

## Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea

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### Abstract

In the present investigation down core variations of heavy metals such as; Zn, Ni, Co, Mn, Fe and Al in a sediment core from Bay of Gorgan adjacent to the Caspian Sea was studied. Inter-relationship amongst various parameters was brought out through correlation coefficients and cluster analysis. The results of present study reveals that Zn, Ni, Co and Mn possess both lithogenous and non-lithogenous sources. The increasing trend of Al towards top of sediment core is indicative higher erosion in the recent years. Interestingly, concentration of all studied metals increases toward core top (except for Fe) that might be indicative of influence of man's activities residing in catchment area of Gorgan Bay and also oil exploration in the Caspian Sea. Further,  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  techniques were used to find out rate of sedimentation. The result of dating is indicative of sedimentation rate between 1.4 to 2.45 mm/yr. based on  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activities respectively.

**Key words:** Heavy metals,  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , core, sediment, Gorgan bay, Caspian Sea

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### Introduction

Bays comprise a complex system involving interplay between various physical, chemical and biological factors (Hutchinson, 1957; Ruttner, 1963; Mortimer, 1941, 1942 and 1971; Sain and Neufield, 1975 and Coker, *et al.*, 1979). Heat and suspended and dissolved substances are factors that can effect the dispersion of trace elements in the waters, and accumulation or mobilization of trace elements in the sediments of Bays (Al-Masri, 2002 and Butman and Bothner, 1998). Trace metals that are derived from lithogenous and non-lithogenous sources can accumulate in the upper 5 to 20 cm of Bay sediment. Such accumulation takes place by biological and geochemical mechanisms (Mortimer, 1942 and 1971; Gorham and Swain, 1965; Mackereth, 1966; Cline and Upchurch, 1973; Farmer, 1991 and Rasmussen, 1994). Upward migration of trace metals may occur because of de-watering due to compaction and unidirectional ion migration, but, to a much greater extent, migration appears to be due to bacterial activity (Cline and Upchurch, 1973 and Coker and Shilts, 1979). Most trace metals tend to enrich in the modern organic sediment relative to inorganic sediment (Henderson, 1995 and Kettles, *et al.*, 1991). This is probably due to

the nature of the metal-organic binding strength and perhaps increased ion-exchange capacity of organic sediments over inorganic types. Thus, the highest and uniform concentrations of trace metals generally occur in the modern-organic sediment of most Bays (Coker, *et al.*, 1979 and 1995 and Friske, 1995). It is important to identify rates and patterns of sedimentation over the past few centuries. With this information a better prediction of the impact of proposed developments and changes to catchment land-use can result. By analyzing sedimentary records, the chronology of deposition can be determined and changes over time in the characteristics of sediments can be identified. Most of the recent changes are a result of clearing for various purposes, causing increased runoff, discharge, catchment erosion and increased sedimentation in lakes receiving basins. One way to gauge how estuaries have been changing is to have a look at their sedimentary records and use the Lead-210 ( $^{210}\text{Pb}$ ) dating method to determine sediment accumulation (Henderson, 1995). In the present investigation, we have tried to establish background or baseline concentration for Zn, Ni, Co, Mn, Fe and Al in the Bay of Gorgan



Figure 1: Sampling areas in the central parts of the Bay

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### Materials and Methods

The Bay of Gorgan that is located on the southern coasts of Caspian Sea is considered as the largest bay of the Caspian sea. Its area is about 400 Km<sup>2</sup> with a maximum length of 70 Km. A maximum depth of 5m is found in Gorgan Bay (Figure 1). The Qarahsoo river is the only important fresh water source flowing into the Bay.

