Natural and Concentration Factor Distribution of Heavy Metals in Sediments of Chah Nimeh Reservoirs of Sistan, Iran

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ABSTRACT The Chah Nimeh reservoirs of Sistan is as one of the main water sources of Zabol City used for drinking, agriculture, industry and livestock purposes. This study aimed to determine the contribution of the natural and concentration factors of heavy metals such as Cd, Pb and Cu in sediment of Chah Nimeh of Sistan. The concentrations of heavy metals in surface sediments were studied in six stations during 2013. To determine the concentration of the heavy metals atomic absorption spectrometer (Contr AA 700) was used. Sequential extraction analysis was applied based on the share of natural and concentration factor sources of heavy metals. Sequential extraction analysis showed that a considerable part of the Pb (63.67%), Cd (55.17%) and Cu (57.17%) were from natural sources. The highest concentrations of Cd and Pb were 0.81 and 5.57 mg kg^{-1}, respectively, obtained in station one and the maximum Cu concentration was observed in station five (37.8 mg kg^{-1}), while the lowest concentration of Cd, Pb and Cu were 0.34, 3.95 and 31.4 mg kg^{-1}, respectively.

Key words: *Environmental pollution, Sequential extraction, Water resources management*

1 INTRODUCTION

Environmental (sediment) systems have become complex due to human activities and natural process as they disturb the natural development and add hazardous elements. Hence, there is a growing public concern over the accumulation of heavy metals in the environment (Sayadi and Sayyed, 2011). Aquatic environments play an important role in the transport and handling of heavy metals from the environment. The heavy metals may be released from natural processes (such as weathering and erosion) and concentration factor activities. Sediments are the natural sinks for many minerals and heavy metals having different origins ranging from lithogenic, pedogenic and anthropogenic sources. Despite complex transport

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mechanisms involving chemical and diagenetic processes, causing downstream dilution and/or alteration of the sediments, riverbeds can provide important information on dominant local contributions, such as geologic anomalies or pollution sources in their catchments (Sayadi *et al.,* 2008; Sayadi and Rezaei, 2014). The importance of the relationship between natural and concentration factor sources of heavy metals in the environments is undeniable. Metals from concentration factor sources after entering the aquatic environment income in the form of inorganic ions or hydrated. In this case, the heavy metals by the physical and chemical with relatively weak bonds are absorbed by sediments. Metals originating from concentration factor sources are due to weak bonds by sediments under different environmental conditions can be easily released into the environment. Human activity has negatively affected water quality and aquatic ecosystems. To evaluate heavy metal pollution sources in sediments in the aquatic environment various methods have been proposed (Rezaei and Sayadi, 2015; Sayadi *et al.,* 2014).

Ololade *et al.* (2008) showed the impact of human activities on the environment. The presence of metals such as Cu, Pb was used as a factor threatening the environment. Bobb and Lester (1994) noted that there were potential for accumulation, detoxification and stabilization of heavy metals in sediments. Sediments of the study area were considered as an indicator of pollution. They also stated that the concentration of heavy metals in sediment, one to three times greater than the heavy metal concentration in water. Since the Chah Nimeh reservoirs of Sistan is as one of the water resources of Zabol City, and used in

different purpose such as drinking water, agriculture, industry and livestock, therefore the study and evaluation of heavy metals in the sediments is necessary. So, this study aimed to determine the contribution of the natural and concentration factor heavy metals such as Cd, Pb and Cu in sediment of Chah Nimeh reservoirs of Sistan.

