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Distribution of Metals, Chemical Partitioning, Pollution and Origins in Riverbed Sediment

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Abstract: Water quality and metal contents of sediments were measured in Zayandeh-Rood River. Zayandeh-Rood is one of the most important rivers of Iran. The river water is used for drinking, industrial and agricultural purposes. The anthropogenic impact on the river over the last three decade has proven to be extremely negative due to the quick development of industry. Physico-chemical parameters of water were measured in study area. Total concentration of metals was measured in bulk sediment samples (0-5cm). Study of water parameters indicated BOD and COD values are more than surface water quality standards in some segments. Sediments analysis revealed some metals accumulation is very close to normal and some beyond threshold limits. Comparing with the maximum background values indicates river is polluted in central segmentation. Higher concentrations of elements were observed in sampling location 4 and 5. Lead was the highest in terms of contamination level, especially after Zarin-Shahr effluents, followed by Nickel. Results indicated the origin of Lead was mainly anthropogenic and for others was lithogenic. I_{poll} Index values indicated a non-polluted and less-polluted environment throughout the river. I_{poll} values are in a well agreement with results of chemical partitioning of metals.

Key words: Pollution · Lead · Nickel · Trace Element · Zayandeh-Rood · Anthropogenic Source

INTRODUCTION

During the last decades, human activities have contributed to increase of pollution and toxic contamination into aquatic environment and accumulation of toxic pollutant includes heavy metals. Sediments of aquatic ecosystems have an important role in adsorption and desorption of dissolved metals and can be a potential source of metal pollution by releasing adsorbed metals during physico-chemical characteristics changes of the aquatic environments [1]. The discharge of heavy metal into aquatic ecosystem has become a matter of concern over the last few decades. [2]. Sediment is known to act as a sink for heavy metal in aquatic systems [3]. Some studies have demonstrated that aquatic sediments are contaminated by heavy metals from industrialized areas; therefore, the evaluation of metal distribution in surface sediments is useful to assess pollution in the aquatic environment [4-7]. Different studies have widely confirmed contamination of river sediment by heavy metals [8-10].

Other studies have been conducted to evaluate the distribution and speciation of heavy metals in sediments [9, 11]. In the few recent decades, increasing industrialization and urbanization activities made the serious problems of pollution in rivers; particularly heavy metals pollution [12, 13]. Heavy metals in aquatic ecosystem and sediments have natural and anthropogenic origin; distribution and accumulation of metals are influenced by sediment texture, mineralogical composition, oxidation -reduction state, adsorption-desorption processes and physical transport. Metals can be adsorbed from the water column into/on fine particle surfaces and participate in various biogeochemical processes and affect the aquatic ecosystems through bioaccumulation and biomagnifications processes and are

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potentially toxic for environment and for human life [14]. In the central area of Iran, Zayandeh-Rood River is a good example of a site where contributions of pollutants from lithogenic sources and anthropogenic activity. The purpose of this investigation is to determine the geochemistry and heavy metal thresholds in the Zayandeh-Rood river sediments to provide additional data and investigate the present level of metal (lead, Cadmium and Nickel) and also determination of origin and chemical partitioning of metal pollution. Trace elements have expanded effect on environment because of their uses in Human's life [15]. For example many kinds of lead compound are used in petrol and Nickel is a toxic heavy metal that is widely used in Iron Molting Factory units and in refineries [2] and Cadmium is widely distributed in rocks, sediments and soils with an average concentration in the earth's crust 0.2 mg/kg. Pollution of soil by Cd can be caused by industrial development and addition of urban wastes and phosphate fertilizers. Cadmium is readily taken up by plants and is passed on in the food chain [16]. One of most important entrance for metals is atmosphere. Other entrance for metal is waste water of industry, farming and home actually [17]. Heavy metal stability in environment produced some special problems. One of the important results of stability is metal expansion in food chain [18, 19].

Trace metals can absorb from the body organs and usually absorbed with passive transition. Metals in aquatic ecosystems are eaten in combination form with organic matter. Many of these metals remain in body and increase the amount of them in life-hood of organisms that is called bioaccumulation [20]. The accumulation of heavy metals has toxic effect on animal and plants [16]. Zayandeh-Rood is the largest river in central part of Iran and it is an important habitat for living organisms and has a main role in diversity of flora and fauna. The river originates from the Zagros Mountain chain in the eastern slope of the Zardkooh Mountain in the Chahar Maahal-VA-Bakhtiari province and ends at the GAVKHOONI Swamp, which is located in about 140 km east of Isfahan [21].

