Assessment of Cd, Cr and Pb Pollution in Sediment and Water of Gheshlagh River, Iran, in September 2013

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ABSTRACT

Background: This study aimed to evaluate the pollution levels of surface water with heavy metals including Pb, Cd and Cr in Gheshlagh River, western Iran.

Methods: Water and sediment were sampled in five monitoring stations with three replicates in time along the river. The concentration of Cr, Pb and Cd in both water and sediment samples were measured with graphite furnace atomic absorption spectrometer (Australia, Varian 220). The Geoaccumulation Index and Pollution Load Index were employed to assess the pollution level of sediments with heavy metals.

Results: The mean value of Cd, Cr, Pb in sediment samples were 0.69, 17.19 and 10.69 $\mu g g^{-1}$ per dry weight, respectively. Water samples contained Cd, Cr and Pb concentration of 1.99, 1.45 and 12.92 $\mu g L^{-1}$, respectively. The Geoaccumulation Index and Pollution Load Index indicates that the sediments were not polluted with Pb and Cr, and unpolluted to moderately contaminated with Cd in Gheshlagh River.

Conclusion: This study concludes that the Gheshlagh River is threatened by heavy metals particularly Cd and Pb.

Keywords: Chemical Water Pollution, Geologic Sediments, Heavy Metals, Iran, Rivers.

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INTRODUCTION

Pollution of the natural environment by heavy metals is a global problem because metals are indestructible and have toxic effects on living organisms especially at high concentrations [1]. Heavy metals enter aquatic ecosystems through natural sources and anthropogenic activities including industrial or domestic sewage, rain runoffs, agricultural activities, landfills, oil pollution, shipping and harbor activities and atmospheric deposits [2]. Heavy metals are first dissolved in water, then adsorbed, and finally accumulated on the bed sediments acting as sinks.

Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota. Contamination is generally lower in water as compared to concentrations in sediments and biota [3]. However, it is noteworthy that metals do not exist in soluble forms for long times and they become mainly as suspended colloids or are fixed by organic and mineral substances [4].

Sediments are mixtures of various components of mineral and organic residues represented as a final sink of heavy metals discharged into the environment. Sediments play an important role in the adsorption of dissolved heavy metals [5]. In addition, sediments can be potential reservoirs of heavy metals by releasing them into the water column under changing physical and chemical conditions [6]. Sediments play a major role in identifying the pollution load of surface water with heavy metals [7].

Adverse effects of contaminants in sediment and water include behavioral changes, increased cancer risk and reproductive toxicity in fish, reproductive failure in fish-eating birds and mammals, and decreased biodiversity in aquatic ecosystem. Human health is endangered when these sediments and water contaminants bioaccumulate in fish and birds edible tissues consumed by humans [8].

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Many studies [9-12] have been carried out on the pollution of rivers with heavy metals in Iran. However, the concentrations of heavy metal in both sediment and water of the Gheshlagh River, Sanandaj city have not yet been studied. This study assessed the current status of Gheshlagh River in terms of pollution level by heavy metals. The objectives of this study were to determine the distribution and concentration of three heavy metals, i.e., cadmium (Cd), chromium (Cr) and lead (Pb) in both water and sediments in the Gheshlagh River, Western Iran.

MATERIAL AND METHODS

Study Area

This study was conducted in the Gheshlagh River, Sanandaj City, Western Iran. The river is approximately 95 km in length and plays an important role in socio-economic development of the region. In addition to wastewater from the surrounding rural villages entering into adjacent streams and the main river course, pollutants and wastewaters of industrial towns and Sanandaj's main sewage plant end directly into the river.

Sample Collection and Analysis

Sampling was carried out in September 2013. Water and sediment samples were collected in five monitoring stations with three replicates along the Gheshlagh River (Fig.1). Latitude and longitude of sampling stations are illustrated in Table 1.

Water samples were collected in acid washed 250 mL plastic bottles from approximately 30 cm below the water surface. Sediment samples were collected using a grab sampler. All containers and equipments were previously soaked in 10% HNO_3 and rinsed thoroughly with deionized distilled water before being used for sampling or analysis [13].

The water samples were filtered using 0.45 µm nitrocellulose membrane filter. Sediment samples were dried at 105 ºC for 24 h to achieve constant weight. Samples were passed through 0.063 mm plastic sieve and stored in polyethylene bottles until chemical. Acid digestion was performed by placing 1 g of sample in a beaker and digesting with 14 mL mixture of concentrated HCl and HNO_3 (from Merck) with a ratio of 10:4 v/v for 8 h at 70 ºC and then 5 mL of concentrated $HClO_4$ was added. The residue was filtered and diluted to 50 mL with double distilled water. The solution was stored in a refrigerator at 4 ºC for analysis [14].

