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Investigation on anthropogenic and natural share of heavy metals in surface sediments of Shadegan wetland

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ABSTRACT: Accumulation of trace metals in sediment can cause severe ecological impacts. The present study determines the elemental concentrations and chemical partitioning of heavy metals in surface sediment of Shadegan wetland. Shadegan wetland is one of the most important wetlands in southwest of Iran and it is in Ramsar-listed wetlands. For this purpose, 7 sampling stations were selected for sediment collection in this wetland during autumn 2011. Physico-chemical parameters including pH, EC, total organic materials (TOM), grain size fraction and elements (Cr, Pb, V,) in sediments were measured. Subsequently, lithogenous and anthropogenic portions of trace metals in sediment, along with Igeo and IPOLL indices were measured. According to obtained results, Pb(25%), and Cr (14 %), had highest anthropogenic portion in study area. More ever, strong and positive meaningful relation between Cr and V shows that Cr has oil origin in the area of the study. Also, measured physico-chemical parameters have no role in controlling the trace elements concentration. The two pollution indices used in the present investigation (Igeo and IPOLL) are indicative of different pollution intensity in Shadegan aquatic environment.

Keywords: *Chromium; Lead; Vanadium; Aquatic environment; Chemical partitioning; Manmade source*

INTRODUCTION

Heavy metals are ubiquitous, highly persistent, and non-biodegradable with long biological half-lives and they can accumulate in soils at environmentally hazardous levels
(Burger *et al*., 2007; Uba *et al*., 2009; Mensi *et al*., 2008; Ahmad *et al*., 2010; Murugesan *et al*., 2008; Sekhavatjou *et al*., 2010). They can decline water and sediments quality and may adversely affect all biological attributes like taxonomic richness, trophic structure, and health of individual organisms (Fernandes *et al*., 2007; Batzias and Siontorou, 2008). Also they can be dispersed and accumulated in plants and animals, and taken in by humans through consumption (Wcislo *et al*., 2002).

Metals in essential and non-essential forms accumulate in nature especially in sediments (Fairbrother *et al*., 2007; Mazeja and Germb, 2009; Muchaa *et al*., 2008; Venugopal *et al*., 2009; Priju and Narayana, 2007; Karbassi *et al*., 2007). Sediments conserve important environmental information (Gutierrez *et al*., 2004) and increasingly are recognized as both carriers and possible sources of contaminants in aquatic systems (Tessier *et al*., 1979).

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). Wetland sediment analyses have been essential in assessing the impact of industrial effluent discharge and in determining processes of metal effluent remediation and the potential of the sediment as a source of pollution (Von der Heyden and New, 2004). Various reports clearly indicated that total concentration of heavy metals is inadequate to assess the behavior and potential risk to the environment. Therefore, information on heavy metal distribution in various chemical forms should be employed to envisage the potential contamination risk and ensuing environmental damage (Fitamo *et al*., 2007).

Chemical speciation can be defined as the identification and quantification of the different chemical species, forms or phases present in sediment. However, the determination of specific chemical species is difficult and often hardly possible (Loska and Wiechula, 2002). Heavy metals are associated with sediments in different ways, and their association determines the mobility and availability (Ahumuda *et al*., 1999). This type of association between metals and the sediments can be understood in detail by sequential extraction techniques (Taghinia Hejabi *et al*., 2011).

In this study, Shadegan wetland is selected for determination of trace elements in sediments and identification of natural and anthropogenic shares. For this purpose Cr, Pb, and V were measured in the bed sediments of the study area. In addition to the above, the determination of the following parameters were carried out in this study: sediment physical structure, lithogenous and anthropogenic portion of metals, pH, ECc and total organic materials (TOM) in all sediments, calculating the pollution intensity indices and statistical analysis of relationships amongst different parameters in Shadegan wetland. Shadegan wetland has a very important role of conserving fauna and flora in southwest of Iran. There is located numerous polluting industries such as petrochemical complexes (about 10 petrochemical complexes) and agro-industry units that release their wastewater in this wetland.