2 MATERIAL AND METHODS
2.1 Study Area
The study area is located in Zabol City which includes 50° ha extent. The first Chah Nimeh is started from Afghanistan border parallel to Sistan River up to six km from Zahak City. The second Chah Nimeh starts from Afghanistan border and ends to the middle of first Chah Nimeh and the third Chah Nimeh is located at west of second Chah Nimeh (Bandab Consulting Engineers, 2003). The area extended between 30^0 45' to 30^0 50' N-latitude and 61^0 35' to 61^0 45' E-longitude. This study with in view of the Chah Nimeh conditions, Two sampling stations from each Chah Nimeh (totally six sampling stations) was selected (Figure 1). The samples are collected in triplicate with the aid of a sediment grab of the Van Veen type. Whereas the sediments are may frequently heterogeneous due to small-scale changes in hydrological regime and geomorphological changes in the catchment area. This variability is minimized by taking five sub-samples, which are mixed together in a composite sample. The samples were dried at room temperature and then crushed by mortar then shredded sediments were passed through sieve of 63 micron.
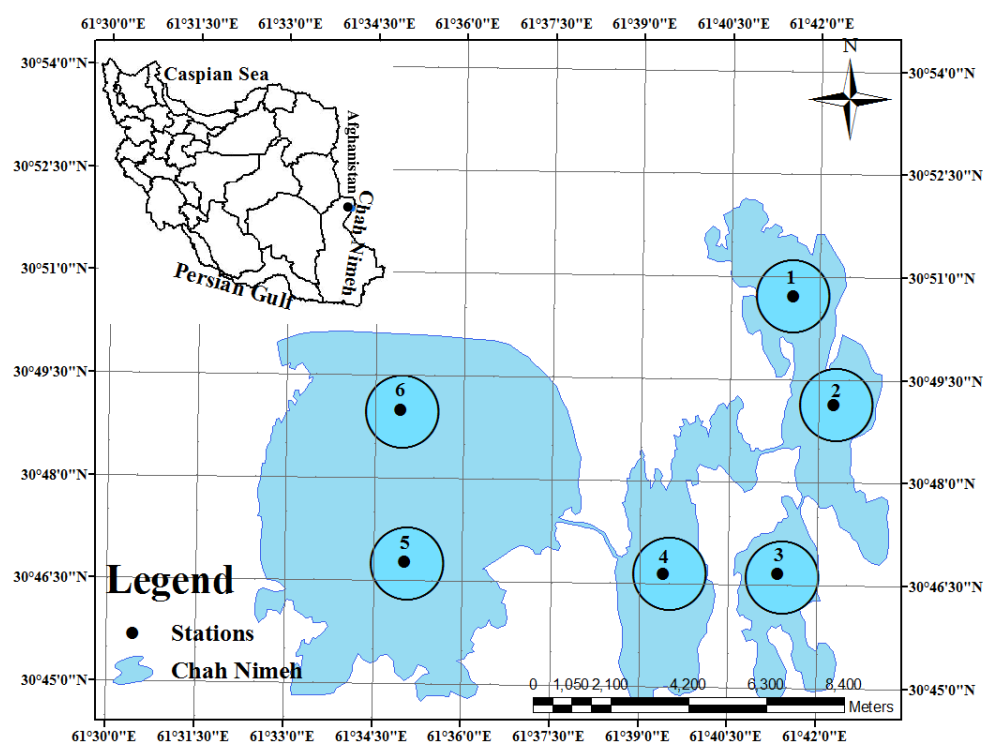
Figure 1 Study area and sampling site locations in the Chah Nimeh reservoirs of Sistan, Eastern Iran

2.2 Sequential extraction analysis

Sequential extraction was performed by four steps procedure defined to investigate the distribution of the element fraction in various sediment samples. (Qiao *et al.,* 2013; Sayadi *et al.,* 2015):

1. Acid-soluble/exchangeable fraction (F1); Sediment sample (1g) was introduced in 20 ml of 11M HOAc and shaken for 16 h at room temperature. The solution and solid phases were separated by centrifugation at 6000 rpm for 20 min. Subsequently, the suspension was filtered through a 0.45-μm membrane filter and the solid residues were preserved for the subsequent extractions.

2. Reducible Fe-Mn oxides and hydroxide fraction (F2); the residue from F1 was leached with 20 ml of 0.1 M $NH_2OH \cdot HCl$ for 16 h.

3. Oxidizable organic matter bound fraction (F3); The residue from F2 was mixed with 5 ml of hydrogen peroxide (30%) and digested at room temperature for 1 h with occasional shaking. A second 5-ml aliquot of hydrogen peroxide was introduced into and digested at 85 °C (water bath) for 1 h. The contents were evaporated to a small volume (1–2 ml). Twenty-five milliliters of ammonium acetate (0.1 ml l^{-1}, adjusted to pH 2 with nitric acid) was added to the cool and moist residue. The sample was then shaken and centrifuged.

4. Residual fraction (F4); the residue from F3 was digested with 5 ml HNO_3 in acid. The contents were heated on a hot plate and evaporated to almost dryness. The resultant solutions were subsequently used to determine the heavy metals. The concentration of Cd, Pb and Cu in different

fractions and the resultant solutions obtained in the different fractions were determined using a Contr AA 700 atomic adsorption spectrophotometer with detection limits for Cd (0.5), Pb (3.5) and Cu (1) mg l^{-1}.

