Environmental Qualitative assessment of rivers sediments

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ABSTRACT: In this study, the concentrations of heavy metals (Ca, Zn, Cu, Fe, Mn, Ni) in thesediment of Shavoor River in Khuzestan Province in Iran has been investigated. After the library studies and field studies, six samples of water and sediment were taken from the river in order to evaluate heavy metal pollution in sediments. To determine the geochemical phases of metals in sediment samples the 5-step method was used for chemical separation. For quantitative assessment of the severity of contamination in the sediments, the geochemical indicators such as enriched factor (EF) and the accumulation index (Igeo) were used. Also, the statistical analyses including methods such as correlation analysis cluster analysis the (CA), were conducted.The results of the experiments showed that the organic matter deposited varies with the average of 2.49 and ranges between 1.95% and 3.43%. Samples showed concentrations of metals such as calcium, iron, manganese, copper and nickel at all the sampling points were below the global average, whereas the concentration of copper was slightly higher than the global scale. Enriched factor (EF) was calculated for the elements revealed that heavy metals are classified as non-infected. The Geo-accumulation Index showed that the studied elements were uninfected peers. Based on the results of multivariate statistical analysis it was concluded that metals such as manganese, copper, iron, nickel and zinc are mainly natural and calcium metal is likely to have an organic origin.

Keywords: *Shavoor River, Pollution, Sedimentation, Water, Khuzestan Province*

INTRODUCTION

Rivers as one of the basic resources of surface water have Ecologic and notable economic value. The Hydro-chemical composition and quality of water and the sediments of river beds have always been influenced by natural (Geologic) and unnatural (Pollution) factors.

The polluting elements entry, based on natural and human activities is one of the most important issues which mankind faces today. Together with the fast industrial and economic growth and producing many kinds of chemical substances as well as the consumption increase, human enters many kinds of contaminants to the nature which endangers both man and environment (Espinoza *et al.,* 2005). The importance of water resources especially surface water for supplying water needs, declares the important need of maintaining them from pollution, with entering effluents to the main system, consisting urban, industrial and agricultural sewage, they contain microbial and contaminants such as heavy metals.

Although the noted metals in low concentration act as micro-nutrients in a food chain , their accumulation in high concentrations cause toxicities and adverse environmental effect and as a result endangers water ecosystem and of course the consumers.

Measuring the heavy metals concentration alone, would not show their pollution intensity. Therefore in recent years to get rid of such problem, the Muller geochemical index is used to measure the intensity of pollution. In addition the accumulation of metal in sediments provides researchers with suitable information about environmental conditions. (Borja *et al.,* 2004; Caeiro *et al.,* 2005; Karbasi and valavi, 2010). Although sediments are ultimate accumulation of heavy metals in aquatic environments, in some cases they can act as sources of contaminations in water themselves (Berkowitz *et al.,* 2008, Izquierdo *et al.,* 1997; Yu *et al.,* 2001). The contaminants remains in the sediment for quite a long time , but due to biological activities and physical and chemical changes they can enter the surface waters , therefore measuring the heavy

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metal concentration can show a real picture of aquatic environment pollution (Karbassi *et al.,* 2010; Karbassi, 1998; Helling, 1990; Chester and Hughes, 1967; Prabu, 2009). To determine the pollution effect, the sources and concentrations of pollutants in aquatic environment need assessment and monitoring Chen and Lin (2001). The amount of pollution in aquatic environment can be determined by analysis of water, sediments and marine organisms. (Chen and Lin, 2001; Hamed and Emara, 2006; Veerasingam *et al.,* 2010; Karbassi and Heidari, 2015).

MATERIALS AND METHODS
Characteristics of the study area
Characteristics of Susa area

The Susa plain is situated in Khozestan province as a low width area in south-north direction. This plain is limited to Karkha River from west, Dez River from east, southern heights of Taghdis shirin Abad from north and to Taghdis Sardar Abad heights south. The Danial Susa city has an area of 3577 square km and is situated in 24 km from south west of Dezfoul and 38 km to Andimeshk and 115 km from north west of Ahwaz. The height of Susa area is 87 meters above the sea level and its distance from Tehran is 774 km.

The catchment characteristics

The Shavoor River is situated in Khozestan province in Danial Susa restrict and Ahwaz. This river catchment has geographical longitude of 48° 10' till 48° 25' in the east and 31° 47' till 32° 19' in the north. The highest point in this area is 100 meters and the lowest point is located in 30 meters above the sea level.

