Heavy Metals Distribution in Fractioned River Sediments — Case Study: Shafaroud River-South West of Caspian Sea

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***Abstract*—Heavy metal contamination of the environmental aria has attracted a great deal of world-wide attention due to their non-biodegradable nature, long-biological half-lives for elimination from the body, their accumulation in the food chain will have a significant effect on human health in the long term.**

The objectives of this study were (1) determine the physical characteristics (sediment size) of surface sediments in Shafaroud, Iran, (2) determine the relation between physical characteristics (grain size) with heavy metals pollution by using cluster analysis and multivariate statistical techniques. Distribution of total concentration of heavy metals are different in fractioned sediments. Metals that have more abundance in particles less than 38 µm (clay and silt) like Cu, Zn and Mn originated from anthropogenic source from sea water that attracted to fine minerals. Other metals like Cr that have more abundance in gravel and sand particles (particles grate than 63 µm) related to natural sources. Also, these metals are found in river's placers.

***Index Terms*—Heavy metal, river sediment, Caspian sea, fractioned.**

I. Introduction

Heavy metal contamination of the environmental aria has attracted a great deal of world-wide attention due to their non-biodegradable nature, long-biological half-lives for elimination from the body, their accumulation in the food chain will have a significant effect on human health in the long term [1]-[3].

Surface sediments are most vulnerable to various pollution including heavy metals due to their ease of access for the disposal of urban and industrial wastewater. Most of heavy metals in aquatic systems are bound to sediments and suspended particulate matter [4]-[7]. Therefore sediment quality has been recognized as an important environmental indicator of water pollution [8], [9] because sediments are the main sink for various pollutants, including metals discharged into the environment [10]-[13]. Also, in order to develop effective aquatic fresh water quality strategies, an in-depth understanding of the factors that affect metal desorption from sediment and the nature of the adsorption and desorption processes is essential.

Based on previous studies and reports, these factors are: Sediment size [14]-[19], Sediment composition [19], [20], Cation exchange Capacity [15], Temperature [21], [22], pH [4], [23], [24], Redox condition[4], [23]-[33], Oxic- Anoxic condition[34], Salinity [35]-[37],Organic matter [3], [4], [14], [38]-[40], Bacterial activity [41]-[43].

The objectives of this study were 1) determine the physical characteristics (sediment size) of surface sediments in Shafaroud river, Iran, 2) determine the distribution of total heavy metals concentration in different river sediment size.

II. Material And Methods

A. Study Area

The study area was south west of Caspian Sea the most important rivers that have been located within Gilan province (Fig. 1). Its catchment area is about 14041km2 and is located between 50°36' 00"and 48°34' 00"E longitude and 38°27' 00"and 36°34' 00"N latitude.

According to Iran Metrological Organization reports, Gilan province is the rainiest provinces in Iran with average 580 mm per year. Diversity of plant and animal species has been visible in Gilan province [44].

The agricultural geography of Gilan can be divided into coastal lowlands; plain areas with rice, tea and tobacco cultivation; foothill lands with tea cultivation and fruit trees and mountainous lands with grains as well as forage plants; based on the altitude parameter. However, the most important agricultural activity centers are the coastal low lands, lands and plain areas situated at less than 100 elevation at open sea level [45].

An important part of massive and humid woods of the Caspian Sea water drainage area [46].

Moreover, water resources of the Gilan region are rain and snow falls. The probability of snowfall at all months of the year is quite high. At hydrological side, the rate of rain is higher in all rivers.

The important and interesting particularities of Gilan Rivers include a massive hydrographic network with a large number of rivers as well as large range of water quantity in the rivers, shortness of the flow and flooding condition at their place of origin. The inundating rivers, by transporting circular stone pieces and blocks and by under-washing the ridges overlooking the farms and orchards, threaten the cultivated areas and gardens. Submit your manuscript electronically for review.

The uncontrolled floods courses can result in water

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penetration, weight increase as well as sliding condition of soil masses. These conditions could cause the houses located at the foothills to crack or to fall down, [47].

Moreover, According to the Iran Ministry of Industries and Mines data 60 active and 19 abounded mines are located in study area That produce heavy metals such as Fe, Pb, Zn, Ti and so on, coal mining activities is as of the examples of mine type in the catchment area.

