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

A. R. Karbassi and R. Amirnezhad

Department of Environmental Science, Graduate School of the Environment and Energy, Science and Research Campus, Islamic Azad University, Tehran, Iran

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}Pb and ^{137}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}Pb and ^{137}Cs activities respectively.

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

** Corresponding Author, E-mail: karbassi@iranenergy.org.ir*

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}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

Figure1: Sampeling areas in the central parts of the Bay

and in the other hand to know about sedimentation rate.

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^2 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^{o} $37^{'}$ $45^{''}$ Long. 53^{o} $05^{'}$ $54^{''}$). 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_3, HCl and $HClO_4$ were used for bulk digestion (Karbassi, 1996). All heavy metal measurement was carried out using aromatic absorption spectrophotimetry 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 19th. and 20th. century bathymetry), short-lived radioisotopes (^{137}Cs, ^{210}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

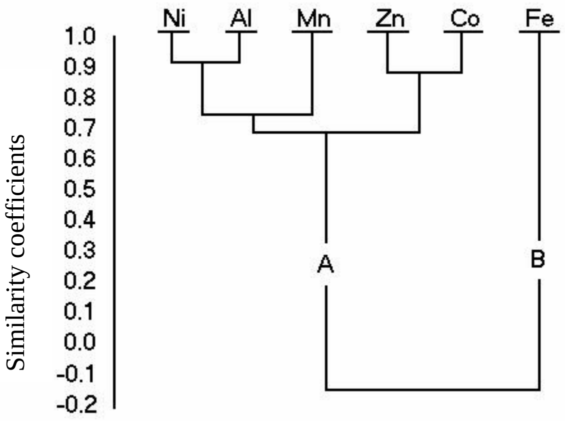

Figure 2: Dendogram of heavy metals in sediment core from Bay of Gorgan

sensing (Amano and Onuma, 2003 and Jetter, 2000). ^{137}Cs activity was counted with a lithium-drifted germanium detector and multi channel analyzer (Huh and Su, 1999). Lead-210 (via its granddaughter ^{210}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_3 acid mixture. To eliminate HF and excess HNO_3, the digestion mixture was evaporated with 2ml H_2SO_4. Then the solid residue was re-dissolved in dilute HNO_3 and the radionuclides scavanged by precipitating Fe and Mn, as in foregoing. Polonium isotopes were separated by spontaneous deposition. Excess ^{210}Pb was calculated as the difference between total ^{210}Po and ^{226}Ra decay (Amidi, *et al.*, 1998). Further, it should be noted that lines 662 KeV for Cs and 609 and 1765 KeV for ^{226}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

	←	ppm		→	← %	→
Depth (cm)	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}Pb and ^{137}Cs are respectively shown in Figures 3 and 4. According to these activities two different sedimentation rate were obtained. ^{210}Pb activity is indicative of sedimentation rate of 1.4 mm/yr.

However, ^{137}Cs activity yields sedimentation rate of 2.45 mm/yr. As ^{210}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}Cs is not questioned but such discrepancies often happens at locations where all the ^{137}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. Theses 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.

