0.74	0.29	–0.85	–0.45	0.31
Max	0.51	1.21	0.05	0.47	0.04	1.14	0.68	–0.55	–0.01	0.8

the results of I_{geo} and I_{poll} show that As, Pb, Cd and Mn have the highest pollution in the Anzali Wetland. On the other hand, results of chemical partitioning method reveal that these metals have the highest anthropogenic portion. According to the studies, the presence of metals such as As and Mn in the sediment of the wetland, in addition to the chemical erosion of rocks, is related to the agricultural activities and the use of fertilizers and fungicides in the farmlands, especially rice fields around the wetland. Wastewater discharge of metal smelting and plating industries, and as well as the wastewater of chemical units such as dyeing industries could be the source of metals such as Cd and Pb in the wetland. (Khosheghbal et al., 2013; Jamshidi-Zanjani and Saeedi, 2013).

Overall, I_{POLL} and I_{geo} indices for metals studied in the eastern and central part of the wetland (Stas A, B and C) have the highest value, which may be due to the high aggregation of anthropogenic sources, such as highly populated cities (Rasht), industrial wastewater and agricultural drainage in the eastern part of the wetland. These indices in the southwestern part of the wetland (Stas D and E) show the lowest value. This can be due to the fact that these stations are located in a protected area and the entrance of pollutants into this section is controlled.

Toxicity of sediment samples were examined with the help of m-ERM-Q. Figure 3 shows the amount of this index at different stations. Samples are in the range of 0.32–0.51. According to the classification, by excluding Al, Fe and Ca from computations and considering only the nine remaining metals a potential of 21% toxicity will be obtained. This index can be presented in the following order at different stations: Station B>Station A>Station C>Station G>Station F>Station E>Station D.

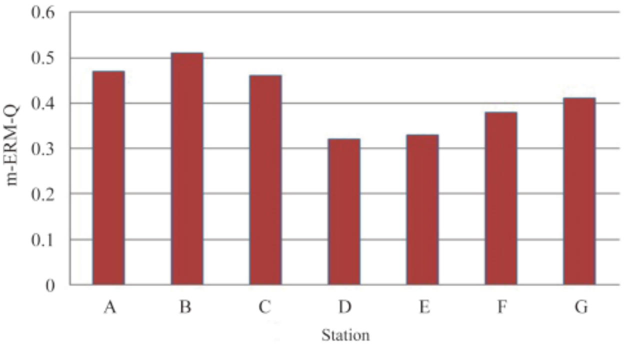

Fig. 3. The spatial distribution of mean ERM quotient (m-ERM-Q) in surface sediments of the Anzali Wetland.

Comparing the value of metals in the studied sediments with ERM value show that, compared to other metals, nickel and chromium can play a greater role in the toxicity of sediment samples for the organisms. However, chemical partitioning studied reveals that 29% of nickel and chromium are anthropogenic, while only 12% of their bulk concentrations are in loosely bonded phase. Hence, the probability of their availability for organisms under normal conditions in aquatic environments is weak. Therefore, chemical partitioning technique is considered as a complementary method to enhance accuracy of the studies related to metal pollution in sediments.

3.4 *Cluster analysis*

The correlation amongst the studied metals in sediments of Anzali Wetland is investigated by cluster analysis (Davis, 1973) (Fig. 4). Cluster analysis has been applied by different researchers to ascertain the relationship between various metals and environmental indicators (Karbassi et al., 2006; Hosseini Alhashemi et al., 2011; Jamshidi-Zanjani and Saeedi, 2013; Zamani Hargalani et al., 2014; Karbassi et al., 2015). Dendrogram of cluster analysis shows four distinctive clusters. Knowing that metals in the same cluster have similar behavior, As, Pb, Cr and Zn in Cluster A join at a very high similarity coefficient to Cd and Co in Cluster B. Many studies show that Ni and V are presented at higher concentrations in oil and therefor they are used as indicators (Karbassi and Amirnezhad, 2004; Khoshnood et al., 2010; Farsad et al., 2011; Vaezi et al., 2015a). Since V and Ni are good indicators of oil pollution, it can be inferred that source of metals in these two clusters are partially derived from oil pollution sources. Although Mn in Cluster C has a correlation with LOI as an indicator of organic materials, chemical partitioning studies do not support its association with organic materials. Although Fe, Cu, Ca and Al form Cluster D, it is difficult to have any interpretation on Fe as it joins other metals with a rather low similarity coefficient. Aluminum is selected as lithogenic fraction since it is mainly derived from Aluminosilicate rocks. And therefor it is applied as lithogenic indicator (Karbassi and Amirnezhad, 2004; Karbassi et al., 2006; Farsad et al., 2011; Zamani Hargalani et al., 2014; Vaezi et al. 2015a). However, it can be stated that Cu and Ca are mainly derived from lithogenic sources for the presence of Al as a good indicator of parent rocks.

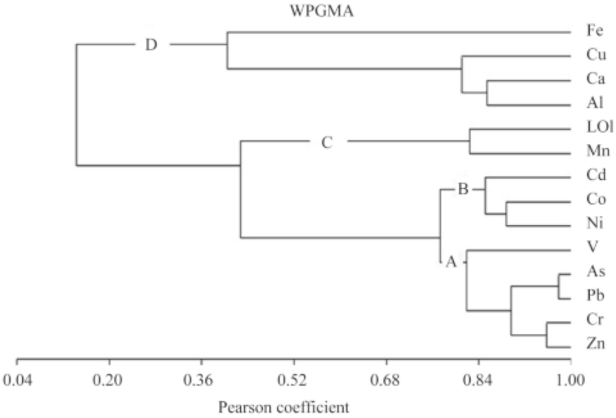

Fig. 4. Dendrogram of cluster analysis for metals in the Anzali Wetland sediments.

4 Conclusions

Various methods and indices are used to assess metal pollution in the sediments of the Anzali Wetland. The studied metals are As, Cd, Cr, Cu, Zn, Ni, Pb, Mn, V, Al and Fe. According to the Geochemical studies in the study area reveal that concentrations of the mentioned metals, except V, are higher than the mean shale concentration and mean crust concentration. The results of indices pollution reveal that the highest concentrations of metals are at the eastern and central stations, while the lowest are at stations located on the south-west of the wetland. Chemical partitioning studies reveal the high percentage of Cd in loose bond phase. This metal has the highest mobility among the studied metals and its low total concentration may have adverse effects on the environment. Since Mn and Pb have the largest share in sulfide phase, probability of their presence in aquatic environments during reduction state, is higher than other metals. A high amount of Pb, As and Zn was also observed in organic bonds. The results of chemical partitioning studies determined that Pb, Cd, Mn and As have the highest anthropogenic portion. The main pollution sources for the wetland are identified to be wastewater from the adjacent industrial centers, polluted water of the Caspian Sea flowing into the wetland through shipping channels, and agricultural activities. The results of this study indicate that the Anzali Wetland is threatened by metals. Moreover, due to fishing and tourism development in the area, ecological risk assessment is also suggested.

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