The concentration of Cr, Pb and Cd in both water and sediment samples were measured with graphite furnace atomic absorption spectrometer (Australia, Varian 220). The limits of detection for Cd, Pb and Cr were 0.01, 0.2 and 0.075 $\mu g g^{-1}$, respectively.

Data Analysis

Kolmogorov–Smirnov test was used to check the normal distribution of data. The relationship between concentrations of heavy metals in water and sediments was determined with Pearson's correlation. The analysis of variance (ANOVA) and Tukey's honest significant difference test was employed to compare monitoring stations. Data analysis was performed with SPSS 19.

The geoaccumulation index (I_{geo}) and pollution load index (PLI) were employed to assess the pollution level of sediment with heavy metals. The geoaccumulation index (I_{geo}) was originally defined by Muller [15] and is widely used to evaluate the degree of contamination or pollution with heavy metals in terrestrial, aquatic and marine environments. The I_{geo} values were calculated for measured metals in sediments using the following equation:

$$I_{geo} = \ln \frac{C_n}{1.5 \times B_n} \quad (1)$$

Where, C_n is the measured concentration of heavy metal in sediment ($\mu g g^{-1}$ dry mass) and B_n is the background value of heavy metal ($\mu g g^{-1}$ dry mass). In this study, B_n was considered as Mean crust given by Karbassi et al. [9] and the background matrix correction factor was considered as 1.5.

Forstner et al. [16] identified geoaccumulation classes and the corresponding contamination intensity for different indices as illustrated in Table 2. Pollution load index for each site was determined by the following (equation) proposed by Tomlinson et al. [17]:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n)^{\frac{1}{n}} \quad (2)$$

Where, n is the number of metals and CF is the contamination factor. Calculated by the following equation:

$$CF\ (\text{Contamination factor}) = \frac{\text{Metal concentration in the sediments}}{\text{Background value of the metal}} \quad (3)$$

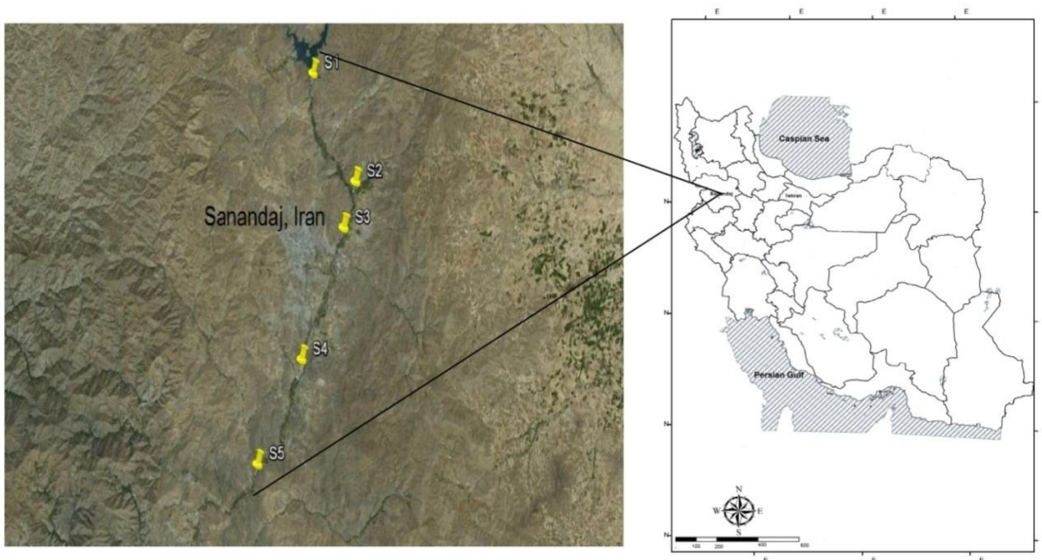

Figure1. Map of the study area showing sampling stations in Gheshlagh River.

Table 1. Latitude and Longitude of sampling stations in the Gheshlagh River.

Stations	Latitude	Longitude
1	46º59′35″	35º24′46″
2	47º09′19″	35º22′26″
3	47º03′14″	35º20′40″
4	47º02′03″	35º18′24″
5	46º58′25″	35º10′9″

Table 2. Geoaccumulation index classification (courtesy of Forstner et al. 1993) [16].

