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Anthropogenic sources of heavy metals in deposited sediments from runoff and industrial effluents, Shiraz, SW Iran

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***Abstract*—Heavy metal contents and contamination degree of deposited sediments from runoff and industrial effluents in Shiraz city, Iran are investigated. Concentrations of the heavy metals display the following decreasing trend: Ni>Cr>Zn>Cu>Mo>Cd. The higher Enrichment factor values (EFs) for all heavy metals belong to drainage deposits collected from densely populated areas. Geo accumulation index (Igeo) results are in agreement with EF. Pearson correlation matrix as well as principal components and cluster analyses are applied on data to identify inter- relationships and sources of the heavy metals. Cd, Cu, Mo, Pb and Cu are positively correlated showing an anthropogenic origin. There is also a positive correlation between Ni, Cr and Mn probably indicating a geogenic source. Principal component analysis is in agreement with Pearson correlation matrix. Cluster analysis classifies the samples into two clusters.**

Keywords- anthropogenic sources; heavy metals; sediment; effluents; Shiraz

I. INTRODUCTION

As the population of urban environments is rapidly increasing all over the world, developing a scientific field of study to monitor all chemical aspects affecting such environments is becoming inevitable. The term urban geochemistry was coined by Thornton in 1990 to describe research activities concerning the role of geochemists at the interface of environmental geochemistry and urban pollution [1]. The discipline of urban geochemistry addresses the complex interactions and interrelationships between chemical elements and their compounds in the urban environment, the influence of past and present human and industrial activity on these and the impacts of geochemical parameters in urban areas on plant, animal and human health [2].

Heavy metals are typical pollutants in urban environments. These elements are of particular concern due to their persistence in the environment and their toxicity to humans [3,4]. The non biodegradability of heavy metals leads to their accumulation in the environment and thus they are also known as 'chemical time bombs' [5]. Sediments, particularly surface sediments, can act as metal pools that release metals to the overlaying water via natural or anthropogenic processes, causing potential adverse health effects to the ecosystems [6,7].

Shiraz (29° 37′ 0″ N, 52° 32′ 0″ E), the sixth most populous city of Iran is located in a synclinal plain in the Zagros Mountains, 1500 meters above sea level, northwest of Fars Province. The population of this city was reported to be 1,227,331 in 2006. A seasonal river (Khoshk River) flows through Shiraz and discharges rain water and industrial effluents in to Maharlu Saline Lake (Fig.1).

In dry seasons, apart from the upstream flows, Khoshk River receives discharges only from the municipal effluents. Maharlu Lake is a saline lake with ecosystem exposed to pollutants from Khoshk River [8]. Khoshk River is apparently a main source of the lake's pollution. Using the Khoshk River wastewater for irrigation in suburban Shiraz has already lead to change in soil quality (pH, organic matter, and exchangeable Ca), increase in heavy metals concentrations in soil and crops, and hence pose potential health risk [9].

The exposed surrounding geological formations include Oligo-Miocene carbonate Asmari Formation, Miocene marly Razak Formation and Plio-Pleostocene conglomerate Bakhtyari Formation.

The main objectives of this study are (1) evaluating heavy metal contents (Cd, Cr, Cu, Ni, Mo, Pb and Zn) in deposited sediments from runoff and industrial effluents; (2) identifying natural and/or anthropogenic sources of the heavy metals; and (3) evaluating degree of contamination in the environment.

II. MATERIALS AND METHODS

A. Sampling and analytical methods

A total of nine samples were collected from sediments deposited from runoff and effluents. Four samples (S1-S4) were collected from drainage channel deposits and, four sediment samples (S5-S8) were collected from Khoshk River. A control sediment sample (S9) was also collected from a river (Ghalat River) in suburban Shiraz. Samples were collected from the upper 5 cm of the deposited sediments. A composite sample was prepared by mixing four subsamples in a polyethylene bag, at each site. Consequently, all samples were air dried and passed through a < 2mm nylon sieve.

The analyses were carried out in an accredited Canadian laboratory (ACME laboratories, ISO 9001:2000) using inductively coupled plasma–mass spectrometry (ICP-MS). Replicate samples were analyzed to assure precision.

