Evaluation of lead and zinc concentration and their changes in surface sediments of Zayanderood River (Iran)

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Abstract
Zayanderood is the only permanent river in central iran and the main feeding source for regional aquifers that plays a key role in providing esfahan province with drinking water. Because of the importance of this river in terms of its various uses and the fact that it receives waste materials from heavy industries, In order to study the motion changes of the potentially poisonous elements of lead and zinc and their effective factors in zayanderood river, Eleven surface sediment samples were taken along the beds of the river course (up stream to down stream). Total metal concentrations were obtained after acid digestion and then analysis was carried out by ICP-AES. The results from the analysis of fine grain sediments (particles smaller than 63 μ) indicate a high concentration of lead and zinc in several sampling stations. The concentrations of zinc & lead have been 494.3 ppm and 40.45 ppm respectively. The separation of human factors from natural ones was done by comparing lead & zinc concentrations at" Zaman khan" bridge station (as the reference sample) with those of the other sampling stations by obtaining the enrichment coefficient. Taking into account the results and coefficients, obtained and comparing those with widely used international standards, it seems the two elements of lead and zinc have not natural sources in some of the stations.

Keywords: Heavy metals, Surface Sediment, Lead, Zinc and Zayanderood River

I. INTRODUCTION

Most environmental regulations have established limitations for total heavy metal concentration in waters so that they do not exceed some quality criteria for the protection of the environment. However, it has been widely recognized that long-term infringement of water quality through release of sediment-bound metals may be of greater significance. Metal contents in sediments are involved in environmental research, where short-term or past-pollution events are not reflected in water analyses. Heavy metal species in the aquatic environment are distributed among water-soluble species, colloids, suspended matter and sedimentary phases. Metal concentration in both river water and sediment are strongly changed by deposition–remobilization processes. Sediments have a high storage capacity for pollutants, in any part of the hydrological cycle far less than 1% of these are actually dissolved in the water; more than 99% are stored in the sediments (Filgueiras et al, 2004).

Trace elements in aquatic systems may be attributed to natural geologic sources or to past and present land uses. Although heavy metals may originate from natural sources, human activities such as mining, agriculture, and urbanization can affect its concentration and spatial distribution (Varkouhi, 2007)

Because of the population increase and more and more need for different water, food, energy, etc sources and the expansion of industrial and agricultural activities, these sources especially those on the surface are increasingly exposed to various pollutants. Heavy metals are some of the most important of such pollutants. Lead is a well-known pollutant of the environment. It is dangerous to the life of man and the ecosystem in general due to its high durability in nature. This element accumulates first in surface soils. Zinc is very mobile along weathering processes, too. It has a high potential for combining with both organic & inorganaic group, and adjusts the biological interactions and analysis of carbohydrates. Sediments gradually accumulate along with the time due to sedimentary processes and may finally be considered as an evidence for pollution (degrees). The amount of heavy metals in different sediment layers indicates how much of these metals existed a how the ecosystem was polluted at the time of the formation of those layers.

Several investigators research about heavy metals in surface sediment. Varkouhi et al, (2006)a and (2007)b determined the relation of lead concentration in streambed sediments to natural and anthropogenic factors in Veysian River. Also, Schenato et al, (2008) research about heavy metals pollution affected by different land using in Brazil. Bravo et al in our research determined Methyl-mercury in freshwater sediments contaminated by a chlor-alkali plant.

The Isfahan province in Iran was chosen for this study because this is one of the most important industrial centers of Iran.

The aim of this work is study the distribution of heavy metals such as Pb and Zn in surficial sediments of Zayanderood River. Because of the importance of this river in terms of its various uses and the fact that it receives waste materials from heavy industries., such as esfahan steel company, mobarake steel complex, polyacril and the other chemical factories, power plants, oil refinery, and military industries, the basis of this study is an examination of the river for pollution with elements like pb and zn and geochemical studies on it. For this purpose, sediments collected 11 different sampling stations upstream and downstream of important industrial areas along the Zayanderood River during spring season 2008.

