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Evaluation of the heavy metal contaminations in water resources in ophiolitic complex of Pangi area, (Kadkan, NW Torbat Hydarieh, Iran)

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Abstract—The extent of transfer, distribution, controlling geochemical factors and enrichment of heavy metals in Pangi area (NW Torbat Hydarieh, Iran) were investigated. Ten heavy metals and metalloids such as manganese (Mn), iron (Fe), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), Copper (Cu) Lead (Pb), Zinc (Zn) were analyzed using AAS and GFAAS. The mean metal pollution index (MPI) and heavy pollution index (HPI), in the Pangi and Targhi area were found to be above the critical pollution index values. Index of metal and heavy metal pollution index showed that 5 samples of water samples, not potable. The results indicate that multiple sources of pollution in the water resources of the region. The two main sources, one associated with the dominant lithology of ophiolite sequence in the region (extensive serpentinites as well as sulfide ores in dikes) and another, mining activities in the region. High values of Fe, As, Cu, Mn and Cr elements associated with lithologic units but high levels of Ni and Cr are associated with mining activities. High levels of Cd associated with fertilizers used in agriculture but high Pb must be obtained from the vehicle exhaust emissions (due to heavy road traffic). The enrichment factor (Ef) of heavy metals was in order of Mn > Fe > Pb >Ni > As > Cu > Cr > Zn > Cd in the study area.

Keywords—Metal Indices, Ophiolite, Pangi, Water Resources

I. INTRODUCTION

Heavy metal contamination is recognized as a major environmental problem and excessive use of heavy metals has led to rapid accumulation of these materials in the environment. Heavy metals are stable and persistent environmental contaminants since they cannot be decomposed or destroyed [2]. Heavy metals can form toxic chemical specieses and contamination of environment by hazardous and toxic metals is harmful for human [9]. Heavy metal concentrations in water resources depend on anthropogenic (mining and industrial and agricultural) activities and land resources (weathering and erosion of rocks) [15].

The Asad Abad - Pangi ophiolite complex consists predominantly of variably serpentinized peridotite plus mafic plutonic and volcanic rocks and volcanosedimentary rocks (Fig. 1). Harzburgite and lherzolites cut by numerous bodies of serpentinite, some of which contain podiform chromites.

There is widespread partial serpentinization throughout the Asad Abad - Pangi ophiolite complex from interaction of the massif with fluids [12]. There are rocks and soils with high concentrations of heavy metals in these units. Serpentine soils derived from the weathering of ultramafic rocks are characterized by Cr concentrations and high concentrations of Fe, Ni, Co, and Cd elements [10]. These soils have low concentrations of P, Na and K, and higher concentrations of Mg and bicarbonates.

In general, serpentine soils have widely varying pH, contain a variety Fe(III) oxides (magnetite and hematite), phyllosilicates (serpentine and chlorite), and clays (smectites and vermiculites), and contain concentrations of Cr (>200 ppm), Ni (>1,000 ppm), and Mn (>200 ppm) exceeding values of non-serpentine soils [10]. Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment [4] and sediments can be sensitive indicators for monitoring contaminants in aquatic environments [11]. The serpentine soils have little stability and contain many heavy metals, as a result, their heavy metals can enter the water resources, the plant life cycle and food chains. So, study the water quality and degree of contamination of heavy metals in environment is necessary. The objectives of the present study were to investigate the extent of transfer, enrichment and accumulation of heavy metals in media as well as to identify the sources of heavy metals along the Rud Shur river basin (NW Torbat Hydarieh, Iran).