MATERIALS AND METHODS

Urban and agriculture run-off pour into this aquatic ecosystem. In this study, 7 sediments sampling stations were selected according to clean areas and pollution sources (Fig.1)

Sediment sampling was done during autumn, 2011. Surface sediment was collected using a Peterson grab sampler. After transportation of samples to laboratory under quality control standards, main parameters were measured as follows:

1. Physico-chemical analysis involving pH, electrical conductivity (EC), total organic matters (TOM) and grain size fraction were done in sediment samples (Allen, 1989). TAL software was used to show the texture of sediment in the area of study (Fig. 2)
2. 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). For total contents of heavy metals, about 0.5 g of the sieved and 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

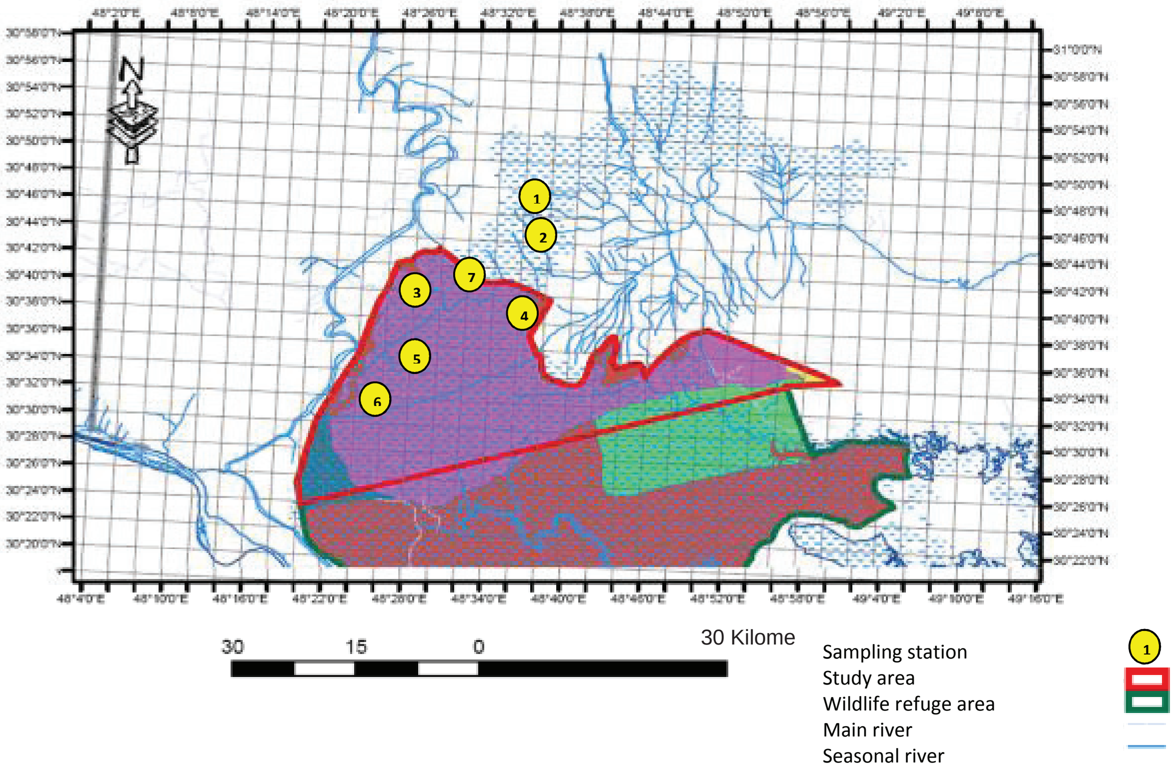

Fig. 1: Sediments sampling stations in Shadegan wetland Iran

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 (Hosseini Alhashemi et al., 2011). Chemical partition studies were conducted in three sequential steps: (1) acetic acid 25%v/v, (2) acetic acid 25% v/v-0.1 M hydroxylamine hydrochloride, and (3) 30% H_20_2 "extraction with 1 M ammonium acetate" (EPA 3050; Tessier *et al.*, 1979; Chester and Hughes, 1967; Gibbs, 1973). All glasses and plastics ware were cleaned by soaking in 10% HNO3 (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.