II. MATERIALS AND METHODS

A. Geographical location of the region studied

From the geological viewpoint, the region studied includes three major geological zones,i, e. zagros, sanandaj- sirjan and central iran. Each of these zones has affected this region with their special characteristics (aghanabati, 2004). The rocks composing the river bottom in the region, mostly include jurrasic sedimentary, and metamorphic rocks and new quaternary alluviums among which fine grained rocks (sedimentary and metamorphic) play a essential role in increasing the concentration of the elements studied naturally in zayanderood (river), moreover, because of high erodibility of the above mentioned formations the amount of fine grains increases along with the river (forstner, 2004), grains.

The watershed of zayanderood river is situated in the middle of the central plateau of iran between $50^{0},02^{/}$ and $53^{0},24^{/}$ east longitude and $31^{0},11^{/}$ and $33^{0},42^{/}$ north latitudes this watershed area about 41550 square kilometers with an average altitude of 2514 meters. Zayanderood is the only permanent river in this basin; it originates from the eastern slopes of zardkouh – e – bakhtiari mount, in central zagros and takes its course in southwest- northeast direction down to zayanderood dam. From this point on, the river change direction toward the south east, and after completing around 435 kilometers and passing through the north of "charmahal" province & esfahan plain, ends in "gavkhouni" marsh about 20km from "varzane" town (jafari, 1997) (Fig.1).

B. Reagents

All reagents were of analytical grade. De-ionized water, further purified using a Milli Q system (Millipore, Molsheim, France) was used throughout Stock standard solutions of metals (1000 mg ml^{-1}) were obtained by dissolving the pure metals. Standard solutions were employed for calibration in the analysis of extracts. Calibration standards made in 1% volume/volume HNO_3 were employed for analysis of digests. HCl, HNO_3 ,$HClO_4$, and HF extra pure were purchased of Merck company.

C. Sample Collection and Analysis

Sampling the sediments of Zayanderood River was done in ten stations along the river in spring 2008 in order to determine the concentrations of lead and zinc and the factors controlling their mobility and carrying them downstream as zayanderood heterogene hydrology, the samples were taken from width of the river as a mixed from the most recently constructed channel.

Approximately 2 kg of sediment were collected at each of the sampling points at the sediment–water interface) surface river sediments (using a plastic scoop and kept in polyethylene containers. Sampling was confined to the upper 10-15cm of streambed sediment to insure that the most recent deposition was being sampled. Once in the laboratory, samples were air dried inside a laminar flow chamber, sieved using nylon sieves (particle diameter <63µ)and then stored in polyethylene bottles at room temperature in a desiccator.

Three samples were taken at each station and the samples average was selected for analysis. Meanwhile, in order to determine the enrichment coefficient and pollution rate, three more sediment samples were chosen at non- polluted (upstream) parts of the river.

The sediment samples were digested with a mixed-acid solution consisting of HCl, HNO_3 ,$HClO_4$,and HF. This procedure (total digestion) is effective in dissolving most minerals, including silicates, oxides and sulfides; resistant or refractory minerals such as zircon, chromite, and some tin oxides are only partially dissolved. Previous investigations using a variety of materials support the completeness of the digestion (Varkouhi et al, 2006). Results are reported for 2 trace elements analyzed by ICP-AES (Varian, 710 ES) (High Resolution Inductively coupled plasma - atomic emission spectroscopy) at the laboratory of scientific and applied research center of the geological survey of iran. Limits of determination (LOD) for the total digestion method as well as a statistical summary of mean values, standard deviations, and median values for four National Institute of Standards and Technology (NIST) standard reference materials are determined.