There are 703 major factories including food industries, chemical industries, plastics and tires, textile, wood and paper machines located in the study area [48].

Shafaroud is the latest River that flows directly into the Caspian sea. This river originates from elevations over than 2800 meters from west to east .The river is constantly full of water and the length of its path from source to sea is about 48 km.

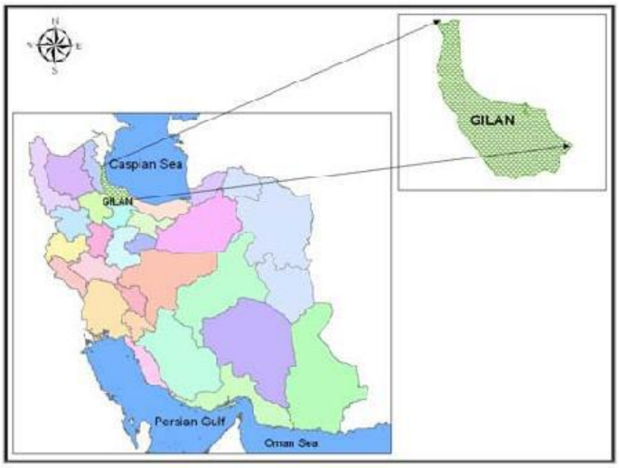

Fig. 1. Study area located in Gilan province in Northern Iran, south of Caspian sea.

B. Sample Collection and Preparation

Primarily, according to the purposes of this research, the geological map of study area has been used. For selection of sampling stations (sampling network), has been tried these stations located on different geological formations. Geographic coordinate of Surface sediment sampling stations have been illustrated in Table I.

TABLE I: GEOGRAPHIC COORDINATE OF SURFACE SEDIMENT SAMPLING STATIONS

Station No.	Geographic coordinate	
	X	Y
1	39.337447	41.62540
2	37.53016	49.10350
3	37.53880	48.91876
4	37.50138	48.79193

Shafaroud's surface sampling size locations has been shown in Fig. 2.

According to above steps, 4 surface sediment samples were taken from the Shafaroud River, Gilan province.

From upstream to estuaries selected for sampling during June 2013.

Samples were collected by Ekman type grab sampler. All samples were transferred to the laboratory in sealed plastic bags under 0 to 4 ℃.

Each sediment sample was divided randomly into two part to allow for grain-size and geochemical analysis.

Grain-size analysis was carried out using wet standard sieving methods for particles larger than 38μmby using sieve shaker (Analysette 3 Pro, Fritsch)and laser grain size analyzer for particles less than 38 μm (Analysette 22, Fritsch) at the Research center for applied geology, Geological Survey of Iran, Sedimentology Laboratory.

