St. Joseph's Journal of Humanities and Science (Volume 4 Issue 1 January 2017) 96-104

St. Joseph's Journal of Humanities and Science
ISSN: 2347 - 5331

http://sjctnc.edu.in/6107-2/


ISSN: 2347-5331

St. Joseph's Journal of Humanities and Science

Volume 3 Issue 1 January 2016

HEAVY METAL CONCENTRATION IN COASTAL SEDIMENTS OF EAST COAST OF TAMILNADU USING ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY (EDXRF) TECHNIQUE

-B. Anitha[a]

- J. ChandraMohan[a]

Abstract

Heavy metal concentrations in coastal environment have been rapidly increased by human activities because the coastal environments are subjected to metal contamination throughout various inputs such as natural, industrial and urban sources. The concentrations of Mg, Al, K, Ca, Ti, Fe, V, Cr & Mn was measured in twenty sampling sites along the East Coast of Tamilnadu by Energy Dispersive X-Ray Fluorescence spectroscopy (EDXRF) technique. Natural background values were used to delineate their derivation as geogenic or anthropogenic. To interpret and assess the contamination status for heavy metals in sediments, four metal pollution indices were discussed using Enrichment Factor (EF). The methodology used has proved to be a useful tool to separate geological and anthropogenic causes of variation in sediment heavy metal content and to identify common pollution sources.

Keywords: Sediment, Heavy Metal, EDXRF, Enrichment Factor, Pollution Indices.

INTRODUCTION

Sediments are ecologically important components of the aquatic habitat and are also a reservoir of contaminants, which play a significant role in maintaining the trophic status of any water body. The coastal sediments provide useful information about environmental and geochemical nature of the marine environment. They are composite minerals consisting of inorganic components, mineral particulates and organic matter in various stages of decomposition (Kucuksezgin *et al*., 2006). Development of industrial activities in coastal zones brought the risk of heavy metal contamination in marine environment (Esen *et al*., 2010). Since the industrial revolution, tremendous amounts of the toxic pollutants have been discarded into coastal environment and sediments of bays and estuaries have huge sinks of heavy metals (Wang et al., 2010). More than 90% of the heavy metal load in the aquatic systems has been found to be associated with suspended particulate matter and sediments (Amin *et al*., 2009).

Sediments act as sinks and sources of contamination in aquatic sytems because of their variable physico-chemical properties. Naturally the sediment contains the major elements (Mg, Al, K, Ca, Ti, Fe) due to earth crust and toxic metals (V, Cr, Mn, Co, Ni and Zn) due to anthropogenic activities. The rapid industrialization in the coastal area increases the heavy metal contamination in sediment samples. Heavy metal accumulation deposited into near shore areas of marine

[a] Department of Physics, C.K.College of Engineering & Technology, Cuddalore - 606603, Tamil Nadu, India.
Email: anithab77@reddiffmail.com, Mobile: +91-9444772120

environments is partitioned between the sediment and water column phases. Further partitioning of metals occurs within the sediment and water column with different ligands (Korfali and Davies, 2004). Hence sediments become large repositories of toxic heavy metals. The distributions, bio-availability and mobility of heavy metals in marine sediments can change natural and anthropogenic impact (*i.e*., parent rock, weathering, transportation, soil erosion) and may be greatly different various aquatic ecosystems.

Therefore, heavy metal pollution is one of the largest threats to marine environment and human health. In many coastal regions adjacent to industrial and urban areas where metals from both geological and man-made sources accumulate together, it can be difficult to determine the proportion of anthropogenic inputs (Ergin *et al*., 1993). The distribution of heavy metals concentration in sediments, water and biological materials are great importance in environmental pollution (Martincic *et al*., 1989). A comprehensive study on both the status of heavy metal pollution and the bio-availability (and mobility) of heavy metals in the sediment environment of east coast of Tamilnadu is important for the sustainable development of the regional economy and for the long-term improvement of public health. Many studies from around the world have used the sediments of the wetlands as an indicator for pollution (Syrovetnik et al., 2007).