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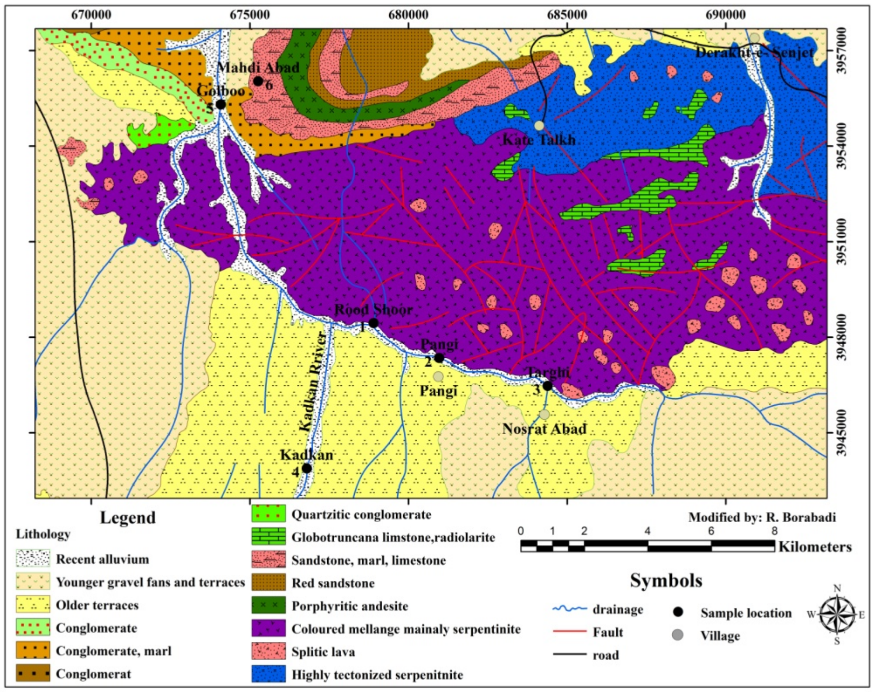

Fig. 1. Geological map of Pangi area (modified from Torbat Hydarieh 1:250000 map) and location of water samples [5]

II. Materials and Metods

Six water samples were collected in order to determine the concentration of heavy metals, physical and chemical properties of samples in water resources. The heavy metal cations (As, Pb, Cd, Ni and Cr) and trace elements were analyzed using an atomic absorption spec. (Spectra AA 220 model) and GFAAS (GTA-110 model) at department of chemistry at Fersowsi University of Mashad, Iran. Charge balance error was calculated for water samples to determine the accuracy of chemical analysis. The precision of analyses based on measurements of certified standards was typically better than 4% with a detection limit and precision of 0.5 mg/L and ±10%, respectively.

III. Results and Discussion

Soils, sediments and water samples collected from the study area were analyzed for hydrochemical characteristics.

Significant variations in the concentration of metals were obtained spatially along the Targhi, Pangi, Golbou and Kadkan area. Ten heavy metals, trace elements and metalloids such as manganese (Mn), iron (Fe), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), Copper (Cu) Lead (Pb), Zinc (Zn) and mercury (Hg) were analyzed (Table I). The concentrations of As, Cd, Ni and Pb were found to be above the highest permissible value but Significant variations in the concentration of heavy metals and trace elements were obtained in the area. Based on the concentration ranges, heavy metals and trace elements were ranked as Mn > Fe > Pb >Ni > As > Cu > Cr > Zn > Cd (Table I).

Table I. The hydrochemical data of samples in the study area

SAMPLE / ELEMENT	1	2	3	4	5	6	Reference Value (WHO)
Ni	127.1	14	582.87	393.7	10	86.6	70
Cd	5.76	10.66	111.92	8.25	5.74	1.08	3
Cr	97.42	34.82	5.37	54.5	24.03	12.86	50
Pb	166	25.15	14.46	41.26	24.31	25.31	10
As	119.3	115.5	14.2	111.4	124	27.3	10

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Mn	195	206	130.57	186.6	114	20.61	400
Cu	117.4	16.7	122.35	70.57	27	18.4	2000
Zn	31.5	17.73	10.13	17.42	19.15	22.1	1500
Fe	183	305	_	201	296	_	1000
EC (µs/cm)	773	557	4440	4650	995	453	1000
TDS (mg/l)	471	351	2798	2929	627	341	500
Eh (V)	0.41	0.37	0.38	0.46	0.43	0.40	_

Heavy metal pollution index is an effective tool to characterize the surface water pollution [14] as it combines several parameters to arrive at a particular value which can be compared with the critical value to assess the level of pollution load [6]. The Metal Pollution Index (HPI) of the waters in Pangi and Targhi regions was higher than that of the other sites. The high HPI in these sites could be due to the weathering of diabasic dykes and serpentinites associated with lenses of chromites. The mining activities from the vicinity lands also add to the sediment pollutant load of the sites.