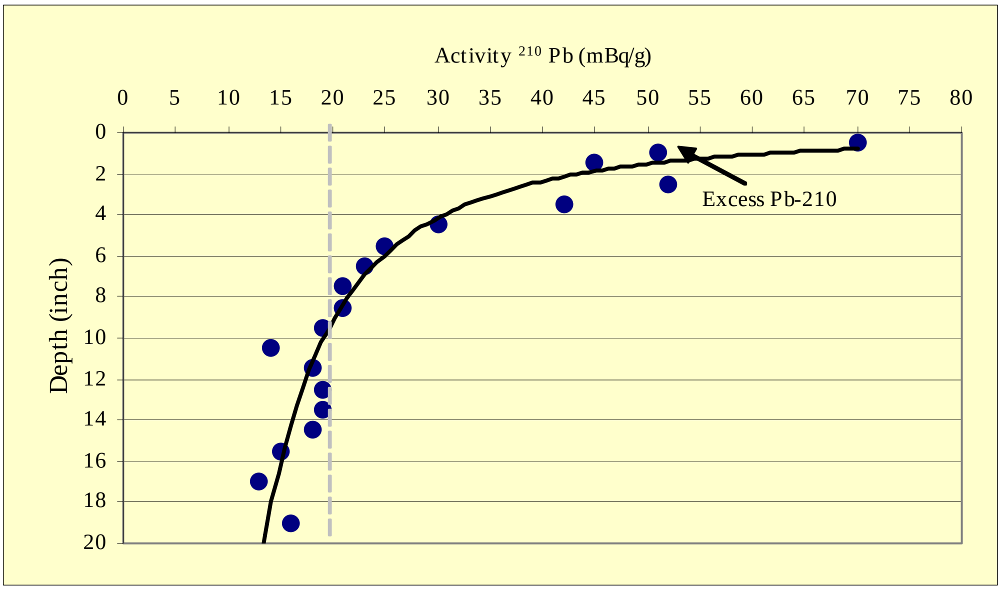

Figure 3: Activity of ^{210}Pb

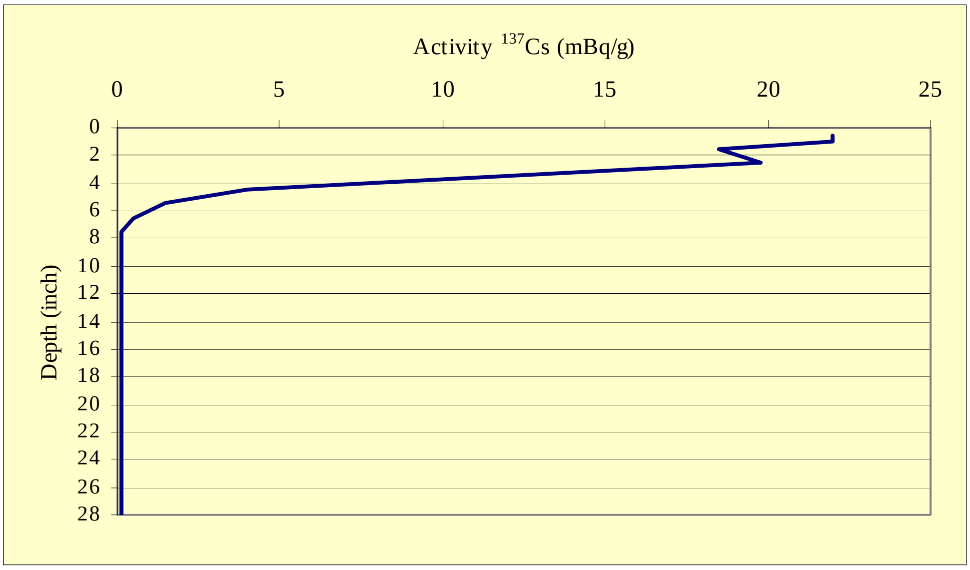

Figure 4: Activity of ^{137}Cs

- 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 ^{210}Pb and ^{137}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 role 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.

