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Full Length Research Paper

Accumulation and bioaccessibility of trace elements in wetland sediments

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Accumulation of trace metals in sediment can cause severe ecological impacts. In this study, determination of elemental concentrations in water and sediment was done. Shadegan wetland is one of the most important wetlands in southwest of Iran and is among the Ramsar-listed wetlands. Wastewaters from industries, urban activities and agricultural run off are released into this unique wetland in the region. In the present investigation, 12 sampling stations were selected for water and sediment collection in Shadegan wetland during winter, 2009. Physico-chemical parameters such as pH, electrical conductivity (EC), turbidity and salinity of water and pH, EC, total organic materials (TOM), grain size fraction and elements (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn) in sediments were measured. Also, macrobenthos communities were identified in sediments due to their important role in ecosystem health. Subsequently, lithogenous and anthropogenic portions of trace metals in sediment, trace elements bioaccessibility, along with I_{geo} and I_{POLL} indices were measured. According to obtained results, trace elements including Cu (39.5%), Pb (26%), Cr (24.1%), Cd (16.4%) and Zn (13.6%) had highest anthropogenic portion in study area. The two pollution indices used in the present investigation (I_{geo} and I_{POLL}) are indicative of different pollution intensity in Shadegan aquatic environment. The low pollution intensity values computed by I_{geo} might be acceptable for metals that have low anthropogenic values (less than 15% of their total concentrations). But higher anthropogenic values (16 to almost 40% of total concentration) for other studied metals show that an I_{POLL} pollution intensity formula is more reliable. Moreover, bioaccessibility concentrations amount for Ni, V, Pb and Co had strong and positive meaningful relationship with Cu, Cr and Cd.

Key words: Heavy metals, accumulation, aquatic environment, I_{POLL} index, Shadegan wetland.

INTRODUCTION

The toxicity of heavy metals has long been of great concern since it is very important to the health of people and ecology (Feng et al., 2008). Metals in essential and non-essential forms are naturally persistent in the environment; they accumulate in nature especially in sediments. The toxicity of metals is highly influenced by geochemical factors that influence metal bioavailability (Fairbrother et al., 2007; David et al., 2007). Priju and Narayana (2007) showed metal enrichment in top 20 cm of sediment core from Vembanad Lake. Heavy metal pollution was reported for Mengkabong Lagoon as a result of human activities (Praveena et al., 2008). Geochemical reactivity of surficial and core sediment in a tropical mangrove ecosystem was reported by Geetha et al. (2008). They concluded that the top 5 cm of aquatic sediment is very reactive. Chibunda (2009) and Chibunda et al. (2010) reported the inhibition of larva growth due to

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the presence of Hg in aquatic sediments of Africa. Grain size is another important factor governing distributions of heavy metals (Zhipeng et al., 2009; Sundararajan and Natesan, 2010). Also, heavy metals can bioconcentrate and bioaccumulate in the food chain and contribute to chronic toxicity (Ahmad et al., 2010). The inorganic pollutants entering water bodies originate from natural and anthropogenic sources (Mdegela et al., 2009) but the occurrence of heavy metals in the environment mainly results from anthropogenic activities (Zhipeng et al., 2009).

Heavy metals have a potential to contaminate soil and water, which can be dispersed and accumulated in plants and animals, and taken in by humans through consumption (Wcislo et al., 2002). Sediments, which play both the source and sink roles, are very important in evaluating the pollution level of heavy metals (Zhipeng et al., 2009; Al-Juboury 2009). Heavy metal contamination of sediments can critically degrade aquatic systems (Charkhabi et al., 2005). Their release from the sediment can make them enter the aquatic ecosystems and bring about severe problems (Mohammed and Markert, 2006). Despite the differences in toxic effects of the metals, their concentrations are reliable indicators of ecosystem health (Singh et al., 2005). Aquatic organisms can bioaccumulate, biomagnificate or biotransfer certain metals to concentrations high enough to bring about harmful effects (Naimo, 1995, Opuene et al., 2008).

In the aquatic environment, sediments have a high storage capacity for contaminants. In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water and more than 99.9% are stored in sediments and soils (Karbassi et al., 2007; Pradit et al., 2009).

Sediments frequently contain higher concentrations of pollutants. They act as carriers and possible sources of pollution due to the fact that heavy metals are not permanently fixed by them and can be released back to the water by changes in environmental conditions, therefore they may become sufficiently polluted to disrupt natural biological communities. Contaminated sediments are known to be responsible for degradation of water quality in the natural waters especially in the shallow and enclosed water systems (Toluna et al., 2001; Venugopal et al., 2009) such as wetlands.

The wetland is an important habitat for many kinds of wildlife (He and Lu, 2001). Wetland habitats contain a multitude of ecological niches and support a wide variety of flora and fauna with different ecological functions. Wetlands provide a diversity of habitats for wildlife which may include many rare, threatened and endangered species (EPW, 2004). Invertebrate communities are important in terms of environmental monitoring biodiversity and ecosystem health. Benthic communities have frequently been employed in environmental monitoring and assessment of heavy metal, with demonstrated changes in macro benthic community structure and composition in response to pollutant impacts (Macfarlane and Booth, 2001).

Contamination of aquatic systems from heavy metals has been an urgent problem worldwide. Spatial surveys of metal contaminant concentrations in sediments are an important step in understanding and regulating the fate and transport of these contaminants, and distribution of these pollutants is critical for environmental management and decision-making (Liu et al., 2006; Christine et al., 2004).

To evaluate the heavy metal burden in the environment and their impact on the ecosystem, it is usually not sufficient to measure only total concentrations, because the mobility, bioavailability and toxicity of metals depend not only on their total concentrations but also on the geochemical fractions in which they occur. Also, most of the researchers have now realized that the toxicity of heavy metals has much to do with the bioavailability and not total concentration (Feng et al., 2008).

In this study, Shadegan wetland is selected for determination of trace elements in sediments and identification of natural and anthropogenic sources shares because of trace elements transfer in upper levels of food chains that can contribute to toxic levels. Also, some animals and plants species that live in this wetland ecosystem are listed in the International Union for Conservation of Nature (IUCN) red list. For this purpose Cr, Cd, Cu, Zn, Pb, Fe, Al, Mn, Ni, V, Co and Mg were measured in the study area. In addition to the above, the determination of the following parameters were carried out in this study: Sediment physical structure, trace elements concentration in sediment and water, lithogenous and anthropogenic portion of metals, concentration of bio-accessibility of trace elements, distribution of macrobenthos community and total organic materials (TOM) in all sediments, modification of I_{POLL} pollution intensity index and statistical analysis of relationships amongst different parameters in Shadegan wetland.

MATERIALS AND METHODS

Study area and sampling stations

Shadegan wetland is one of the most important wetlands that is located in southwest of Iran. It has a very important role of conserving fauna and flora in this area. A lot of polluting industries such as petrochemical complexes (about 10 petrochemical complexes) release their wastewater in this wetland. Also, urban and agriculture run-off pour into this aquatic ecosystem. In this study, 12 sediments sampling stations were selected. Figure 1 shows Shadegan wetland location in Iran and sediments sampling stations in the area of study.