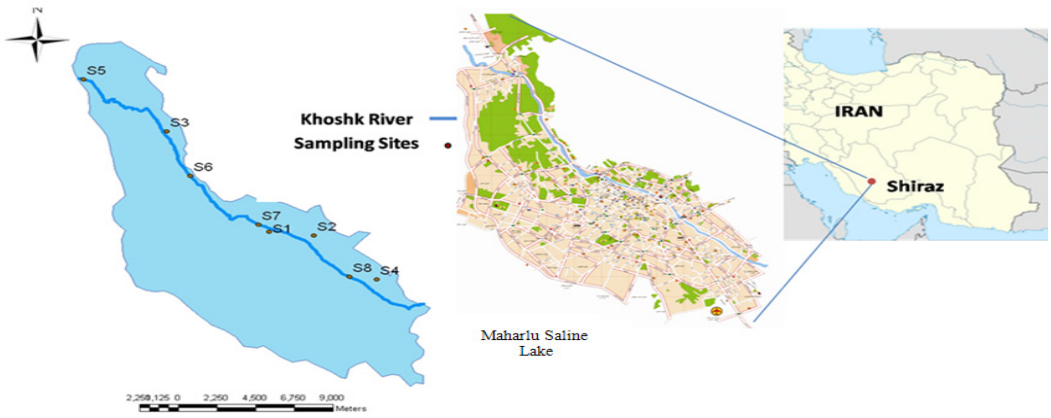

Figure 1.Study area and sampling sites

B. Data analysis

Enrichment factor (EF) calculation is a common approach to estimate anthropogenic impact on sediments [10] .EF is calculated as follows:

$$EF = [(Mc/Mr)]s / [(Mc/Mr)]b \quad (1)$$

Where M_c is the content of contamination. M_r is the content of reference elements, *s* is the sample, and *b* is the background. A reference element is often used as a conservative element. The most commonly used elements are Al, Fe, Mn, Sc, Ti, etc. [11]. In this study, Mn is used as a reference element as it mainly originates from natural lithogenic sources.

Igeo is used to calculate metal contamination level in all samples. The index is calculated as:

$$Igeo = \log_2 1.5\ Cn / Bn \quad (2)$$

Where *C*n is the concentration of the element in the samples, Bn is the background value of the element, and the factor 1.5 is used to take into account the possible lithological variability.

Cluster and factor analyses are applied on all samples to cluster different sampling stations with similar heavy metal contents. Hierarchical cluster analysis dendrogram of samples is presented using Average Linkage (Between Groups) method.

III. RESULTS AND DESCUSSION

Table I. shows descriptive statistics of elemental concentration in sediment samples. Metal concentrations are Cd, 0.1–48 mg/kg; Cr, 56.7–124 mg/kg, Cu, 13.95-168.98 mg/kg; Mo, 0.93-3.8; Ni 60.2-142 mg/kg; Pb, 5.21-158.52 mg/kg and Zn, 3320.5-230.3 mg/kg. Cu, Pb, and Zn show high concentrations in the samples (S1-S4). Highest concentrations of these heavy metals are at sampling site S4, while Ni and Cr show steady trends.

The median values for heavy metal concentrations display the following order in a box plot: Ni>Cr>Zn>Cu>As>Mo> Cd (Fig. 2).

The EF values revealed enrichments for all elements (Table II). Significant enrichments for Cu, Pb, Zn, Ni, and Cd belong to deposited sediments along drainage channels (S1-S4) collected from the populated areas of the city. This is probably due to heavy traffic (automobile emissions, wear and tear of tires) and auto workshops littered with old rusty vehicles and lubricant oils.

The sample S4 with highest EF values for Pb, Cu, Zn, Ni and Cd is collected from a drainage channel deposit in an area with numerous automobile workshops. In general, samples (S1-S4) are more enriched in the investigated heavy metals in comparison with samples (S5-S9) which are collected along Khoshk River. Ni is significantly enriched and Cu, Cd and Cr are classified as moderately enriched along Khoshk River. The main sources of heavy metals in the Khoshk River are municipal, domestic, and illegal discharges of industrial effluents [8].