Method

To do the field survey and sampling from the environment, it is essential to be familiar with the region and the influenced areas. First of all the geologic and topographic maps were studied and after preliminary visit and defining the access ways, the water and river sediments samplings conducted. After collecting the samples, several experiments were done in order to define water physico-chemical parameters and determine the heavy elements concentration in sediments.

Sampling

First the access ways to the river were studied and after preliminary field survey and with respect to land use and natural terrain, access to specific sampling stations and water and sediment sampling was carried out by existing standards in April 2013.

The river water sampling took place in 6 chosen stations, from the beginning of the river to its entrance point in Bamdej pond. The samples were stored in poly ethylene containers of 1 L. capacity from depth of 15 to 20 centimeters below water surface. Before each sampling, the poly ethylene containers were washed with river water twice. The sampling point situation as well as the the geographical water sampling station along the Shavoor River are shown in Fig. 1 and Table 1.

To analyze the datas in current research and determine their relationship with eachother the classification of the measured variables have been used by statistic methods such as correlation and hierachical cluster analysis as well as clustering the datas by using the software MVSP. All calculations and census experiments were done by census software SPSS (version 18)

Equation (1): $I_{geo} = Log_2 \left[\dfrac{Cn}{Bnx1.5} \right]$ (1)

Cn : current element concentration in soil and sediment
Bn : element concentration in Shale
1.5 : Shale correction factor

If the chemical separation statistic is available, Muller formula can be optimized or modified. Since the

Table 1: The geographical water sampling station along the Shavoor River

Number	Station	Longitude	Latitude
1	Radadeh	E48° 12' 31''	N32° 17' 51''
2	Farmandari bridge	E48° 14' 33''	N32° 11' 04''
3	Shahid dastgheib village	E48° 16' 35''	N32° 05' 49''
4	Shavoor bridge	E48° 18' 01''	N32° 03' 31''
5	Shavoor dam	N48° 26' 23''	N31° 50' 52''
6	Bamdej lagoon	E48° 27' 15.8''	N31° 49' 54''
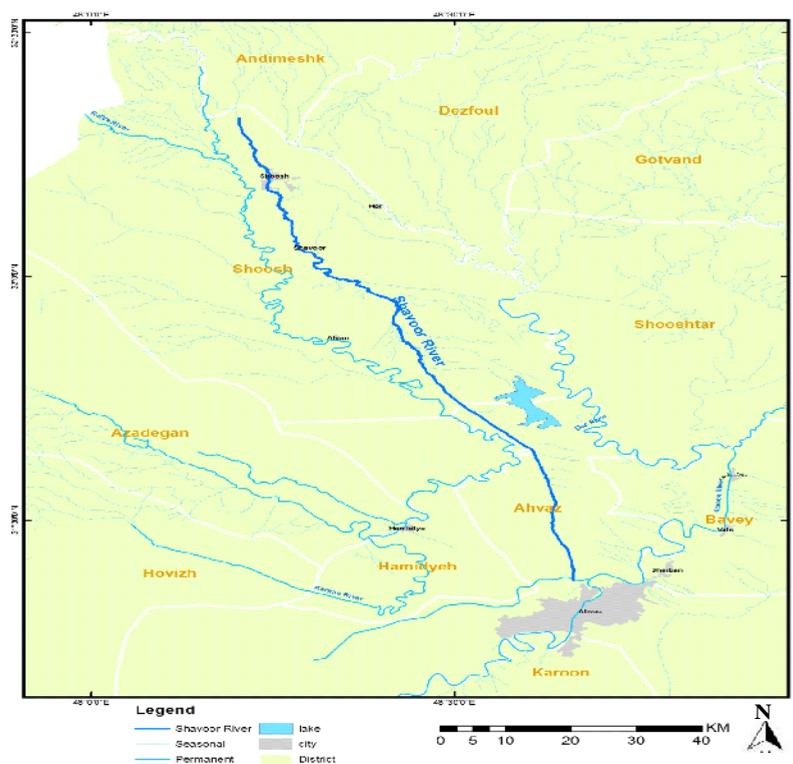
Fig. 1: The sampling point situation in Shavoor River

chemical separation method separates manual part from natural one, the exact deal of Bn is found. Thus the Muller formula was changed By Karbassi in 2007 as follows:

Equation (2) : $\quad I_{Poll} = Log_2 \left[\dfrac{Cn}{Bn} \right]$ (2)

According to this index, the sediment contaminations are divided in to seven categories. In this study the element Fe is considered as the reference element. Based on this fact the enriched factor is calculated from the following equation:

Equation (3): EF= [(M/Fe) sample /(M/Fe) mane] (3)

Using, 5- stage separation in this study, the concentration of the studied elements were defined in percent of the total concentration of poor phases sulphide, organic-metal, resistant and within lattice phase are calculated.