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]

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

   I_{geo}= Log_2 [Cn/Bn1.5×]

   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).

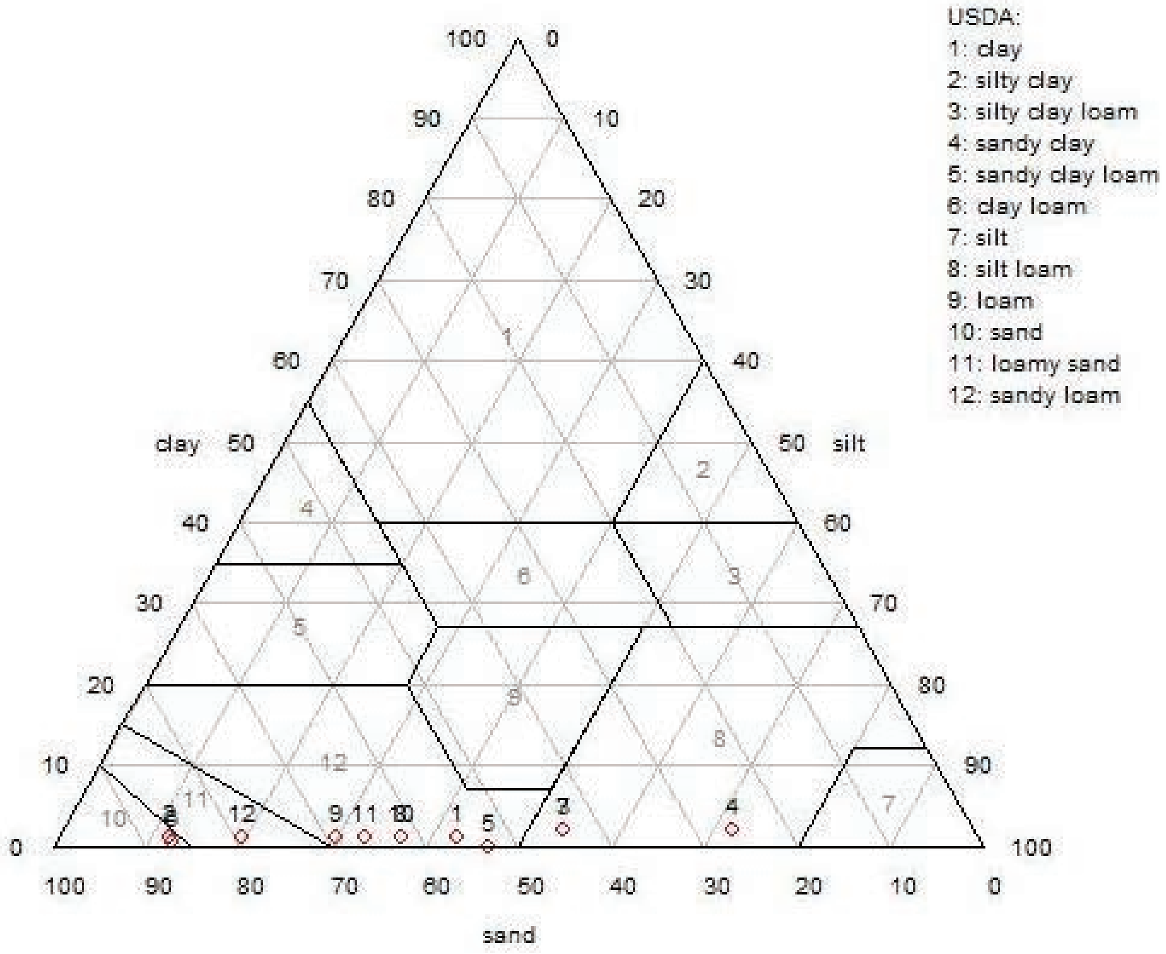

Fig. 2: Texture of sediments in the area of study

RESULTS AND DISCUSSION

Table 1 shows physical characteristics of water and sediments in Shadegan wetland.