Analytical methods

Sediment and water sampling was done during winter, 2009. Surface sediment was collected using a Peterson grab sampler. In the same site, two replicate samples for benthic invertebrate community assessment were collected. After transportation of samples to laboratory under quality control standards, main parameters were measured as follows:

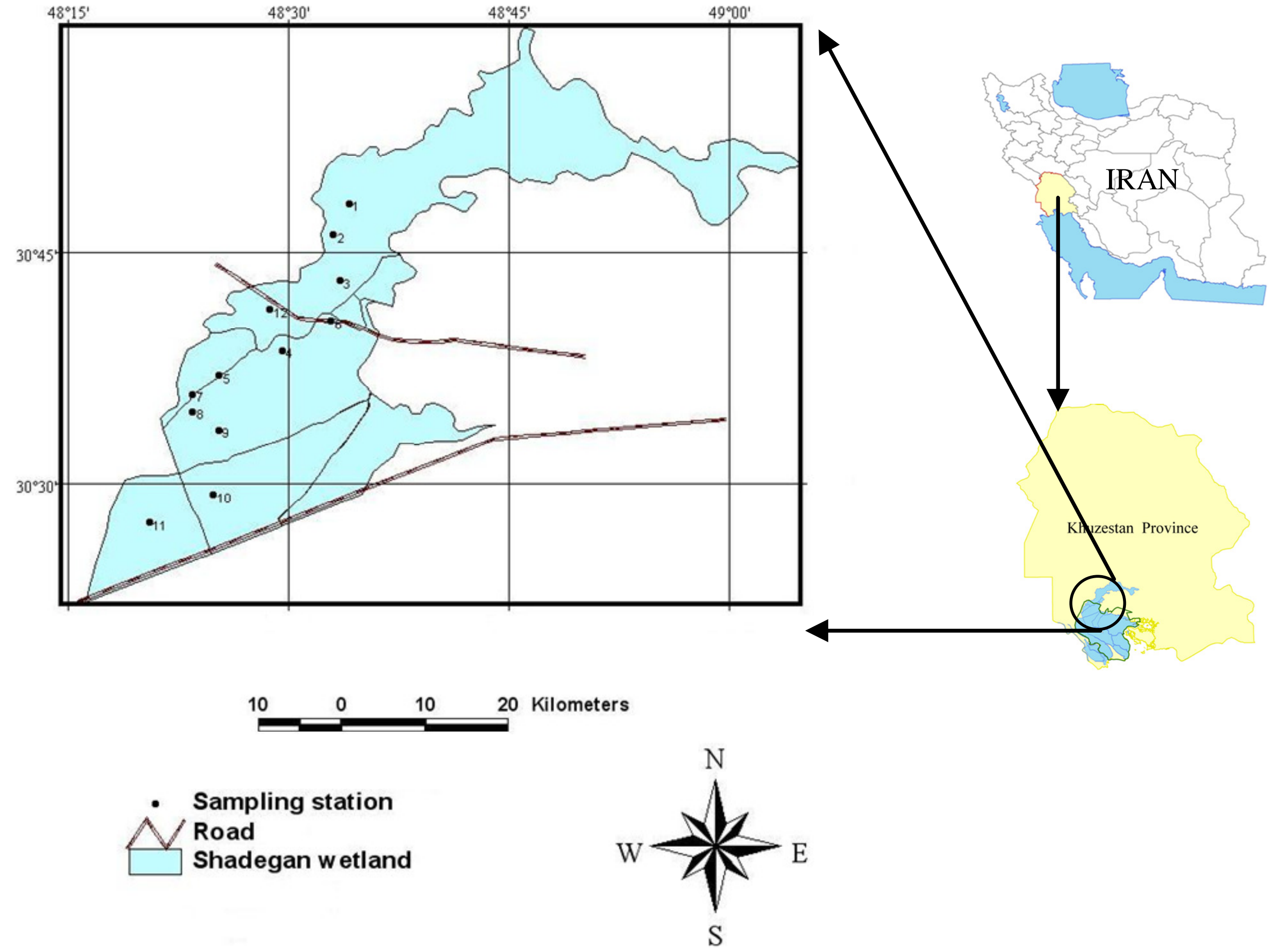

Figure 1. Sediments sampling stations in Shadegan wetland in Iran.

1. Water samples were filtered through Whatman (0.45 µm) membrane filters (in order to examine the dissolved fraction), acidified (pH <2) and stored at 4°C (Jain et al., 2005). Subsequently, samples were analyzed by inductively coupled plasma atomic emission spectrometry (PerkinElmer, ICP AES; Macfarlane and Booth, 2001).
2. Physico-chemical analysis involving grain size fraction (Allen, 1989; ASTM, 1992), pH, electrical conductivity (EC) and total organic matters (TOM; Allen, 1989) were done in sediment samples.
3. Sediments preparations were performed by air-drying and then passing samples through a 63-µm mesh (equivalent to a No. 230 sieve, ASTM E-11). TAL software was used to show the texture of sediment in the area of study (Figure 2). The sieved sediments were powdered. About 0.5 g of the powdered sample was placed in a beaker containing 5 ml of 3:1 HNO_3 to HCl and covered with a watch glass. Then, sample was heated until most of the liquid had evaporated, and allowed to cool before 3 ml of Per-chloric acid ($HClO_4$) was added. The cover was replace and heated again till evaporation of most of the liquid. Finally, samples were cooled to room temperature before being filtered. The filtrates were transferred to 50 ml volumetric flasks and brought to volume with 1 N HCl. Chemical partition studies were conducted in four sequential steps: (1) Acetic acid 25%v/v, (2) acetic acid 25% v/v-0.1 M hydroxylamine hydrochloride, (3) 30% H_20_2 "extraction with 1 M ammonium acetate" and (4) hot 50% HCl (EPA 3050; Tessier et al., 1979; Chester and Hughes, 1967; Gibbs, 1973). Determination of trace elements bioaccessibility in sediments was done by adding 10 g of sediments to NaOH (1 N) and acetic acid aqua at pH 5. Then samples were shaken for 30 min and refluxed for 24 h. The filtrates were transferred to 50 ml volumetric flasks. All glasses and plastics ware were cleaned by soaking in 10% HNO_3 (v/v) for about 24 h, followed by soaking and rinsing with deionized water (Milli-Q). All chemicals used in the experiment were of analytical-reagent grade or better.
4. To determine macro benthic community structure and composition, sediments were sieved on-site through 1 mm mesh, and macro benthic invertebrates collected were preserved in 5% buffered formalin. In the laboratory, samples were rinsed, sorted from sediment and transferred to 60% ethanol (Macfarlane and Booth, 2001). The identification of macrobenthos species was done through standard keys (Eleftheriou and McIntyre, 2008, DE Bruyne, 2003, Rouse and Pleijel, 2002).