Sediment geoaccumulation index, Igeo	I_{geo} class	Intensity of contamination
< 0	0	Practically uncontaminated
> 0-1	1	Uncontaminated to moderate
> 1-2	2	Moderately contaminated
> 2-3	3	Moderately to strongly contaminated
> 3-4	4	Strongly contaminated
> 4-5	5	Strongly to very strong contamination
> 5	6	Very strong contamination

RESULTS

The concentrations of Cd, Cr and Pb in water and sediment samples are presented in Tables 3. The highest and lowest concentrations of Pb in water samples were determined at stations 5 and 2, respectively. Mean concentration values of Pb were 20.08 μgL^{-1} and 2.40 μgL^{-1} in stations 5 and 2, respectively. The concentration of Pb ranged from 18.74 to 21.30 μgL^{-1} in station 5 and from 1.10 to 3.80 μgL^{-1} in station 2. The concentrations of Pb in station 2 and other stations were significantly different ($P < 0.01$), while concentrations of Pb in stations 1, 4, 3 and 5 were not ($P > 0.05$) (Table 3).

The highest and the lowest concentrations of Pb in the sediment samples were measured at stations 1 and 3, respectively. Mean concentration values of Pb were 12.50 μgL^{-1} and

8.50 μgL^{-1} in stations 1 and 3, respectively. The concentration of Pb ranged from 11.50 to 14 μgL^{-1} in station 1 and from 8 to 9.10 μgL^{-1} in station 2. There were significant differences among the stations 1, 4 and 5 and stations 2 and 3 in the sediment samples with regard to Pb concentration ($P < 0.05$) (Table 3).

The concentration of Cd in the water of station 3 was the highest amongst the stations with a mean value of 6.12 μgL^{-1}. Cd value ranged from 5.8 to 6.44 μgL^{-1} in station 3. The lowest Cd concentration in water was at station 4 with a mean value of 0.29 μgL^{-1}(0.07 to 0.73μgL^{-1}). There were significant difference between station 3 and other stations with regard to Cd concentration in the water ($P < 0.01$). We found the same trend for Cd level between station 4 and the other stations ($P < 0.05$) (Table 3).The concentrations of Cd in the sediments of stations 3 and 2 were the highest and the lowest amongst the stations, respectively. The mean values of Cd were 1.49 and 0.26 μgg^{-1} in stations 3 and 2, respectively. The value of Cd ranged from 0.79 to 2.1μgg^{-1} and from 0.12 to 0.5μgg^{-1}in stations 3 and 2, respectively. There was a significant difference between the station 3 and other stations with regard to Cd level in the sediment ($P < 0.05$) (Table 3).

The highest and lowest concentrations of Cr in water were measured in stations 5 and 4 with a mean value of 2.14 μgL^{-1} and 0.13 μgL^{-1}, respectively. There was significant difference between station 4 and other stations in relation to Cr content in the water ($P < 0.05$) and also we discovered significant difference between station 3 and station 5 in terms of Cr content in water ($P < 0.05$) (Table 3).

The highest and lowest concentrations of Cr in the sediment were determined at stations 3 and 2 with mean values of 20.46 and 14.26 μgg^{-1}. Cr values ranged from 17 to 22.40 μgg^{-1} and from 13.6 to 15.2 μgg^{-1} in station 3 and 2, respectively. There was significant difference of Cr levels in the sediments of station 2 and stations 1 and 3 ($P < 0.05$). There was significant difference between station 3 and stations 2 and 4 in the sediment for Cr content ($P < 0.05$) (Table 3).

Table 3. Mean, ±SD and range concentrations of Pb, Cd and Cr in the water (μgL^{-1}) and sediment (μgg^{-1}, dry weight) samples from the Gheshlagh River.