D. Statistical analysis

All analyses were performed on triplicate samples and statistical analysis data (presented as mean ± SD) were subjected to analysis of variance (ANOVA). The data were tested for homogeneity of variances at a significance level of $P < 0.05$ and probability values of less than 0.05 were considered as statistically significant (one-way ANOVA). For pairwise comparisons between lead and zinc concentrations in any station paired t-test were performed. SPSS version 11.5 (SPSS Inc., Chicago, IL, USA) was used for statistical analysis.

III. RESULTS AND DISCUSSION

Streambed sediment is the best indicator for assessing the occurrence and spatial distribution of heavy metals on a watershed wide scale in the zayanderood River study unit and for developing relations between study units and land use.

The pb and zn concentrations show a significant increase related to the samples taken from no polluted spots (table1) the enrichment rate and the percentage of the effect of non-natural agents in the distribution of polluting elements in the sediment, have been calculated based on a comparison of the concentration of those elements with non- polluted samples from upstream. Thus, pb concentration levels are highest at polchoum and zarinshahr stations respectively while zn. Levels have been abnormally high only at polchoum station.
The raise in pb and zn concentrations (40 ppm and 634.2 ppm) respectively in zayanderood sediments (based on statistical background) and the raise in enrichment rate (Eby, 2004; Miller, 2008) all show the effect of human on the existing pollution in zayanderood sediments. Table 2 shows the enrichment coefficient obtained for the elements studied. Table 3 shows geochemical correlation between the polluting elements, studied in this paper. The positive correlation of elements together is indicative of releasing, transfering and sedimenting of these elements under similar condition, and their low corelation with the AL element can indicate a lack of dependence of these elements on mother elements and amount of geochemical background of the region. In general in environmental analyses, the enrichment rate is used to distinguish the effect of man-generated factors from natural factors in a basin which may be an expression of the effect of external (man –made) factors.
In this study, the element Al has been considered as reference (Eby, 2004) due to its geochemical nature and insignificant changes it shows in geochemical environments.

IV. CONCLUSION

Changes in the concentration of elements in Zayanderood River (from zayanderood dam to Gavkhouni marsh) are in the first place, a function of the distance of sampling points from polluting sources (entrance of industrial, agricultural, and urban wastes). After that, these changes are controlled by the geological formations (i.e.fine shally rocks) composing this basin (especially the river bottom) and the amount of fine grain sediments.
The results from the analysis of the samples taken from industrial areas, especially high amounts of zn (494.3ppm) and pb (40.46ppm) at polchoum and zarinshahr stations and high enrichment rates shown for these elements well prove this idea. These enrichments, especially after the waste from south Esfahan treatment plant and various industrial, agricultural and urban sources enter the river, show a significant increase. The enrichment rates more than many indicate the effect of man-generated activities on Zayanderood River. The exchange rate of potentially poisonous elements in sediments is a lot higher than in water environments. Because of the long durability of these elements, polluted soils can not easily be freed from pollution & their removal may take hundreds or thousands of years. For this reason, and taking into account the direct relationship of human beings and organisms with water and sediments of Zayanderood River, special administrative programs with the purpose of reducing pollution are required.