A Nuclear Analytical Technique (NAT) such as energy dispersive X-ray fluorescence (EDXRF) is a dominant experimental tool for elemental composition assessment of the environmental samples. This is a non-destructive and multi-elemental in nature with a large throughout of specimens. This technique is useful for the short and long-range sampling studies and provides accurate elemental concentration data. In the present work, we used EDXRF as a very suitable technique for large area screening because it is fast and requires small quantity of a sample. Some other authors have also used energy dispersive X-ray fluorescence (EDXRF) for soil and sediment elemental analysis (Ravisankar *et al*., 2014; Chandrasekaran *et al*., 2015; Obiajunwa *et al*., 2002).

STUDY AREA

Table-1 : The Geographical Latitude and Longitude for the Sampling Locations

S. No.	Location ID	Latitude (N)	Longitude (E)	Location
1.	CTK	11°46'13.71"	79°49'8.37"	Thazhankuda
2.	CDM	11°43'57.67"	79°48'46.41"	Devanampattinum
3.	COT	11°43'4.67"	79°48'36.20"	Singarrathoppu
4.	CAP	11°35'8.08"	79°47'37.32"	Ayyampet
5.	CSP	11°32'47.99"	79°47'34.60"	Samiyarpet
6.	CPT	11°31'20.40"	79°47'50.09"	Parangipet
7.	CPM	11°24'40.18"	79°50'41.73"	Pichavaram
8.	KDM	11°22'49.64"	79°50'53.33"	Kodiyampalayam
9.	NPZ	11°19'59.41"	79°51'23.09"	Pazhaiyar
10.	NSI	11°13'50.66"	79°52'29.62"	Sirkazhi
11.	NPB	11° 8'37.30"	79°53'7.83"	Poombukar
12.	TRGB	11° 1'32.53"	79°53'20.28"	Tharangambadi
13.	PKK	10°54'56.72"	79°52'45.28"	Karaikal
14.	NGR	10°49'17.00"	79°53'11.67"	Nagore
15.	NAP	10°44'43.39"	79°53'27.71"	Akkaraipettai
16.	VLK	10°41'4.92"	79°54'17.98"	Velankanni
17.	TPI	10°37'45.19"	79°55'58.98"	Thirupoondi
18.	VKT	10°34'8.75"	79°56'39.88"	Vettaikaranthoppu
19.	VED	10°23'46.29"	79°59'31.46"	Vedaranium
20.	KODI	10°20'41.64"	80° 0'29.34"	Kodiyakkarai

Sediment samples were collected along the Bay of Bengal coastline, from Thazhankuda (Cuddalore) to Kodiyakkarai coast during the pre-monsoon condition. Table 1 represents the geographical latitude and longitude for the sampling locations at the study area. Sampling locations were selected to collect representative samples from all along the study area. The coastal region of this area has been a highly productive area rich in marine fauna. Recent industry developments during the last two decades in Cuddalore, Karaikal, Nagapattinam and Velankanni coastal towns include offshore oil production, chemical, fertilizer processing plants and more than 300 small scale industries, all located in this region. The recent development of a minor harbor in Nagapattinam town is very important because it acts as the main fishing harbor with heavy movement of fishing and naval vessels in this region. The study area is also drained by the tributaries of river Cauvery which runs through many industrial towns and its tributaries, i.e., river Nandaiar, Puravandayanar, Vettar, Uppanar pass through the agricultural belt of Tamilnadu state and finally drain into the Bay of Bengal in this coastal sector.

MATERIALS AND METHODS

Sample Collection and Preparation

Sediment sample were collected by a Peterson grab sampler from 10m water depths parallel to the shoreline. The grab sampler collects 10cm thick bottom sediment layer from the seabed along the 20 locations (Fig. 1).

Uniform quantity of sediment samples were collected from all the sampling stations located between an average interval of 3NM (Nautical mile). Care was taken to ensure that the collected sediments were not in contact with the metallic dredge and the top sediment layer was scooped with an acid washed plastic spatula. Sediment samples were stored in plastic bags and kept in refrigeration at -4ºC until analysis. The samples were sub-sampled using the coning and quartering method. The sub-samples were air-dried and larger stone fragments (>20mm largest diameter) or shells were removed. The samples were air dried at 105ºC for 24 h to a constant weight and were not separated <63 µm in order to identify the geochemical concentrations in the whole bulk fraction as the study area is dominated by sandy layers in many places. Then samples were ground into a fine powder for 10-15 min, using an agate mortar.

