Caspian J. Env. Sci. 2008, Vol. 6 No.2 pp. 133~140

CJES
Caspian Journal of Environmental Sciences

[Research]

Land use effects on heavy metal pollution of river sediments in Guilan, southwest of the Caspian sea

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ABSTRACT
Studies have showed the River Siahroud is the main contributor to the present pollution of Anzali Wetland in Guilan. Therefore, this study was initiated to evaluate the spatial distribution of metals pollution on the River Siahroud sediments in Guilan.Surfacial river sediment samples along this river were taken during five consecutive seasons at eight sampling stations and analyzed for availability of Fe, Mn, Pb, Zn, Cu, Cr, Cd metals. Canonical correlation demonstrated that the total organic carbon (TOC) was of great importance in co-precipitation of Zn while Cu and Pb were mainly related to hydrous iron oxides. Also, in the interest of pollutant finger printing, factor analysis showed that extractable Zn, Cu, Fe, Cd and Mn were attributed to the present agricultural fields while industrial site of Rasht City was the major contributing factor for the extended levels of Cr in the study area. Moreover, Pb level was mainly relevant to urban landuse in Rasht. Cluster analysis demonstrated that there was a rising metal pollution level in the River Siahroud from upstream to downstream suggesting that Anzali Wetland pollution could be highly related to loading of heavy metals by the River Siahroud sediment.

Keywords: Canonical correlation; Cluster analysis; heavy metal pollution; Siahroud River, River pollution.

INTRODUCTION
River sediments are essential and integral parts of any river ecosystem. They provide the substrate for living organisms and through interaction with overlying waters such as nutrient cycling playing important roles in aquatic ecosytems (Tiedemann, *et al.*, 1988). On a qualitative basis, sediment analysis can be used favorably to estimate point sources of pollutants that are being discharged into surface waters. The pollutants, which do not remain in water column or solution, could be absorbed rapidly by particulate matters and thereby they also could escape any detection by water monitoring schemes (Meiggs, 1980).

Therfore, contaminants are not necessarily permanently fixed by sediments but they also may be recycled through biological and chemical agents within both the sedimentary compartment and the water column. For instance, sediment aspects played only a marginal role until it was recognized that recycling from bottom deposits can be a significant factor in the nutrient budget of an aquatic system (Forstner, 2002). So, besides water analysis, sediment data are important factors that should be taken into account when we conduct environmental monitoring programs in river ecosystems (Bormann and Likens, 1979).

The River Siahroud is located in Siahroud watershed and Guilan province in north of Iran and on the southwestern coastal plain of the Caspian Sea. It is a notorious polluted water system which endangered both human and river organisms in this province (Shirinfekr, 2001). The unsustainable development in Siahroud Watershed, especially in the surounding of Rasht City, the capital of Guilan province, during the past few decades has turned this water ecosystem into a deteriorating condition aggravated (Shirinfekr, 2001). There is a couple of contributing factors responsible for this environmental degradation. In one hand, the land clearance in the upstream forests results in soil erosion accompanies by discharging of the highly polluted effluents into the water course through industrial sites and agriculture (Shirinfekr, 2001). Rasht city, the most populated urban area and the captical of the province with a population of about one million with surrounding 300 villages, is located in the center of this watershed releasing contaminated sewage into this river as well. Rasht industrial city in the northwest of the main city with nearly 500 small and mid-size factories also contributes to the present level of river pollution (Year Census of Guilan provice, 2000).

Moreover due to the gentle slope of the river bed after Rasht City during its way toward Anzali Wetland, an international endangered water body in the list of Ramsar Convention, any possibility for self-purification is aborted in a way that it has become the most important external polluting source of the wetland (Rahnamai, 1995). In recent years, eutrophication in this wetland, which is a winter habitat for more than tens of thousands of migratory birds, has insightfully plagued this water body too (Mansouri, 2000).

Thus, the importance of the river quality sediment in Siahroud Watershed is indispensable for a sound and sustainable management of Siahroud Watershed. Despite the fact that several fellow researches have worked on the water quality parameters of the River Siahroud (Shirinfekr, 2001., Tavakoli and Sabetraftar, 2002), no studies have been carried out to examine the important role of the river sediments on the pollution of this river. Therefore, the objetive of this study was to address the distribution of bioavailabe heavy metals as the most perilous pollutants in the stream sediments and the importance of eutrophication of Anzali Wetland as it might relate to the nutrient status of the river sediments.