Table 1: Physical characteristics of sediment in Shadegan wetland.

Station No.	TOM %	EC ms/cm	pH	GS fractions % Sand	Silt	Clay
1	18.5	20.2	7.21	55.1	44.1	0.8
2	20.2	20.4	7.20	84.3	15.4	0.3
3	10.1	34.3	7.15	25.9	72.2	1.5
4	17.3	17.5	7.11	84.3	15.3	0.3
5	21.5	69.6	7.58	65.7	33.6	0.7
6	20.4	58.9	7.55	62.3	36.9	0.8
7	30.7	53.1	7.41	75.7	23.8	0.5
Min	10.1	17.5	7.11	25.9	15.3	0.3
Max	30.7	69.6	7.58	84.3	72.7	1.5
Average	19.9	37	7.4	55.1	34.5	0.7

As shown in Fig. 2, most of the stations have sandy loam and loamy sand textures. Total organic matter contents ranges from 10.1 to 30.7% with mean value of 19.9%. The very high contents of TOM may be indicative of massive amount of wetland plants and dead macro benthoses. Total concentration of trace elements in Shadegan bed sediment is provided in Table 2.

Table 2: Total concentration of trace elements (mg/kg) in Shadegan wetland sediments.

Station No.	Cr	Pb	V
1	7.4	11.3	31.7
2	8.1	16.4	50.6
3	7.4	16.1	31.5
4	7.2	16.1	30.5
5	2.1	12.7	24.8
6	5.8	10.7	19.0
7	6.3	17.2	20.5
Min	2.1	10.7	19.0
Max	8.1	17.2	50.6
Average	6.3	14.3	29.8
Crust Ave.*	100	14	135

* Bowen 1979

The mean concentration of V (29.8 mg/kg) was highest among other elements in sediments. It should be pointed out that V is 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 Pb content is more than mean crust concentrations that may be indicative of anthropogenic sources for these elements.

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.

The results of the three-step chemical partitioning for trace elements are shown in Table 3. Metals are found in various sedimentary phases. Majority of 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: Pb (4.3 mg/kg)> V (3.09 mg/kg)> Cr (1.4 mg/kg); Sulfide ions: V (1.08 mg/kg)> Pb (0.53 mg/kg)> Cr (0.015 mg/kg); Organic ions: Cr (0.9 mg/kg)> V (0.7 mg/kg). Lead does not have any concentration in this phase.

Table 3: Chemical partitioning of trace elements (mg/kg) in Shadegan sediments

Station No.	Cr a	Cr b	Cr c	Pb a	Pb b	Pb c	V a	V b	V c
1	1.4	0	1.1	5.5	0	0	3.2	1.0	0
2	1.4	0	1.6	3.3	0.9	0	2.0	2.4	1.4
3	1.5	0	1.6	2.8	0.8	0	3.4	0	2.1
4	1.5	0.1	1.4	3.5	1.5	0	3.6	0.2	0.3
5	1.4	0	0.6	4.5	0	0	3.5	1.4	0
6	1.3	0	0	3.8	0	0	2.4	0.3	1.1
7	1.3	0	0	6.6	0.5	0	3.3	2.2	0
Min	1.3	0	0	2.8	0	0	2.0	0	0
Max	1.5	0.1	1.6	6.6	1.5	0	3.6	2.4	2.1
Mean	1.4	0.015	0.9	4.3	0.53	0	3.09	1.08	0.7

a, Loosely bonded ions; b, Sulfide bonded ions; c, Organo-metalic bonded ions.

