
Accumulation and sources of heavy metals in the sediments of Kashaf Rood River

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Abstract: Rivers and wetlands which act as natural absorbents and food filters are important aquatic ecosystems. Kashaf Rood River is a seasonal river in Khorasan Razavi province that has many branches such as Ferizi, Zoshk, Torogh, Kardeh and Radkan Rivers. The aim of this study was to evaluate the concentration and the source (natural and man-made) of heavy metals in surface sediments of Kashaf Rood River. The results showed that the organic part of man-made has no significant contribution to the distribution of Hg in the river while the sulphide part is distributed as the organic phase in the environment because of the very close similarity coefficient with organic part. For Cr the man-made part and organic part have a similarity with each other and have a weaker relation with exchange able and sulphide parts. The results on the Pb also showed that natural resources have no role in the release of Pb in river because its similarity to other parts is very low but it is identical to Cr in other parts. It also became clear that there is a significant difference at 99% level in all four stages of chemical methods for all three metals and also all stations except Pb in the exchangeable and sulphide stages. It was found that the Station4 (Hemat Abad) the highest concentration of Hg. Station5 (Alteimoor) has the highest concentration for Cr. Station2 (Parkand Abad) has the highest concentration of Pb.

Key Words: Heavy metals, Kashaf Rood River, Chemical methods, Stations

Introduction

The importance of aquatic habitats as irreplaceable ecosystems and the maintenance of biological diversity in many species of animals and plants are considered valuable. Heavy

metals include two essential and non-essential elements that are significant in ecological toxicology, so these elements have high stability and are able to cause toxicity in living

organisms (Storelli *et al.*, 2005). Today, due to the impact of human activities on water quality and environmental regulations and issues that have emerged in relation to water pollution, water quality necessary to have great significance (Singhal and Gupta., 1999 ; Jones, 1993). Today the environmental pollution caused by heavy metals is a problem on a global scale (Nriagu and Pacyna, 1988). The use of heavy metals in various industries increases their concentrations in air, water and soil, in addition, the effect of heavy metals accumulation variability and its impact on the health of the biosphere made it too important. (Babaei and Khodaparast, 2007; Nadafi *et al.*, 2006). The sources of these metals in sediments can be caused by natural processes or human activities such as industrial and urban wastewater, fossil fuel combustion, industrial activities and products (Noori and Ferdowsi, 1992; Namminga and Wilhm, 1976). Sediments gradually accumulate on each other over the years and in the process of sedimentation and finally will be considered as the stabilizer of air pollution levels in aquatic ecosystems (Khorasani *et al.*, 2005). Sediments are a reservoir for heavy metals in aquatic ecosystems, which introduce these elements into the water and this can be a potential source of pollution. The study of heavy metals in aquatic environments has shown that heavy metals are not soluble in water for a long time

and are mostly in pending colloids or have been mixed with organic and inorganic materials (Kabata and Pendis, 2001). Due to the toxic effects and the accumulation in different species of fish and even for getting into the food chain, heavy metals are important. These elements are very stable and usually their analysis in the environment takes a long time (Karbassi *et al.*, 2010).

Bing *et al.* (2011) did a study for Historical trends of heavy metals (Cd, Cr, Cu, Pb, Zn, Hg) contamination and their sources in lacustrine sediment from Xijiu Lake, Taihu Lake Catchment in China. The result show that sources of Cr in the sediment were mainly from natural inputs, while other metals, especially Cd, were predominantly derived from anthropogenic sources (Bing *et al.*, 2011).

In the study that Dou *et al.* (2012) did in surface sediments of the eastern Beibu Bay, South China Sea for Distribution, enrichment and source of heavy metals (Zn, Cr, Pb, Cd, Cu, Hg and As). The results showed that in comparison, Zn, Cr, Pb, and partly Cu are predominantly sourced from lithogenic components and Hg and As are mainly from organic matter related to anthropogenic input (Dou *et al.*, 2012).

Harguinteguy *et al.* (2013) studied heavy metals, Co, Cu, Fe, Mn, Ni, Pb, and Zn in surface water and sediments in relation to agricultural practices in the Xanaes River

(Córdoba, Argentina). These results suggest that the levels of pollutants in the river came in pulses from the riverbank. Also these results show the able use of *M. aquaticum* as a suitable accumulation biomonitor at the early stages of heavy metal pollution in rivers (Harguinteguy *et al.*, 2013). The primary objective of this study was therefore to compare the concentrations of the metals mercury (Hg), chromium (Cr) and lead (Pb) appearing in the different fractions of soils derived from sediment of river and determine the source of these metals (man-made and natural) and also the mean difference of these metals in various stages of chemical separation.