MATERIALS AND METHODS

Study Area

Siahroud Watershed is located in Guilan province in the north of Iran and southwest of the Caspian Sea coastal plain (Figure 1). Minimum and maximum elevations of the watershed are -20 to 800 m from the see level.The annual precipitation and temperature in this watershed are 1356 mm and 15.8 ^{o}C, respectively (Shirinfekr, 2001). Due to the presence of available water resouces, this area has a high potential for different uses including agriculture, industry, residential and recreational activities. Moreover to increase job opportunities in the province, a major area is turned into an industrial site in the middle reaches of the river. The effects of the landuse changes in the recent decades are not well known yet and it requires urgent need for more studies. The agriculure is mostly located in the low land areas, however since the rice cultivation is the major crop, the amount of runoff from this type of cultivation is significant. In this watershed there are 3 cities and about 300 villages with a population of nearly one million and a population density of about 20 presons per kilometer (Year Census of Guilan provice, 2000).

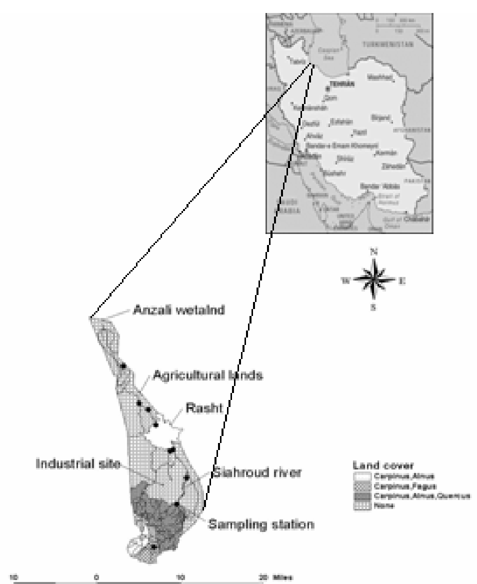


Fig 1. Location map of the River Siahroud in Siahroud Watershed, Guilan province south of Caspian Sea, showing the sampling sites, land cover and landuses.

Sampling Procedures and Analysis

The composite river sediment samples were taken from top 0-10 cm during five consecutive seasons in the year 2002 and 2003 from eight selected sampling stations along the River Siahroud. The selection of the sampling stations were based on viniciy to the major land-uses such as forest, industry, residential and agriculture landuses in the watershed. Procedure of Page and his colleagues (1982) was followed to determin chemical properties in the liquid phase. After coarse removal fragments from the sediment samples and air drying, the samples were analyzed for available Fe, Mn, Pb, Zn, Cu, Cr, Cd metal content and the levels of TOC, pH using the above procedure. The 0.5 mm air-dried samples with addition of 20 ml of DTPA (extracting agent) extraction solution were extracted for metals and analyzed by atomic absorption spectrascopy (AAS)using appropriate standards (AAS, GBC-902 Model, Australia). The 0.5 mm samples, avoiding contact with iron or steel, were analyzed for TOC using wet oxidation and digestion by the Walkly-Black method (Walkley and Black, 1954).

Statistical Methods

Multivariate analysis of canonical correlation, factor analysis (Shuxia, *et al*., 2003), and cluster analysis were used to find out the reactions of heavy metals among sediment and water phases. These statistical methods identify the main pollutant sources along with elucidation of the pollution trends in the watershed.

Canonical correlation

The aim of canonical correlation is to identify pairs of new axes, called canonical variates, (i.e., Wi and Vi), with each pair resulting into two new variables, where one variable is a linear combination of the X variables and the other variable is a linear combination of the Y variables such that: (1) the correlation between Wi and Vi is maximum, and (2) each set of the new variables is uncorrelated with other sets of new variables. In this case, rather than examining numerous correlations between the two sets of variables to discern the associations among them, each set is first reduced to a few linear combinations and only the correlations between a few linear combinations are interpreted (Sharma, 1996). In this study SAS system (version 6.12) was used to perform canonical correlation analysis.