Statistical Analysis

1. To assess the intensity of metal contamination in Shadegan wetland sediments, the pollution index (Karbassi et al., 2008) was calculated using:

$$I_{POLL} = Log_2\ (Cn / Bn)$$

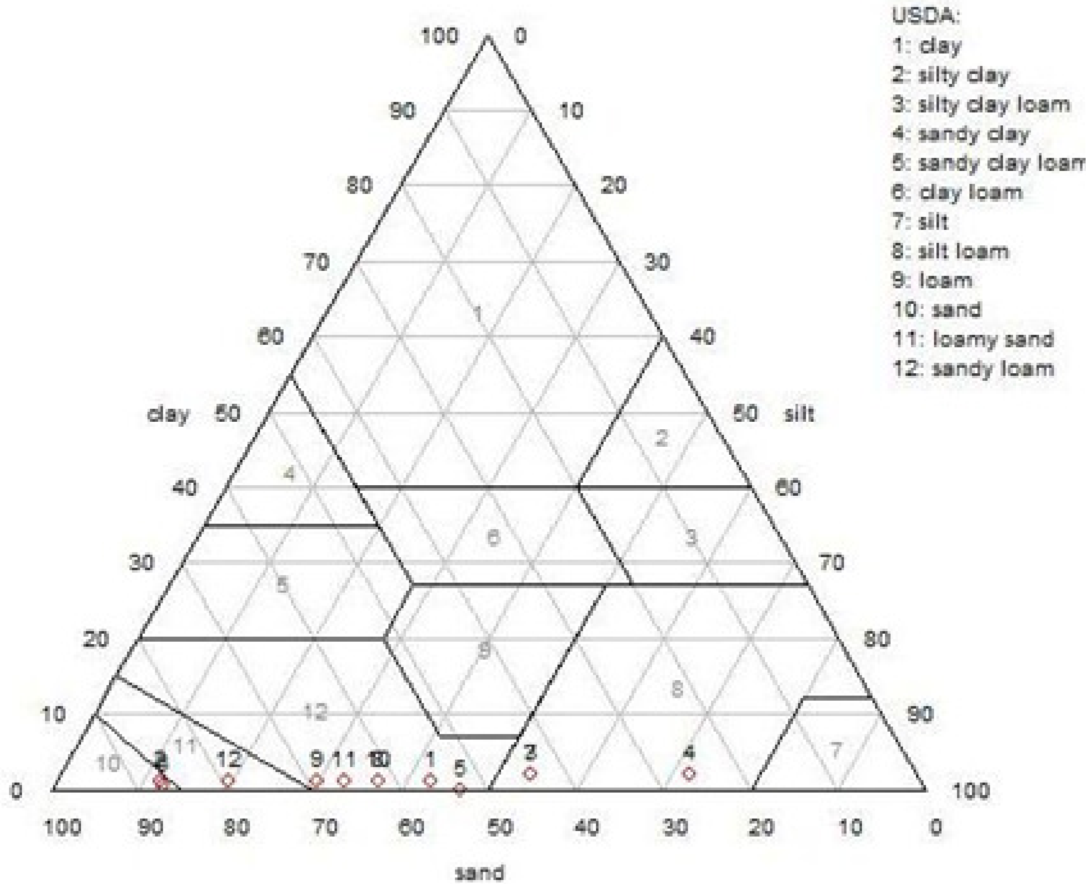

Figure 2. Texture of sediments in the area of study.

Where, Cn is the total elemental content in sediments and Bn is the lithogenous portion of element.

$$Igeo = Log_2 (Cn / Bn \times 1.5)$$

Where, Cn is the total elemental content in sediments, Bn is the concentration of metals in shale and 1.5 is a factor for normalization of background metals concentrations in shale.

2. To understand the relationship amongst various metals and environmental indicators, Multi Variable Statistical Program (MVSP) was used. This analytical software is frequently used by various researchers (Karbassi et al., 2004, 2008).

RESULTS

Table 1 shows physical characteristics of water and sediments in Shadegan wetland. As shown in Figure 2, most of the stations have sandy loam and loamy sand textures. Total organic matter contents ranges from 7.5 to 30.7% with mean value of 18.5%. The very high contents of TOM may be indicative of massive amount of wetland plants and dead macro benthoses. Salinity of water ranges from 15 to 42.5 ppt. The lowest salinity is seen in stations 1 to 6, while the highest ones can be found at stations 7 to 12. The pH of water increases as salinity does. The lower salinities and pHs might be due to the presence of upper stations in the study area that are closer to natural water resources and as they distribute in wetland, the salinity of water increases because of various pollution effluents and human activities.

Elemental concentrations (Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, Fe, Al and Ca) in the water samples of Shadegan wetland are shown in Table 2. As this table indicates, the mean concentration of elements in water shows the following pattern: V>Pb>Ni>Cu>Co>Mn>Zn>Cr>Cd. The area of study is having many oil reservoirs as well as about 10 petrochemical complexes. Therefore, the highest amounts of V and Ni can be justified by the activities of the above mentioned sources. The high Pb contents can be attributed to the old batteries that are frequently disposed by fishermen in the area of study as well as the municipal waste disposal in the vicinity of Shadegan wetland. Also, it should be pointed out that the maximum concentration of Pb, Ni, Zn and Mn are seen in station 8, where most urban wastewater is discharged into wetland. As Table 2 shows, the amount of trace elements in water is relatively high in Shadegan wetland; although in other sites in the world, higher concentrations of trace elements

Table 1. Physical characteristics of water and sediment in Shadegan wetland.

Station no.	Sediment						Water			
	TOM (%)	EC (ms/cm)	pH	GS fractions %			Salinity (ppt)	EC (ms/cm)	pH	Turbidity (NTU)
				Sand	Silt	Clay				
1	18.5	20.2	7.21	55.1	44.1	0.8	15.0	93.0	7.5	5.0
2	20.2	20.4	7.20	84.3	15.4	0.3	15.0	93.0	7.5	6.5
3	17.5	34.1	7.19	44.2	54.7	1.1	15.0	93.7	7.5	1.0
4	10.1	34.3	7.15	25.9	72.7	1.5	15.0	86.3	7.5	4.8
5	19.8	35.5	7.06	52.6	46.5	0.9	16.0	89.9	7.7	1.4
6	17.3	17.5	7.11	84.3	15.3	0.3	15.0	91.6	7.6	9.5
7	7.5	52.8	7.33	44.6	54.3	1.1	39.0	85.7	8.8	2.3
8	20.4	58.9	7.55	62.3	36.9	0.8	39.0	92.5	8.6	2.0
9	16.9	59.5	7.54	68.5	30.9	0.6	39.0	87.7	8.6	3.2
10	22	67.5	7.56	62.4	36.8	0.8	42.5	91.7	8.7	2.9
11	21.5	69.6	7.58	65.7	33.6	0.7	36.0	87.0	8.8	4.1
12	30.7	53.1	7.41	75.7	23.8	0.5	40.0	90.0	8.5	3.0
Min	7.5	17.5	7.06	25.9	15.3	0.3	15.0	85.7	7.5	1.0
Max	30.7	69.6	7.58	84.3	72.7	1.5	42.5	93.7	8.8	9.5
Average	18.5	41.3	7.29	60.5	38.7	0.8	27.2	90.2	8.1	3.8

Table 2. Total concentration of trace elements (µg/l) in the water of Shadegan wetland.