Using a Pheleger type corer, a sediment sample of 70 cm length was collected at the central part of the Bay (Lat. 36° 37' 45" Long. 53° 05' 54"). The core was sliced into identify the increments (top 10 cm intervals and rest of sediment core at 5 cm intervals) for geochemical and dating studies. Sediment samples were powdered using agate mortar and pestle. Acids of analytical reagents including HF, HNO<sub>3</sub>, HCl and HClO<sub>4</sub> were used for bulk digestion (Karbassi, 1996). All heavy metal measurement was carried out using aromatic absorption spectrophotometry model Perkin Elmer at university of Science and Technology in Iran. A variety of approaches have been used to study patterns and processes of bay sedimentation. These include the following methods used to study the geological record of sediment: geophysical surveys (determining

Holocene rates of the past 7,500 years of estuarine sedimentation), bathymetric surveys (comparing 19<sup>th</sup> and 20<sup>th</sup> century bathymetry), short-lived radioisotopes (<sup>137</sup>Cs, <sup>210</sup>Pb) and other chemical markers (useful for the past century), and pollen stratigraphy (mainly *Ambrosia*, ragweed pollen) correlated with land-use changes (documenting post-colonization–land clearance rates).

Monitoring methods not included in the present introduction include instrumental measurement of total suspended solids in water samples and satellite imagery and remote

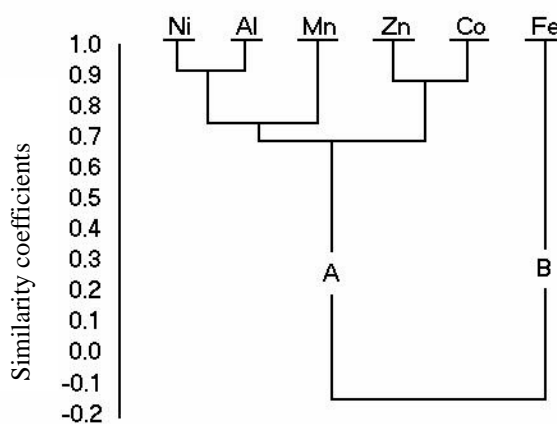


Figure 2: Dendrogram of heavy metals in sediment core from Bay of Gorgan

sensing (Amano and Onuma, 2003 and Jetter, 2000).  $^{137}\text{Cs}$  activity was counted with a lithium-drifted germanium detector and multi channel analyzer (Huh and Su, 1999). Lead-210 (via its granddaughter  $^{210}\text{Pb}$ ) was determined separately in the solution and solid residue resulting from the carbonate analysis. The solutions were separated by settling and decant. The dried residue was transferred to a micro wave digestion bomb, spiked with the same isotopic traces and totally dissolved with micro wave heating of a HF-HNO<sub>3</sub> acid mixture. To eliminate HF and excess HNO<sub>3</sub>, the digestion mixture was evaporated with 2ml H<sub>2</sub>SO<sub>4</sub>. Then the solid residue was re-dissolved in dilute HNO<sub>3</sub> and the radionuclides scavenged by precipitating Fe and Mn, as in foregoing. Polonium isotopes were separated by spontaneous deposition. Excess  $^{210}\text{Po}$  was calculated as the difference between total  $^{210}\text{Po}$  and  $^{226}\text{Ra}$  decay (Amidi, *et al.*, 1998). Further, it should be noted that lines 662 KeV for Cs and 609 and 1765 KeV for  $^{226}\text{Ra}$  were used.

## Results

Concentrations of Zn, Ni, Co, Mn, Fe and Al are presented in Table 1. As seen in the Table, concentrations of all studied metals except for Fe increase towards top of the sediment core. Many researchers have used

sediment cores to study the behavior of metals (Bellucci, *et al.*, 2003; Bertolotto, *et al.*, 2003; Al-Masri, *et al.*, 2002; Borretzen and Salbu, 2002; Weis, *et al.*, 2001; Lee and Cundy, 2001 and Karbassi, 1996 and 1989). A very low concentrations of Fe and Al in sediment core when compared with those of mean crust is indicative of low detritus input into the Bay of Gorgan. Concentration of Zn at the bottom of sediment core is very close to mean crust. However, the highest concentration of Zn (at the top of sediment core) is almost 1.5 fold higher than mean crust. Figure 2 Shows diagram of cluster analysis amongst studied metals. Cluster "A" consists of five metals namely Ni, Al, Mn, Zn and Co. It can be seen that origin of Ni and Mn is mainly from lithogenous sources taking into account Al as indicator of detritus matters. However, much of Co concentration could have been derived from anthropogenic origin due to its very high similarity coefficients with Zn. It should be pointed out many researchers use Zn as oil pollution indicator in the absence of V (Karbassi, 1989, 1993 and 1996).