RESULTS AND DISCUSSION

The heavy metal concentration (Ca, Zn, Cu, Fe, Mn, Ni) and some of their related statistical indexes

(mode , median , standard deviation (SD)) are shown in Table 2. Also the heavy metals concentration in Shavoor River with the World Mean Sediment (W.M.S) a concentration, average earth crust and shale are compared.

The concentration of calcium in sediments in all the stations are almost the same and only in the third station, little amount is added to it. The percentage of calcium average in Shavoor river sediments is 31.1 and the calcium concentration in all stations in the study area is less than WMS as well as the earth' s crust. iron average concentration in Shavoor river sediments in 33.2 and the concentration of this element in all stations in all area is less than WMS as well as the earth' s crust and average shale. The concentrations of iron and manganese are almost constant in all the stations. The highest amounts are observed in are station 3 (512.7 mg /kg) and the lowest amounts observed in station 2 (482.4 mg/kg). the amount of copper in sediments is fluctuated and in samples 3, 5 and 6 is higher than WMS. The highest amount of this element in station 5 (34.1 mg/kg) which is higher than the average amount

Table 2: Heavy metals concentration measured in sediment samples

Station	Mn (mg/kg)	Ni (mg/kg)	Fe (%)	Cu (mg/kg)	Zn (mg/kg)	Ca (%)	LOI (%)
1	482.4	41.19	2.41	30.42	52.65	1.22	1.95
2	496.1	44.1	2.49	32.29	59.7	1.16	1.2
3	512.7	44.18	2.47	33.2	59.24	1.93	2.18
4	483.9	45.4	2.21	21.56	48.12	1.15	2.78
5	501.5	47.52	1.94	34.01	62.43	1.21	2.5
6	494.4	47.27	2.46	33.81	61.39	1.22	3.43
Median	495.25	44.79	2.43	32.74	59.47	1.215	2.34
Average	495.16	44.94	2.33	30.88	57.25	1.315	2.49
SD	11.30	2.35	0.21	4.75	5.62	0.3	0.54
Minimum	482.4	41.19	1.94	21.56	48.12	1.15	1.95
Maximum	512.7	47.52	2.49	34.01	62.43	1.93	3.43
W.M.S*	770	52	¼	33	95	4.1	–
Average earth crust	770	55	4.17	39	67	3.15	–
Average shale	850	68	4.72	45	95	1.6	–

*: Bowen (1979)

in WMS (33 mg/kg). nickel concentration changes between 41.19 to 47.52 in sediment samples and the average sediment concentration is 44.94 mg/kg in Shavoor river.

Two quantitative assessment of the intensity of contamination in sediment are used geochemical enrichment factors (EF) and geo-accumulation index (Igeo). The Igeo formula loading shows that there is no pollution in this river. Table 3 indicates the comparison of the results of pollution indexes.

The average concentration of elements in upper crust as well as Iron concentration is considered as a reference element for calculating the enrichment factor (Hernandez *et al.,* 2003).

In this study geochemical enrichment factor (EF) and geo-accumulation (I_{geo}) are used for a quantitative assessment of the intensity of contaminations in sediments (Fig. 2). Also for a better understanding in terms of heavy metal contamination in region sediments, I_{POLL} index is used. The result of comparison of pollution indexes as well as pollution intensity of heavy metals in Shavoor river sediments are presented by the Mooler and Karbasi formulas in Table 4. The intensity of heavy metals contaminations in sediments of the region according to Mooler and Karbasi pollution indexes are very low and with no contamination.