Materials and methods

Study area

First, a one-day visit from the river was done to identify the locations and available stations. Sampling sediments in the Kashaf Rood River (36° N latitude and 59° E longitude) was done in Mashhad in Khorasan Razavi province after determining different stations (Fig. 1) in March 2012. The stations were Ferdowsi bridge station, Parkhand Abad station, Sis Abad station, Hemat Abad station and Alteimoor station.

Sediment sample collection and analysis

Samples of sediment were collected from the river bed from five stations. Due to the

shallow river, all river bed sediment samples were collected directly by plastic containers and we didn't need to use of Niskin Sampler for sampling of water and Grab for sediments. Sediment samples were transferred into plastic tubs after the removal. For water samples we used 65% HNO₃ to prevent biological activity in water bottles before transfer to the laboratory. A total of 5 (1 sample from each station) sediment samples were collected from upstream to the station 5. The complete digestion (total) and 4-step chemical separation (fraction) was used for digestion of sediment samples, because the chemical separation was the most reliable method for estimating the pollution and identifying the sources of trace elements and the type of their relations with various types of sediments. This method investigates the sources of elements to see if they are terrestrial or non-terrestrial. The chemical separation increases the estimation of contaminant potential in sediments (Karbassi *et al.*, 2010). For sediment digestion in the four-phase extraction method (the exchangeable phase, the sulfide phase, the oxidation of organic material phase, the resistant phase) 10 grams of each sample was selected and for the sediment digestion in the the exchangeable phase, ammonium acetate (NH₄CH₃COO) 1 M was used. For the sulfide phase hydroxyl amine hydro chloride (NH₃OHCL) 0.25 M and HNO₃ 65% were used. For the oxidation phase



Fig.1: The Satellite location of sampling stations along the Kashaf Rood River

hydrogen peroxide (H_2O_2) 35% and 37% HCL were used. For the resistant phase $HClO_4$ (72-70 percent) was used (Ebrahimpour and Mushrifah, 2008 and 2009; Naji *et al.*, 2010). The quality assurance and quality control were assessed using duplicates, method blanks and standard reference materials, Stock Solution Standard (1ml = 1000 micg/l Hg, Pb, Cr BDH Chemical Ltd Poole England (Spectrosol). The recovery rate for Hg was 94% and for Cr and Pb were respectively 96% and 109%. At the end, to measure the concentrations of all samples of graphite furnace atomic absorption Perkin-Elmer AA3030 model was used. Because of loose links exchange able stage, sulphide and oxidation of organic matter they are related to man-made phase and if we subtract them from total concentration, we can get natural phase or the resistant stage, we used the following formulas 1 and 2.

Statistical analysis

The following formulas were used to calculate the man-made phase and natural

phase (Karbassi *et al.*, 2010):

- 1) Man-made phase = exchange able stage + Sulphide + Oxidation of organic matter
- 2) Natural phase = man-made phase - the total concentration of metal

Cluster Analysis is a series of multivariate methods which is used to find true groups of data or stations. In clustering the objects are grouped such that similar objects fall into the same class (Reghunath *et al.*, 2002). In this study for determine of objects whit same class used Cluster Analysis. We used Difference of Means for showing the difference in concentration at the all station. EXCEL and SPSS statistical software for the analysis of the results was used.

Results and Discussion

The results of experiments of determining the amount of heavy metals in surface sediment samples from the stations under study are shown in tables 1 to 3 and figures 2 to 10.

Figures 2, 3 and 4 show that the highest percentage in all three metals (Hg, Cr, Pb) in the method of chemical separation is dedicated

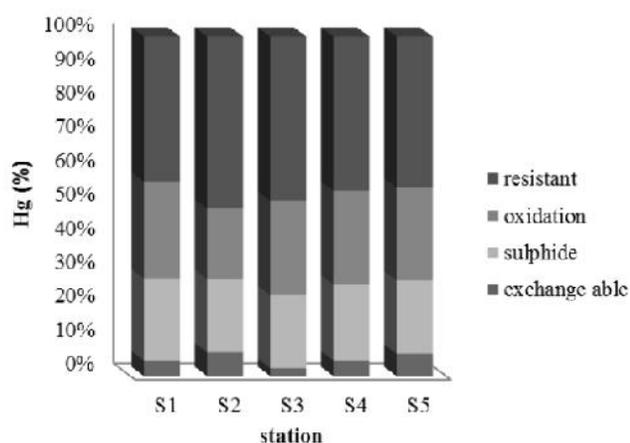


Fig. 2: Determination of Hg percentage in various stages of chemical separation of sediments

