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Concentration Measurement and Evaluation of Mobility of Heavy Metals of Zayandeh-Rood River Sediments

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Metallic contaminants associated with sediments showed various behaviours depending on physicochemical conditions. Zayandeh-rood is one of the most important rivers of the centre of Iran. It sources from Zagros Mountains in Charmahal Bakhtiari province and flowing about 350 km, ends to the Gavkhooni marsh in the east of Isfahan. So far, many researches have been conducted to measure the concentration of heavy metals in the environmental samples all over the world and for this purpose, different methods have been proposed. Although several reports have been released concerning the amount of heavy metals concentrations in the air, water or food stuffs, there is less information available about the concentration of heavy metals in the sediments of the rivers and their mobility. The required samples for this research have been taken from 5 different areas: Zaman Khan Bridge, Falavarjan, Vahid Bridge, Ziar and Varzane. Two samples were collected from each of these regions. A five-step sequential extraction procedure, modified from the Tessier method, was applied to the determination of some heavy metals (Cu, Mn, Cd, Ni, Co, Cr, Zn and Pb) in sediment in order to evaluate the potential mobility of fixed metals. The amount of heavy metals were measured utilizing atomic absorption spectrometer (model AA-220, Varian) equipped with graphite oven GTA-110 and the accuracy of part per billion (ppb). A considerable amount of heavy metals exists in the sediments of Zayandeh-rood. These metals and specially manganese, cadmium and nickel have higher poisonous and carcinogenicity effects and mobility. These results therefore help to improve the waste management of such contaminated sediments.

Key Words: Mobility evaluation, Heavy metals, Sediment, Zayandeh-rood river, Sequential extraction procedure.

INTRODUCTION

The determination of trace elements in environmentally significant solid substrates has attracted special attention as a point of reference for toxicity assessment. Elements present at even minimal concentrations can exert fundamental influence on vital functions proportion to their amounts. During the last two decades, analytical chemist have come to realize that the impact of metal ions on the environment cannot be

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evaluated by measuring merely the total concentration of individual species, because the mobility, the bioavailability and the ultimate impact of anthropogenic metal ions on ecological systems and biological organisms largely depend on their chemical forms, their types of binding, the reactivity of their links with particulate forms as well as on the soil-solution equilibriums at the solid-water interface[1-4].

Zayandeh-rood is considered as one of the most important rivers of the center of Iran passing Charmohal Bakhtiari and Isfahan provinces. Its source is located in the Zagros Mountains to the Gavkhuni marsh[5]. It sources from Zagros Mountains in Charmahal Bakhtiari province and ends to the Gavkhooni marsh in the east of Isfahan.

The length of the river is about 350 km and several industrial units and farms have been spread around the river in the above mentioned provinces[5]. Most of the agricultural and industrial effluents are discharged into the river and make the water polluted[6]. The main resources of the discharge of heavy metals into the environment are iron and steel industries, power stations, combustion of rubbishes and the exhaust pipes of cars[6].

Nowadays, the poisonous effects of heavy metals are well recognized and determination of the amount of which in environmental samples is of considerable importance. In the last decade, a great deal of information has been released about the harmful effects of heavy metals on human health[7-9]. Since the heavy metals agglomerate in the sediment of the river water and are separated by a shock or a change in the physico-chemical conditions of water, the measurement and evaluation of their mobility in the sediment of the river are of great importance[10-13]. In order to evaluate the mobility of heavy metals from sediments, various sequential extraction procedures have been developed. The number of steps in these extraction varies from 3 steps to 6 steps and the extraction procedures adopted can show different results[12-17], which has been widely adopted by a large group of specialists[12-19]. Five-step sequential extraction method was applied in this research study. Sediment samples were taken from five different areas of the river. These parts of rivers are near anthropogenic contributions such as river discharges. Five-step method and spectrometric atomic absorption with graphite oven (GF-AAS) were applied simultaneously to extract heavy metals (Cu, Mn, Cd, Ni, Co, Cr, Zn and Pb) and measure their mobility. The purpose of this study was to develop and examine the merits of a method of sequential selective extraction for partitioning particulate trace metals into chemical forms likely to be released in solution under various environmental conditions.

EXPERIMENTAL

The required samples were collected from surface sediment in the depth of 0-5 cm of the river from 5 different regions. Two samples were taken from each region with an average distance of 10 meter from each other using echman instrument. Sampling areas were Zamankhan Bridge, Falavarjan, Vahid Bridge, Ziar and Varzane.

Samples were dried in a thermostatic oven in the temperature of 105 °C. Dried samples were ground in a mortar and made homogeneous and then they were shifted before doing the 5-step sequential extraction method to measure the concentration of heavy metals. The following five steps sequential extractions were applied.

Step-1: Exchangeable heavy metals. At first, 12 mL of 1.0 M sodium acetate solution was added into the 3 g of dried sample and stirred continuously for 1 h by the use of a shaker. In order to separate liquid phase from solid phase, test tubes containing samples, were centrifuged in a centrifuge apparatus for about 15 min. The liquid phase was transferred into a 25 mL volumetric flask and was made voluminous by the double distilled water.