As these five elements are clustered together, one may infer that both lithogenous and anthropogenic sources have contributed to the concentrations of studied metals.

Table 1: Concentrations of heavy metals in sediment core from Bay of Gorgan

Depth (cm)	ppm				%	
	Zn	Ni	Co	Mn	Fe	Al
1	95.5	35.2	15.8	516.0	0.94	0.80
5	97.9	34.1	14.9	487.7	1.03	0.78
8	88.9	32.9	12.3	483.7	1.03	0.74
10	86.6	30.9	13.1	488.9	1.03	0.76
15	88.0	32.0	12.5	502.1	1.02	0.78
20	90.9	36.9	13.8	568.2	1.04	0.80
30	78.5	36.2	11.7	441.5	1.02	0.77
45	81.5	33.7	12.1	489.6	1.04	0.72
55	76.7	24.2	11.3	428.2	1.01	0.58
70	67.6	24.2	10.9	413.1	1.01	0.55
Mean	85.2	32.0	12.8	482.0	1.00	0.73
Std (+,-)	9.20	4.50	1.60	45.00	0.03	0.08
Mean Crust	65.0	56.0	24.0	716.0	4.32	7.96

Iron that forms an individual cluster “B” joins metals of cluster “A” at a very low and negative similarity coefficient. Thus, origin of Fe needs further investigation by means of chemical partitioning techniques. Activities of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  are respectively shown in Figures 3 and 4. According to these activities two different sedimentation rate were obtained.  $^{210}\text{Pb}$  activity is indicative of sedimentation rate of 1.4 mm/yr.

However,  $^{137}\text{Cs}$  activity yields sedimentation rate of 2.45 mm/yr. As  $^{210}\text{Pb}$  method performs best in relatively quiet depositional environment such as marsh lands (Orson, *et al.*, 1992 and Amano and Onuma, 2003), bays and lakes (Robbins and Edgington, 1975; Ambers, 2001 and Thomson, 2002), we consider it in the further discussion. However, merits of  $^{137}\text{Cs}$  is not questioned but such discrepancies often happens at locations where all the  $^{137}\text{Cs}$  concentrations are low or near detection limit (Jeter, 2000; Guevara and Arribere, 2002 and Aslani, *et al.*, 2003). If length of sediment core from Gorgan Bay (70 cm) is divided by sedimentation rate (1.4 mm/yr.), it could be computed that collected core sample is representative of 500 years time span. The variation in concentrations of heavy metals during last 500 years is depicted in Figure 5 (a, b and c).

As shown in Figure 5 (a to c), the concentrations of all metals except for Fe decrease towards bottom of sediment core. This is indicative of human influence on the

eco-system of Gorgan Bay in the last 500 years. It should be pointed out that increase in the concentration of some trace metals such as Zn is mainly due to oil activities in the Caspian Sea. However, an increase in the concentration of Al might be attributed to higher erosion in the area of study that is mainly due to more agricultural activities and improper catchment’s management. Based on the present investigation base-line values for metals is proposed in the discussion and conclusions section of this paper. However, for more accurate baseline data, chemical-partitioning technique is suggested. By this technique, association of metals with various sedimentary phases would be known (Karbassi, 1993 and Karbassi and Shankar, 1993). Thus, a more reliable data can be provided for further investigations.