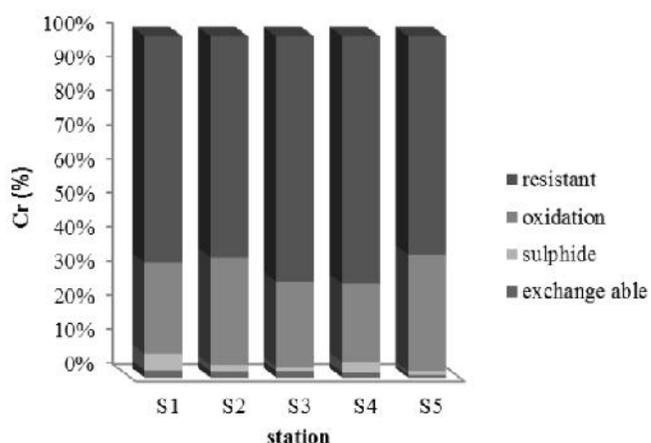


Fig. 3: Determination of Cr percentage in various stages of chemical separation of sediments

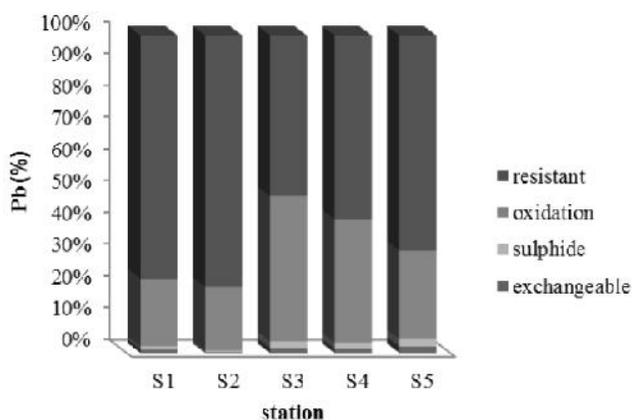


Fig. 4: Determination of Pb percentage in various stages of chemical separation of sediments

Tab.1: Heavy metals concentrations (Mean ± S.D) in sediment by total digestion method (total)

| stations | Hg | Cr | Pb |
|----------|----------|-----------|-----------|
| 1 | 25.5±0.4 | 470.2±0.9 | 270.2±0.3 |
| 2 | 23.5±0.5 | 695.2±0.2 | 490.4±0.5 |
| 3 | 25.1±0.8 | 645.1±0.3 | 156.1±0.2 |
| 4 | 24.6±0.2 | 722.6±0.4 | 205.3±0.6 |
| 5 | 23.4±0.1 | 950.5±0.6 | 170.2±0.8 |

to the resistant stage and the lowest percentage is dedicated to the exchange able part. Figure 3 shows the highest percentage in the resistant stage for Cr, and figure 4 show the lowest percentage for exchange able phase for Hg. Figure 2 shows that the highest percentage of Hg is at station 2 (50.6%) and is related to the resistant part and the lowest percentage of Hg is at station 3 (2.3%) and is related to the exchange able part. It can be seen in figure 3 that the highest percentage of Cr is at station 3 (72.1%) and 4 (72.4%) and is related to the resistant stage, while the lowest percentage of the metal is at the station 5 (0.7%) and exchange able parts. It is estimated from figure 4 that the highest percentage of Pb is at station 2 (79%) and the resistant stage and also the lowest percentage of Pb is at station 2 (0.2%), and the exchange able stage. Generally the following trend in the percentage of metals in various stages of chemical separation was obtained:

Resistant stage > Oxidation stage > Sulphide stage >
Exchange able stage

The above results with the results of the investigation, Chandra Sekhar (2003) in India, Ebrahimpour and Mushrifah (2008) in Malaysia, Kim (2009) in Korea and Naji (2010) in Malaysia, that used chemical separation can be matched. It seems that because the resistant stage is related to the natural section and in

fact the resistant stage is equal natural section, in more of study area in the world has the maximum amount while the exchange able stage that related to man-made section has the minimum amount. Table 1 also shows that Cr has a higher concentration in sediments than other metals (Hg and Pb). Also table 1 shows that lowest change is related to Hg, but Cr and Pb have much change. In comparison the result of table 1 with the work of Lashkaripour *et al.* (2009), the amount of Cr and Pb in this study has more concentration of wells near the river, but the amount of Hg is lesser.