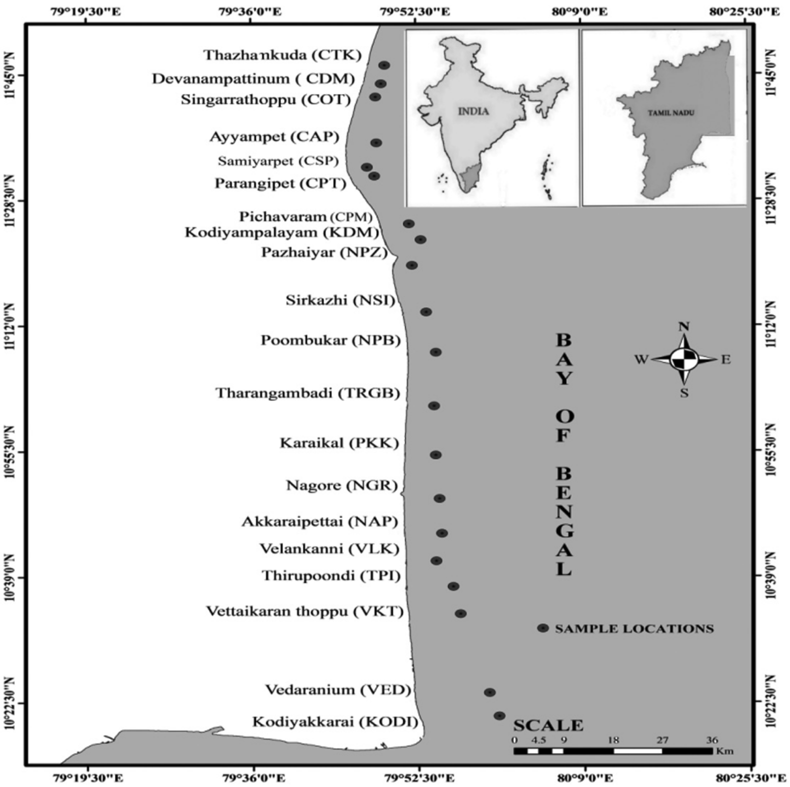

Fig. 1. Sediment samples collected at various locations from the east coast of Tamilnadu, India

All powder samples were stored in desiccators until they were analyzed. One gram of the fine ground sample and 0.5 g of the boric acid (H_3BO_3) were mixed. The mixture was thoroughly ground and pressed to a pellet of 25mm diameter using a hydraulic press (20 tons) (Ravisankar *et al*., 2011).

EDXRF Technique

The prepared pellets were analysed using the EDXRF available at Environmental and Safety Division, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, Tamilnadu. The instrument used for this study consists of an EDXRF spectrometer of model EX-6600SDD supplied by Xenemetrix, Israel. The spectrometer is fitted with a side window X-ray tube (370W) that has Rhodium as anode. The power specifications of the tube are 3-60kV; 10-5833μA. Selection of filters, tube voltage, sample position and current are fully customizable. The detector SDD 25mm^2 has an energy resolution of 136eV ± 5eV at 5.9keV Mn X-ray and 10-sample turret enables keeping and analysing 10 samples at a time. The quantitative analysis is carried out by the In-built software nEXT. A standard soil (NIST SRM 2709a) was used as reference material for standardizing the instrument. This soil standard obtained from a follow field in the central California San Joaquin valley. The soil standard (reference material) (NIST SRM 2709a) analysis value are given in Table 2. The typical EDXRF spectrum for sediment (Pichavaram-CPM) is shown in Fig. 2.