	Pb			**Cd**			**Cr**		
Water	**Mean**	**±SD**	**Range**	**Mean**	**±SD**	**Range**	**Mean**	**±SD**	**Range**
1	10.86[b]	3.58	8.7-15	1.22[b]	0.53	0.7-1.76	1.7[ab]	0.17	1.6-1.9
2	2.4[c]	1.35	1.1-3.8	1.16[b]	0.18	1-1.37	1.84[ab]	0.61	1.18-2.4
3	21.95[a]	2.81	18.75-24	6.12[a]	0.32	5.8-6.44	1.45[b]	0.22	1.23-1.67
4	9.34[b]	0.77	8.7-10.2	0.29[c]	0.37	0.07-0.73	0.13[c]	0.03	0.1-0.17
5	20.08[a]	1.28	18.74-21.30	1.19[b]	0.1	1.1-1.3	2.14[a]	0.29	1.87-2.45
Average	12.92	-	-	1.99	-	-	1.45	-	-
WHO	10	-	-	3	-	-	50	-	-
Sediment									
1	12.5[a]	1.32	11.5-14	0.57[b]	0.46	0.2-1.1	18.56[ab]	2.45	16.2-21.1
2	8.93[b]	1.15	7.8-10.1	0.26[b]	0.2	0.12-0.5	14.26[c]	0.83	13.6-15.2
3	8.5[b]	0.55	8-9.1	1.49[a]	0.66	0.79-2.1	20.46[a]	3	17-22.40
4	11.56[a]	0.47	11.2-12.1	0.47[b]	0.54	0.12-1.1	15.2[bc]	1.01	14.3-16.3
5	11.96[a]	0.8	11.2-12.8	0.68[b]	0.09	0.6-0.79	17.46[abc]	0.56	17-18.1
Average	10.69	-	-	0.69	-	-	17.19	-	-
Mean word sediments	19	-	-	-	-	-	70	-	-
Mean crust	14	-	-	0.3	-	-	100	-	-

[a,b,c] : Means with the same letters in each column for each metal are significantly different at $P < 0.05$.
The concentrations of heavy metals were expressed on dry weight basis for sediments.

DISCUSSION

The industrial activities in Sanandaj City has increased during the past two decades which caused pollution of Gheshlagh River its adjacent environment. The main sources of heavy metals contamination of Gheshlagh River are industrial wastewaters discharged from various industries such as chicken slaughterhouses, industrial towns as well as agricultural lands, landfills' leachates and wastewater treatment plant of Sanandaj City. The pH value in Gheshlagh River varied between 5 and 6.2. Low pH of water can be attributed to discharge of acidic wastes from industrial and agricultural sites into surface waters.

The mean concentrations of metals in water at all sampling stations in descending order were: Pb > Cr > Cd, except for sampling stations 2 and 3 where Cd concentration was higher than Cr level. Furthermore, the metal concentrations in sediments in descending order were: Cr > Pb > Cd. Pearson correlation coefficient matrix indicated a positive significant correlation ($r = 0.607$, $P < 0.05$) between Pb and Cd values. Moreover, Pearson correlation showed insignificant ($P > 0.05$) correlations between Cr and Pb ($r = 0.225$), Cr and Cd ($r = 0.155$) in water samples (Table 4). There was a positive significant correlation ($r = 0.655$, $P < 0.01$) between Cr and Cd values. In addition, there were negative but nonsignificant correlations ($P > 0.05$) between Pb and Cd ($r = -0.297$) and Cr (r = -0.053) in sediment (Table 4).

The mean concentrations of Pb were higher in the sediments at stations 1, 2 and 4 than that of water. However, the mean concentrations of Pb in the water of stations 3 and 5 were higher than that of sediments. There was a positive significant relationship ($r = 0.654$, $P < 0.01$) between Pb in water and Cd in sediment. Additionally, there was significant relationship ($P < 0.05$) between Pb in water and Cr in sediment. There was also negative significant relationship ($r = -0.597$, $P < 0.05$) between Pb in sediment and Cd in water. The levels of Pb in water, at stations 1, 3 and 5 in Gheshlagh River were higher than the World Health Organization limit (2011) [18]. However, Pb concentrations at all sampling stations were lower than the mean world sediments and mean crust levels.

The mean Pb concentration in water of five sampling sites in Gheshlagh River was lower than Khoshk River [10], but higher than that Shur River [9]. Mean Pb concentrations in sediment samples from five monitoring sites in Gheshlagh River were lower than Khoshk River [10], Shur River [9] and Han River [19], but higher than Cauvery River [7].

The mean concentrations of Cd in water were higher than the sediments at all sampling stations except for station 4. There were high positive correlations ($P<0.01$) between Cd in water and Cd ($r = 0.705$) and Cr ($r = 0.672$) in sediments. The results indicated that the levels of Cd in water, at all stations (except for station 3) in Gheshlagh River were lower than the recomended levels by WHO [18]. In case of sediment samples, Cd concentrations at all stations (except for station 2) were higher than the mean crust levels. Mean Cd concentration in water from the five sampling sites were lower than Khoshk River [10], but higher than the Cd level in Shur River [9]. The mean Cd concentration in sediment samples from all sites were lower than Khoshk River [10], Shur River [9] and Cauvery River [7], but higher than Cd level in Han River [19].

Table 4. Pearson's correlation coefficient of Pb, Cd and Cr in water and sediment samples from the Gheshlagh River.