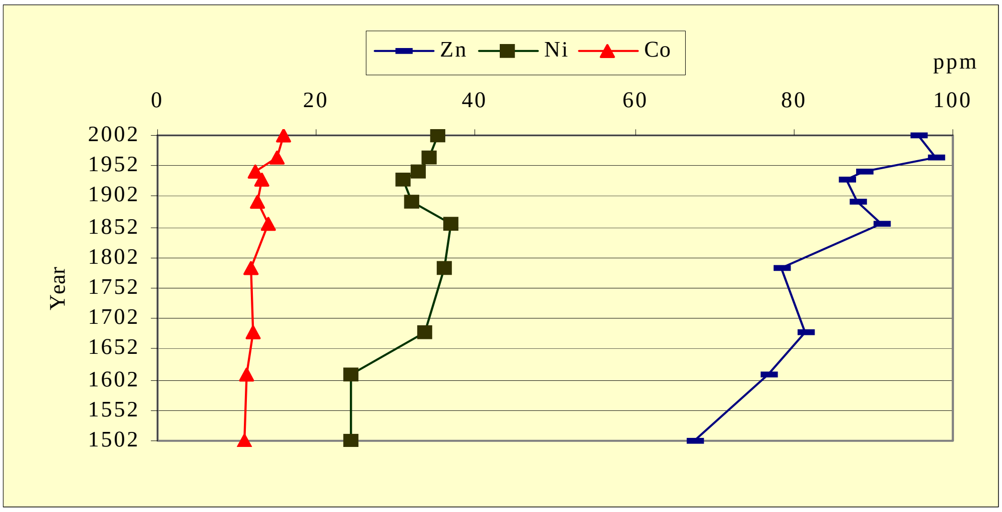

Figure 5 (a): Down core variations of Zn, Ni and Co concentrations through span of time

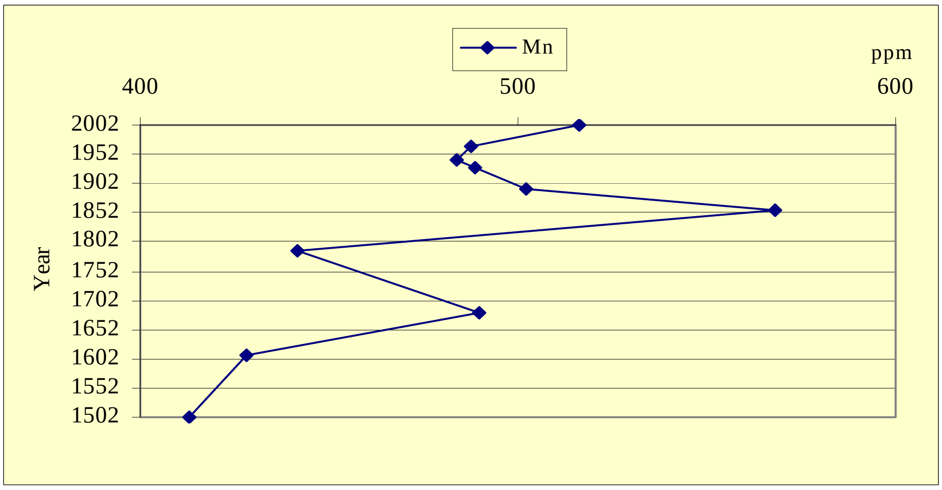

Figure 5 (b): Down core variations of Mn concentrations through span of time

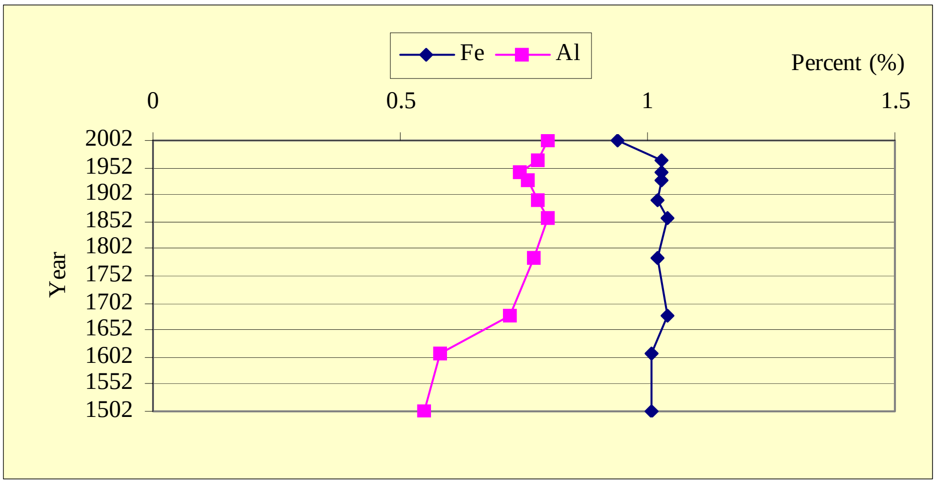

Figure 5 (c): Down core variations of Fe and Al concentrations through span of time

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}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.