Table-2 : Analysis of Soil Standard-NIST SRM 2709a by EDXRF (mg kg^{-1})

Element	Certified Values	EDXRF Values
Mg	14600	14900 ± 1000
Al	72100	68400 ±2300
K	20500	19100 ± 700
Ca	19100	16500 ± 500
Ti	3400	3100 ± 100
Fe	33600	33900 ±1200
V	110	98.8 ± 6.59
Cr	130	112.1 ± 4.01
Mn	529	568.2 ± 19.85
Co	12.8	12.8 ± 0.55
Ni	83	69.3 ± 2.98
Zn	107	127.9 ± 4.88

RESULTS AND DISCUSSIONS

Heavy Metal Distribution in the Sediments of East Coast of Tamilnadu

The determined heavy metal concentration for 20 coastal locations of east coast of Tamilnadu by energy dispersive X-ray fluorescence (EDXRF) is given in Table 3. As can be seen from Table 3, the mean metal concentrations existed in the following order of Al>Fe>Ca>K>Mg>Ti>Mn>Cr>V>Zn>Ni>Co in the east coastal sediments. The heavy metal concentration varies from 800-10100 mg kg^{-1} for Mg; from

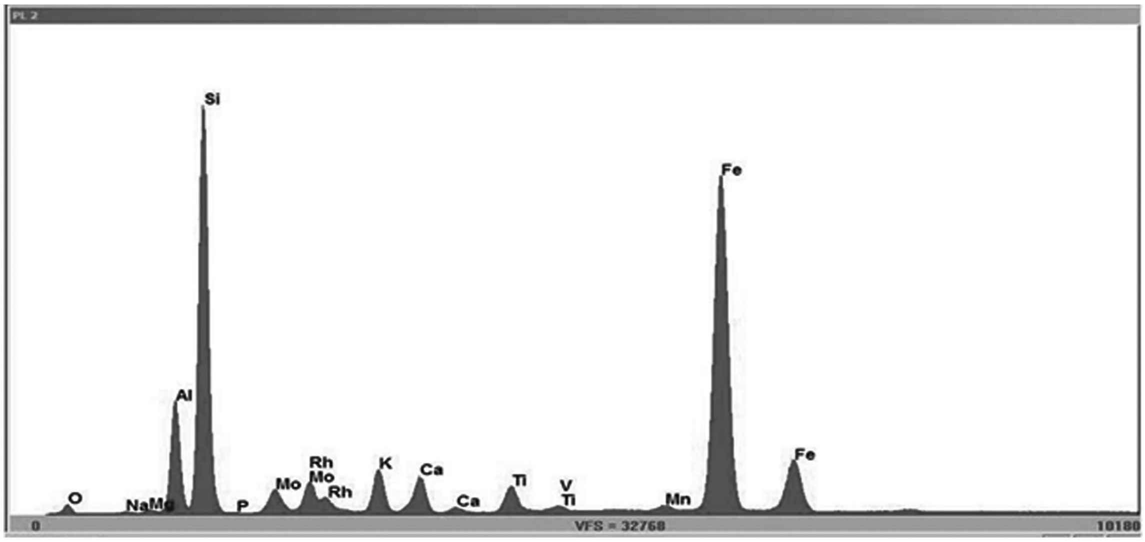

Fig. 2. Typical EDXRF Spectrum of Sediment Sample (Pichavaram-CPM) of the East Coast of Tamilnadu, India

38600-70600 mg kg^{-1} for Al; from 12100-16100 mg kg^{-1} for K; from 8900-29100 mg kg^{-1} for Ca; from 1000-21200 mg kg^{-1} for Ti; from 7900-47100 mg kg^{-1} for Fe; from 30.1-314.6 mg kg^{-1} for V; from 38.1-312.6 mg kg^{-1} for Cr; from 159.8-1171.3 mg kg^{-1} for Mn.

Assessment of Sediment Contamination by Pollution Indices

In the interpretation of geochemical data, choice of background values plays an important role. Many authors have used the average shale values or the average crustal abundance data as reference baselines. The best alternative is to compare concentrations between contaminated and mineralogical and texturally comparable, uncontaminated sediments (Varol, 2011). In this study, four different indices were used to assess the degree of heavy metal contamination in sediments of the east coast of Tamilnadu.