To classify the variables based on similarities and proximity, cluster analysis is usually used (Everitt, 1980). The elements or variables that have the same geochemical behavior or similar origins are placed in the same cluster. As it is shown in Fig. 3, five elements consisting Cu, Zn, Fe, Ni and Mn which have positive

Table 3: The comparison of the results of pollution indexes

Pollution indexes	I_{geo}	I_{POLL}	EF
Cu	0	1.1	1.16
Ni	0	1.2	0.10
Mn	0	0.85	0.92
Zn	0	1.1	1.35
Fe	0	0.58	1.09
Ca	0	1.7	0.57
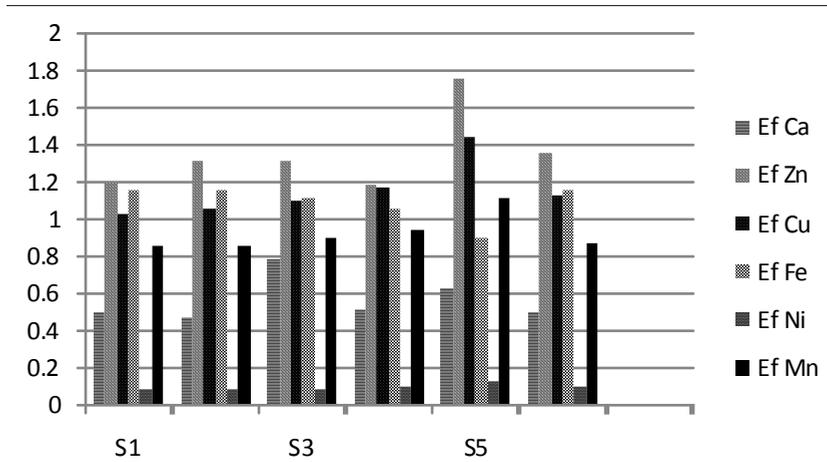
Fig. 2: Enrichment factor (EF) of heavy metals present in Shavoor rivers's sediments
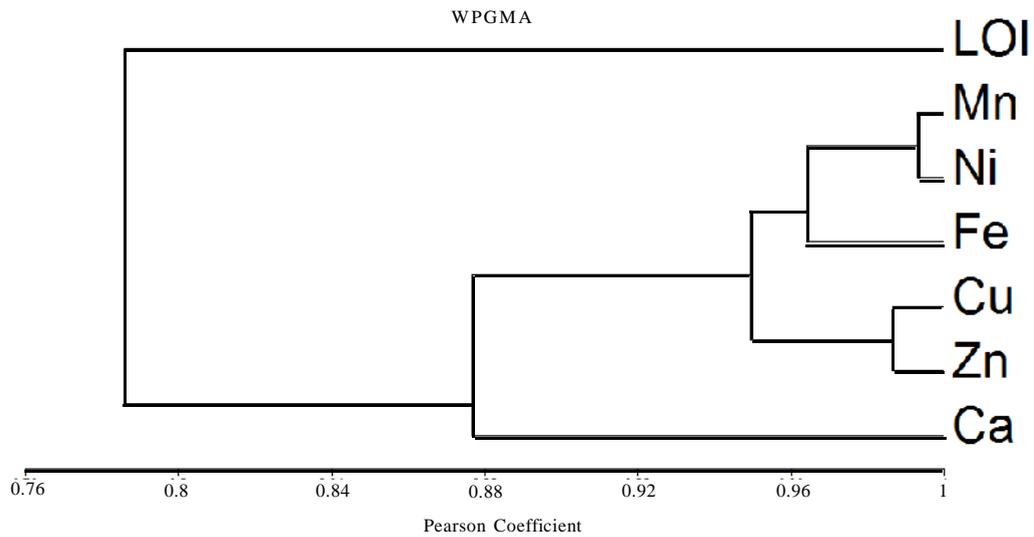
Fig. 3: The tree diagram of the studied metals in Shavoor river's sediments

and meaningful similarity coefficients are connected to each other and because Iron is the terrestrial element, it could be concluded that the origin of other four elements are terrestrial too. Calcium has both mineral and organic origin and since calcium and LOI have positive and meaningful similarity coefficients, we can conclude that calcium has organic origin. Calcium or similar origins as one biological index and since this element is connected to five other elements with a meaningful and positive similarity coefficient, it can be started that the presence of biological material influence on the control of the element concentration and causing the condensation of the elements.

After the chemical separation results were obtained, the results of first three phases (loose phases, sulphide and organic-metal) were added together and then subtracted 10% of the total concentration from the result. The final digit is considered as artificial phase.