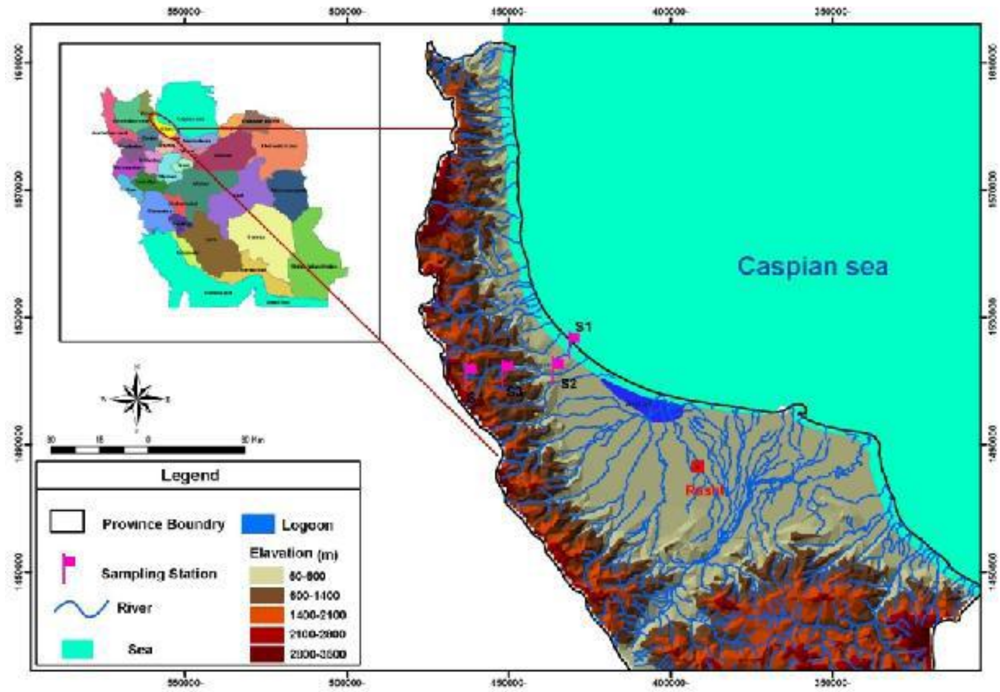

Fig. 2. Location of sediment sampling stations in Shafaroud river.

C. Laboratory Analysis

1) Grain size analysis

The 4 collected rivers samples were separated into ten particle size ranges as follow: <38μm, 38-63μm, 63-125μm, 125-250μm, 250-500μm, 500μm-1mm, 1-2mm, 2-4mm, 4-8mm and >8mm.

Grain size analysis was done by wet sieve shaker. But according to purposes of this research, only six particle Size ranges (<38μm, 38-63μm, 63-125μm, 125-250μm, 250-500μm, 500μm-1mm) were selected for chemical analysis.

2) Chemical analysis

a) Preparation of samples and digestion

Homogenous and powdered samples, bulk and fractional, (0.5 g) are treated with an oxidizing mixture (HNO_3/HCl/ HF) according to ASTM test methods (ASTM-D4698-92-2013).

Metal concentrations (Fe, Al, Ca, Mn, Cu, Zn, Cr, Pb, Ni, Cd, V and Co) in solution are determined by an

Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP-OES-730).

Standard quality control procedures were followed to maintain accuracy and reliability of the laboratory analysis.

Precision and accuracy of metal analyses and the digestion procedure was monitored using internal standards, certified reference material (standard sediment sample-GBW01-12) and quality control blanks.

III. Results and Discussion

A. Sediment Particle Size and Metal Pollution

Total metal concentrations (Fe, Al, Ca, Mn, Cu, Zn, Cr, Pb, Ni, Cd, V and Co) and statistical parameters of 4 samples across the six particle size ranges, <38μm, 38-63μm, 63-125μm, 125-250μm, 250-500μm and 500-1000μm are presented in Table II.

TABLE II: Total Heavy Metal Concentration in Fractioned Sediments

Sampling station	Sediment size(μm)	Total concentration(ppm)								
		Cu	Zn	Cr	Fe	Mn	Pb	Ni	Cd	Al
1	<38	52.06	183.60	218.04	56488.57	1371.43	17.34	110.15	1.27	85162.98
	38-63	51.66	187.47	205.72	61756.84	1290.11	35.00	109.04	1.12	83635.68
	63-125	54.46	141.51	308.41	67219.91	921.31	14.42	118.04	1.35	99379.06
	125-250	47.53	136.33	500.14	69530.39	1085.43	11.50	107.88	0.05	73764.50
	250-500	46.68	94.22	620.32	72033.99	1126.39	8.38	85.05	0.05	72823.69
	500-1000	53.80	80.72	264.90	62086.04	938.96	8.90	71.89	0.05	79468.87
2	<38	49.24	182.02	219.46	61212.16	1419.08	16.42	120.23	0.05	88302.01
	38-63	-								
	63-125	52.93	153.82	327.85	73243.12	978.31	12.21	114.48	1.54	105923.00
	125-250	46.63	154.63	777.26	91631.46	1207.47	14.65	166.08	1.31	71771.71
	250-500	45.14	134.28	874.05	88542.91	1180.50	12.03	166.45	1.27	68301.27
	500-1000	47.99	93.04	613.41	73317.69	996.67	11.34	139.19	0.05	69953.47
3	<38	62.00	194.87	271.97	65015.25	1388.41	18.90	152.86	1.36	94650.68
	38-63	43.87	109.74	222.21	60393.88	900.36	16.54	109.60	0.05	72183.67
	63-125	55.50	117.07	461.80	82222.56	1151.78	22.90	140.81	1.82	89535.06
	125-250	52.96	115.38	918.50	90064.38	1247.25	14.84	161.16	0.05	66975.99
	250-500	51.15	108.40	860.74	81454.66	1155.57	15.59	156.03	0.05	67024.24
	500-1000	50.15	94.76	658.40	72855.91	1042.53	11.82	172.69	0.05	68079.47
4	<38	67.27	375.86	339.59	68645.64	944.30	24.01	215.15	1.50	81539.68
	38-63	53.26	253.29	254.86	61528.91	988.13	26.87	147.00	0.05	72311.72
	63-125	53.57	175.39	197.98	52201.78	711.40	15.80	101.09	1.02	72893.05
	125-250	45.36	133.28	370.08	56255.30	747.91	14.61	155.15	0.05	65123.98
	250-500	46.82	101.32	365.70	56941.22	769.26	13.56	193.31	0.05	65218.51
	500-1000	48.09	92.65	323.35	56191.19	756.21	13.42	194.06	0.05	66300.82
Earth crust content		**47.00**	**83.00**	**83.00**	**46500.00**	**1000.00**	**16.00**	**58.00**	**0.13**	**80500.00**