REFRENCES

[1] Aghanabati, s,Geology og Iran, Geological and explorations survey of Iran pub, 2004.
[2] Bravo., A.G, Bouchet., S, Angureano., Y, Zopfi,J, Methylmercury concentrations and sulphate-reducing bacteria in freshwater sediments contaminated by a chlor-alkali plant: Babeni Reservoir, Romania, RECENT ADVANCES in ENVIRONMENT, ECOSYSTEMS and DEVELOPMENT.
[3] Eby, G.N , Principle of environmental Geochemistry., Thompson, 515 P, 2004.
[4] Farkas, A; Erratico, C; Vigano, L., Assessment of the environmental significance of heavy metal pollution in surficial sediments of river Po, Chemosghere, Vol 68, N 4, 2007, 761-768 P.
[5] Filgueiras., A.V, Lavilla., L, Bendicho., C, Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River) Galicia, Spain (using chemometric analysis: a case study, Science of the Total Environment 330 (2004) 115-129
[6] Forstner, U.,. Sediment dynamics and pollutant mobility in river: An interdisciplinary approach, lake and reservoirs: Research and management , vol 9, 2004, 25-40 P.
[7] Kabata pendias,A; Mukherjee A.B, Trace elements from soil to human, Springer Verlag, 2007, 561.
[8] Miller,J. contaminated rivers, Speringer verlag, 2007, 418P.
[9] Owens.PN, Batalla.R.J, Fine-Grained sediment in River systems:Environmental significance and management issues,River Res.Applic.21, 2005,693-717.
[10] Varkouhi., S, Geochemical Evaluation of Lead Trace Element in Streambed Sediments, Proceedings of the WSEAS Int. Conf. on Waste Management, Water Pollution, Air Pollution, Indoor Climate, Arcachon, France, October 14-16, 2007
[11] Varkouhi., S, Lasemi., Y, Kangi., A., Geochemical Evaluation of Toxic Trace Elements in Recent Wind Driven Sediments of Zahedan Catchment Area, Proceedings of the 5th WSEAS International Conference on Environment, Ecosystems and Development, Venice, Italy, November 20-22, 2006.
[12] Schenato., F, Schröder., N, Martins., F, Assessment of Contaminated Soils by Heavy Metals in Municipal Solid Waste Landfills in southern Brazil, WSEAS TRANSACTIONS on ENVIRONMENT and DEVELOPMENT, Issue 9, Volume 4, 2008.

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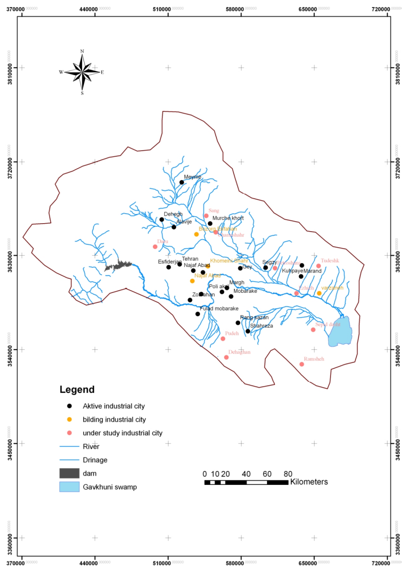

Fig 1. a- The map of zayanderood watershed and distributaries

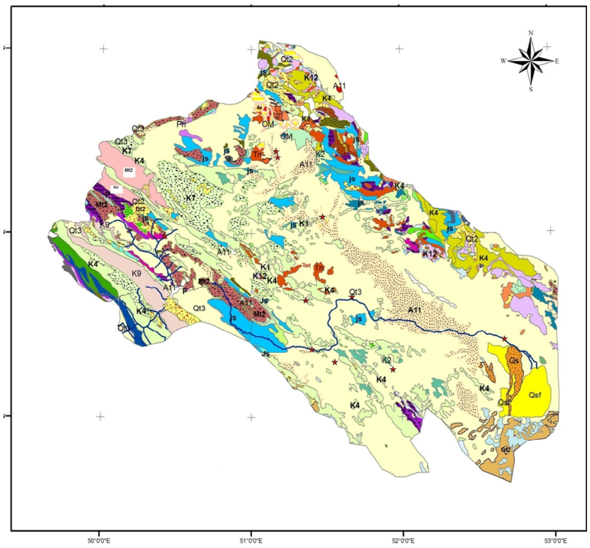

Fig. 1.b- the geological map of zayanderood watershed with different formations in route of river and sampling stations