2.3 Statistical analyses
All statistical analyses were computed by using SPSS 16. To determine the significant differences among study parameters, one-way analysis of variance with post hoc Tukey's were also used.

3   RESULTS AND DISCUSSION
Tables 1 to 3 show average concentration of the sequential extraction of metals from sediments with standard deviation.

Table 1 Mean±SD concentrations of Cd (mg kg^{-1}) at three replications in sediments of Chah Nimeh reservoirs in Sistan, Iran

| Stations	Acid-soluble/exchangeable fraction (F1)	Reducible Fe-Mn oxides and hydroxide fraction (F2)	Oxidizable organic matter bound fraction (F3)	Residual fraction (F4)
1	0.07±0.003	0.09±0.001	0.22±0.013	0.43±0.021
2	0.04±0.002	0.07±0.005	0.19±0.01	0.31±0.011
3	0.03±0.002	0.06±0.006	0.07±0.007	0.19±0.009
4	0.04±0.003	0.05±0.006	0.10±0.011	0.21±0.014
5	0.06±0.004	0.08±0.009	0.21±0.014	0.40±0.018
6	0.05±0.003	0.07±0.007	0.20±0.012	0.35±0.06
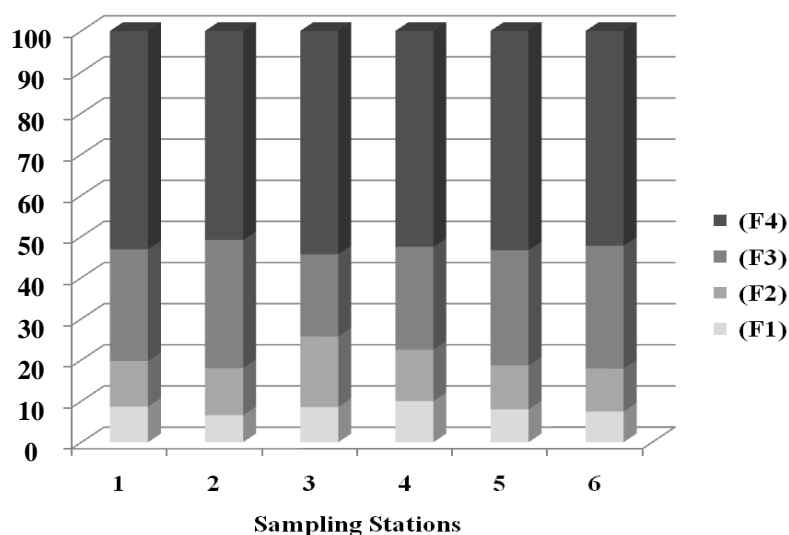
Figure 2 Percentage of sequential extraction of Cd in sediments of Chah Nimeh reservoirs in Sistan, Iran

The mean concentration of Cd sequential extraction in sediments are presented in Table 1, which showed that the highest amount of the Cd on the exchangeable fraction (0.07 mg kg^{-1}) was obtained in station 1 and station 3 had the lowest concentration (0.03 mg kg^{-1}). The highest and lowest concentrations of Cd in F2 were 0.09 and 0.05 mg kg^{-1} which is measured at stations 1 and 4 respectively. Cd in F3 and F4 has the highest concentration (0.22 and 0.43 mg kg^{-1} respectively) at station 1, while the lowest

concentrations of Cd were 0.07 and 0.19 mg kg^{-1} respectively, at station 3. Cd distribution in various fractions showed the same patterns for each sediment samples (Figure 2). These results are consistent with the findings of Dongting Lake, central China (Yao, 2008) and Qayen area Iran (Sayadi *et al.,* 2015). Overall, a total of six stations, the mean concentration of Cd in the four-phase of sequential extraction is as follows:

F4 (0.31 mg kg^{-1})> F3 (0.16 mg kg^{-1})> F2 (0.07 mg kg^{-1})> F1 (0.048 mg kg^{-1}).