Table-3 : Heavy Metal Distribution in the Sediments

Location ID	Mg	Al	K	Ca	Ti	Fe	V	Cr	Mn	Co	Ni	Zn	PLI
CTK	8800	66100	15600	29100	5100	22100	80.2	86.4	477.9	7.9	30.8	48.8	0.66
CDM	4100	48200	14100	14100	2100	9600	35.3	38.5	187.2	3.5	24.2	26.8	0.33
COT	3200	47900	13300	14700	2600	10600	44.6	45.6	216.1	3.8	23.9	28.1	0.36
CAP	4400	52100	13600	14300	3200	14800	48.3	77.5	297.8	5.5	31.5	34.4	0.45
CSP	4600	54000	14100	15400	2700	14100	45.5	66.2	271.4	5.2	29.5	36.4	0.43
CPT	6100	60000	13900	18300	3900	19700	64.8	101.8	425	7.1	37.4	47.3	0.58
CPM	9500	56700	13400	17300	13800	37200	223.9	232.9	745.1	12.8	41.6	69.7	1.00
KDM	1700	42900	15500	9900	1100	8600	31.1	38.1	180.9	2.9	29.1	26.4	0.28
NPZ	800	38600	13900	8900	1000	7900	30.1	38.9	159.8	2.8	27.6	26	0.24
NSI	4900	48100	14900	13100	2200	12500	40.7	63.6	257.1	4.6	26.9	32.8	0.40
NPB	2400	43500	15000	12000	1800	11300	35.4	61.2	232.3	4	25.9	29.8	0.34
TRGB	7900	61300	15400	21000	15400	38200	238.6	271.8	811.3	13	42.7	65.6	1.05
PKK	7700	70600	14300	24600	21200	47100	314.6	312.6	1171.3	16.6	44	87.3	1.25
NGR	6200	56800	16100	20200	5100	20000	91.1	141.2	445.1	7	35.6	49.3	0.65
NAP	8100	58000	15400	18900	5200	20400	77.1	120.1	451.9	7.4	34	44.6	0.64
VLK	6700	43000	12100	12200	1900	10600	39.8	62.5	232.4	4	25.8	32.9	0.38
TPI	9300	59700	13600	20600	10200	29900	155.7	174.7	680	10.5	38.9	64.6	0.87
VKT	7900	58300	14100	20000	2600	16200	52.3	105.2	342.8	5.9	33	39.1	0.52
VED	10100	57500	13000	20900	5700	22500	102.5	142.9	531.3	8.1	34.3	44.7	0.70
KODI	5300	57900	13100	20300	4200	18800	77	121.9	433.3	6.7	32.8	38.1	0.57
Average	5985	54060	14220	17290	5550	19605	91.43	115.18	427.5	6.965	32.48	43.63	0.59
Standard values	15000	80000	26600	22100	4600	47200	130	90	850	19	68	95	

4.2.1. Enrichment Factor (EF)

Enrichment Factor (EF) is a useful tool in determining the degree of anthropogenic heavy metal pollution (Simex and heltz, 1981). The EF is computed using the below relationship:

$$EF = \frac{\left(\frac{C_X}{C_{Al}}\right)_{sample}}{\left(\frac{C_X}{C_{Al}}\right)_{reference}} \text{ - - - - - - - - -(1)}$$

In this study, Aluminum (Al) was used as the reference element for geochemical normalization because of the following reasons: (1) Al is associated with fine solid surfaces, (2) its geochemistry is similar to that of many trace metals and (3) its natural concentration tends to be uniform. When the EF value is in the range of $0.5 \leq EF \leq 1.5$, it suggests that the metals may be entirely as a result of crustal materials or natural weathering processes but when $EF > 1.5$, it suggests that a significant portion of trace metals are provided by other sources (Harikumar and Jisha, 2010). Some other EF categories are recognized: < 1 background concentration, 1–2 depletion to minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, 20–40 very high enrichment and > 40 extremely high enrichment (Bam et al., 2011). According to Zhang and Liu (2000), EF values between 0.05 and 1.5 indicate that the metal is entirely from crustal materials or natural processes, whereas EF values higher than 1.5 suggest that the sources are more likely to be anthropogenic.

