



Research Journal of
**Environmental
Toxicology**

ISSN 1819-3420



Academic
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Heavy Metals (Co, Cr, Cd, Ni, Pb and Zn) in Sediment of Gorganrud River, Iran

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ABSTRACT

Most of the industrial, urban and sewage discharges are released into Gorganrud River, Iran without any previous treatment. The aim of this study was to assess the levels of heavy metals (Co, Cr, Cd, Ni, Pb and Zn) in sediment collected from ten sampling stations along the Gorganrud River. The concentrations of heavy metals were determined using Inductively coupled plasma mass spectrophotometer (ICP-MS). The results demonstrated that concentrations of heavy metals showed significant difference ($p < 0.05$) along the river. Concentrations of Co, Cr, Cd, Ni, Pb and Zn ranged from 6.13 to 19.56, 26.66 to 78.33, 0.12 to 0.27, 17.66 to 57.76, 9.00 to 20.83, and 1.06 to 81.83 ppm, respectively. This assessment would help establish pollutant loading reduction goal and the total maximum daily loads and consequently contribute to preserve public health in the Gorganrud River.

Key words: Sediment, pollution, river

INTRODUCTION

There are principally three reservoirs of metals in the aquatic environment: water, sediment and biota. Metal levels in each of these three reservoirs are dominated by a complex dynamic equilibrium governed by various physical, chemical and biological factors. Among these three reservoirs the sediment is the major repository for metals, in some cases, holding over 99% of the total amount of metal present in the system. The study of river sediment is a valuable method of studying environmental pollution with heavy metals (Tang *et al.*, 2010). Rivers play major roles to the community especially in the fishing industry and a source of water supply for people residing within the vicinity of the area. River contamination either directly or indirectly will affect humans as a final consumer. Although some of heavy metals are required as micronutrients, it can be toxic when present higher than the minimum requirements. Heavy metals have been introduced into rivers through geological origin (Kaushik *et al.*, 2009) and factory waste outlet point discharge. Anthropogenic metals may consistently retain within the water bodies or may be taken up by organisms such as plankton, benthos or fish and finally transferred to humans. This is essential to understand the source of heavy metal pollution for future environmental planning strategies. River bed sediments act as both carriers and source of contamination in an aquatic environment; not only play an

important role in river water pollution but can also provide a record of river's pollution history (Tsai *et al.* 2003). Many studies were carried out on concentration of heavy metals in sediment of rivers in other world areas (Diagomanolin *et al.*, 2004; Okonkwo and Mothiba 2005; Olivares-Rieumont *et al.*, 2005; Szalinska *et al.*, 2006; Kaushik *et al.*, 2009; Vasile *et al.*, 2010; Tang *et al.*, 2010) whereas little information is available in the rivers of Iran. The objective of this study is to assess the levels of heavy metals in sediments from Gorganrud River.

MATERIAL AND METHODS

Study area: Gorganrud Great River is one of the most important rivers of Caspian Sea river basin which is originated from Narchi Mountains with 1875 m height and Bilikoooh with 1598 m height in 37 km distance from Kalaleh. Gorganrud irrigates the North area of Gorgan plain and in Mahichopaghli which nears with Khajehnafas, flows to Caspian Sea from East coast. The length of Gorganrud is 325 km. annual mean volume which is estimated in Basir Abad hydrometer station for a 20 years period is equal to 450 MM. Maximum discharge peak in Gorganrud is $3000 \text{ m}^3 \text{ sec}^{-1}$ which was occurred in flood event in August 2001 (Fig. 1).

Collection and analysis of samples: Ten sediment samples were collected in the spring of 2010. Figure 1 shows the location of the sampling sites. At each station three sediment samples were collected using a Peterson grab. The samples were transported to the laboratory according to standard protocols. Concentrations of heavy metals (Co, Cr, Cd, Ni, Pb and Zn) were determined by inductively coupled plasma mass spectrophotometer (ICP-MS, Acme Lab, Canada).