Table 4: The comparison of heavy metals contamination intensity in Shavoor river sediments by Muller and Karbasi formulas

Element	I_{geo}	Average of I_{POLL}	Guide contamination intensity	Contamination intensity in I_{geo}	Contamination intensity in I_{POLL}
Cu	0	1.1	1<No contamination	No contamination	Low contamination
Ni	0	1.2	2-1Low contamination	No contamination	Low contamination
Mn	0	0.85	3-2Moderate contamination	No contamination	No contamination
Zn	0	1.1	4-3high contamination	No contamination	Low contamination
Fe	0	0.58	5-4severe contamination	No contamination	No contamination
Ca	0	1.7	5>Very severe contamination	No contamination	Low contamination

Table 5: The amount of man-made (%)

Station	Ca	Fe	Zn	Mn	Ni	Cu
1	63.39	15.7	49.7	38.5	25.3	53
2	62.58	17	51.2	32.7	25.2	54.5
3	80.47	16.1	57.5	46	46.1	61.6
4	61.8	12.8	49.2	41.6	53.3	48.1
5	67.29	19.9	63	50.2	57.9	63.6
6	67.57	23.1	55.7	47.7	56.7	64.8
Average	67.1	17.4	54.3	42.7	44	57.6

Table 6: The amount of terrestrial phase (%)

Station	Ca	Fe	Zn	Mn	Ni	Cu
1	35.61	84.3	50.3	61.5	74.7	47
2	37.42	83	48.8	67.3	74.8	45.5
3	19.53	83.9	42.5	54	53.9	38.4
4	38.2	87.2	50.8	58.4	46.7	51.9
5	32.71	81	37	49.8	42.1	36.4
6	32.43	76.9	44.3	52.3	43.3	35.2
Average	32.6	69.1	45.6	57.2	45.2	42.4

According to the obtained amount of artificial phase in Table 5, the minimum amount is for iron and the maximum is for calcium.

In Table 6, the terrestrial phase results have been presented in which, the maximum amount is for Iron and the minimum amount is for calcium. The percentage of man-made phase:
Ca(67.1%)> Cu(57.6%)> Zn(54.3%)> Ni(44%)> Mn(42.7%)>Fe(17.4%)
The percentage of terrestrial phase :
Fe(69.1%)> Mn(57.2%)> Zn(45.6%)> Ni(45.2%)> Cu(42.4%)>Ca(32.6%)

CONCLUSION

The sediment organic material with the average of 2.49, show domain between 1.9% (in station 1) to 3.43% (in sample 6). Generally positive and high correlation of this parameter with nickel shows that by increasing of organic material, the absorption of this metal in river sediments (specially the final samples) has been increased. The study of the concentration of the samples indicates that metals such as calcium, iron, manganese, copper and nickel in all sampling points have less than concentration of WMS, and only copper concentration is slightly

higher than global sediment concentration. Enrichment factor (EF) of calcium is in a range without enrichment. Enrichment factor for zinc elements in all stations are in the poor enrichment area. Manganese is in a normal range without enrichment, has a minimum absorption which indicates environment with no pollution. Enrichment factor for copper in all samples ranging which the amount of enrichment in station 5 is more than other stations. Enrichment factor for Iron is poor in all stations except in station 5 which is less than the others and is in area without enrichment. nickel is clean and free of contamination with respect to enrichment coefficient. Geo-accumulation index is used to access the pollution intensity in the sediments, in which all the elements are placed in uncontaminated area.

The results of elements chemical separation shows that an average of 67 % of calcium has natural origin (mineral) and about 33 % of it caused by man-made activities (organic). The maximum amount of calcium in all specified stations is released in loose bond and the minimum amount is in within lattice bond. An average of 83% of Iron has natural origin and about 17% is man-made. The maximum amount of Iron in all stations is release in resistant bond and minimum amount is in the within lattice bond. An average of 54% of zinc is man-made origin and about 46% caused by natural activities. The maximum concentration of zinc in the stations 1, 2, 4 and 6 is in a strong bond in stations 3 and 5, the maximum amount of zinc concentration is released minimum concentration of zinc in organic metal bond. An average of 57% of copper has man-made origin and about 43% of that is caused by natural activities. The maximum amount of copper in all stations except the final station is released in resistant bond and the minimum amount is in within lattice bond. An average of 44% of nickel has man-made origin and about 56% of that is caused by natural activities. The maximum amount of nickel in all stations is released in resistant bond and the minimum amount of that is in within lattice bond. 43% of manganese has man-made origin and about 57% of it caused by natural activities. The maximum amount of Manganese in all stations is released in resistant bond and the minimum amount of that is in organic metal bond.

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