The Enrichment Factor (EF) values of all the sediment samples of present study area are given in Table 4. The sediment samples at the location of Thazhankuda (CTK) was moderately enriched with Ca (2.45); minimal enriched with Ti (1.48) and Cr (1.16). Also, the sediment samples from Pichavaram (CPM) was moderately enriched with Ti (4.68), Cr (3.65) and V(2.43); minimal enriched with Ca (1.70), Fe (1.21) and Mn (1.24), the sediment samples from Tharangambadi (TRGB) was moderately enriched with Ti (4.83) and Cr (3.94); minimal enriched with Ca (1.90), V (2.40) and Mn (1.25). Similarly, significant enrichment is observed in Ti (5.77), V (2.74) and Cr (3.94); minimal enriched with Ca (1.94) and Mn (1.56) for Karaikal (PKK); moderate enrichment for Vedaranium (VED) is observed in Ti (3.29) and Cr (2.60). The presence of heavy metal in remaining locations is due to the presence of crustal materials. Among the 20 locations, the three location Pichavaram (CPM), Tharangambadi (TRGB) and Karaikal (PKK) sediment samples are moderately enriched by the elements Ca, Ti and Cr due to wastewater from human activities. The EF values of Ti were found to be highest and that of Co is lowest among the determined metals. Finally the EF value for metals studied in the sediment samples of the East Coast of Tamilnadu is "minimal to moderate enrichment".

Total EF values followed the order of Ti > Cr > Ca> V> K> Mn> Ni> Zn> Fe> Mg >Co. The variation of enrichment factor values along the east coast of Tamilnadu is shown in Fig 3.

Pollution Load Index (PLI)

The Pollution Load Index (PLI) represents the number of times by which the heavy metal concentrations in the sediment exceeds the background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample (Priju and Narayana, 2006). For the entire sampling site, pollution load index (PLI) has been determined as the n^{th} root of the product of the n CF:

$$PLI = \left(CF_1 \times CF_2 \times CF_3 \times \text{---} \times CF_n\right)^{1/n} \text{ - - - - - - (2)}$$

This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When PLI > 1, it means that pollution exists; if PLI < 1, there is no metal pollution (Tomlinson *et al.*, 1980; Chandrasekaran *et al.*, 2015). The pollution load index (PLI) ranged from 0.24 to 1.25 (Table 3). According to the mean PLI value (0.59), the east coast of sediments was practically not polluted. But the sediments of Pichavaram (CPM) with 1.00; Tharangambadi (TRGB) with 1.05; Karaikal (PKK) with 1.25 were moderately polluted by investigated metals. Other sites where PLI was less than 1 and must be classified as not polluted. Pollution indices and their assessments are given in the Table.3.

Table 4 : The EF Values of Heavy Metals in Sediment Samples of East Coast of Tamilnadu, India

S. No	Location ID	Location	Mg	K	Ca	Ti	Fe	V	Cr	Mn
1.	CTK	Thazhankuda	0.78	0.79	2.45	1.48	0.62	0.75	1.16	0.68
2.	CDM	Devanampattinum	0.50	0.98	1.63	0.84	0.37	0.45	0.71	0.37
3.	COT	Singarrathoppu	0.39	0.93	1.70	1.04	0.41	0.57	0.85	0.42
4.	CAP	Ayyampet	0.50	0.87	1.52	1.18	0.53	0.57	1.32	0.54
5.	CSP	Samiyarpet	0.50	0.87	1.58	0.96	0.48	0.52	1.09	0.47
6.	CPT	Parangipet	0.60	0.77	1.69	1.25	0.61	0.66	1.51	0.67
7.	CPI	Pichavaram	0.99	0.79	1.70	4.68	1.21	2.43	3.65	1.24
8.	KDM	Kodiyampalayam	0.23	1.20	1.28	0.49	0.37	0.45	0.79	0.40
9.	NPZ	Pazhaiyar	0.12	1.20	1.28	0.50	0.38	0.48	0.90	0.39
10.	NSI	Sirkazhi	0.60	1.03	1.51	0.88	0.48	0.52	1.18	0.50
11.	NPB	Poombukar	0.32	1.15	1.53	0.80	0.48	0.50	1.25	0.50
12.	TRGB	Tharangambadi	0.76	0.84	1.90	4.83	1.15	2.40	3.94	1.25
13.	PKK	Karaikal	0.64	0.68	1.94	5.77	1.24	2.74	3.94	1.56
14.	NGR	Nagore	0.64	0.94	1.98	1.73	0.65	0.99	2.21	0.74
15.	NAP	Akkaraipettai	0.82	0.89	1.81	1.72	0.65	0.82	1.84	0.73
16.	VLK	Velankanni	0.92	0.94	1.58	0.85	0.46	0.57	1.29	0.51
17.	TPI	Thirupoondi	0.92	0.76	1.92	3.29	0.93	1.60	2.60	1.07
18.	VKT	Vettaikaranthoppu	0.80	0.81	1.91	0.86	0.51	0.55	1.60	0.55
19.	VED	Vedaranium	1.03	0.75	2.02	1.91	0.72	1.10	2.21	0.87
20.	KODI	Kodiyakkarai	0.54	0.75	1.95	1.39	0.60	0.82	1.87	0.70
Average			0.63	0.90	1.74	1.82	0.64	0.97	1.80	0.71
Minimum			0.12	0.68	1.28	0.49	0.37	0.45	0.71	0.37
Maximum			1.03	1.20	2.45	5.77	1.24	2.74	3.94	1.56