Step-2: Connected to the carbonates. 12 mL of 1.0 M sodium acetate solution was added to the remaining solid phase of the first step. The pH of 1 M sodium acetate solution had been stabilized in the pH 5 by adding acetic acid. The procedure was followed by stirring for *ca.* 5 h and centrifuge. Similar to the first step, liquid phase was transferred to 25 mL volumetric flask and made voluminous by the double distilled water.

Step-3: Connected metals to the iron and manganese oxides. 20 mL of 0.04 M hydroxylamine hydrochloride in 25 % (v/v) of acetate acid was added to the remaining solid phase of the second step and stirred for *ca.* 16 h. (Like the previous steps, liquid phase was transferred to a 25 mL volumetric flask and 25 mL volumetric flask was made voluminous by the double distilled water). The experiment was conducted at 96 ± 3 °C temperature by the continuous shaking.

Step-4: Connected to the organic materials and sulfides. 3 mL of 0.02 M nitric acid and 5 mL of 30 % hydrogen peroxide, pH of which was changed to 2 by nitric acid was added to the remaining solid phase of the third step. The mixture was heated in thermostatic bath at 85 ± 2 °C temperature for *ca.* 2 h. Again 3 mL of hydrogen peroxide (30 %) was added to the sample and once more heated in the same preceding conditions for *ca.* 2 h with a little shake. After cooling, 5 mL of 3.2 M ammonium acetate solution in 20 % nitric acid was added and sample was made voluminous by the two times distilled water until 20 mL and it was shaken continuously for *ca.* 0.5 h. Liquid phase was transferred to a 25 mL volumetric flask and 25 mL volumetric flask was made voluminous by the double distilled water.

Step-5: Connected to silicate structures of solid particles. Remaining solid substance of the 4th phase was transferred to the poly tetrafluoroethylene (PTFE) container to which 10 mL nitric acid (C) was added under the extractor hood. Having covered PTFE by watch-glass, it was heated on the hot plate to reduce the volume of solution to the half. Then 2 mL HF acid (C) was added to the sample and heated to be dried. For the second time, 5 mL of nitric acid (C) was added and heated to make the volume of sample half. Then the solution was cooled, diluted and filtered. The filtered solution was transferred into the 25 mL volumetric flask and was made voluminous by the double distilled water.

Measurement method: In order to measure concentration of heavy metals the atomic absorption spectrometry method with graphite oven was used. Measurements were conducted by the atomic absorption spectrometer (model AA-220) made by Varian company, equipped with graphic oven GTA-110. The wave lengths that were used include Mn 279.5 nm, Cu 324.8 nm, Zn 213.9 nm, Cd 228.8 nm, Co 240.7 nm, Ni 232.0 nm, Pb 217.0 nm and Cr 357.9 nm.

RESULTS AND DISCUSSION

Since the concentration of heavy metals were not the same in the sediment of the different points of the river and the water pollution was not similar in the different parts, samples were taken from five different areas along the river and the concentration of heavy metals of each region was determined distinctly.

In fraction 1 (exchangeable metals), in all of the stations concentrations found for exchangeable in all of the heavy metals except Mn (1.25 μg/g) are lower than their respective detection limits. In this fraction concentration percentage of Cd, Co and Mn are more than another heavy metals.

In fraction 2 (metals bound to carbonates), concentration of Mn, Ni and Co in different stations are more than another heavy metals. Concentration of Cd, Cu and Pb are inconsiderable. In third fraction, concentration percentage of Cd, Co and Mn in that manner are more. But quantity of Mn, Ni and Zn are more than others.

It is observed that high quantity of Mn, Zn and Ni in fraction 4 and concentration percentage of Cd, Mn and Co is more than rest. In residue fraction, high concentration of all trace elements has been observed but concentration percentage of Cd, Co and Ni are more than others. The concentration of Mn, Zn and Ni are more than other heavy metals.

In all of the 5 sampling station, almost concentration of Mn, Zn and Ni are more than another heavy metals. Cd, Cu and Cr showed minimum concentration in this river. The amount of heavy metals in the sediment of the river as follows:

$$Mn > Zn > Ni > Pb > Cr > Co > Cu > Cd$$

Table-1 indicate the results of 5 step sediment analyses in different sampling areas. If we consider the mobility of metals equal to the concentration percentage of released in the 1st and 2nd phases of 5-step sequential extraction, the mobility of metals in the sediment of the river is as follows:

$$Cd > Co > Mn > Cu > Ni > Cr > Pb > Zn$$

There is considerable concentration of heavy metals observed in the sediment of the river and because of the poisonous effects of metals, quality control of water is of great importance. Because of the mobility of poisonous heavy metals and the location of treatment plants of drinking water of Isfahan and Yazd in the vicinity of the river, quality control of water seems more essential.