Sample no.	Cd	Cr	Cu	Mn	Zn	Co	Ni	Pb	V
1	1.02	1.64	35.75	12.41	5.48	18.00	25.30	95.60	222.70
2	0.30	2.81	23.21	9.69	4.11	15.75	21.80	72.10	153.80
3	0.41	0.00	22.40	7.35	13.07	13.40	21.45	63.50	191.90
4	5.27	23.21	18.79	29.32	12.87	17.60	25.10	89.20	226.60
5	0.76	3.78	26.70	9.33	3.30	18.40	24.40	89.10	101.60
6	0.97	1.22	31.61	20.49	3.47	17.30	23.00	99.20	145.60
7	0.94	4.65	31.60	13.42	3.37	20.20	25.70	105.90	373.70
8	1.20	20.72	0.00	31.72	21.12	23.30	28.90	116.85	285.50
9	0.37	4.87	27.40	24.56	3.36	21.70	27.40	98.50	195.60
10	0.00	7.26	19.29	26.52	5.42	21.10	25.30	101.80	268.30
11	0.87	6.30	28.47	22.71	2.55	23.30	28.70	116.20	354.00
12	0.90	4.43	31.70	15.50	3.30	22.80	26.20	108.75	290.63
Min	0.00	0.00	0.00	7.35	2.55	13.40	21.45	63.50	101.60
Max	5.27	23.21	35.75	31.72	21.12	23.30	28.90	116.85	373.70
Mean	1.08	6.74	24.74	18.59	6.79	19.40	25.27	96.39	234.16

in water is reported (Hall and Pulliam, 1995; Forero et al., 2009; Ozturk et al., 2009; Baldantoni et al., 2004; Pascoe et al., 1996).

Total concentration of trace elements in Shadegan bed sediment is provided in Table 3. The concentrations of Mn (310.6 mg/kg), Ni (46.1 mg/kg), Zn (36.4 mg/kg) and V (32.1 mg/kg) were highest among other elements in sediments. It seems that high concentrations of Ca in station 6 are dependent on maximum density of live macro benthoses community in this station. It should be pointed out that Ni and V are known as index of oil pollution (Karbassi and Amirnezhad, 2004), and since Shadegan wetland is located in an oil field, such indices can be useful for the interpretation of data. Also Cd and Pb contents are more than mean crust concentrations that may be indicative of anthropogenic sources for these elements. Gathered results from other locations of the world show that the mean concentration of studied elements in Shadegan wetland is almost high and in some cases higher than other sites. For instance, Ni concentration is more than that in Southern Baltic Sea (1.2 mg/kg; Hendozko et al., 2010), Gulf of Paria (4.8 mg/kg; Norville 2005), Montevideo Harbour (300 mg/kg; Muniz et al., 2004) and Lake Michigan (18.8 mg/kg;

Table 3. Total concentration of trace elements in Shadegan wetland sediments.

Station no.	Cd	Cr	Cu	Co	Mn	Ni	Pb	V	Zn	Ca	Al	Fe
	mg/kg									%		
1	4.9	7.4	18.3	10.8	222.0	58.1	11.3	31.7	33.7	1.4	1.8	1.9
2	5.0	8.1	28.3	14.1	340.0	74.0	16.4	50.6	39.1	2.2	2.7	2.4
3	5.0	9.4	33.8	17.4	420.1	24.7	18.8	58.8	44.4	2.3	3.1	3.2
4	4.9	7.4	18.9	12.1	332.2	33.5	16.1	31.5	37.4	1.5	2.3	2.2
5	4.8	7.8	20.1	11.9	292.3	79.2	15.7	43.8	33.9	1.3	2	2.3
6	5.5	7.2	14.7	9.9	306.7	62.5	16.1	30.5	29.6	9.4	1.6	1.8
7	4.8	49.1	4.9	10.2	353.4	66.1	10.4	29.0	96.3	1.9	2.2	1.9
8	3.8	2.1	6.0	7.0	335.3	40.5	12.7	24.8	25.7	2	2.1	1.2
9	3.8	13.4	4.6	8.9	365.2	50.1	13.3	23.4	35.2	2.2	2.1	1.5
10	3.8	24.4	13.0	7.4	304.6	31.7	12.2	21.9	30.9	2	1.6	0.1
11	4.9	5.8	6.4	3.8	302.6	17.8	10.7	19.0	12.4	2.4	1.1	0.6
12	4.7	6.3	8.3	5.8	153.1	27.6	17.2	20.5	18.8	2.6	1.3	0.9
Min	3.8	2.1	4.6	3.8	153.1	17.8	10.4	19.0	12.4	1.3	1.1	0.1
Max	5.5	49.1	33.8	17.4	420.1	79.2	18.8	58.8	96.3	9.4	3.1	3.2
Mean	4.7	12.4	14.8	9.9	310.6	47.1	14.2	32.1	36.4	2.6	2.0	1.7
Mean crust[a]	0.3	100	25	50	-	75	14	135	75	4.1	8.2	4.6

[a]Bowen, 1979.

Table 4. Bioaccessibility concentration of trace elements (mg/kg) in Shadegan sediments.

Station no.	Cd	Cr	Cu	Co	Mn	Ni	Pb	Zn	V	Ca	Mg
1	0.23	0.29	0.34	0.10	7.55	0.14	0.33	0.23	0.57	16.97	5.44
2	0.23	0.28	0.35	0.11	4.71	0.15	0.35	0.20	0.61	12.70	5.31
3	0.23	0.28	0.34	0.09	7.48	0.13	0.33	0.17	0.70	12.93	5.47
4	0.23	0.18	0.25	0.11	0.33	0.13	0.52	0.17	0.81	16.55	9.01
5	0.23	0.28	0.35	0.10	6.93	0.12	0.25	0.18	0.65	16.20	9.47
6	0.23	0.29	0.35	0.11	6.20	0.15	0.00	0.16	0.71	17.15	7.23
7	0.23	0.30	0.37	0.37	3.66	0.28	0.92	0.15	1.95	14.85	8.58
8	0.23	0.34	0.42	0.82	5.21	0.73	3.43	0.15	3.98	16.45	7.99
9	0.25	0.33	0.51	0.79	5.84	0.92	5.12	0.18	3.92	12.25	3.87
10	0.22	0.26	0.27	0.05	22.66	0.09	0.14	0.29	0.48	16.43	8.47
11	0.23	0.26	0.27	0.10	16.18	0.11	0.45	0.26	0.80	14.85	8.44
12	0.22	0.26	0.26	0.11	13.00	0.13	0.57	0.27	0.78	19.50	8.28
Min	0.22	0.18	0.25	0.05	0.33	0.09	0.00	0.15	0.48	12.25	3.87
Max	0.25	0.34	0.51	0.82	22.66	0.92	5.12	0.29	3.98	19.50	9.47
Mean	0.23	0.28	0.34	0.24	8.31	0.26	1.03	0.20	1.33	15.57	7.30

Carter et al., 2006). Also, Cd content is higher than that in Qatar and Bahrain coastal sediments (0.9 and 0.18 mg/kg respectively; Mora et al., 2004). Accumulation of Co in Shadegan sediment is more than other sites (Hendozko et al., 2010; Mora et al., 2004). In addition, V and Mn concentrations are significantly higher than other sites near Persian Gulf and Oman Sea (Mora et al., 2004). But in Milltown Reservoir Wetland, the concentration of Zn (1426 mg/kg; Pascoe et al., 1996) is higher than that of the study area. Generally, it seems that release of various contaminants such as industrial, agricultural and urban waste waters in Shadegan wetland, led to high accumulation of most of the studied trace elements than other sites in the world.