Statistical analysis: Statistical analysis of data was conducted using SPSS statistical package program (Ver.16). Data were subjected to homogeneity of variance and normal

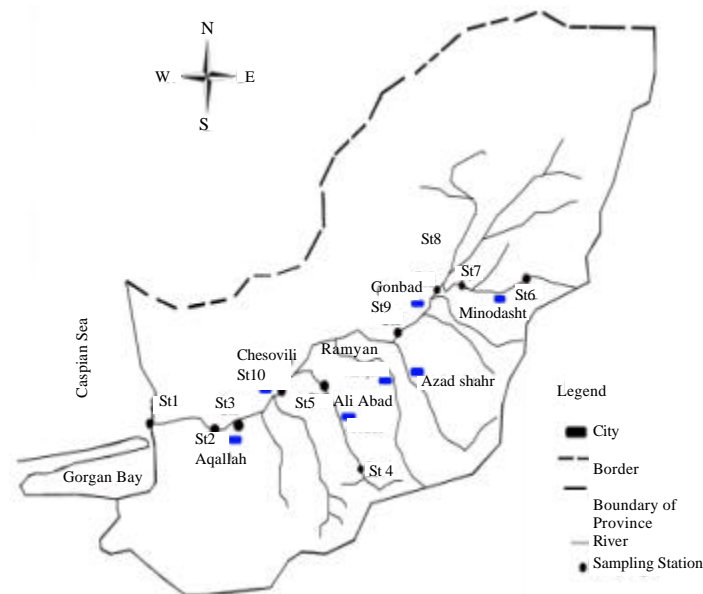


Fig. 1: Study area in Gorganrud River, Iran

distribution tests. One-way analysis of variance (ANOVA) was used for statistical comparisons and Cluster analysis was used for input data. A value of $p < 0.05$ was considered to be statistically significant. Correlations between variables were established by Pearson's coefficient for linear correlation (r) at $p < 0.001$.

RESULTS

Data for metal concentrations in the sediment samples are presented in Table 1. The mean concentrations of Co, Cr, Cd, Ni, Pb and Zn were significantly different between sampling sites ($p < 0.05$), (Table 2). Maximum concentrations of Co, Cr, Cd, Ni and Pb were recorded in station 1 whereas maximum concentration of Zn was recorded in station 10. Minimum concentrations of Co, Cr, Cd, Ni and Pb were recorded in station 6 whereas minimum concentration of Zn was recorded in station 10 (Table 2). between 9, 8, 7, and 5 as well as 2 and 3 in addition to 4 and 10 in sampling sites. There was also no significant difference in Cr concentrations between 9, 8, 7, 5, 3 and 2 as well as 1 and 10 in sampling sites (Table 1).

Results of cluster analysis revealed two major clusters; Cluster 1 includes stations 1 and cluster 2 that includes the stations 2, 3, 4, 5, 7, 8, 9 and 10 (Fig. 2). As shown in Table 2, a significant

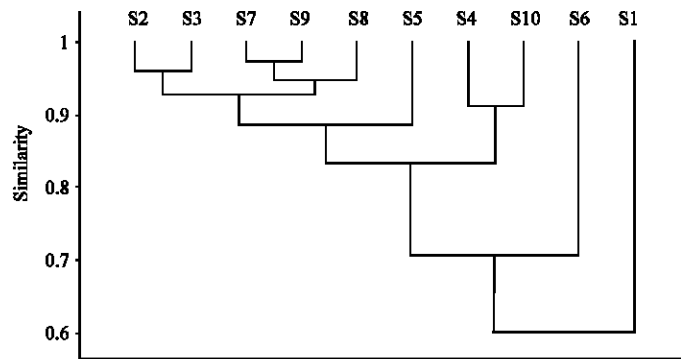


Fig. 2: Dendrogram indicating relatedness of sites with heavy metal contamination among the fifteen sampling stations

Table 1: Comparison and concentration (mean±sd) of heavy metals in different sampling sites of Gorganrud River