MATERIALS AND METHODS

Water samples and riverine bulk sediment samples (0-5cm) were collected from spring 2011(May) to autumn (November) at six predetermined locations (Figure 1) using plastic dishes. Samples immediately fixed and sent to laboratory for measuring physico-chemical parameters (Table 1). Related standard method [22] was used for Physico-chemical analysis of water samples. The sediment samples sealed and stored immediately at 4°C. The grain size less than 63 micron meter was chosen for analyzing [8, 23]. Sediment grains powdered and acid digestion carried out for determination of total metal content by HF-HNO3-HCl-HClO4 [24]. A blank was prepared for each digestion program, then samples were filtered and diluted for analyze [25]. Chemical partitioning study carried out in four sequential steps1: acetic acid 25% v/v; steps 2: acetic acid 25% v/v- 0.1M hydroxylamine hydrochloride; steps 3: 30% H2O "extraction with 1M ammonium acetate" and step 4: hot 50% HCl [26]. Total metals concentrations (Pb, Cd, Ni) were measured using Varian Spectra AA-220

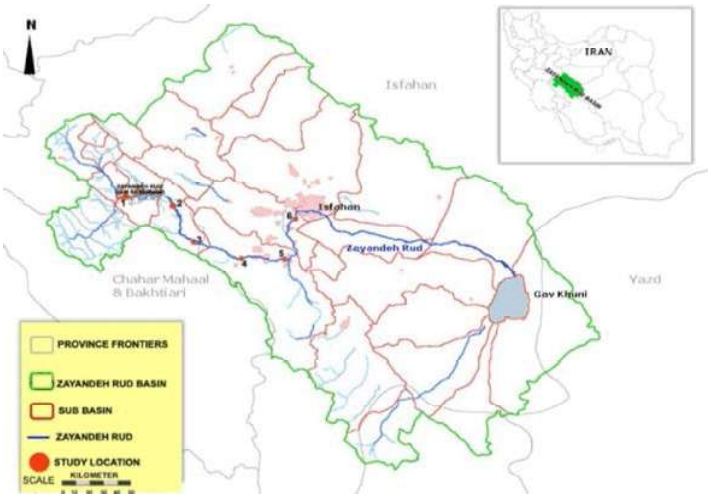

Fig. 1: Locations of water and sediment samples in Zayandeh-Rood River

Table 1: Physico-Chemical characteristics of water of Zayandeh-Rood-2011Station number

	Minimum	Maximum	Average	Standard deviation
pH	6.9	8.7	7.50	0.60
EC (µmho/cm)	388	4355	1278.50	1529.50
TDS (mg/lit)	241	2058	766.50	728.65
DO (mg/lit)	6.03	8.33	7.49	0.82
Nitrate (mg/lit)	1.1	2.1	1.36	0.37
Phosphate (mg/lit)	0.02	0.036	0.06	0.07
Ca (mg/lit)	288	400	232.17	96.83
Mg (mg/lit)	88	216	142.00	44.52
BOD_5 (mg/lit)	2	8.3	3.62	1.87
COD (mg/lit)	4.7	16.8	12.38	4.56

atomic absorption spectrophotometer. Samples were analyzed in duplicate for Cd and Ni [27]. Blanks and duplicates were run with the samples in a similar way for quality assurance of the laboratory analysis. The accuracy of analysis was about ±5 % for all elements. A standard sample (MESS-1) was analyzed in the same manner for analysis accuracy check. Results showed less that 5% error in analysis. Cluster analysis is a multivariable statistical method and it was used to find the origin of heavy metals and identification of the metals association. The Weighted Pair Group method (WPG) was used to identify clustering tendencies among the samples [25].

RESULTS AND DISCUSSION

The results of water analyze was presented in Table 1. There were apparent differences in measured parameters from site to site. pH variation from 6.9 to 8.7 indicates neutral nature of river water in the most segmentation. There was significant difference in calcium value between the sampling locations. The highest value of the calcium was observed at station 2 (400 mg/lit). Generally, the higher calcium contents are attributed to calcareous nature of the soil and microorganisms which play an important role in the calcium exchange at the interface between sediment and overlying water.

Heavy metals concentration in sediments of riverbed was represented in Figure 2. Sediment quality guideline (SQG) was used to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guideline [28]. According to Figure 2, the maximum value of Pb concentration in station 5(40.2 mg/kg) was observed that doesn't exceed the SQG standard level. The concentration of Nickel with value of 21.2 mg/kg was the highest at station 4 and the lowest concentration was measured at station 1 (2.6 mg/kg).