According to geo accumulation index (Table III) Samples S1-S3 are moderately contaminated with Cu and uncontaminated to moderately contaminated with Pb. Sample S4 shows moderately to heavily contamination for all analyzed heavy metals except Cr and Mo. Samples S5-S8 are not contaminated with Cu, Mo, Pb and Zn. However, they show no contamination to moderate contamination regarding Cr, Cd and Ni.

Table I. Descriptive statistics of sediment samples

Statistics	Cd	Cr	Cu	Mo	Ni	Pb	Zn
Mean	0.26	72.26	68.25	1.82	87.06	39.25	87.20
Median	0.23	68.90	34.8	16	84.5	8.6	53.8
Std.Deviation	0.12	20.48	56.34	0.98	25.11	50.47	79.36
Minimum	0.11	56.7	13.95	0.93	60.20	5.21	20.50
Maximum	0.48	124	168.98	3.80	142	158.52	230.30

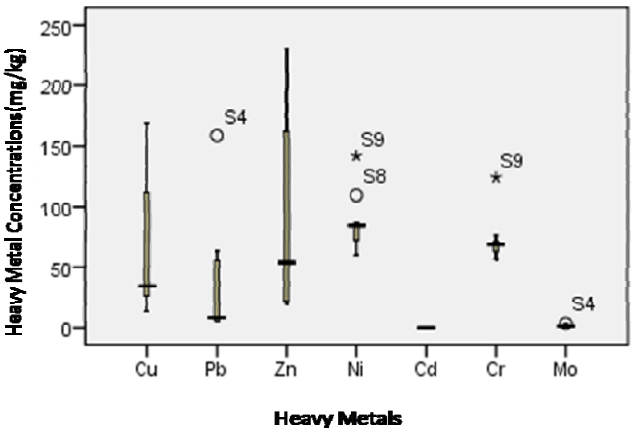

Figure 2. Heavy metal concentrations (mg/kg)

Fig. 3 shows a dendrogram summarizing all samples. Cluster A includes samples S5, S6, S7 and S8 (sub- cluster A1) which are collected along the Khoshk River and S9 (sub-cluster A2) which was taken from Ghalat River (control site).

Cluster B includes samples S1, S2, S3 (sub-cluster B1) collected from populated areas; and S4 (sub-cluster B2) collected from part of the city with numerous automobile workshops. It can be concluded that Khoshk River sediments are less affected by anthropogenic activities, since they fall in the same cluster as the control site (Ghalat River). Classifying S4 as a sub-cluster is due to severe anthropogenic effects resulting from automobile workshops.

Pearson correlation analysis was performed to assess possible similar sources of the metals. The heavy metals with positive correlation were considered to have similar sources.

Table II. Heavy metals enrichment factor at different sampling sites

Samples	Cd	Cr	Cu	Mo	Ni	Pb	Zn
S1	6.14	3.83	10.65	2.66	7.59	5.01	5.54
S2	6.94	2.88	7.28	3.51	5.36	5.65	4.07
S3	9.96	5.35	11.69	3.70	10.47	7.25	3.06
S4	10.10	3.71	12.75	4.78	10.80	14.95	6.12
S5	4.29	3.85	1.09	1.51	8.42	0.51	0.61
S6	3.10	2.94	1.90	1.28	6.89	0.48	0.48
S7	4.71	6.43	3.12	1.96	10.02	0.85	0.85
S8	3.12	2.47	0.78	0.84	7.43	0.55	0.49