Factor analysis

Factor analysis is motivated by the fact that measured variables can be correlated in such a way that their correlations may be reconstructed by a smaller set of parameters, which could represent the underlying structure in a concise and interpretable form. The principal motivation for using factor analysis, however does apply in the possibility of a meaningful interpretation of the data, particularly in exploratory analysis when using the so-called unrestricted factor models, which contrary to their names, embody restrictions of a fundamental nature (Basilevsky, 1994). In this study, Minitab statistical software release 13 was utilized for factor analysis.

Cluster analysis

Cluster analysis is to group observations into clusters so that in which each cluster is as homogeneous as possible with respect to the clustering variables. The first step in cluster analysis is to select a measure of similarity. Next, a decision is made on the type of clustering technique to be used such as a hierarchical or a nonhierarchical clustering. Third, the type of clustering method for the selected technique is determined such as centroid method in hierarchical technique. Fourth, a decision regarding the number of clusters is made. Finally, the cluster solution is interpreted based on the aims of the study (Sharma, 1996). Hence, the mean value of the all five seasons have been used. The sampling stations were compared given all the measured variables in an aggregate (Das and Acharya, 2003). Minitab statistical software (release 13) was used to carry out cluster analysis.

RESULTE AND DISCUSSION

General Sediment Quality

The results of the measured parameters are listed in Table 1. As shown, the sediment pH values range from 6.99 to 7.25 with an anverge of 7.14 showing a nearly neutral reaction for the sediments. The values of TOC range from 0.58 to 2.04 with an anverge of 1.00 percent, showing a relatively large range of TOC for the sediments in this river system. The heavy metal contents were measured in the liquid state as extractable metals and reported in mg per liter. The mean values of extractable Fe and Mn are 72.02 and 45.52 mg/l, respectively. Whereas, the average values of extractable Zn, Pb, Cu, Cr, and Cd were 10.44, 7.16, 4.02, .143, and

.061 mg/l, respectively. These values show enrichment loading of heavy metals in the sediment of the River Siahroud.

Heavy Metals of River Sediments

Metal release from sediments at the sediment-water inteface is largely controlled by Eh and pH of a sediment system (Peters *et al*., 1997). Metals such as copper, cadmium, lead, and zinc can be moblized during oxidation of anoxic or at low pH sediments through oxidation of sulfide phases (Kerner and Wallmann, 1992) and oxidation of organic matter (Forstner and Patchineelam, 1980). So, apart from heavy metal concentrations, during sampling some other factors such as TOC and pH should be mentioned to document the release of metals from the sediment to solution and vice versa.

Considering the aforesaid discussion, canonical correlation was utilized in an attempt to investigate the importance of these reactions in the River Siahroud. For this purpose, at the first step, TOC and pH were considered as criterion variables while other heavy metals were reserved for the predictor variables to document the importance of organic matter and acidity in displacement of the trace elements between solid and dissolve phases in the water-sediment system. Statistical significant tests for the elicited canonical variates according to the F-test mindicated that only the first canonical variate was statistically significant at 0.05 level. Thus, just the result of first canonical variate was interpreted. The standardized canonical coefficients of first canonical variate for the predictor variables (Table 2) suggested that Zn is more influential in forming the first canonical variate whereas that of the criterion variables implying that TOC is more important.

Therefore, it may be concluded that organic matter is of great importance in co-precipitation of the soluble Zn in the river. Generally, zinc in soil solution is very low, ranging between 2 and 70 ppb, half of which is in stable complexes with organic matter in the solution. In this field, the humic and fulvic acid fractions are prominent in Zn absorption (Tisdale *et al*., 1993). This may imply that leaching of this heavy metal is associated with loading of organic matter from the fields into the river ecosystem.

In addition, the current reactions among heavy metals should be taken into account in the transformation among dissolved and particulate phases, as well. One of the common reactions is absorbtion of heavy metals on hydroxide metals, especially iron and manganese hydroxides.

There are corollary of facts that hydrous iron oxides are often amorphous, whereas manganese generally occures as poorly crystallized brinesite or todorkite minerals. Since hydrous Mn and Fe oxides have considerable absorption capacity and affinity for many trace metals such as Cu, Pb, Zn and Cr, these metals largely absorb at these oxide phases (Das, 2003).