Generally, bioaccessibility of trace elements in sediment are low except for Ca (15.57 mg/kg), Mg (7.30 mg/kg), Mn (8.31 mg/kg), V (1.33 mg/kg) and Pb (1.03 mg/kg) (Table 4). The higher concentrations of Ca, Mg and Mn may not pose environmental risks since they are considered as essential elements for the growth of organisms (Freitas et al., 2006). The results of the three-step chemical partitioning for trace elements are shown in

Table 5. Chemical partitioning of trace elements (mg/kg) in Shadegan sediments.

Station	Cd			Cr			Co			Cu			Mn			Ni			Pb			V				Zn	
no.	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1	1.6	0.0	0.0	1.4	0.0	1.1	1.0	0.1	0.0	4.4	0.0	0.4	13.5	0.0	0.0	2.8	0.0	0.3	5.5	0.0	0.0	3.2	1.0	0.0	5.7	1.0	0.0
2	1.2	0.0	0.0	1.4	0.0	1.6	0.7	0.4	0.0	5.0	0.0	0.0	12.7	0.0	0.0	0.7	1.3	2.4	3.3	0.9	0.0	2.0	2.4	1.4	4.8	0.5	0.0
3	0.7	0.0	0.4	1.5	0.0	1.1	0.5	0.2	0.0	3.0	0.3	0.4	22.7	0.0	0.0	1.8	0.3	2.2	2.4	0.9	0.0	2.3	1.2	3.1	2.5	2.3	0.0
4	1.2	0.0	0.0	1.5	0.0	1.6	0.6	0.0	0.0	3.8	0.0	0.1	27.9	0.0	0.0	1.5	0.1	1.6	2.8	0.8	0.0	3.4	0.0	2.1	2.7	33.7	0.0
5	1.2	0.0	0.0	1.4	0.0	1.4	0.8	0.2	0.0	3.1	0.7	0.3	21.4	0.0	0.0	2.1	0.3	0.0	3.9	1.6	0.0	2.6	1.7	0.4	2.9	3.9	0.0
6	1.2	0.2	0.0	1.5	0.1	1.4	0.7	0.1	0.0	3.3	0.0	0.4	32.1	0.0	0.0	1.9	0.2	0.6	3.5	1.5	0.0	3.6	0.2	0.3	2.4	2.3	0.0
7	1.2	0.0	0.0	1.5	0.0	1.2	0.7	0.2	0.0	4.7	0.0	0.0	27.9	0.0	0.0	2.0	0.0	0.0	4.1	0.8	0.0	2.9	0.3	0.8	3.2	2.6	0.0
8	1.2	0.0	0.0	1.4	0.0	0.6	0.7	0.0	0.0	5.9	0.0	0.0	21.8	0.0	0.0	1.8	0.0	0.0	4.5	0.0	0.0	3.5	1.4	0.0	3.7	1.4	0.0
9	1.2	0.0	0.0	1.4	0.0	0.0	0.8	0.0	0.0	4.5	0.0	0.0	25.0	0.0	0.0	1.8	0.0	0.0	4.2	2.4	0.0	2.7	0.3	0.0	2.5	2.6	0.0
10	1.1	0.0	0.0	1.5	0.2	0.0	1.1	0.0	0.0	9.2	0.0	0.0	19.0	0.0	0.0	2.2	0.0	0.0	5.2	0.0	0.0	4.7	0.0	0.0	4.5	1.0	0.0
11	1.1	0.0	0.0	1.3	0.0	0.0	0.6	0.0	0.0	3.8	0.0	0.0	43.4	0.0	0.0	1.1	0.0	0.0	3.8	0.0	0.0	2.4	0.3	1.1	2.0	1.3	0.0
12	1.2	0.0	0.0	1.3	0.0	0.0	0.5	0.0	0.1	3.3	0.2	0.7	6.3	0.0	0.0	1.2	0.0	0.3	6.6	0.5	0.0	3.3	2.2	0.0	3.1	0.1	0.0
Min	0.7	0.0	0.0	1.3	0.0	0.0	0.5	0.0	0.0	3.0	0.0	0.0	6.3	0.0	0.0	0.7	0.0	0.0	2.4	0.0	0.0	2.0	0.0	0.0	2.0	0.1	0.0
Max	1.6	0.2	0.4	1.5	0.2	1.6	1.1	0.4	0.1	9.2	0.7	0.7	43.4	0.0	0.0	2.8	1.3	2.4	6.6	2.4	0.0	4.7	2.4	3.1	5.7	33.7	0.0
Mean	1.2	0.0	0.0	1.4	0.0	0.8	0.7	0.1	0.0	4.5	0.1	0.2	22.8	0.0	0.0	1.7	0.2	0.6	4.1	0.8	0.0	3.0	0.9	0.8	3.3	4.4	0.0

a, Loosely bonded ions; b, sulfide bonded ions; c, organo-metalic bonded ions.

Table 5. Metals are found in various sedimentary phases. Majority of the metal content is loosely bonded ions, sulphides and organo-metallic bonds (over 90%) which originated from anthropogenic sources (Karbassi et al., 2008). These data were grouped based on mean concentration of the elements associated with various sedimentary phases as follows: Loose ions: Mn (22.8) > Cu (4.5 mg/kg) > Pb (4.1 mg/kg) > Zn (3.3 mg/kg) > V (3 mg/kg) > Ni (1.7 mg/kg) > Cr (1.4 mg/kg) > Cd (1.2 mg/kg) > Co (0.7 mg/kg); sulfide ions: Zn (4.4 mg/kg) > V (0.9 mg/kg) >Pb (0.8 mg/kg) > Ni (0.2 mg/kg) > Cu and Co (0.1 mg/kg). Other elements do not have any concentration in this phase; Organic ions: Cr and V (0.8 mg/kg) > Ni (0.6 mg/kg) > Cu (0.2 mg/kg). Other elements do not have any concentration in this phase.