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References

Al-Masri, M. S., A. Aba, H. Khalil, and Z. Al-Hares, Sedimentation rates and pollution history of a dried lake: Al-Oteibeh Lake. Science of the Total Environment, ***293*** *(1-3):177-189, 2002*

Amidi, J., M. M. Beithollahi, and M. Asefi, Calibration of gamma spectrometer with high pure germanium detector. IRNA-NRPD Technical Report, 1998

Amano, H. and Y. Onuma, Depth profiles of long lived radionuclides in Chernobyl soils sampled around 10 years after the accident. Journal of Radio analytical and Nuclear Chemistry, ***255*** *(1): 217-222, 2003*

Ambers, R. K. R., Using the sediment record in a western Oregon flood-control reservoir to assess the influence of storm history and logging on sediment yield. Journal of Hydrology, ***244*** *(3-4): 181-200, 2001*

Aslani, M .A. A., S. Aytas, S. Akyil, G. Yaprak, G. Yener, and M. Eral, Activity concentration of cesium-137 in agricultural soils. Journal of Environmental Radioactivity, ***65*** *(2): 131-145, 2003*

Bellucci, L. G., B. El Moumni, F. Collavini, M. Frignani, and S. Albertazzi, Heavy metals in Morocco Lagoon and river sediments. Journal de Physique, ***IV 107*** *(Pt. 1): 139-142, 2003*

Bertolotto, R. M., B. Tortarolo, M. Frignani, L. G. Bellucci, S. Albanese, and C. Cuneo, Heavy metals in coastal sediments of the Ligurian sea off Vado Ligure. Journal de Physique, ***IV 107*** *(Pt. 1): 159-162, 2003*

Borretzen, P. and B. Salbu, Fixation of Cs to marine sediments estimated by a stochastic modeling approach. Journal of Environmental Radioactivity, ***61*** *(1):1-20, 2002*

Butman, B. and Bothner, M. H., Predicting the Long-Term Fate of Sediments and Contaminants in Massachusetts Bay. U.S. Geological Survey Fact Sheet, 172-97, 1998

Coker, W. B. and Shilts, W. W., Lacustrine geochemistry around the north shore of Lake Superior: Implications for the evaluation of the effects of acid precipitation: In Current Research, Part C, Geological Survey of Canada, Paper 79-1C: 1-15, 1979

Coker, W. B., Hornbrook, E. H. W. and Cameron, E. M., Lake sediment geochemistry applied to mineral exploration: In Geophysics and Geochemistry in the search for Metallic Ores; Peter J. Hood, editor; Geological Survey of Canada, Economic Geology Report 31: 435-478 1979

Coker, W. B., Kettles, I. M. and Shilts, W. W., Comparison of mercury concentrations in modern lake sediments and glacial drift in the Canadian Shield in the region of Ottawa/Kingston to Georgian Bay, Ontario, Canada: Water, Air and Soil Pollution, 80: 1025-1029, 1995

Farmer, J. G., The perturbation of historical pollution records in aquatic systems: Environmental Geochemistry and Health, 13 (2): 76-83, 1991

Cline, J. T. and Upchurch, S. B., Mode of heavy metal migration in the upper strata of lake sediment: In Proceedings of the 16th Conference on Great Lakes Research. International Association on Great Lakes Research, ***1:*** *349-356, 1973*

Friske, P. W. B., Effects of limnological variation on element distribution in lake sediments from Tatin lake, central British Columbia - implications for the use of lake sediment data in exploration and environmental studies: In Current Research 1995-E, Geological survey of Canada, ***4:*** *59-67, 1995*

Gorham, E. and Swaine, D., The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments: Limnology and Oceanography, ***10****: 268-279, 1965*

Guevara, S. R. and M. Arribere, Cs-137 dating of lake cores from the Nahuel Huapi National Park, Patagonia, Argentina: Historical records and profiles measurements. Journal of Radioanalytical and Nuclear Chemistry ***252*** *(1): 37-45, 2002*