Table II. Mean Heavy metal pollution index (HPI) in the study area

Parameters	Mean	Desirable maximum value	Highest permissive value	Unit weightage (W_i)	Q_i	$Q_i \times W_i$
Fe	164.1	300	1000	0.003	42.799	0.128
Mn	142.3	100	400	0.01	32.895	0.328
Pb	49.4	10	50	0.1	12.65	1.265
Ni	202.3	70	200	0.014	51.62	0.722
As	85.2	10	50	0.1	148	14.800
Cu	62.1	500	2000	0.002	33.32	0.666
Cr	38.2	50	100	0.02	98.47	1.969
Zn	19.7	500	1500	0.0002	49.99	0.014
Cd	38.2	3	10	0.33	139	45.87
HPI=116.76				**$\sum W_i$ =0.584**		**$\sum Q_i \times W_i$=68.20**

The geo-accumulation (I_{geo}) was calculated using Müller's equation [8]: $I_{geo}=\log_2[C_n/(1.5C_{Ref})]$, where C_n is the measured total concentration of the studied metal *n* in the sediment and C_{ref} is the geochemical background values (the reference value) of metal *n*. The average background concentrations of Fe, Mn, Fe, Pb, Ni, As, Cu, Cr, Zn and Cd obtained from [13] are used in this study. The average Igeo of 6 samples in the area suggests that the Pangi area is strongly contaminated with heavy metals.

As enrichment factor (EF) is a powerful tool to distinguish between anthropogenic and lithogenic contribution of heavy metals [3], an attempt was made to calculate enrichment factors to classify contamination level and to determine the degree of modification in the composition from source to environment in the study area. The enrichment factor is defined as following (using iron as a reference element): $EF = (C_n/C_{Ref})_S/(C_n/C_{Ref})_{background\ S}$, where C_n is the value of element *i* in the sample of interest and C_{Ref} is the value of selected reference sample.

Table III. Average, minimum and maximum metal values of enrichment factor and geoaccumulation index ($I_{geo.}$) values of the study area

		Fe	Mn	Pb	Ni	Cu	Cr	Zn	Co	Mg
EF	Max.	14.54	11.78	1.22	6.56	3.98	5.97	1.96	3.78	20.26
	Min.	10.22	5.23	0.56	2.98	2.13	2.43	1.06	1.98	11.98
	Mean	13.01	7.76	0.99	4.24	2.99	4.09	1.29	2.67	15.54
Igeo.	Max.	30.26	22.09	2.88	8.09	5.46	7.83	2.97	5.94	37.98
	Min.	10.98	11.90	1.67	6.77	3.56	6.16	1.44	4.01	20.65
	Mean	19.78	17.88	2.07	7.33	4.96	6.89	1.99	4.59	25.96

III. CORRELATION COEFFICIENTS OF HEAVY METALS

The regression analysis of the heavy metals showed some positive and negative relationships between the soils and water media (Table IV). The Pearson correlation coefficients of heavy metals between the soils and water media showed several metal pair correlations (Table IV). Arsenic concentration values are significant correlated with those of Fe (r=0.938), Mn (r=0.662), Cu (r=-0.194) and Cd (r=-0.649). Ni values are significant correlated with those of Cr (r=0.593), and Cd values are significant correlated with those of Cu (r=0.606). Zn values are significant correlated with those of Fe (r=0.202) and Mn (r=0.094). The determination coefficient (r^2) of the metals indicated Fe and As to be more dependable to each of the medium than in the other metals (r = 0.938). Hydrous oxides of Fe and Mn on particulate surfaces are

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significant carriers for Zn in aquatic systems [4]. The relationship between Zn bound to the Mn and Fe oxides and present Mn ore deposits in the area, suggesting that Fe-Mn oxides may be the main carriers of Zn from the ophiolitic complex to the water resources.