Percentage of anthropogenic portion of different metals in bed sediments of Shadegan wetland is provided in Table 6. Also, comparison of this portion is shown in Figure 3. As this figure indicates, the most and lowest anthropogenic portion of trace elements, relates to Cu and Cr, respectively. Table 7 shows the results of collected benthic invertebrate (no benthic invertebrate is found in station 10 and 11, so they are not included in Table 7). Only a few species have been found in the study area. It is obvious that the number of dead Strachoda and Gastropoda are very high in bed sediments. As some researchers have determined, the reason for the fewness of benthic invertebrate may bebad living environment that is caused by heavy pollution (Li et al., 2006). So due to different water pollution sources in Shadegan wetland and oil reservoirs around this area, the condition of benthic macrobenthos is unsuitable in Shadegan bed sediment.

To determine the intensity of pollution in bed sediments of Shadegan wetland, I_{geo} and I_{POLL} indices were calculated. The results which are given in Table 8 clearly indicate that I_{geo} fails to bring out the intensity of pollution in the study area. The reason for its inability is that I_{geo} uses the concentrations of shale for comparison. Since the geological settings of an area can differ from others, I_{geo} cannot furnish the right information. On the other hand, I_{POLL} shows pollution intensity of moderate to very high (except for Co) that are not only compatible with the anthropogenic portion of the elements but also, is in accordance with the macro benthic studies. It should be pointed out that the very high pollution intensity (I_{POLL} = 8) for Mn could be due to the mobile nature of Mn in sediments. The chemical partitioning studies may

Table 6. Comparison of anthropogenic portion of trace elements in Shadegan sediments (% of anthropogenic to total contents of metals in bulk digestion).

Station no.	Cd	Cr	Co	Cu	Mn	Ni	Pb	V	Zn
1	22.4	24.3	0.0	16.1	0.0	0.0	39.1	3.1	9.8
2	14.0	27.2	0.0	7.6	0.0	0.0	15.5	1.5	3.6
3	12.0	18.1	0.0	0.9	0.0	7.3	7.7	1.1	0.9
4	14.3	32.4	0.0	10.4	0.0	0.0	12.4	7.5	87.4
5	14.6	25.6	0.0	10.4	0.0	0.0	24.8	0.7	10.0
6	16.4	31.9	0.0	15.3	0.5	0.0	21.0	3.4	5.7
7	14.6	4.5	0.0	86.7	0.0	0.0	37.1	3.9	0.0
8	21.1	85.7	0.0	87.7	0.0	0.0	25.3	9.7	9.7
9	21.1	9.7	0.0	88.4	0.0	0.0	39.7	2.8	4.5
10	18.8	6.1	4.9	60.5	0.0	0.0	32.4	11.6	7.8
11	12.2	12.1	5.3	49.3	4.3	0.0	25.9	10.2	16.9
12	14.9	11.1	0.6	39.9	0.0	0.0	31.1	16.9	6.9
Min	12.0	4.5	0.0	0.9	0.0	0.0	7.7	0.7	0.0
Max	22.4	85.7	5.3	88.4	4.3	7.3	39.7	16.9	87.4
Mean	16.4	24.1	0.9	39.5	0.4	0.6	26.0	6.0	13.6

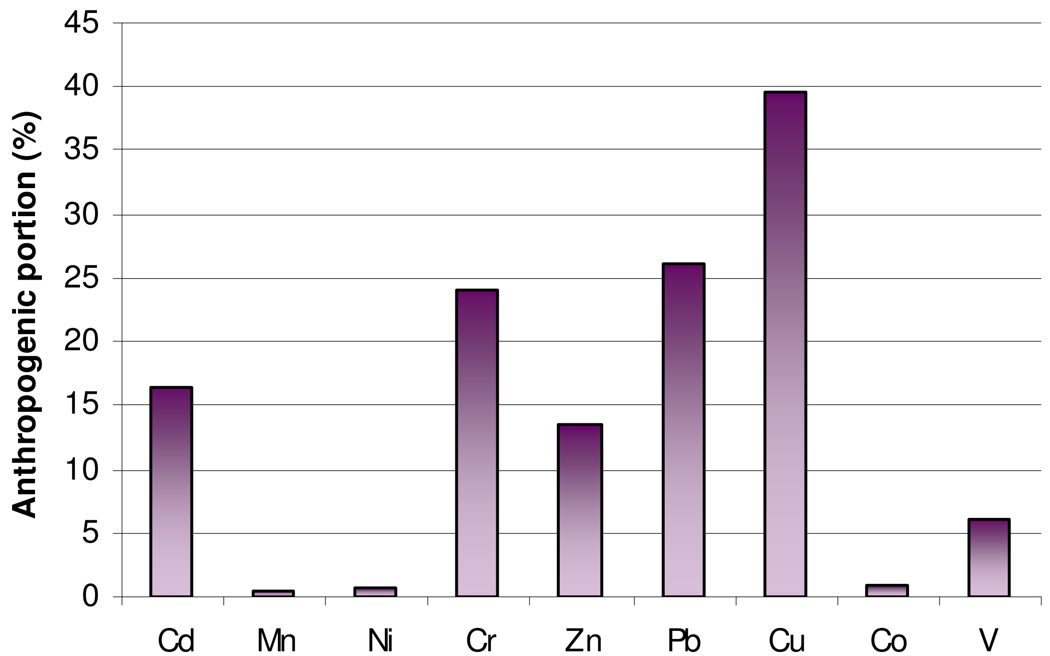

Figure 3. Anthropogenic percentage of trace elements in bed sediments of Shadegan wetland.

show higher values for Mn and therefore higher pollution intensity is found by I_{POLL}.

DISCUSSION

Figure 4 shows relationships between metals and physical parameters in the water of Shadegan wetland. It is clear that Co, Ni, Pb and V are strongly related to pH and salinity characteristics in water (cluster "B"). Cluster "A" shows similar relationships amongst Cd, Cr, Mn and Zn in water of Shadegan wetland. Also, turbidity and Cu have same behavior although this is quiet weak. Base on bioaccessibility cluster analysis, most of the trace elements (Pb, Ni, V, Co, Cu, Cr and Cd) have same behavior and positive strong relation (cluster "A"). It reveals that increase in pollution discharge in the study area can enhance adsorption of trace elements in

Table 7. Number of collected macro benthoses in sediments of Shadegan wetland.

Macrobenthos	Station no.									
	1	2	3	4	5	6	7	8	9	12
Chironomidae	3	31	13	11	0	130	13	0	10	15
Strachoda	0	15	16	3	0	17	0	0	0	1
Nematoda	0	20	0	0	1	2	0	0	0	0
Oligochaete	0	6	0	2	0	87	0	0	0	0
Dead Gastropoda	350	100	100	50	200	80	0	50	30	0
Dead Strachoda	0	0	500	30	150	100	0	0	0	300
Sum	353	172	629	96	351	416	13	50	40	316

Table 8. Comparison of different pollution indices in Shadegan wetland sediments.