### Discussion and Conclusion

Data to determine trends is commonly gathered by long-term programs that monitor environmental media such as air, water, fish and surface sediments. These monitoring programs can continue for years or even decades.

Although aluable, this long-term monitoring can suffer from several shortcomings. These are:

- Such programs can not evaluate conditions prior to the time they were initiated.

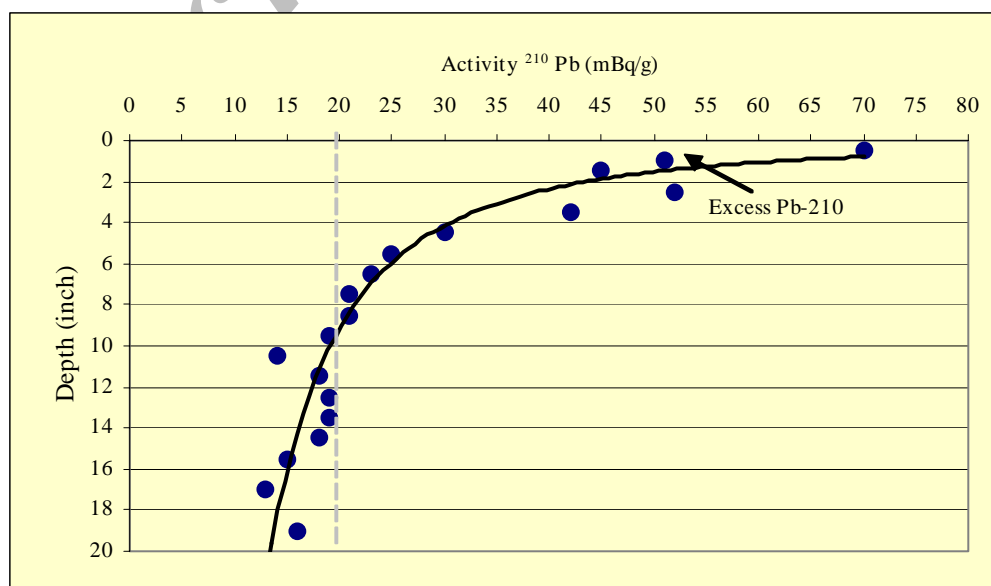


Figure 3: Activity of  $^{210}\text{Pb}$

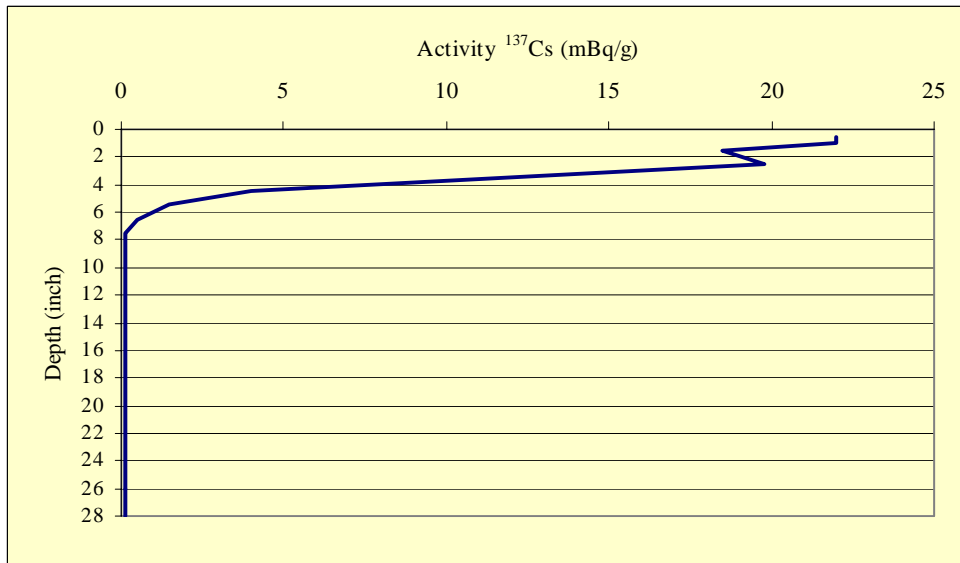


Figure 4: Activity of <sup>137</sup>Cs

- Changes in sampling and analytical methods can void or compromise comparison with earlier data.