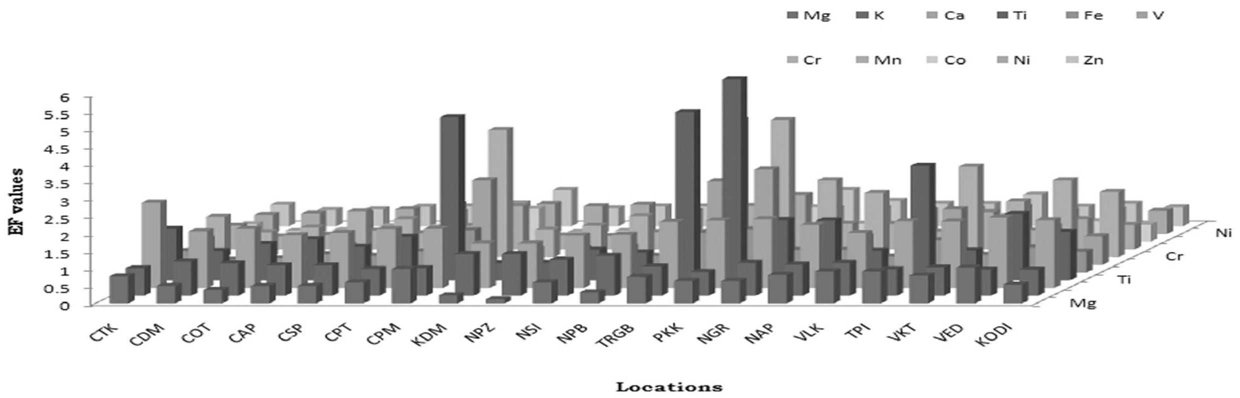

Fig. 3. Enrichment Factor Values in Sediment Sample of the East Coast of Tamilnadu, India

CONCLUSION

Distribution and ecological risk for Mg, Al, K, Ca, Ti, Fe, V, Cr, Mn, Co, Ni and Zn in sediment samples collected from 20 locations in the east coast of Tamilnadu were studied. The results showed that the sediments are not polluted by Mg, Al, K, Ca, Ti, Fe, V, Mn, Co but slightly enriched with Cr, Ni and Zn due to anthropogenic activities. The sediments of Pichavaram (CPM), Tharangambadi (TRGB) and Karaikal (PKK) were moderately polluted by investigated heavy metals due to anthropogenic inputs. From pollution assessment indices sediment samples are moderately polluted by heavy metals Ti and Cr due to human activities in coastal areas. Significant positive correlation ($p < 0.01$) among all measured metals except K showed that the major sources of those metals are probably related. This shows that sediments are contaminated by those heavy metals can affect adversely sediment-dwelling organisms. Consequently, continuous monitoring and efforts of remediation are might be required to improve the coastal environment near industrialized areas.