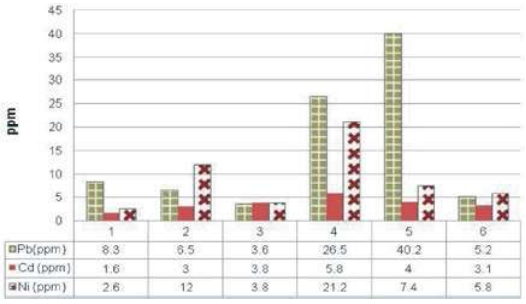

Fig. 2: Average concentration of heavy metals in Zayandeh-Rood river bed sediments at sampling locations

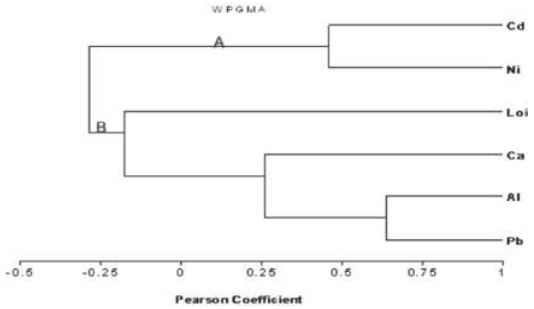

Fig. 3: Dendrogram of cluster analysis for heavy metals in river bed sediments of Zayandeh-Rood

Cadmium concentration exceeds the SQG standard level of freshwater sediments in location 3, 4 and 5. Cluster analysis was used to identify the similarities, inter-relations in metals and their origins.

Figure 3 shows dendrogram summarizing samples from 6 sampling location which were grouped into significant clusters of statistically similarity. Dendrogram of cluster analysis depicts two distinct clusters namely "A" and "B". The close relations among Al and Pb indicate their similar behaviors in the nature. The positive significant similarity between Aluminum and Lead can

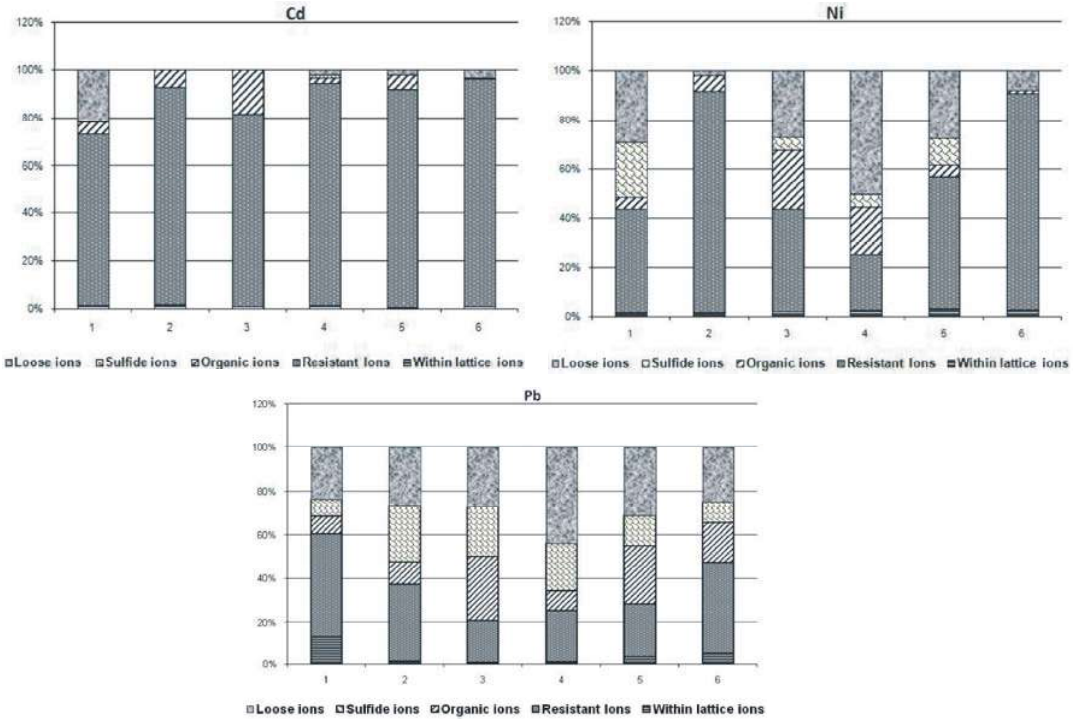

Fig. 4: Chemical Partitioning patterns of Cd, Ni and Pb in sediments of sampling locations in Zayandeh-Rood

Table 2: IPoll values and anthropogenic portions of metals pollution in riverbed sediments