Table 2 Mean±SD concentrations of Pb (mg kg^{-1}) at three replications in the sediments

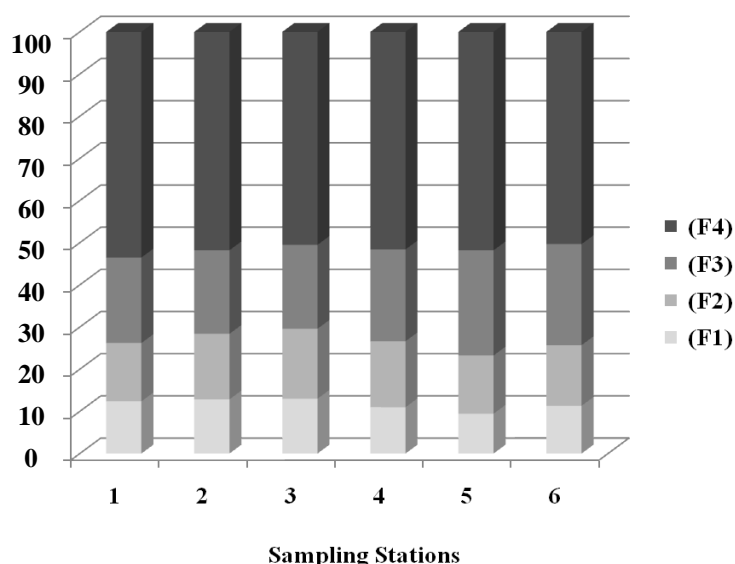| Stations	Acid-soluble/exchangeable fraction (F1)	Reducible Fe-Mn oxides and hydroxide fraction (F2)	Oxidizable organic matter bound fraction (F3)	Residual fraction (F4)
1	0.69±0.019	0.77±0.08	1.13±0.06	2.98±0.096
2	0.72±0.047	0.87±0.099	1.11±0.08	2.9±0.78
3	0.51±0.032	0.65±0.011	0.78±0.07	1.98±0.2
4	0.52±0.042	0.74±0.099	1.03±0.09	2.44±0.11
5	0.50±0.041	0.73±0.092	1.32±0.08	2.74±0.63
6	0.52±0.042	0.66±0.099	1.1±0.012	2.31±0.54

Figure 3 Percentage of sequential extraction of Pb in the sediments of Chah Nimeh reservoirs Sistan

The mean concentration of Pb sequential extraction in sediments are presented in Table 2, which showed that the highest amount of the Pb on F1 and F2 (0.72 and 0.87 mg kg⁻¹) were obtained in station 2 and station 5 had the lowest concentration (0.50 mg kg⁻¹) at F1 while the lowest concentration of Pb for F2, F3 and F4 were recorded in station 3. The highest amount of Pb in F3 (1.32 mg kg⁻¹) were found at station 5 and the lowest average of 0.87mg kg⁻¹ was at station 3. F4 lead to high levels of Pb (2.98 mg kg⁻¹) at station 1 and the lowest level (1.98 mg kg⁻¹) at station 3. Amazingly, as figure 3 shows, the distribution of Pb in the stations showed a strong similarity with the F4. The results of this study are consistent with the findings of Shantou Bay, China (Qiao *et al.,* 2013). As well, in the paddy sediments, a large fraction of Pb was bound in F3, and the second most important fraction was the F3 (Wong *et al.,* 2002). Average amount of Pb in the mean concentration in the four-phase of sequential extraction has been obtained in

this way: F4 (2.55 mg kg⁻¹)> F3 (1.07 mg kg⁻¹)> F2 (0.73 mg kg⁻¹)> F1 (0.57 mg kg⁻¹).

As Table 3, the highest and lowest of Cu in F1 are at stations 1 (3 mg kg⁻¹) and 2 (1.2 mg kg⁻¹) respectively. The highest concentration of Cu (5.2 mg kg⁻¹) in F2 was observed at station 5, while the lowest value (2.4 mg kg⁻¹) found in the station 4. The highest concentration of Cu (8.8 mg kg⁻¹) in F3 was obtained at station 2 while the lowest concentration (6.2 mg kg⁻¹) was at station 3. The highest concentrations of Cu (21.6 mg kg⁻¹) at F4 in station 5 and the lowest concentration of Cu (17.5 mg kg⁻¹) was obtained in station 3.

In the sampling stations were found in large quantities during the F4 (Figure 4). These results are consistent with the findings of other researchers (Huang *et al.,* 2013). The mean concentration of Cd in the four-phase of sequential extraction is as follows: F4 (20.05 mg kg⁻¹)> F3 (7.78 mg kg⁻¹)> F2 (4.55 mg kg⁻¹)> F1 (2.68 mg kg⁻¹).