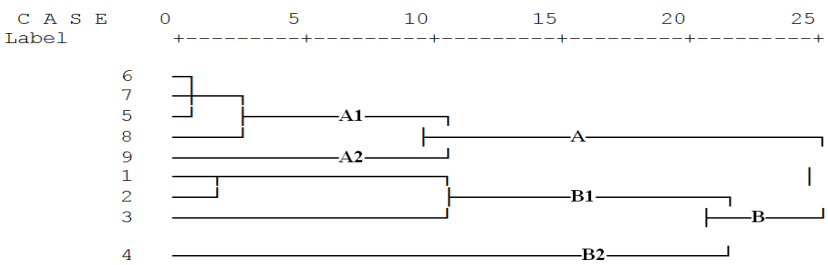

Figure 3. Hierarchical cluster analysis dendrogram of sediment samples

Table III. Geo accumulation index values of heavy metals

Sample	Cd	Cr	Cu	Mo	Ni	Pb	Zn
S1	0.79	0.11	1.59	-0.41	1.10	0.50	0.64
S2	1.38	0.11	1.45	0.40	1.00	1.08	0.61
S3	1.34	0.45	1.57	-0.09	1.41	0.88	-0.36
S4	1.68	0.39	2.17	0.76	1.27	2.40	1.11
S5	0.55	0.40	-1.43	-0.96	1.53	-2.53	-2.26
S6	0.34	0.27	-0.37	-0.93	1.49	-2.35	-2.36
S7	0.09	0.54	-0.50	-1.17	1.50	-2.37	-2.38
S8	0.62	0.28	-1.38	-1.27	1.87	-1.90	-2.05

Table IV. Correlation coefficient between analyzed heavy metals

Elements	Cu	Pb	Zn	Ni	Cd	Cr	Mo	Mn
Cu	1							
Pb	0.919[a]	1						
Zn	0.941[a]	0.894[a]	1					
Ni	-0.58	-0.48	-0.55	1				
Cd	0.864[a]	0.891[a]	0.794[b]	-658	1			
Cr	-0.27	-0.23	-.0273	0.85a	-0.5	1		
Mo	0.895[a]	0.944[a]	0.898[a]	-0.444	0.873[a]	-0.137	1	
Mn	-0.35	-0.23	-0.202	0.807[a]	-0.4	0.641	-0.116	1

Table IV. shows that Cd, Cu, Mo, Ni, Pb and Cu are positively correlated which suggests a common pollution source. There is also a strong positive correlation between Ni, Cr and Mn.

Factor analysis applied on the data accounts for 93.5% of the total variance and set the data through three factors with Eigen values greater than unity (Table V). Based on rotated component matrix using principle component analysis with Varimax rotation, Pb, Cu, Zn, Mo and Cd (with high loadings) are placed together within Factor 1 explaining 63.6% of total variance. This factor is considered as "anthropogenic factor".

As already monitored rubber tire wear, auto workshops, electroplating industries, gasoline combustion, as well as domestic wastewater are probably the major sources of these metals. Factor 2 which explains 29.7% of the total variance is mainly composed of Cr and Ni. This factor is a "natural factor", since Razak Formation which comprises an important fraction of the river sediments contains high concentration of Ni and Cr[12] .

Table V. Rotated component matrix using principle component analysis, rotation Varimax method

	Principle components	
Heavy metals	***Factor1***	***Factor2***
Cu	0.939	-0.237
Pb	0.963	-0.156
Zn	0.925	-0.218
Ni	-0.371	0.891
Cd	0.839	-0.442
Cr	-0.061	0.981
Mo	0.974	-0.084

IV. SUMMARY AND CONCLUSION

Drainage channel deposits are moderate to significantly contaminated with all analyzed heavy metals, while Khoshk River sediments are moderately to significantly contaminated with Ni, Cd and Cr. Khoshk River sediments are less affected by anthropogenic activity in comparison with drainage channel deposits. S4 is classified as a sub-cluster due to intense anthropogenic effects resulting from numerous auto workshops. Factor analysis applied on sediment samples indicate that except for Ni and Cr which have geogenic source, all analyzed heavy metals (Cd, Cr, Cu, Mo, Ni, Pb and Zn) come from anthropogenic sources. Pearson correlation matrix also indicate strong positive correlation between the heavy metals, suggesting a common source for the positively correlated heavy metals.

Considerable heavy metal concentrations in collected samples pose a threat to the health of local population in time and environmental impacts of these elements is approved in many research studies. Since the drainage channels discharge water into Khoshk River and this river is finally discharged in to Maharlu Saline Lake (host of migrant birds and other living species) is also threatened.

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