Therefore, in the next step, Zn and Mn were considered as the criterion variables and the other heavy metals as a predictor to examine the importance of these two heavy metals in co-precipitation reactions. Like that of the TOC and pH, in this case, again only one significant canonical variate was retained and interpreted.

Table 1. Sediment quality and some selected heavy metals in the River Siahroud taken from eight sampling stations in five consecutive seasons in 2002 and 2003.

Season	Statistics	Fe	Mn	Zn	Cu	Cd	Pb	Cr	TOC	pH
					(mg/l)				(%)	
Winter 2002	Avg.	62.2	86.76	14.9	2.61	0.049	6.7	0.100	0.83	7.22
	Std.	19.56	31.11	21.76	2.01	0.018	3.91	0.037	0.82	0.28
Spring 2002	Avg.	65.2	36.11	4.8	2.82	0.053	7.0	0.236	0.59	7.03
	Std.	41.68	13.50	3.87	2.72	0.022	4.47	0.055	0.66	0.35
Summer 2002	Avg.	42.1	23.60	6.4	3.35	0.116	5.4	0.063	1.28	6.99
	Std.	5.70	0.666	4.39	2.27	0.073	5.51	0.033	1.40	0.42
Fall 2002	Avg.	106.0	47.79	15.2	7.93	0.042	9.70	0.125	1.47	7.25
	Std.	11.48	4.97	12.96	6.81	0.036	8.12	0.078	2.04	0.28
Winter 2003	Avg.	84.6	33.32	10.9	3.38	0.047	7.00	0.190	0.82	7.19
	Std.	25.57	8.08	8.21	2.78	0.020	3.84	0.088	1.00	0.37

Table 2. Standardized canonical coefficients for heavy metals related to pH and TOC concentration.

Predictor Variables	V1	Criterion variables	W1
Fe	-0.118		
Zn	0.717	pH	-0.334
Pb	0.035	TOC	0.766
Cu	0.367		
Mn	0.012		

Table 3. Standardized canonical coefficients for Mn and Fe heavy metals associated with the river sediments of Siahroud River.

Predictor variables	V1	Criterion variables	W1
Zn	-1.394		
Cu	1.184	Mn	-0.044
Pb	1.529	Fe	1.043
Cd	0.088		
Cr	-0.467		

The results showed that Zn had a high negative standardized coefficient whereas Cu and Pb had the biggest positive coefficients among predictor variables (Table 3). On the other hand, Fe was more important in the criterion variables. To summerize, we may be concluded that co-precipitation of Pb and Cu were more likely associated with Fe hydroxide as they had a low coefficient in the first variate. As mentioned before that of the Zn was mainly related to organic matter, thus it showed a high negative coefficent in this variate.

This finding could be addressed in such a way that, a number of observers have reported on the absorption affinity of different metal cations for hydrous oxides. There is evidence that absorption tendency of divalvent transition elements by hydrous oxides often follows the Irving-Williams order (Kinniburgh, *et al*., 1989) at which Cu has the most absorption tendency. Moreover, based on this order, the overall absorption affinity by ferric oxyhydroxide is as followes; Pb>Cu>Cd>Zn>Ni>Ca (Kinniburgh, *et al*., 1989). Therefore, to some extent this affinity confirms our conclusion in this study.

In this regard, Foster *et al*., (1994) in a study on heavy metals in fluvial and reservoir sediments in Sowe catchement in England indicated that Pb was the least soluble form and Zn was the most soluble forms. Moreover, Vande Meent and his colleagues (1995) demonstrated significant associations between organic components of sediments and heavy metals deposited in freshwater sedimenttion basins of the Rhine River.

Because of the negative effects of heavy metals in aquatic environments, their pollutant sourcing in watershed is of the great importance in River Siahroud system too. For this purpose, factor analysis was used accompanied by the extraction of four major factors which encompassed 98.3 percent of the total observed variance as shown in the varimax rotated factor loadings for the heavy metals in Table 4. For the first factor, accounted for 41.1 percent of total variance, Fe, Zn, Cu and Mn had a high loadings which were 0.768, 0.660, 0.821, 0.884, respectively. In this regard, station 8 represented a high score implying that the amounts of foregoing trace metals at this station are higher than the other selected stations (Table 4 and Table 5).