Table 3 Mean±SD concentrations of Cu (mg kg⁻¹) at three replications in sediments of Chah Nimeh reservoirs Sistan, Iran

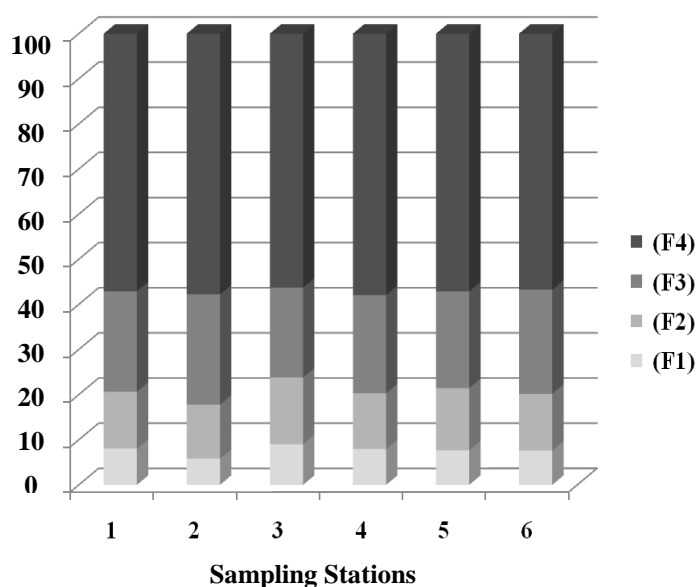| Stations	Acid-soluble/exchangeable fraction (F1)	Reducible Fe-Mn oxides and hydroxide fraction (F2)	Oxidizable organic matter bound fraction (F3)	Residual fraction (F4)
1	3.0±0.31	4.7±0.62	8.3±0.13	21.3±1.4
2	2.1±0.12	4.3±0.19	8.8±0.74	20.8±1.8
3	2.8±0.08	4.6±0.39	6.2±0.34	17.5±1.3
4	2.7±0.29	4.2±0.17	7.4±0.81	19.7±0.83
5	2.9±0.84	5.2±0.53	8.1±0.36	21.6±1.6
6	2.6±0.34	4.3±0.62	7.9±0.93	19.4±1.3

Figure 4 Percentage of sequential extraction of Cu in the sediments of Chah Nimeh reservoirs Sistan

Figures 2 to 4 show percentage distribution of sequential extraction of Cd, Pb and Cd in the sediments of Chah Nimeh in Sistan. The percentage of Cd, Pb and Cu in the four-phase of sequential extraction was measured as follows F4>F3>F2>F1. The heavy metals distribution in various fractions showed same patterns at different sampling stations.

Given the direct relationship between the solubility of metals and bio-available of heavy metal, the bio-availability of the metals in the four-phase of sequential extraction is as follows F1>F2>F3>F4.

To determine the significant differences at different fraction of heavy metals, a one way analysis of variance (ANOVA), Tukey's honest significant difference test was employed. The results showed that, there were significant differences at different fraction for Pb, Cd, and Ni (P-value<0.01). As Table 4 showed there were no significant differences at F1 with F2 and F2 with F3 for Cd and Pb. While, there were significant differences between other fraction of Cd, Pb and Cu. As Rajaei *et al.* (2012) confirmed there were

significant differences between Cd, Pb and Cu in the most of Chah Nimeh reservoirs samples. The same result also obtained by Javan *et al.* (2015).

The sum of heavy metals concentration in F1, F2 and F3 are known as the concentration factor form while the difference between the sum of these with a total metal concentration are known as the natural source (Karbassi *et al.,* 2005).

As Table 5 showed in the study area natural process are play a key role to releasing the heavy metals in the environment, as Pb has the highest percentage (63.67%) of natural process. Cd, Pb and Cu contents are controlled by a long term lithogenic activity connected with weathering and erosion activities, which results in large-scale chemical anomalies (Sayadi *et al.,* 2010).

Similar results were obtained for cadmium, as over 40 % of metal was present in the exchangeable phase and 63 % of the total concentration for lead occurred in the residual phase (Javan *et al.,* 2015).