Trace element	Cd	Cr	Cu	Co	Mn	Ni	Pb	V	Zn
I_{geo}	3.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I_{POLL}	2.6	2.9	2.2	0.00	8	7.9	2.0	4.4	3.0

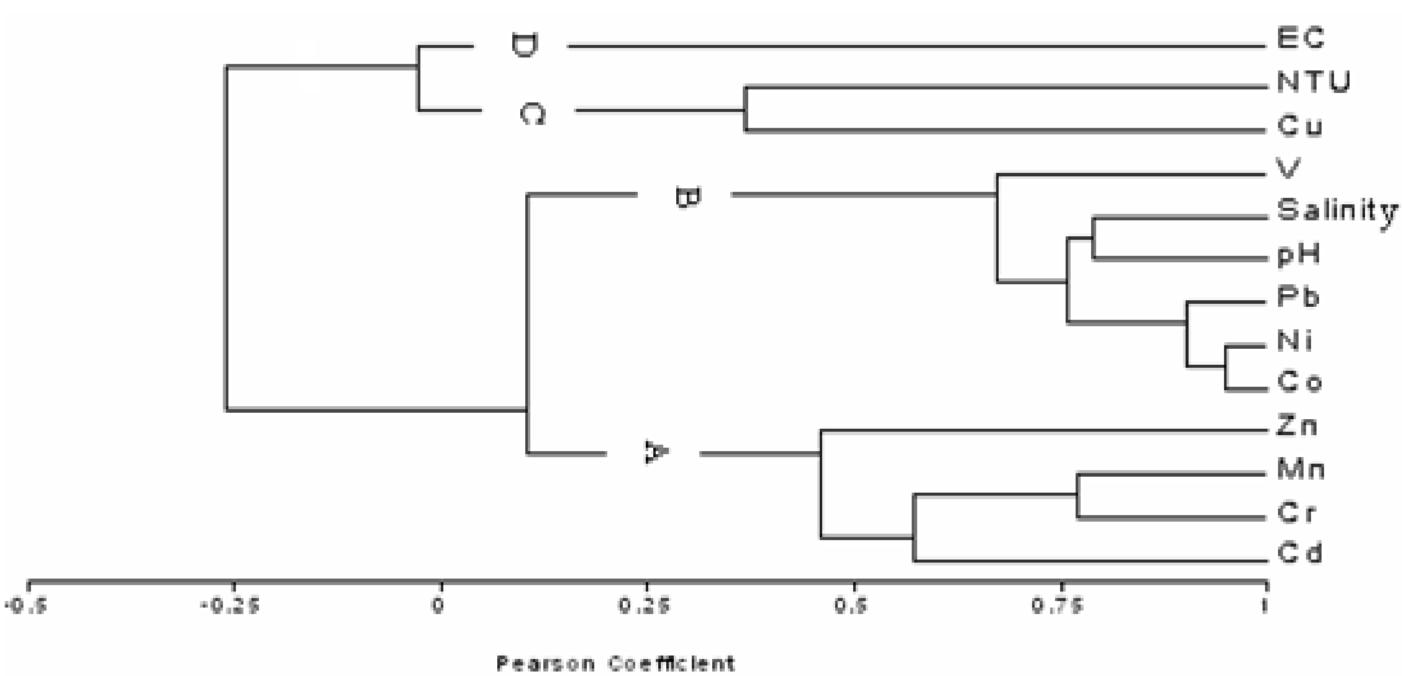

Figure 4. Dendogram of cluster analysis amongst trace elements in water of Shadegan wetland.

organisms. Relationship amongst different trace elements in sediments is shown in Figure 5. Cluster "B" involving Cu, Co, V, Fe, Al and Pb have a significant similarity co-efficient and same behavior. In addition, Mn has positive meaningful relationship by other elements in cluster "B" but this is relatively weak. Also, Ca and Cd have positive relation with each other in cluster "A" but in cluster "C", Cr and Zn have strong positive meaningful relationship. Moreover, Figure 5 reveals that TOM (cluster "D") does not have any relation with other parameters. Figure 6 presents the cluster analysis of trace elements bio-accessibility in sediments of Shadegan wetland. Trace elements of cluster "A" have high positive relationship to each others. Beside, cluster "C" shows that Zn and Mn have positive meaningful relationships with TOM. Also, as Figure 7 shows, Strachoda, Chironomidae and Oligo-chaete are related to Ca accumulation in sediments (cluster "B"). Based on clusters "C" and "D", dead Strachoda and Gastropoda are linked to Cu and Cr and Zn, TOM and Mn, respectively. Beside, Nematoda has

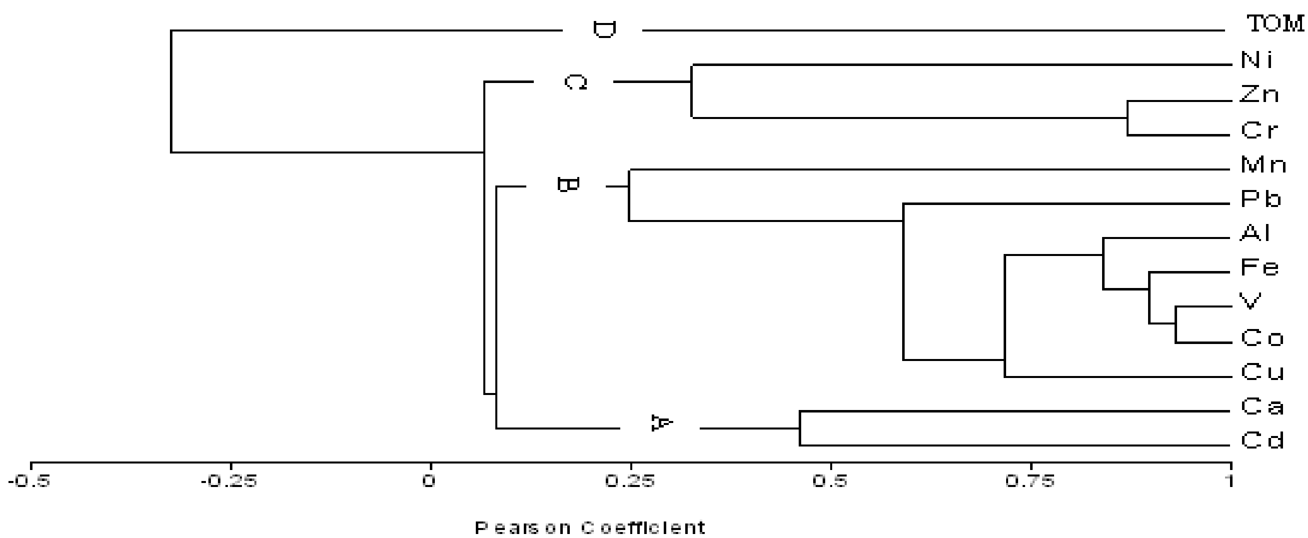

Figure 5. Dendogram of cluster analysis amongst trace elements in sediments of Shadegan wetland.