The total concentrations of 8 heavy metals in the river sediment samples collected from 5 different points are shown in Fig. 1.

TABLE-1
CONCENTRATION OF HEAVY METALS IN DIFFERENT STATIONS (µg/g)

	Mn	Cu	Zn	Cd	Pb	Cr	Ni	Co
Station No. 1								
Step1	1.25	0.07	0.08	0.22	0.45	0.33	0.48	0.51
Step2	2.53	0.34	0.24	0.32	0.30	0.43	1.03	0.85
Step3	10.16	1.16	10.13	0.21	1.25	0.89	1.75	1.14
Step4	30.22	1.24	14.09	0.17	8.15	2.32	19.82	0.12
Step5	36.8	4.86	14.87	0.96	8.75	4.61	17.93	7.87
Station No. 2								
Step1	0.25	0.00	0.00	0.13	0.39	0.09	0.35	0.53
Step2	2.96	0.33	0.52	0.47	0.25	0.20	1.53	1.39
Step3	7.52	1.19	8.93	0.26	3.05	1.21	1.50	1.75
Step4	25.11	1.04	13.56	0.21	7.90	3.16	18.26	0.98
Step5	46.71	5.25	15.37	0.84	9.04	9.75	16.34	8.56
Station No. 3								
Step1	1.72	0.14	0.00	0.14	0.37	0.10	0.41	0.49
Step2	2.13	0.22	0.31	0.29	0.33	0.38	1.47	0.95
Step3	7.21	0.67	8.11	0.20	3.60	2.81	1.22	1.57
Step4	15.63	0.67	11.22	0.22	7.08	3.08	14.93	0.77
Step5	22.55	4.22	11.50	0.50	10.12	7.44	15.01	8.21
Station No. 4								
Step1	2.24	0.12	0.11	0.20	0.16	0.26	0.53	0.49
Step2	4.38	0.34	0.37	0.22	0.28	0.46	1.37	0.85
Step3	8.37	0.56	7.92	0.28	3.22	2.76	1.14	1.36
Step4	14.88	0.23	12.61	0.21	6.51	3.12	13.16	0.73
Step5	20.89	4.73	19.00	0.47	9.23	6.81	14.49	8.14
Station No. 5								
Step1	2.08	0.10	0.11	0.15	0.10	0.21	0.41	0.67
Step2	3.03	0.28	0.22	0.30	0.24	0.22	1.08	0.89
Step3	9.69	0.50	7.18	0.27	1.10	1.74	0.89	1.44
Step4	10.76	0.17	13.21	0.13	5.14	3.10	12.86	0.84
Step5	18.54	3.86	13.50	0.60	9.82	8.89	9.98	8.46

Concentration of Mn in sampling site 1 and 2 is high because Navid manganese is near this two sampling sites. Concentration of Pb, Cr, Zn, Cu, Cd and Co is approximately constant in all of the sampling sites but the concentration of Mn, Zn and Ni is more than other elements. These results (except Pb) are agreed with Talebi *et al.*[20].

Conclusion

Regarding to the results obtained from the 5-step sequential extraction and the analysis of samples, we can judge about the mobility of heavy metals. The study of heavy metals mobility is of considerable importance when pH of the river is not constant or whenever the industrial sewages with acidic pH are discharged into the

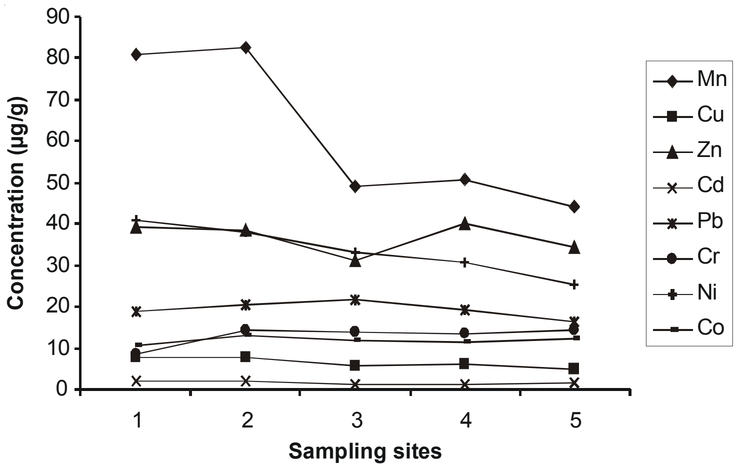

Fig. 1. Concentration of heavy metals associated with sediments at different points

river and cause sudden shocks. Those metals which have higher mobility and have agglomerated in the sediment of the river for a very long time cause restriction in the consumption of water. As the results of this research study revealed great amount of the metals in the sediment of the river indicate and due to the dangers resulting from heavy metals, preventing from the discharge of industrial sewage particularly acidic sewage and controlling the pH of water along the river specially above the treatment plants of drinking water of Isfahan and Yazd is of greats importance.

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