

Assignment of Concentration of Heavy Metals (Cr, Zn, Cd, Pb) In Sediments of Gorgan Bay and South East the Caspian Sea (Golestan Province– Iran)2010-2011

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Abstract Heavy metals have been studied after their entry into water and absorption and accumulation in sediments in the Gorgan Bay and South East the Caspian Sea four season during 1 year from 2010-2011. The aim of this study is the comparison and analysis of heavy metals in sediment in eastern coast of the Caspian Sea and Gorgan Bay. For achievement to this goal had been measured concentrations of some heavy metals Lead (Pb), Cadmium (Cd), Zinc (Zn) and Chrome (Cr) from sea bed layers were measured. Atomic absorption apparatus was used and then analyzed all of data with analysis of variance (ANOVA) Technique in software. The results show that the highest level of metals Maximum concentrations of these elements in sediments were observed in station 1(Zn)(1213±13) , in station 4(Pb)(1021±11), in station 4(Cd)(302±8), in station 4(Cr)(315±8) µg/kg in that order.

Keywords Heavy metals, Sediment, Gorganbay, Caspian Sea

1. Introduction

Coastal areas reflect the processes of oceanic, atmospheric and underground systems. Coastal habitats are naturally affected by human activity and the environmental components of such habitats may be directly or indirectly affected by such activities (Brown and McLachan,1995). Industrial developments have had advantages but also caused many problems including major pollution of the seas which has caused environmental degradation and has threatened marine life (Aminiranjbar and Colleagues 2005). Human activity may increase concentration of heavy metals in coastal sediments and at the same time areas of high rural and industrial activity will lead to increase of such sediments in such areas creating high concentrations of pollutants (Luoma,1983),(Savvdeset,et.at,1995).Bealsact as transfer

environments for active biogeochemicals. Heavy metals show strong reaction to particles and therefore the presence and destiny of soluble metals is dependent on the reaction of floating organic and nonorganic metal solutions. The total concentration of many types of organic and nonorganic metals in sea water is dependent on chelating (Abdul-wahab and Jupp, 2009).Contamination of sediment problems leads to serious environmental problems and serves as a platform for contaminants that can persist for long periods of time (Savvides, et.al, 1995). Marine animals can accumulate metals through sea water, suspended particles, sediments and food chains (Luoma, 1983). Permanent contaminants such as metals may be transferred to higher levels in the food chain through environmental expansion. The levels of these contaminants, due to environmental socialization of species, are generally much higher in marine physico than the surroundings. As many of these species climb the food chain to become food for man, awareness of this aspect is vital. Coastal and beal areas generally turn into collection points for many types of contaminants including heavy metals (kasuba and Rozgaj,2000 ; Suzuki et. al, 2001,Lam et. al.,1997). The most common heavy metals in marine systems are Lead (Pb), Cadmium (Cd), Zinc (Zn) and Chrome (Cr). These elements are poisonous to organisms above normal levels. In water columns, heavy metals must first be absorbed by phytoplankton, bacteria, algae and small organisms and then travel through the food chain to bigger animals and finally enter the human body. The over concentration of such elements in fish, other marine life and plants will cause negative effect. The greatest negative effects of heavy metals on man are known to be stress and nerve related complications; heart artery and vein system difficulties; blocking of body contaminant eradicators (Colon, skin, kidney, etc.), immune system hormonal glands and digestive system. In the case of marine life there are incomplete. some and drastic effects such as reduction of growth, behavioral changes, genetic alterations and death of fish.



Figure 1. Location of the sampling stations of experiments

2. Materials & Methods

The present study was carried out for a period of 4 seasons (for 1 year from 2010-2011). Sampling stations were chosen according to table 1 and fig. 1 due to differences in the eco-system analyzed, which presented differences in the sea, Gorgan bay and beal of Gharehsoo river. The sampling took place on a seasonal basis. In assignment of sampling stations two points of interest stood out:

- 1) possible places covered by the sea, Gorgan bay and River.
- 2) Site wastewater pollutants from various sources.

Table 1. Location of the sampling stations of experiments

Row	Station name	Latitude	Longitude
1	Sea (Opp. Gorgan river)	36° 52' 42"	59° 50' 39"
2	Sea (Tower)	36° 52' 48"	59° 51' 12"
3	Interaction of sea with bay	36° 52' 57"	59° 52' 34"
4	Bay (Khoozin Canal)	36° 53' 06"	59° 55' 30"
5	Bay (Jahanshahi)	36° 53' 18"	59° 56' 02"
6	Gharehsoo River Delta	36° 53' 01"	59° 54' 00"
7	Gharehsoo River	36° 52' 46"	59° 51' 53"
8	Gharehsoo River	36° 50' 31"	59° 46' 32"