Figure 1-b- (Continued) The geological map legend

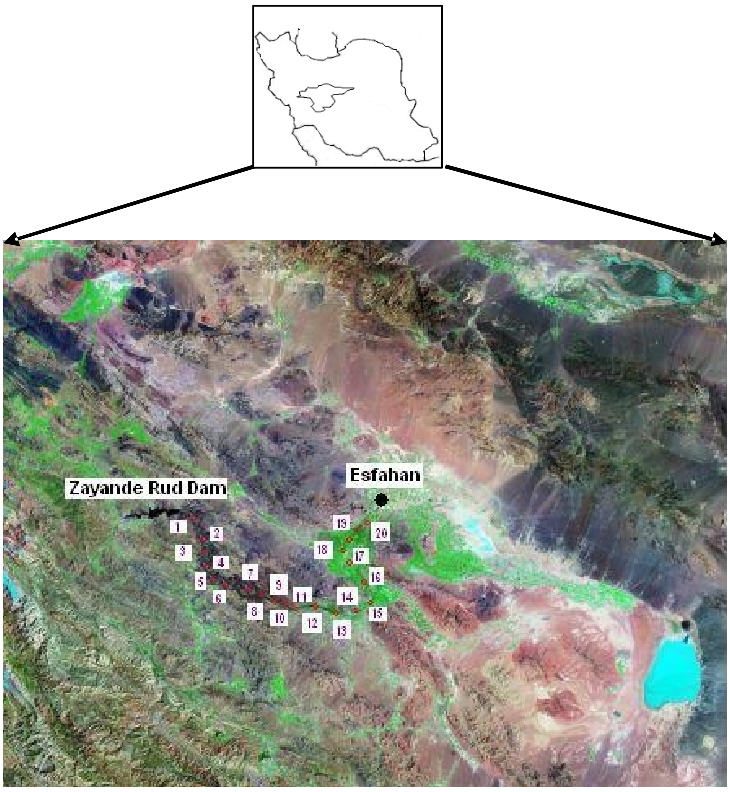

Fig. (1-c) - Geographical position of region and sampling stations

Table.1- concentration of lead and zinc in sediments of Zayanderood River

Sample site		Pb (ppm)	Zn (ppm)
Zaman khan	Standard sample	13.1	63.25
Cham aseman	1	13.45	76.09
Zarin shahr	2	38.37	74.91
Baba mahmood	3	19.66	73.9
Felavarjan	4	36.83	151.5
Ghadir	5	33.46	141.9
Choum	6	40.46	494.3
Ziar	7	26.13	149.4
Sharif abad	8	15.6	75.73
Ejie	9	15.98	65.59
Varzane	10	15.66	78.7

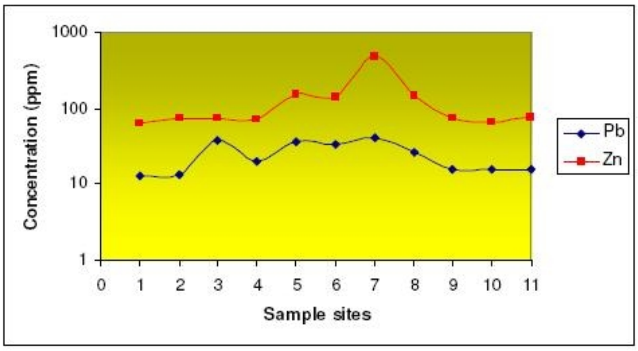

Fig. 2 shows the changing trend of the elements studied in the sediments of Zayanderood River

Table.2- calculated enrichment coefficient for studied elements in Zayanderood River

(Ef) Sample sites	Pb (ppm)	Zn (ppm)
Cham aseman	1.03	1.2
Zarin shahr	3.93	3.18
Baba mahmood	1.5	1.16
Felavarjan	2.81	2.4
Ghadir	2.56	2.24
Choum	3.09	7.82
Ziar	2	2.36
Sharif abad	1.19	1.2
Ejie	1.22	1.04
Varzane	1.2	1.24

Table.3- correlation coefficient of studing elements in sediment of Zayanderood River

	Pb	Zn	Al
Pb	1		
Zn	0.21	1	
Al	-0.22	-0.43	1