In some cases, analyses of sediment cores can be used to overcome these shortcomings. Concentrations of persistent pollutants (especially metals, radionuclides and refractory organic compounds) can be measured in successive layers within cores. Dating techniques including use of radioactive isotopes like <sup>210</sup>Pb and <sup>137</sup>Cs can be used to estimate the age of these layers. By combining concentration data, extended records of pollutant concentrations in sediments can be reconstructed. The eco-system of Bay of

Gorgan is influenced both by water intrusion from the Caspian Sea and to a lesser extent by fresh river waters. Both oil and agricultural activities have left considerable impacts on the eco-system of Bay of Gorgan. If Zn is considered as an indicator of oil pollution then it can be inferred that oil activities in the Caspian Sea might have contributed to the concentration of Zn. In spite of the fact that concentrations of Ni, Co and Mn stands well below those of mean crust but as a general rule the concentrations of these metals increases towards top of sediment core. Such increase in the concentration of metals may be indicative of human influence on aquatic environment of Bay of Gorgan.

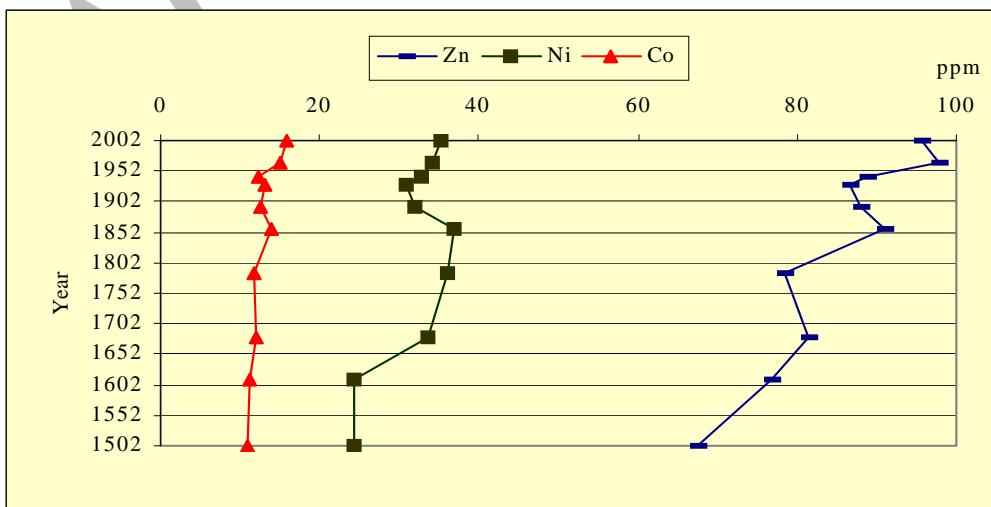


Figure 5 (a): Down core variations of Zn, Ni and Co concentrations through span of time