Henderson, P. J., The geochemistry of Lake Winnipeg long cores and bottom sediment samples: Namao cruise 94-900: Geological Survey of Canada, Open File Report ***5:*** *3113, 1995*

Huh, C. and Su, C., Sedimentation dynamics in the east China sea elucidated from Pb-210, Cs-137 and Pu-239-240. Marine Geology, ***160:*** *183-196, 1999*

Hutchinson, G. E., A Treatise on Limnology; Volume 1, Geography, Physics and Chemistry: Wiley and Sons, New York, 1015, 1957

Jetter, H. W., Determining the ages of recent sediments using measurements of trace radioactivity. Terra et Aqua, ***78:*** *21-28, 2000*

Karbassi, A. R., Geochemical and magnetic studies of riverine, estuarine and marine sediments. Ph.D. thesis, Mangalore University, India, 196, 1989

Karbassi, A .R., Geochemistry of a sediment core and applications of analysis in interpretating data. The 16 th International Geochemical Exploration Symposium, Beijing, China, 1993

*Karbassi, A. R. Geochemistry of Ni, Zn, Cu, Pb, Co, Cd, V, Mn, Fe, Al and Ca in sediments of North Western part of the Persian Gulf. Intl. J. Env. Studies, **54:** 205-212, 1996*

Karbassi, A. R., and Shankar, R., Geochemistry of two sediment cores from west coasts of India. IAWQ Sediment Conference, Milwaukee, U.S.A, 1993

*Kettles, I. M., Shilts, W. W. and Coker, W. B., Surficial geochemistry south-central Canadian Shield: Implications for environmental assessment: In Geochemical Exploration 1989, Part II (A. W. Rose and P.M. Taufen, Editors), Journal of Geochemical Exploration, **41** (1/2): 29-57, 1991*

*Lee, S. V. and A. B. Cundy, Heavy metal contamination and mixing processes in sediments from the Humber Estuary, Eastern England. Estuarine Coastal and Shelf Science, **53** (5): 619-636, 2001*

Mackereth, F.J.H., Chemical investigation of lake sediments and their interpretation: Proceedings of the Royal Society, 161: 285-309, 1965

*Mortimer, C. H., The exchange of dissolved substances between mud and water in lakes. Part III and IV: Journal of Ecology, **30:** 147-207, 1942*

*Mortimer, C. H., Chemical exchanges between sediments and water in the Great Lakes - speculations on probable regulatory mechanisms: Limnology and Oceanography, **16** (2): 387-404, 1971*

*Orson, R. A., Simpson, R. L., Good, R. E., A mechanism for the accumulation and retention of heavy metals in tidal freshwater marshes of the upper Delaware River estuary. Estuarine Coastal and Shelf Science, **34**: 171-186, 1992*

*Rasmussen, P. E., Current methods of estimating mercury fluxes in remote areas: Environmental Science and Technology, **28** (13): 2233-2241, 1994*

*Robbins, J. A. and Edgington, D. N., Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochim Cosmochim Acta, **39**: 285-304, 1975*

Ruttner, F., Fundamentals of Limnology: University of Toronto Press, Toronto, 295, 1963

Sain, K.S. and Neufeld, R.D., A dynamic model of bio-geochemical cycle of heavy and trace metals in natural aquatic systems: Paper presented at the Second International Symposium on Environmental Biogeochemistry, Burlington, Ontario, Canada, 20, 1975

*Thomson, J., F.M. Dyer, and I.W. Croudace, Records of radionuclides deposition in two salt marshes in the United Kingdom with contrasting redox and accumulation conditions. Geochimica et Cosmochimica Acta **66** (6):1011-1023, 2002*

*Weis, D.A., J.C. Callaway, and R.M. Gersberg, Vertical accretion rates and heavy metal chronologies in wetland sediments of the Tijuana Estuary. Estuaries **24** (6A): 840-850, 2001*