For Sampling using Ekman Grabber with surface of 225cm². After each impact of the grabber with the desired area the contents were taken and placed in plastic containers, labeled with specifications and kept in a refrigerator until measuring. It should be noted that 3 samples were taken of sediment at each station and samples were prepared from the resultant 1 kg of the samples. Sampling and testing was according to the standard book methodology. In line with this research to establish the level of metals using the digestion method, a mixture of nitric acid and chloric acid was used. In guidelines no. 1 a summary of the stages of analysis and preparation of samples is shown according to

this method. To eliminate interference, a 10% potassium solution was used. Reflux and heating reactions substantially increased the percentage of metal absorption (Trefry, 1976). Also, for preparation of the standard solution pure metal or high concentration salts were used. To reduce the probable absorption of ions of metal in digested solutions in the inner layers of the containers until time of measurement of the metals contained therein, PE bottles were used (Betti-1988, Sansoni, 1978). To measure heavy metals in digested samples a Swipe Absorption Spectrometer possessing nuclear exposed flame (FAAS) model (Shimadzu AA-670/GU-8) with a deuterium lamp was used. The accumulation of metals was measured using the Standard Curve method (according to concentration and absorption Volumes). The study compares data on sediments after first obtaining the average levels \pm standard deviation ($X \pm SD$) in terms of distribution and then compares their quantity with each other in order to explain the results from a PRISM statistical software and one way analysis of variance (ANOVA) and the results were group compared the results at $P < 0.05$ were considered acceptable difference criteria.

3. Results

Heavy metals in sediment samples: Results of the analysis of sedimentary bed of the southeast coast of the Caspian Sea represent accumulated values of 2 elements, zinc ($1213 \pm 13 \mu\text{g/kg}$) at Station 1 and Pb ($1021 \pm 11 \mu\text{g/kg}$) at station 4 compared with chromium ($315 \pm 8 \mu\text{g/kg}$) at station 4 and cadmium ($302 \pm 8 \mu\text{g/kg}$ dry sediment) at station 4 (table 2). As specified in the table, the values are almost uniform in the fluctuation of highest levels of elements observed in the sampling stations (Figure 2), where the concentration values of all elements at station 3 at the meeting point of seawater and the Bay is considerable.

Table 2. Concentrations of heavy metals in sediment samples ($\mu\text{g}/\text{kg}$ dry weight)

Station	Pb		Cd		Cr		Zn	
	Max	Min	Max	Min	Max	Min	Max	Min
1	687±7	528±6	126±4	106±4	282±5	127±6	1213±13	824±9
2	721±6	489±4	293±6	131±6	232±6	98±4	926±7	721±7
3	721±7	234±3	159±3	102±3	281±4	175±7	986±8	721±6
4	1021±11	324±5	302±8	98±4	315±8	141±5	1012±11	481±3
5	927±9	412±3	201±7	102±2	302±7	89±3	875±5	702±5
6	726±6	624±8	181±4	121±5	179±4	99±4	1015±12	609±5
7	915±7	521±5	181±3	69±3	241±3	197±8	902±7	517±4
8	598±5	408±5	100±2	63±1	104±1	63±2	598±4	402±2

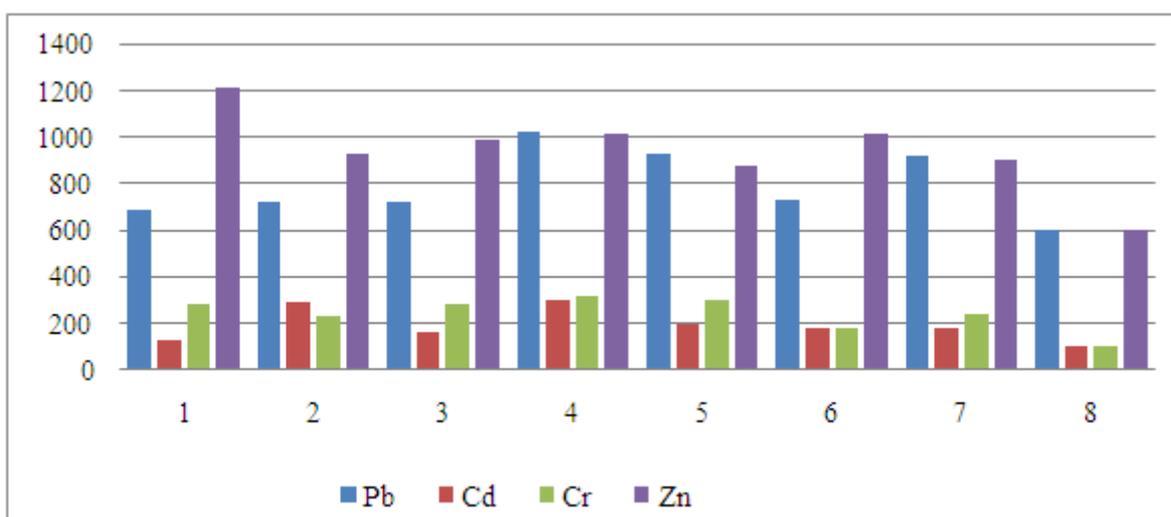


Figure2. Fluctuation of highest levels of elements in the stations

Table 3. Comparison of concentration of metals existing in sediments of Gorgan Bay with concentrations of Same Metals in Sediments in the Rest of the World ($\mu\text{g}/\text{g}$ of Dry Weight)