The average percentage of anthropogenic and natural share of trace elements in studied stations of bed sediments in the area of the study is presented in Fig. 3. As shown in Fig. 3, the highest and the lowest amounts of anthropogenic share are related to

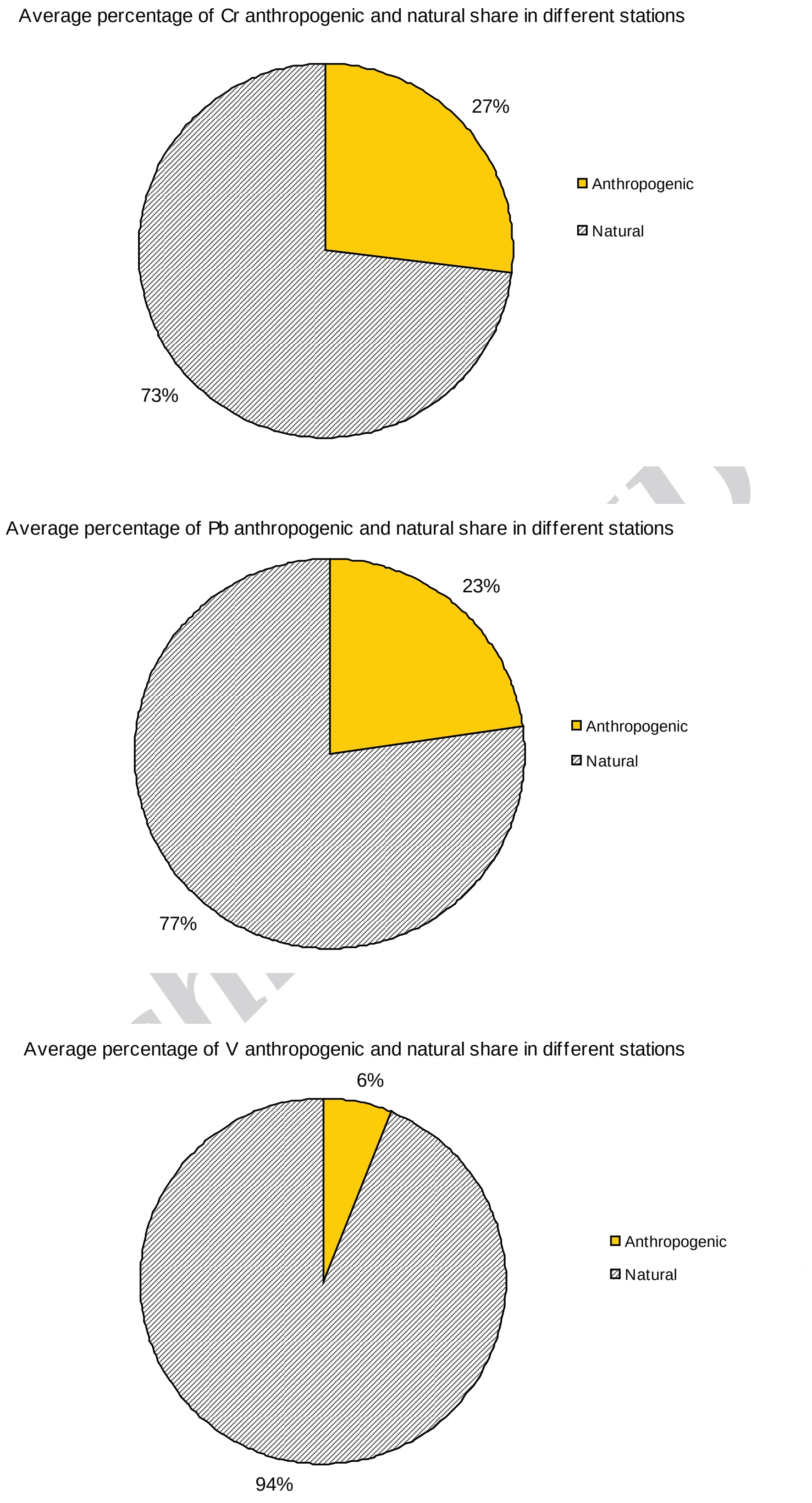

Fig. 3: Anthropogenic and natural percentage of trace elements in bed sediments of Shadegan wetland.

chromium and vanadium, respectively.

Also high anthropogenic share of Pb (23%) adjusted the various manmade sources of this element in the studied area.