	Lead					
Study location	St1	St2	St3	St4	St5	St6
Anthropogenic	29.40%	52.80%	69.00%	64.50%	61.70%	42.70%
Ipoll value	0.50	1.08	1.69	1.49	1.38	0.80
	Cadmium					
Study location	St1	St2	St3	St4	St5	St6
anthropogenic	16.90%	0.00%	8.40%	0.00%	0.00%	0.00%
Ipoll value	0.89	0.00	0.90	1.51	0.58	0.00
	Nickel					
Study location	St1	St2	St3	St4	St5	St6
Anthropogenic	29.40%	52.80%	69.00%	64.50%	61.70%	42.70%
Ipoll value	0.27	0.00	0.13	0.00	0.00	0.00

represent lithogenic origin of Lead, partly. There is a weak relationship between two branches which means negative relation and can be concluded that the elements of branches A and B originates from different sources.Comparison among the Cd concentration averages and "earth Crust" shows that cadmium levels in sediments have no significant difference with mean earth crust. Pb and Ni concentrations are mostly lower than mean earth crust and "world sediments" same as sediments of Shefa-rud river, Iran [8]. According to Figure 3, Ca, Al and Pb were co-relatable, which shows that Ca and Pb content in sediment were not only due to its presence in the parent rocks but also due to anthropogenic effluents and biological matter partly. This result confirms the combination of metal affiliation of vary origins. Kalbsi and Mousavi (2000) obtained the same result in Zayandeh-Rood [29].

Chemical partitioning patterns of metals were shown in Figure 4. In the present study, the resistant ion was predominant for metals in the study area. After resident Ions, Pb was mostly concentrated in loose ions. It is the most important phase in sediment toxicology studies.

Loose ion for Pb is predominant in sampling point 4(43.8%). Only small amounts of Cd were bound to the lose ion (0-21.6%) & organic fraction (0.5-18.4%) and no amount of Cd was bound to the sulfide ions. The dominance of the resistant ion for Ni is clearly over the other fractions (71.7-95.1%). There is some discrepancy between results of cluster analysis and those of chemical partitioning studies (Figure 4). The results of chemical partitioning studies were grouped into natural and anthropogenic ones. Also, pollution intensity was subjected to I_{poll} analysis (Table 2). The I_{poll} values are compared with the percentile of pollution obtained from chemical partitioning studies.

CONCLUSION

Seasonal and spatial variations in the concentrations of selected metals in Zayandeh River sediment were investigated. The major sources of pollution of Zayandeh-Rood River are industrial wastewaters, along with urban and agricultural runoff. Pollution status of Zayandeh-Rood was not published before; other information was only available in rare cases [30, 31]. The riverbed sediment of Zayandeh-Rood is polluted in central parts of river by human activities. Also previous studies indicated the major sources of metal in Zayandeh-Rood are agricultural, municipal and industrial effluents [29, 30]. Accumulation of cadmium in sampling location 3, 4 and 5 can make a serious problem for aquatic organism and Humans. Previous investigations on metal accumulation showed accumulation of Lead and Cadmium in the rice irrigated by zayandeh-Rood water [32] and accumulation of lead and zink in the liver of some edible fishes in Zayandeh-rood [33].

Study of geological units in the study area has governed the concentration of trace metals mostly are lower than mean crust. We used cluster analysis and found out there is some discrepancy between chemical partitioning results and those of cluster analysis. For example chemical partitioning studies didn't show considerable affinity amongst Pb, Ni and Cd and organic matters. Pb didn't show significant affinity toward organics in the cluster analysis but it's originated from organic sources partly as shown in chemical partitioning studies. Considering Aluminum as an indicator of alumina silicate source, Pb has been incorporated into the river bed sediments from the same source unlike the Pb in sediments of Shefa-Rud [8] and Zayandeh-Rood, Iran [29]. Cadmium and Nickel is not originated from alumina-silicate source although chemical partitioning of Ni and Cd showed that these elements mostly originated from lithogenic sources. Although total amounts of the heavy metals investigated were found to be normal, station3, 4 and 5 showed accumulation of cadmium beyond threshold limits presented by SQG standard level, assumes greater significance such as Kabini River, India [34]. The overall results of metal fractions and chemical partitioning represented the major source of metal contamination in Zayandeh-rood is anthropogenic; Comparison among the other studies confirmed this result [30]. Pollution intensity of I_{poll} Index was used to show sediments quality. This Index values indicate a clean environment throughout the river course for Ni and Cd (except of study location 5) and low polluted environment for Pb (except of study location 1 and 6). These values are in a well agreement with results of chemical partitioning data. I_{poll} values indicated that the river quality is degraded due to station 3 to 5.

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