Area	Hg	Pb	Al	Cd	Sources
Distribution in Crust	0/08	12.5	81300	0.2	Dabiri,2000
Beal Sediments in Savana,USA	Na-1.9	0.41-0.95	17-560	Na-1.2	Kumar et al.,2008
Caspian Sea, IRI	0.02-0.09	11.30-24.6	-	0.1-0.2	Demora and sheikh oleslami 2002
Caspian Sea, Azerbaijan	0.05-0.45	12.2-28.6	-	0.1-0.2	" "" " "
North West of Persian Gulf	0.19	23.5	-	2.1	SabzAlizadeh2008
Bandar Imam Sediments	1.4	6.97	30500	0.5>	SajadAbdollahiMamoran, 2009
Ezmir Bay	0.05	8.5	-	0.03	Aksu et al., 2008

4. Discussion

As observed from the results of table 2, the levels of each element under study is different in each station $\mu\text{g}/\text{kg}$ dry weight sediment penetrate the compared to the Witness Caspian Sea control station (Zn 1213 ± 13 , Pb 1021 ± 8 , Cr 315 ± 8 , Cd $302 \pm 8 \mu\text{g}/\text{kg}$ dry weight sediment) and GharaSoo River station (Zn 598 ± 4 , Pb 598 ± 5 , Cr 104 ± 1 and Cd $100 \pm 2 \mu\text{g}/\text{kg}$ dry weight sediment) are the uniformity differences in that Lead and Zinc concentrations in the three regions compared to the two elements Chromium and Cadmium are higher. Comparing the results of the research by Jackson in 1990 which has calculated the maximum levels of lead and copper in the sediment bed of Bay Women in Alaska (levels have been stated.) shows that the element Lead has been observed in the area of research. Average levels of heavy metals in sediments in the research area is lower than the results obtained by Bortleson for the sediments of Lake Roosevelt. the levels of copper, Lead and zinc in the sediments of this lake were respectively obtained as 85 and 310 and 970 mg/kg where such a level rate was at a critical level for organisms identified in the region (Bortleson, 1992). It was also noted that the high level of heavy elements in the area in marine life which was the result of presence of elements in the sediment bed of the environment is indicative of the occurrence of a contamination crisis in the flora and fauna. Comparison of results obtained in the research area, the above research and standards presented indicate that the levels of these elements in the bed sediments of the research area are not at dangerous levels for the marine life (Akhondian, 2001). Levels of Lead, Zinc, Cadmium, Chromium in the sediment of Station 7, the entry point of urban wastewater and agricultural sewage are respectively in 915 ± 7 , 902 ± 7 , 181 ± 3 , $241 \pm 3 \mu\text{g}/\text{kg}$ which trend in the case of the elements Lead and Cadmium have been reduced slightly at the next station, But the levels of Lead and Chromium in sediments from West to East show a growth trend. Therefore, considering the results obtained maximum contamination is observed near the coast and stations located at entry points of Gharesoor river. Once more "due to entry of urban sewage From kordkoy city estate and agricultural waste in the area the level of Lead, Zinc, Cadmium, Chromium in the sediment bed of station 8 has increased and previous to that in the area of stations 6 and 7 which is the entry point of contaminants Gharehsoor river, the level of absorption and accumulation of heavy metals has reached maximum levels in the sediments beds in the area. Therefore, in consideration of the results obtained maximum contamination occurs near the coast and at entry points of the Gharehsoor river. Comparison of the average levels of heavy metals in the sediment beds of the southern coast of Caspian Sea with standards presented indicates the average level of Lead and Chromium in the sediments of the area is below that of standard sediment deposits in the ocean. But the level of Zinc is almost twice that of Lead and Cadmium is at the average standard of oceanic sediment deposits. The average level of all heavy elements in the sediments of the area is

above the standards presented for surface sediments the reason for which may be said to be the effect of nature as well as natural contamination or land construction in the area plus coastal sediment accumulation. (table:3). In consideration of the high level of heavy elements in the sediments and entry varied contaminants to the area through urban, rural, industrial and agricultural sewage in the water board of the area and rivers leading to it, especially Gharasoo river and its natural effect on the marine life of the area, it seems vital to assess and determine the levels of heavy elements among the fish residing in the area. In reviewing the results of analysis of sediments and fish at Tigris River in Turkey there was indication that the accumulation of Lead in fish and sediments was a high level. The level of lead in sediments of Lake Roosevelt was announced at 310 mg/kg (Bortleson, 1992). To control heavy metal occurrence at the surface of water, in sediment and fish of the Caspian Sea the quality control of water of fish farms must be researched and the result of the analysis from fish farms and industry on the environment must be taken into account. Therefore, this level of heavy metals in the soil and sea entering through rain and rivers from farming and industrial areas must be analyzed. Also, farmers and people must be given training in the case of formulation of pesticides and fertilizers as well as residential waste control entering rivers and the sedimentation process in the sea. Another vital requirement is creation of reference laboratories for periodic analysis of contaminants.

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