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 4 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, therefore, I_{geo} cannot furnish the right information. On the other hand, I_{POLL} shows pollution intensity of moderate to high that are compatible with the anthropogenic portion of the elements.

Table 4: Comparison of different pollution indices in Shadegan wetland sediments

Pollution indices \ Trace elements	Cr	Pb	V
I_{geo}	0	0	0
I_{POLL}	2.9	2.0	4.4

CONCLUSION

Fig. 4 presents relationship amongst different trace elements and physico-chemical parameters in sediments. Cluster "A" involving pH, EC, and TOM have a significant similarity coefficient and same behavior. V and Cr have positive meaningful relationship together in cluster "B". This can be representative of this issue that oil materials have controlling role in chromium contents in Shadegan wetland. Also, Pb has positive relation with elements in cluster "B" but it is weak. Finally, all clusters show that physico-chemical parameters have no control on trace elements accumulation in the area of the study.

To sum up the findings, we concluded that TOM ranges 10.1% to 30.7%. The high percentage (mean average 19.8%) of TOM can be indicated the high load of vegetative materials and macrobenthoses in the bed sediment of Shadegan wetland. High amount of EC was shown in southern stations that receive the highest rural wastewaters. The texture of sediments in the Shadegan wetland falls within sandy loam and silt loam. The results of bulk digestion show that average concentration of Cr (6.3 mg/kg) is very lower than mean crust (100 mg/kg), but chemical partitioning analysis indicated that 27% of Cr is from anthropogenic sources. Though due to high anthropogenic share of Cr, the sources of this element (used batteries, fossil fuels and etc.) should be control in Shadegan wetland.

As well, mean levels of lead (14.3 mg/kg) was more than mean crust (14 mg/kg). Also, 23% of Pb originated from manmade sources in the study area. So, the most probable source of lead that is petroleum should be more considered and controlled. Although the mean level of vanadium showed the highest among other two elements, but the chemical partitioning analysis indicated that just 5% of this element is related to anthropogenic

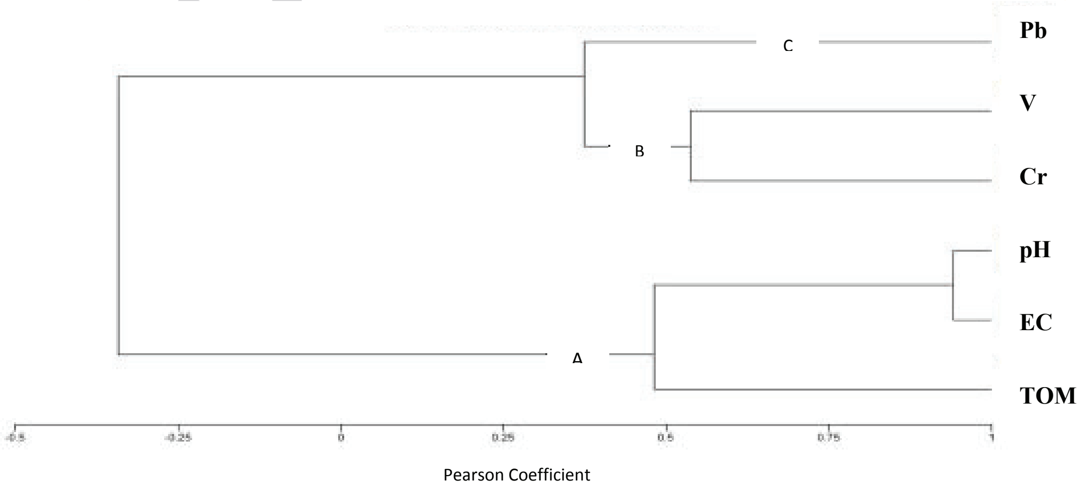

Fig. 4: Dendogram of cluster analysis amongst trace elements in sediments of Shadegan wetland

sources and the natural reservoirs of oil in the area of the study is responsible for V release.

The obtained results clearly show that oil pollution has led to severe pollution in the wetland. The results of 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.

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