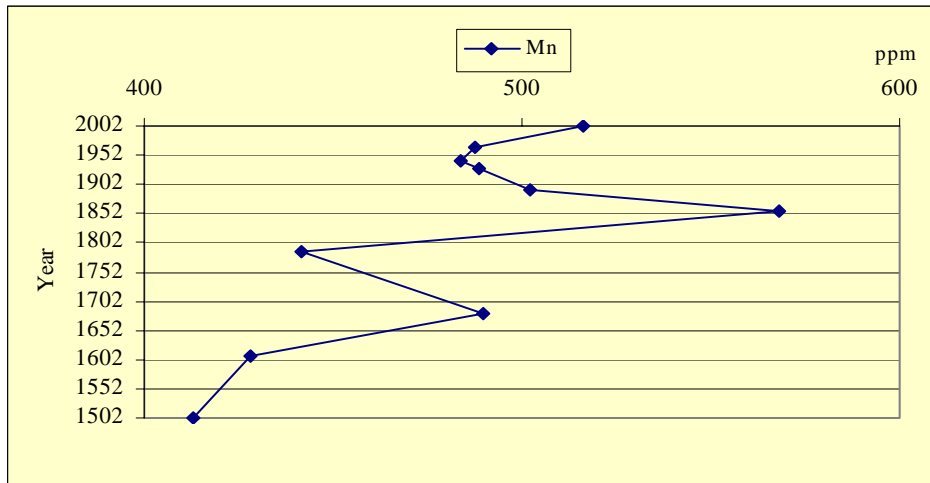


Figure 5 (b): Down core variations of Mn concentrations through span of time

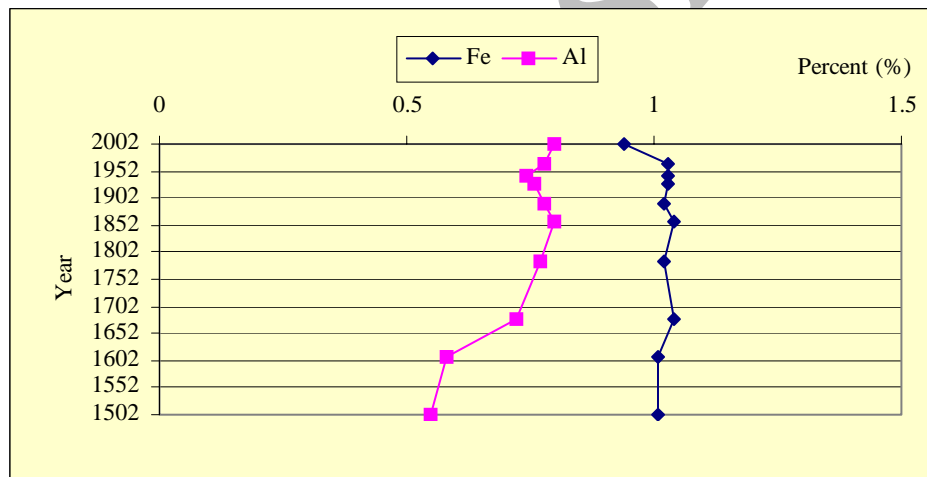


Figure 5 (c): Down core variations of Fe and Al concentrations through span of time

Many parts of Caspian Sea have undergone anoxic conditions for discharge of municipal as well as industrial discharges. Under anoxic conditions, Mn can be mobilized and finds its way into the overlying waters. As a great part of Gorgan Bay's water is supplied by the Caspian Sea, it could be inferred that higher concentrations of Mn at the top of sediment core has been derived from its mobilization in the Caspian Sea. It is proposed the following concentrations as baseline or background values for further investigators whom wish to follow trends of pollution in future. These values correspond to data obtained for metals at 500 years ago. The baseline values are Zn=68 ppm, Ni=24 ppm, Co=11 ppm, Mn=413 ppm, Fe=1% and Al=0.55%. It is much safer to use  $^{210}\text{Pb}$  technique for dating of sediment in Bays. More attention must be paid to themanagement of catchment area tos

minimize soil erosion. Further studies must consider chemical-partitioning techniques. Also longer sediment cores must be obtained from Bay of Gorgan for detailed climatological studies through pollen analysis.

### Acknowledgements

Authors wish to appreciate Marine Wing (Department of the Environment) for financial assistance to carry out  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ . Dr. Beitollahi from Iran Atomic Energy Organization helped us a lot for sediment core dating. Dr. M. Saeedi from University of Science and Industry kindly helped us to carry our geochemical analysis. Thanks to Dr. I. Bayat and Dr. S. M. T. Sadatipour from Department of Marine Science for their fruitful discussions on dating aspects.

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