High Cr values were also measured at Pangi and Targhi area, indicating a transport in to the water resources as weathering products of drainage basin ophiolitic complex. High Cr values were measured in Asad Abad water resources were also attributed to natural weathering of ultramafic rocks and mining activities [1]. High concentrations of heavy metals at Pangi area, which is close to Golbo area in the main water outlet, indicate the sources of these metals as effluents from ophiolitic complex and mining activities.

Table IV. Correlations between the heavy metals in the study area

	Ni	Cd	Cr	Pb	As	Mn	Cu	Zn	Fe	pH	EC	TDS
Ni	1											
Cd	.801	1										
Cr	.593	-.458	1									
Pb	-.170	-.299	.919**	1								
As	-.528	-.649	.690	.408	1							
Mn	.092	-.016	.653	.410	.662	1						
Cu	.714	.606	.385	.516	-.194	.350	1					
Zn	-.582	-.686	.785	.855*	.454	.094	.034	1				
Fe	-.564	-.539	.389	.124	.938**	.624	-.372	.202	1			
pH	.689	.451	.495	.435	.155	.668	.880*	-.063	.002	1		
EC	.930**	.621	-.153	-.264	-.276	.213	.553	-.631	-.300	.695	1	
TDS	.932**	.621	-.165	-.274	-.290	.196	.546	-.635	-.312	.683	1.000**	1

The results of the mean Cd, Pb, As and Ni in water samples was higher than WHO standards. Index of metal and heavy metal pollution index showed that 5 samples of water samples, not potable. The results indicate that multiple sources of pollution in the water resources of the region. The two main sources, one associated with the dominant lithology of ophiolite sequence in the region (extensive serpentinites as well as sulfide ores in dikes) and another, mining activities in the region. High values of Fe, As, Cu, Mn and Cr elements associated with lithologic units but high levels of Ni and Cr are associated with mining activities. According to the (1), coating insoluble manganese oxides on soils and sediments in the saturated zone is a transformation factor of Cr(III) to Cr(VI):

$$2Cr^{+3} + 3MnO_2 + 2H_2O \longrightarrow 2HCrO_4^{-} + 3Mn^{+2} + 2H^{+} \quad (1)$$

As Cr(VI) adsorbed by cationes such as Mn and Manganese compounds are important absorbent of Cr, it can be deduced that the chromium in water resources must contain significant amounts of Cr(VI) and is in the form of chromate (CrO_4^{2-}).

As well as, oxidation of arsenopyrite is occured based on reaction (2) which arsenic, iron and sulfate enter the solution [7]:

$$4FeAsS(s) + 13O_2 + 6H_2O \rightarrow 4H_3AsO_4\,(aq) + 4Fe^{2+} + 4SO_4 \quad (2)$$

High levels of Cd associated with fertilizers used in agriculture but high Pb must be obtained from the vehicle exhaust emissions (due to heavy road traffic).

IV. CONCLUSION

Metal and heavy metals indices of Pangi soils were calculated using hydrochemical data. Results indicate that serpentinites and serpentine soil qualities in the most regions were polluted and few low polluted. From Pangi village to Kadkan city, soil qualities varied from low polluted to unpolluted.

- The positive correlation between iron and arsenic (r = 0.938) and high levels of sulfate in water resources can be attributed to the alteration of sulfide minerals and hydrothermal veins.
- The positive correlation between Mn and Cr (r = 0.653) in water resources and high levels of Mn in the water indicated the possibility that Mn causes the oxidation of Cr (III) to the more toxic form of Cr (VI).
- Combination of metal concentration analysis and correlation analysis were used as an effective tool for the characterization of the sources of the pollutants in the Pangi area.
- High values of Fe, As, Cu, Mn, Ni and Cr elements associated with lithologic units and originated from ophiolitic complex but high levels of Ni and Cr are associated with

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mining activities. Pb and Cd were found to have anthropogenic origin but Zn and Cu showed mixed origin from both natural and anthropogenic sources.

- The enrichment factor (Ef) of heavy metals was in order of Mn > Fe > Pb >Ni > As > Cu > Cr > Zn > Cd in the study area.

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