Table 4 Statistical results (ANOVA) of different fraction of Cd, Pb and Cu concentration at six sampling sites

Sequential extraction		P-value for Cd	P-value for Pb	P-value for Cu
Acid-soluble/exchangeable (F1)	Reducible Fe-Mn oxides and hydroxide(F2)	0.921	0.600	0.011
	Oxidizable organic matter bound(F3)	0.014	0.004	0.000
	Residual(F4)	0.000	0.000	0.000
Reducible Fe-Mn oxides and hydroxide (F2)	Acid-soluble/exchangeable(F1)	0.921	0.600	0.011
	Oxidizable organic matter bound(F3)	0.053	0.063	0.000
	Residual(F4)	0.000	0.000	0.000
Oxidizable organic matter bound (F3)	Acid-soluble/exchangeable(F1)	0.014	0.004	0.000
	Reducible Fe-Mn oxides and hydroxide(F2)	0.053	0.063	0.000
	Residual(F4)	0.002	0.000	0.000
Residual (F4)	Acid-soluble/exchangeable(F1)	0.000	0.000	0.000
	Reducible Fe-Mn oxides and hydroxide(F2)	0.000	0.000	0.000
	Oxidizable organic matter bound(F3)	0.002	0.000	0.000

Table 5 Percent natural and concentration factor sources on the distribution of heavy metals in sediments

Heavy metals	Concentration factor (%)	Natural process (%)
Cd	44.83	55.17
Pb	36.33	63.67
Cu	42.83	57.17

4 CONCLUSION

Sequential extraction techniques used to identify the main binding sites, the strength of metal binding to the particulates and the phase associations of elements in sediment. So, it recognizes the amount of anthropogenic metals in contrast to their natural origin. In the present research, the percentage of Cd, Pb and Cu in the four-phase of sequential extraction was measured as follows Residual> Oxidizable organic matter bound> Reducible Fe-Mn oxides and hydroxide> Acid-soluble/exchangeable. Given the direct relationship between the solubility of metals and bio-available of heavy metal, the bio-availability of the metals in the four-phase of sequential extraction was as follows F1>F2>F3>F4. So, the heavy metals in the sediments of Chah Nimeh reservoirs Sistan were relatively stable. In the study area natural processes play a key role to release the heavy metals in the environment, as Pb has the highest percentage of natural process. Cd, Pb and Cu contents are controlled by a long term lithogenic activity connected with weathering and erosion activities.

5 ACKNOWLEDGMENT

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توزیع پراکندگی طبیعی و فاکتور غلظت عناصر سنگین در رسوبات چاه نیمه سیستان، ایران

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چکیده چاه نیمه سیستان یکی از منابع اصلی آب شهر زابل است که برای آشامیدن، کشاورزی، صنعت و دامپروری استفاده می‌شود. هدف از این مطالعه تعیین سهم طبیعی و فاکتور غلظت عناصر سنگین (کادمیوم، سرب و مس) در رسوبات چاه نیمه سیستان می‌باشد. غلظت عناصر سنگین در رسوبات سطحی شش ایستگاه در سال ۱۳۹۳ مورد بررسی قرار گرفت. برای تعیین غلظت عناصر از دستگاه جذب اتمی (Contr AA 700) استفاده شد. آنالیز چند مرحله‌ای برای تعیین سهم طبیعی و فاکتور غلظت عناصر مورد استفاده قرار گرفت. نتایج آنالیز چند مرحله‌ای نشان داد که سهم قابل توجه‌ای از غلظت عناصر سنگین سرب (۶۳/۶۷٪)، کادمیوم (۵۵/۱۷٪) و مس (۵۷/۱۷٪) مربوط به فعالیت‌های طبیعی می‌باشد. بیش‌ترین غلظت کادمیوم (۰/۸۱ میلی‌گرم بر کیلوگرم) و مس (۵/۵۷ میلی‌گرم بر کیلوگرم) در ایستگاه یک به‌دست آمد و بیش‌ترین غلظت مس (۳۷/۸ میلی‌گرم بر کیلوگرم) در ایستگاه شماره پنج مشاهده شد. کم‌ترین غلظت کادمیوم و سرب و مس به‌ترتیب ۰/۳۴، ۳/۹۵، ۳۱/۴ میلی‌گرم بر کیلوگرم به‌دست آمد.

کلمات کلیدی: آلودگی محیط‌زیست، تجزیه چند مرحله‌ای، مدیریت منابع آبی