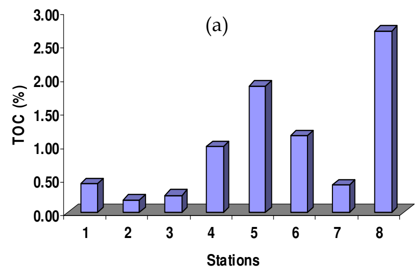
Table 4. The varimax rotated factor loadings for the heavy metals in Siahroud River sediment.

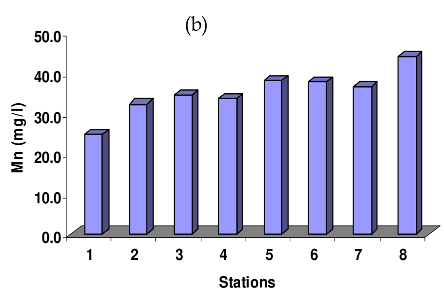
Heavy Metals	Factor1	Factor2	Factor3	Factor4	Cummunality
Fe	0.768	0.133	0.433	0.442	0.991
Zn	0.660	0.481	0.366	0.391	0.954
Pb	0.505	0.426	0.369	0.653	0.999
Cd	0.324	-0.031	0.927	0.180	0.997
Cr	0.194	0.956	-0.055	0.154	0.970
Cu	0.821	0.508	0.235	0.043	0.989
Mn	0.884	0.139	0.281	0.300	0.970
Variance	2.878	1.624	1.454	0.923	6.879
% Total Variance	41.1	23.2	20.8	13.2	98.3

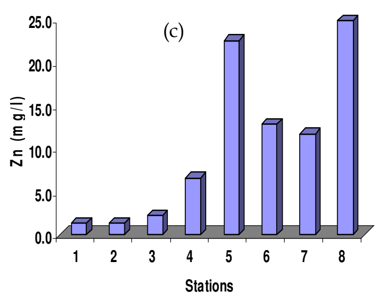
Table 5. Factor scores of the selected heavy metals associated with the river sediments of Siahroud River.

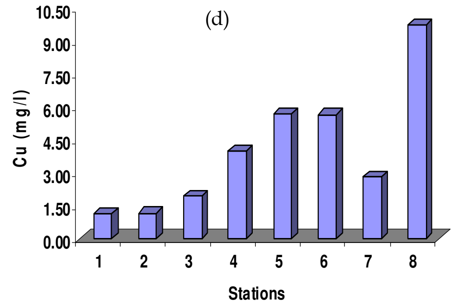
Stations	Factor1	Factor2	Factor3	Factor4
Stat.1	-1.365	0.165	-0.432	-0.873
Stat.2	-0.351	-0.921	-0.543	-0.236
Stat.3	0.218	-1.102	-1.139	0.186
Stat.4	-0.654	1.11	0.749	-1.164
Stat.5	-0.242	1.360	-0.033	1.870
Stat.6	0.732	0.373	-1.023	0.238
Stat.7	-0.300	-1.266	1.792	0.776
Stat.8	1.963	0.279	0.631	-0.797

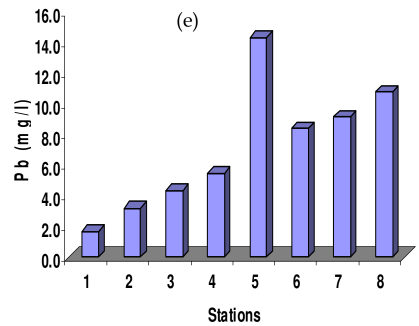
As mentioned and as shown this station is located in the agricultural area with paddy fields as the most prominent cultiavation. Soil waterlogging in these paddy fields will reduce O_2 and lower redox potential which increases the solubility of Mn^{2+}. Moreover, addition of organic matter in these fields as manure and rice straw, may supply as chelating agent that aids in maintaining the solubility of these micronutrients. In the other words, the presence of organic matter can increase Fe^{2+} solubility in the waterlogged soils in the primarily form of Fe $(OH)_2^+$ (Tisdale *et al*., 1993). Both of these phenomena will result into leaching of Mn and Fe into the river system and into its sediment. However, according to the results canonical correlation TOC and Fe $(OH)_2^+$ are the main contributing factors for co-precipitation of Zn and Mn in this river system (Figure 2). Consequently, the extended levels of Fe, Mn, Zn, and Cu occur in this river reach.