REFERENCES

1. Amin, B., Ismail, A., Arshad, A., Yap, C.K., Kamarudin, M.S., 2009. Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. Environ. Monit. Assess. 148, 291–305.
2. Bam, E.K.P., Akiti, T.T., Osea, S.D., Ganyaglo, S.Y., Gibrilla, A., 2011. Multivariate cluster analysis of some major and trace elements distribution in an unsaturated zone profile, Densu river Basin, Ghana. Afr. J. Environ. Sci. Technol. 5, 155–167.
3. Chandrasekaran, A., Ravisankar, R.,Harikrishnan, N., Satapathy, K.K., Prasad, M.V.R., Kanagasabapathy, K.V., 2015. Multivariate statistical analysis of heavy metal concentration in soils of Yelagiri Hills, Tamilnadu, India - Spectroscopical approach. Spectrochim. Acta Part A. 137, 589–600.
4. Ergin, M., Bodur, M.N., Ediger, V., Yemenicioglu, S., Okyar, M., Kubilay, N.N., 1993. Sources and dispersal of heavy metals in surface sediments along the Eastern Aegean Shelf. Bolletino di Oceanologia: Teorica ed Applicata, 11, 27-43.
5. Esen, E., Küçüksezgin, F., Uluturhan, E., 2010. Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. Environ. Monit. Assess. 160, 257-266.
6. Harikumar, P.S., Jisha, T.S., 2010. Distribution pattern of trace metal pollutants in the sediments of an urban wetland in the southwest coast of India. Int. J. Engg. Sci. Technol. 2, 840–850.
7. Korfali, S.I., Davies, B.E., 2004. Speciation of metals in sediment and water in a river underlain by limestone: role of carbonate species for purification capacity of rivers. Adv. Environ. Res. 8, 599-612.
8. Kucuksezgin, F., Kontaş, A., Altay, O., Uluturhan, E., Darılmaz, E., 2006. Assessment of marine pollution in Izmir Bay: Nutrient, heavy metal and total hydrocarbon concentrations. Environ. Int. 32, 41-51.
9. Martincic, D., Kwokal, Z., Stoeppler, M., Branica, M., 1989. Trace metals in Sediments from the Adriatic sea. Sci. Total Environ. 84, 135–147.
10. Obiajunwa, E.I., Pelemo, D.A., Owolabi, S.A., Fasasi, M.K., Johnson-Fatokun, F.O., 2002. Characterisation of heavy metal pollutants of soils and sediments around a crude-oil production terminal using EDXRF. Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Inter. Mat. Atoms. 194, 61–64.
11. Priju, C.P., Narayana, A.C., 2006. Spatial and temporal variability of trace element concentrations in a tropical lagoon, southwest coast of India: Environmental Implications. J. Coast. Res. 39, 1053–1057.
12. Ravisankar, R., Naseerutheen, A., Chandrasekaran, A., Bramha, S.N., Kanagasabapathy, K.V., Prasad, M.V.R., Satpathy, K.K., 2014. Energy dispersive X-ray fluorescence analysis of ancient potteries from Vellore District Tamilnadu, India with statistical approach. J. Radiat. Res. Appl. Sci. 7, 44 -54.
13. Ravisankar, R., Chandrasekaran, A., Kiruba, S., Raghu, Y., Prasad, M.V.R., Satpathy, K., Maheswaran, C., 2011. Energy dispersive X-Ray fluorescence (ED-XRF) analysis of ancient potteries of Tamil Nadu. Archi. Appl. Sci. Res. 3, 289-295.
14. Simex, S. A., Helz, G. R., 1981. Regional geochemistry of trace elements in Chesapeake Bay. Environ. Geol. 3, 315–323.

15. Syrovetnik, K., Malmstrom, M.E., Neretnieks, I., 2007. Accumulation of heavy metals in the Oostriku peat bog, Estonia: determination of binding processes by means of sequential leaching. Environ. Pollut. 147, 291–300.
16. Tomlinson, D. L., Wilson, J. G., Harris, C. R., Jeffrey, D. W., 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Hel-gol. Mar. Res. 33, 566–575.
17. Varol, M., 2011. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. J. Hazard. Mat. 195, 355–364.
18. Wang, S., Jia, Y., Wang, S., Wang, X., Wang, H., Zhao, Z., Liu, B., 2010. Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China. J. Environ. Sci. 22, 23-31.
19. (Zhang, J., Liu, C.L., 2000. Riverine composition and estuarine geochemistry of particulate metals in China-weathering features, anthropogenic impact and chemicalfluxes. Estuar. Coast. Shelf Sci. 54, 1051–1070).