Table 2 shows that Hg has a higher percentage of man-made sources than natural sources, while the natural source is higher for two metals of Cr and Pb. This matter shows that more of Hg is distributed by activities that related to human. In figure 5 it can be seen that the branches of natural and man-made sources are very close together and also the branches of sulphide and oxidation are too close together while the branches (sulphide and oxidation) have a weaker relation with exchange able parts. Figure 6 shows the branches of man-made and oxidation and also the branches of sulphide and exchange able are close together while all the branches have a weak relation with the natural source. The cluster analysis of Pb (Fig. 7) is similar to Cr, but there is a lower percentage of similarity between the other parts and the natural source.

Tab. 2: The contribution of natural and man-made sources in the distribution of heavy metals in sediments.

| Heavy Metals | Mean of total concentration (ppb) | Man-made (%) | Natural (%) |
|--------------|-----------------------------------|--------------|-------------|
| Hg | 24.4 | 53.7 | 46.1 |
| Cr | 696.7 | 32.2 | 67.6 |
| Pb | 258.4 | 29.8 | 70.1 |

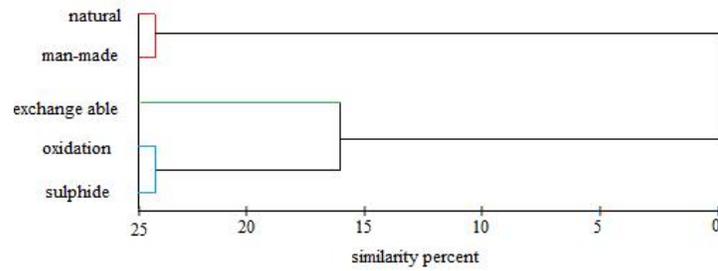


Fig. 5: Cluster analysis of Hg.

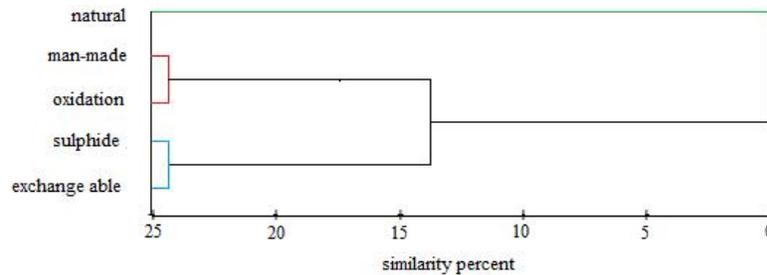


Fig. 6: Cluster analysis of Cr.

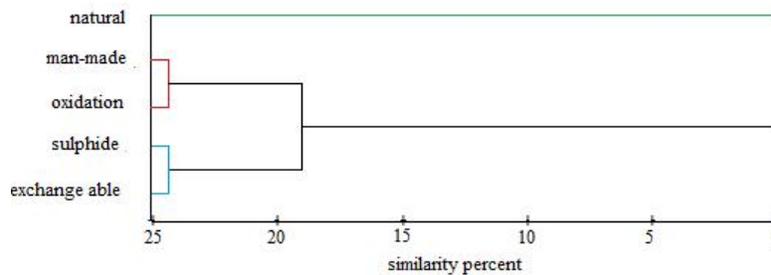


Fig. 7: Cluster analysis of Pb.

It can be deduced from Figures 8 and 9 that the highest pollution for Hg and Cr are at stations 4 and 5 that this matter shows the role of these stations in pollution of these metals in the river. It seems that Agricultural wastes including surplus pesticides and fertilizers and electroplating industries at stations 4 and 5 have an important role for pollution of these metals in the river. But Figure 10 show that the stations 1 and 2 have important role in pollution of pb. For Pb the Parkand Abad refinery at the

station 2 has an important role in the pollution of this metal in the river. Table 3 shows that there is a significant difference in the level of 99% in all four stages of chemical separation method and for all three metals, Hg, Cr, Pb and also all stations except Pb in the exchangeable and sulphide stages that have significant difference in the level of 95%. This suggests that there is a high difference in metal concentrations between stations in all four stages.