1) <38μm

Total concentrations of all metals are higher than those of earth's crust except for Mn in sampling station 4.

2) 38-63μm

Total concentrations of all metals are higher than those of earth's crust content except for Cu(sampling station 3), Mn(sampling stations 3 and 4), Cd(sampling stations 3 and 4) and Al(sampling stations 3 and 4).

3) 63-125μm

Total concentrations of all metals are higher than those of earth's crust content except for Mn (sampling stations 1, 2 and 4), Pb (sampling stations 1, 2 and 4) and Al(sampling stations 4).

4) 125-250μm

Total concentrations of all metals are higher than those of earth's crust content except for Cu(sampling stations 2 and 4), Mn(sampling station 4), Pb(sampling station1), Cd(sampling stations 1,3 and 4) and Al(sampling stations 3 and 4).

5) 250-500μm

Total concentrations of all metals are higher than those of earth's crust content except for Cu(sampling stations 1 and 4), Mn(sampling station 4), Pb(sampling station1, 2, 3 and 4), Cd(sampling stations 1,3 and 4) and Al(sampling stations 2, 3 and 4).

6) 500-1000μm

Total concentrations of all metals are higher than those of earth's crust content except for Zn(sampling station 1), Mn(sampling station 4), Pb(sampling station1, 2, 3 and 4), Cd(sampling stations 1, 2, 3 and 4) and Al(sampling stations1, 2, 3 and 4).

Total metal concentration in sediment particle fractioned as percent is presented in Table III.

According to Table III, higher level of metal concentrations in percent were found in particle less than 125 μm, except for Cr, Fe and Ni.

The minimum content of metals were detected in particles less than 125 μm except for Zn, Pb and Cd. For Cu, Cr, Fe, Mn, Ni and Al minimum content were found in particles larger than 125 μm.

TABLE III: TOTAL METAL CONCENTRATION IN SEDIMENT PARTICLE FRACTIONED AS PERCENT

Particle Size- μm	Cu	Zn	Cr	Fe	Mn	Pb	Ni	Cd	Al
<38	**19.57**	**27.43**	10.31	15.90	**21.07**	20.66	18.66	23.07	19.64
38-63	**12.63**	16.13	**6.71**	**11.62**	**13.07**	**21.13**	**11.40**	10.60	**12.81**
63-125	18.37	17.22	12.74	17.39	15.47	17.61	14.79	**28.50**	**20.66**
125-250	16.34	15.81	25.22	**19.45**	17.63	14.98	18.40	14.02	15.59
250-500	16.11	12.84	**26.74**	18.91	17.40	13.36	**18.73**	13.84	15.35
500-1000	16.98	**10.58**	18.28	16.73	15.36	**12.26**	18.02	**9.98**	15.94

- The highest and lowest values are highlighted

IV. CONCLUSION

Distribution of total concentration of heavy metals are different in fractioned sediments. Metals that have more abundance in particles less than 38 μm(clay and silt) like Cu, Zn and Mn originated from anthropogenic source from sea water that attracted to fine minerals.

Other metals like Cr that have more abundance in gravel and sand particles (particles grate than 63 μm) related to natural sources. Also, these metals are found in river's placers.

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