	Water Pb	Sediment Pb	Water Cd	Sediment Cd	Water Cr	Sediment Cr
Water Pb	1					
Sediment Pb	.002	1				
Water Cd	.607*	-.597*	1			
Sediment Cd	.654**	-297	.705**	1		
Water Cr	.225	-.098	.155	.089	1	
Sediment Cr	.595*	-.053	.672**	.655**	.248	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

The mean concentrations of Cr in the sediments were higher than that of water at all monitoring stations. The levels of Cr in water were lower than the WHO [18] standard limit. In reguard to sediment samples, Cr concentrations at all stations were lower than the mean world sediments and mean crust limits. Mean Cr concentration in water from all sampling sites in was lower than the Cr level in Khoshk River [10]. Mean Cr concentrations in sediments from all sites were lower than Cr levels in Khoshk River [10], Cauvery River [7] and Han River [19].

Demirak et al. [20] studied heavy metal accumulation in sediments and water from a stream in southwestern Turkey and reported mean levels of Cd, Cu, Pb, Zn and Cr for sediment samples as 0.8, 13, 83.6, 37 and 19.7 $\mu g g^{-1}$, respectively. Meanwhile, the mean levels of Cd, Cu, Pb, Zn and Cr for water samples were 0.171, 0.365, 0.405, 1.051 and 0.092 $\mu g L^{-1}$, respectively. The mean levels of Cd, Pb and Cr concentrations for sediment in the mentioned stream in southwestern Turkey were higher than the data obtained in this study, but the mean levels of Cd, Pb and Cr concentrations for water were lower than our findings.

Wang et al [21] mentioned that the average contents of Cu, Pb, Zn, and Cd in the water and sediments of Yellow River were 0.0029, 0.0081, 0.0083 and 0.00045 $mg L^{-1}$ for water and 18.485, 16.125, 78.531 and 0.58

6 $\mu g g^{-1}$ for sediment, respectively. Except for Pb in sediments, the average levels of Cd and Pb concentrations for sediments and water in Yellow River were lower as compared to our findings.

Dundar and Altundag [22] reported that the mean values of Pb, Zn, Cd, Ni, Cr, Cu in water samples in the lower Sakarya River were 1.786 0.173 0.236 1.050 0.027 0.851 $\mu g g^{-1}$; and in sediment samples were 2.640, 9.990, ND, 13.520, 8.870, 4.630 $\mu g g^{-1}$, respectively. The mean levels of Cr, Cd and Pb concentrations for sediment and water in lower Sakarya River were lower than our findings.

The calculated geoaccumulation index (I_{geo}) values in the Gheshlagh River are presented in Table 5. The I_{geo} consists of seven categories ranging from unpolluted to very highly polluted class [23]. The I_{geo} values for Gheshlagh River sediments indicated that the sediments were not polluted (class 0) with Pb and Cr. In case of Cd, it varied from unpolluted to moderately contaminated. Cadmium values were moderately contaminated at station 3 (class 2), to moderate (class 1) at stations 1, 4, 5 and unpolluted at station 2 (class 0).

The values of Pollution Load Index (PLI) obtained for sediments are summarized in Table 5. The PLI values of lead and chromium at all stations in the Gheshlagh River were low (< 1). The PLI calculated for Cd in the sediments of the study river were more than 1 at stations 1, 3, 4 and 5 but PLI values of Cd were lower than 1 at station 2.

CONCLUSION

This study provides knowledge on metal concentration levels in the sediments and water of the Gheshlagh River, Sanandaj city. The study reveals that there is considerable variation in the concentrations of heavy metals in water and sediments samples. These variations may be due to agricultural activities and industrial wastewaters discharged from various industries into river at different locations. The Gheshlagh River is threatened by some heavy metals such as Cd and Pb. Precautions need to be taken in order to prevent further heavy metal pollution. Additionally, biomonitoring is necessary for this River to evaluate the heavy metal contents of water if is used for potable or agricultural purposes. These baseline data are important in designing the management and conservation policies of the Gheshlagh River.

Table 5. Geoaccumulation (I_{geo}) and Pollution Load Index lead (PLI) of Pb, Cd and Cr in the sediments of the Gheshlagh River.

Stations	I_{geo}			PLI		
	Pb	Cd	Cr	Pb	Cd	Cr
1	-0.51	0.24	-2.08	0.88	1.51	0.18
2	-0.85	-0.52	-2.35	0.63	0.73	0.14
3	-0.90	1.20	-1.99	0.60	4.61	0.20
4	-0.59	0.05	-2.28	0.82	1.01	0.15
5	-0.56	0.41	-2.15	0.85	2.51	0.17

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