Tab. 3: The analysis of Hg, Cr and Pb variance in various stages of chemical separation (ppb).

| Hg | | | | | |
|---------|----|---------------|----------|-----------|-----------|
| S.O.V | df | Exchange able | Sulphide | Oxidation | Resistant |
| station | 4 | 1.07** | 1.61** | 6.5** | 2.9** |
| error | 8 | 0.02 | 0.07 | 0.1 | 0.1 |
| CV (%) | - | 7.92 | 3.74 | 3.73 | 2.14 |
| Cr | | | | | |
| station | 4 | 13.4** | 122.9** | 18069** | 35203** |
| error | 8 | 0.1 | 0.12 | 0.13 | 0.09 |
| CV (%) | - | 3.32 | 2.36 | 0.18 | 6.63 |
| Pb | | | | | |
| station | 4 | 1.58** | 1.78** | 1706** | 53745** |
| error | 8 | 0.1 | 0.11 | 0.51 | 0.07 |
| CV (%) | - | 11.45 | 9.79 | 0.95 | 0.14 |

** Significance at the 99% level.

Conclusion

The results indicate that for Hg the sulphide part is released in the environment as organic phase because of the very close similarity

coefficient with organic part. The man-made and organic parts for Cr have a very close similarity with each other and have a weaker

relation with exchange able and sulphide parts. This shows that the man-made sources of Cr in the environment have been as organic phase

and then in a relation with exchange able and sulphide parts and the natural part has a weaker relation with the above-mentioned

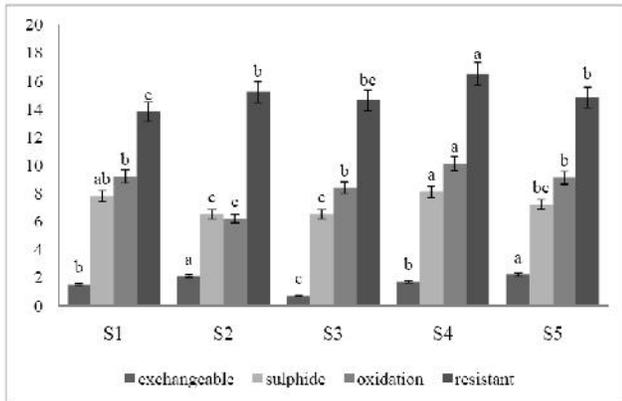


Fig. 8: The mean difference of Hg in various stages of chemical separation (ppb).

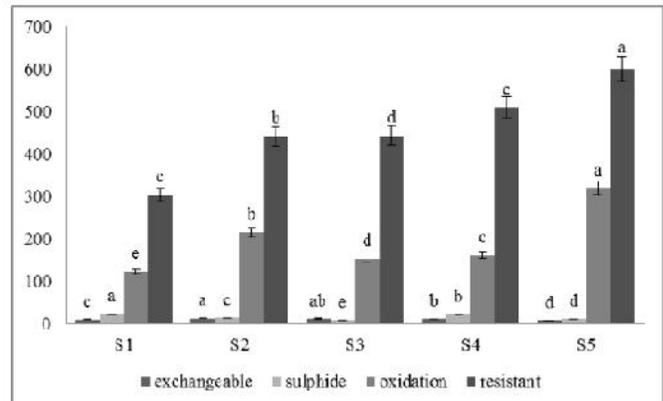


Fig. 9: The mean difference of Cr in various stages of chemical separation (ppb).

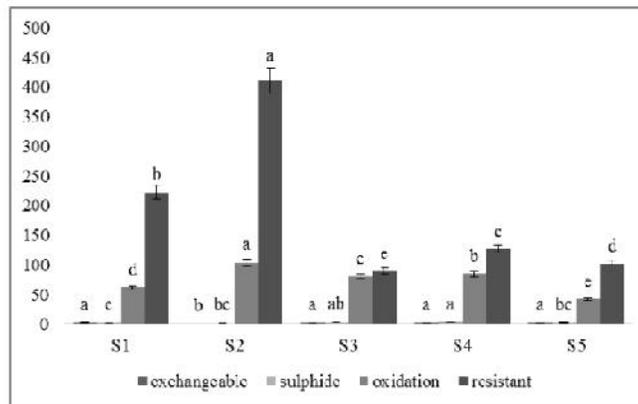


Fig. 10: The mean difference of Pb in various stages of chemical separation (ppb).

parts. We can say that natural resources have virtually no role in the release of Pb in the river, because its similarity percentage is very low than other parts, but the other parts are almost the same as Cr. It can be deduced for Hg that the highest value for sulphide, oxidation and

resistant parts is at station 4. This represents a very high proportion of station 4 in the pollution of this metal in the river. For Cr the oxidation and resistant stages which have the highest value happens at station 5, that this shows the role of this station in the pollution of Cr. For Pb

the most contribution is related to oxidation and resistant stages at station 2 which show the pollutant role of this station for this metal.

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