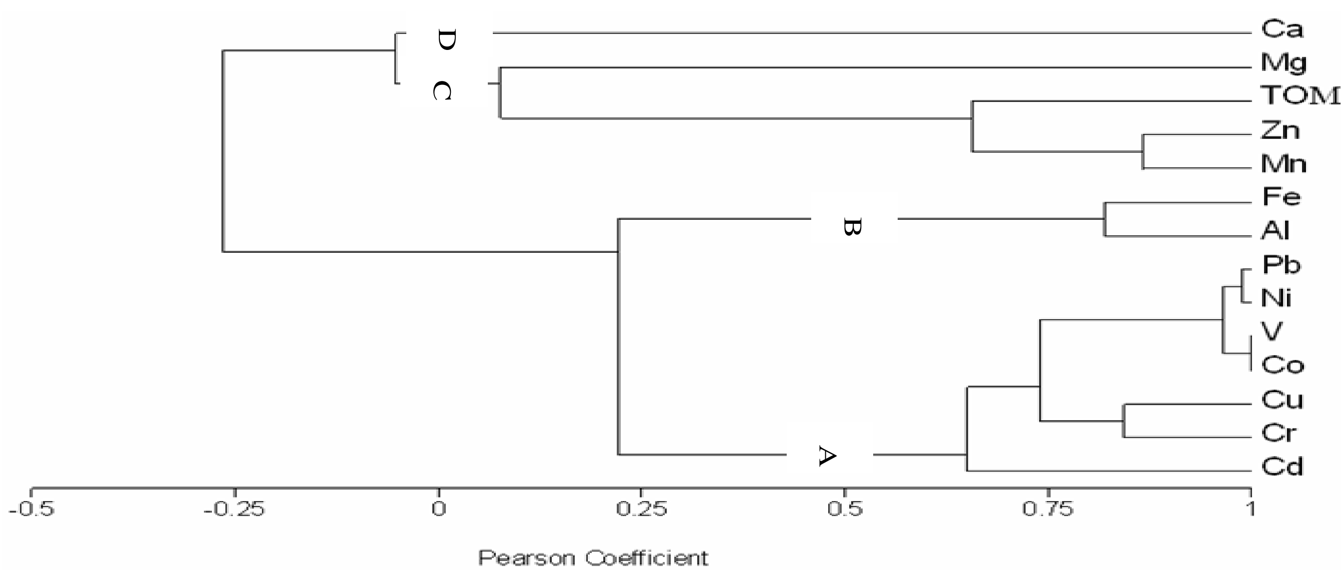

Figure 6. Dendogram of cluster analysis for trace elements bioaccessibility in sediments of Shadegan wetland.

positive relationship with Fe, Al and Cd (cluster "A"), probably, because Shadegan benthic invertebrates are sensitive to other pollution sources such as toxic materials and oil contaminants.

To sum up the findings, we concluded that the texture of sediments in the Shadegan wetland falls within sandy loam and silt loam. The salinity of water ranges from 15 to 42.5 ppt. The general pattern of dissolved elemental concentrations (V>Pb>Ni>Cu>Co>Mn>Zn>Cr>Cd) does not show any anomaly.

Calcium contents of sediments are highlydependent on the density of macro benthos community. The low concentrations of calcium could be indicative of lower biological productivity in the area of study. The results of the present investigation clearly showed that comparison of metals in the sediment with mean crust cannot furnish useful information. The obtained results clearly show that oil pollution has led to severe pollution in the wetland. The results of the present study also show that I_{POLL} index can be effectively used to show environmental pollution more meaningfully. Since I_{POLL} uses background concentrations of metals within the area of study, it provides better results than other pollution indices. Though cluster analysis is an efficient tool to know the inter relationship amongst various parameters, it fails to provide quantitative information.

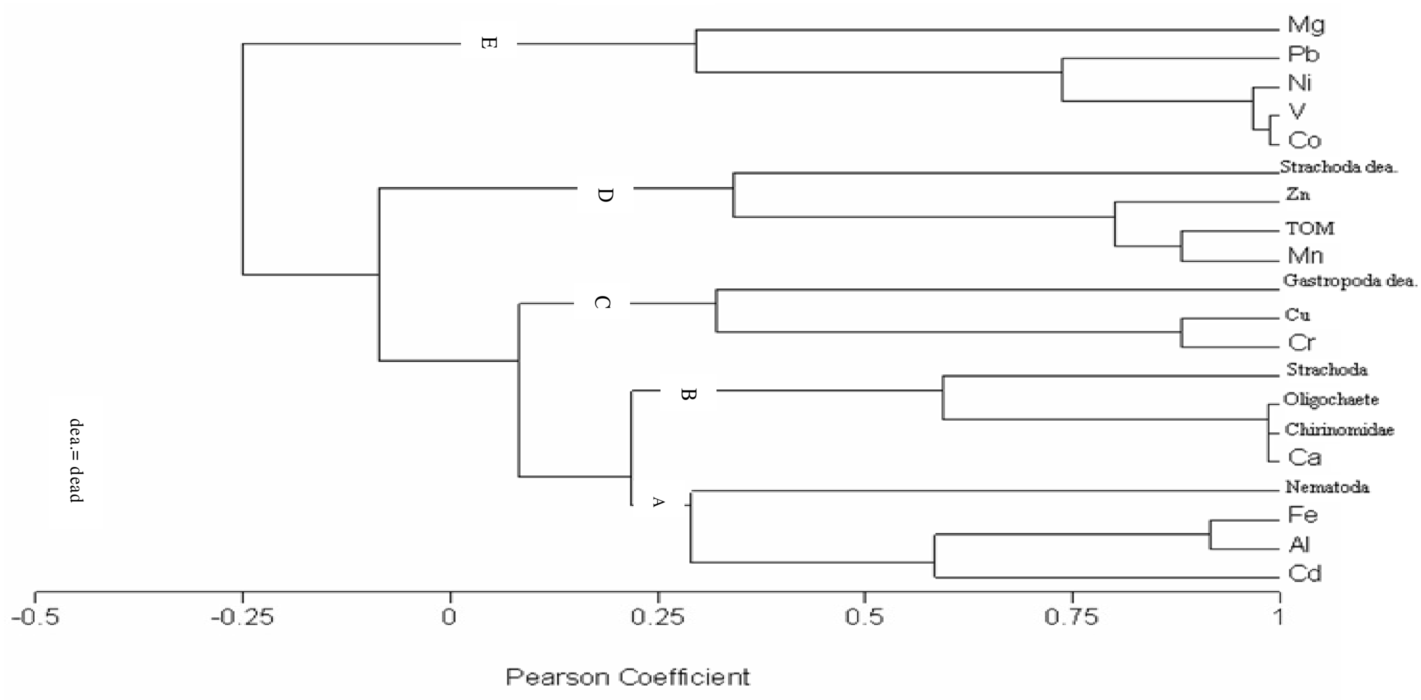

Figure 7. Dendogram of cluster analysis amongst trace elements bioaccessibility in sediments and macro benthose communities of Shadegan wetland.

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