Stations	Heavy metals					
	Co	Cr	Cd	Ni	Pb	Zn
1	19.56±2.60 ^e	78.33±8.02 ^d	0.27±0.03 ^f	57.76±7.48 ^d	20.83±2.21 ^e	1.06±3.80 ^f
2	13.46±0.20 ^c	47.66±3.21 ^{bc}	0.17±0.02 ^{bc} ^d	35.26±0.96 ^{bc}	14.33±0.85 ^f	66.90±3.35 ^d
3	13.53±0.70 ^c	40.66±6.42 ^b	0.19±0.005 ^d	33.10±3.68 ^{bc}	13.16±1.25 ^{bf}	63.40±6.31 ^{cd}
4	16.90±0.55 ^d	57.33±4.72 ^c	5±0.01 ^b	36.26±2.02 ^c	14.33±0.70 ^f	81.30±2.60 ^e
5	11.03±0.20 ^b	39.66±1.15 ^b	0.19±0.00 ^{cd}	28.63±0.83 ^b	14.46±0.76 ^f	85.73±7.47 ^e
6	6.13±0.51 ^a	26.66±.57 ^a	0.12±0.01 ^a	17.66±1.12 ^a	9.00±0.10 ^a	35.66±2.66 ^a
7	10.06±0.32 ^b	39.00±1.00 ^b	0.16±.005 ^b ^d	28.53±.61 ^b	12.40±.87 ^{bf}	52.40±1.57 ^b
8	10.83±1.09 ^b	47.66±5.13 ^{bc}	0.15±0.005 ^b	32.93±3.84 ^{bc}	11.56±1.06 ^b	56.90±6.51 ^{bc}
9	10.56±0.47 ^b	42.33±1.52 ^b	0.16±0.00 ^{bf}	31.40±1.05 ^{bc}	12.20±1.38 ^{bc}	51.46±2.29 ^b
10	16.20±1.92 ^d	75.66±11.59 ^d	0.23±0.03 ^e	53.00±7.23 ^d	17.83±2.43 ^d	81.83±9.84 ^e
Average	12.83±3.91	49.50±16.53	0.18±0.04	35.4±11.78	14.01±3.39	68.21±20.50
Continental crust ¹	10	35	0.098	20	20	71

Values followed by the same letter are not statistically different among the groups ($p > 0.05$). ¹For comparison, we report the composition of the continental crust proposed by Taylor and McLennan (1985)

Table 2: Simple correlation analysis between heavy metal concentration in the sediment of Gorganrud River

Heavy metals	Co	Cr	Cd	Ni	Pb
Cr	0.901**				
Cd	0.789**	0.821**			
Ni	0.907**	0.977**	0.888**		
Pb	0.895**	0.903**	0.908**	0.939**	
Zn	0.865**	0.805**	0.819**	0.804**	0.906**

** Correlation is significant at the 0.01 level

positive correlation ($p < 0.001$) was found between all of the heavy metals in sediment 1) was found between all of the heavy metals in sediment.

DISCUSSION

The main sources of pollution of the river are urban, agricultural and industrial wastewaters. In this study heavy metal concentrations were determined at ten stations along the river (upstream stations and downstream). The results revealed higher concentrations of heavy metals (Co, Cr, Cd, Ni and Pb) at downstream stations (St1) compared to upstream stations. Several studies also revealed these facts. Olivares-Rieumont *et al.* (2005) and Kaushik *et al.* (2009) proved this finding in Almendares River and Yamuna River, respectively. Several sources for the increased metal concentrations appear likely. Chemical fertilizers containing Ni and Pb are used in agricultural industries of the regions around Gorganrud River. Cr and Ni compounds are used as pigments in the painting industry and as anti-fouling agents (Ramelow *et al.*, 1992). The waste water of these industries is discharged to Gorganrud River directly, without any remediation; only a simple physical screening is being performed. The major sources of pollution in agricultural wastewater are fertilizers containing heavy metals such as Cd, Pb, Cr, Zn, and Ni (Spencer and Green, 1981). Our results also revealed that concentration of Zn was higher in station 5 and 6 compared to other stations. We found that in this study concentration of Cd, Cr, Co and Ni was higher compared to continental crust (Table 2). These high concentrations reflect the influence of anthropogenic activities. In decreasing order of magnitude, the average of concentration of heavy metals are: Zn (68.21) > Cr (49.50) > Ni (35.4) > Pb (14.01) > Co (12.83) > Cd (0.18). Cadmium compounds enter the water bodies from the discharge of effluents from paint manufacturing industries where cadmium also is used to produce excellent color from rechargeable battery (Spencer and Greene, 1981). Effluents from cadmium plating industries in the urban area of Gorganrud River (Fig. 1) are responsible for the presence of this metal in Gorganrud River. Concentration of Co ranged from 6.13 to 10.83 ppm in the sediment upstream of Gorganrud River (St6 to St9) whereas concentration of Co was obtained 19.56 ppm pling point 1. The highest level of chromium was obtained at sampling point 1 and the lowest level of chromium was obtained at sampling point 6. Cr contamination is originated by plating companies located in urban of Gorganrud River. Nickel also originates from the Ni plating processes and lead may result from the anodes used in the Cr plating tanks. Our result also revealed two major clusters: cluster 1, which represents highly contaminated sites and cluster 2, which represents sites of moderate and lower heavy metals levels in the sediments. In terms of the contamination of the stations under study, Cr and Zn seem to be the most problematic pollutant followed by Ni, Pb, Co and Cd. In general, heavy metal levels in the river were high, but varied widely among sampling stations.

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