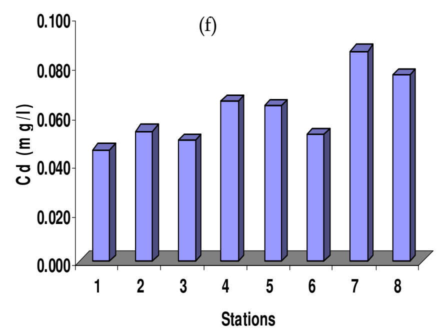












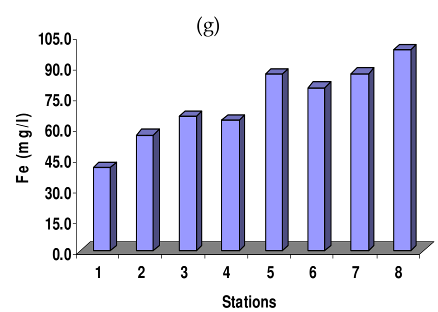


Fig 2 (a-g). Spatial variations of extractable heavy metals of the sediments at the sampling stations along the River Siahroud.

The second factor highly loaded with Cr meanwhile, both stations four and five had a high score in this factor too (Table 4, Table 5 and Figure 2). This demonstrates that these stations are the major contributing ones for the elevated amount of this trace element into the river. These stations were in industrial and urban sites. Thus, industrial effluents and domestic sewages could be attributed to extended level of Cr into the river system.

The third factor marked positively with Cd while station 7 had a high score in this factor, as well (Table 4, Table 5 and Figure 2). As noted,_this station is located in the agricultural area and depending on the sources of raw materials or deposits, from which phosphorus fertilizers are made, they may contain elevated levels of Cd (Williams and David, 1976). Therefore, Cd elevated level and its pollution in lower reaches of the river could be related to phosphorus fertilizer used in the arable fields and paddy soils. Finally, the fourth factor had a high positive loading in Pb accompanied by high score of the fifith station (Figure 2). This station is located in Rasht City neighbourhood and near the major transit road connecting this city to the capital of the country and hence the vehicle-Pb related pollution sources could be significant source of Pb into the river sediment. Similar relation was proposed by some other researchers such as Sunderi (1991) and Bai and Kumar (1997).

Pollution Zonation of the River Siahroud Route

Sampling stations along the River Siahroud were subjected to cluster analysis using single linckage method for the heavy matals. On the contrary, the cluster analysis results of the heavy metals indicated that there are four different zones along the River Siahroud which contain contrasting levels of sediment pollution (Figure 3).

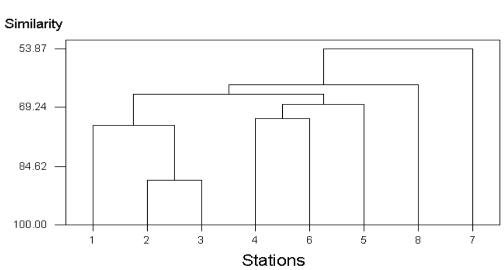


Fig 3. Dendrogram of cluster analysis of the heavy metal contents in the sediment sampled at 8 stations along Siahroud River.

The first cluster is comprised of stations 1, 2, and 3 that was characterized as the least polluted zone. The second zone was made up of stations 4, 5 and 6 at which the level of sediment pollution was higher than that of the previous zone. The third cluster was station 7 that the level of pollution was higher than the two aforesaid zones. The last section contains the fifth and the eighth stations implying the most polluted zone. This indicates that urban and agricultural sections of the river sediment are the most polluted zones and therefore these landuses could be the most important contributing areas for the heavy metal pollution of the River Siahroud sediments.

ACKNOWLEDGEMENTS

The authors are grateful to the Research and Education Organization of Ministry of Jihad-Agriclture of Iran for the financial support during this study. We are also grateful to the Agriculture and Natural Resources Research Center of Guilan province for their collaboration during the field works. The help of Mr. Sheikh-al-Aslam from Guilan Soil and Water Laboratory is greatly appreciated.

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Received: Jan. 15- 2007, Accepted Feb. 11- 2008)