Assessment of Heavy Metal Pollution And Potential Ecological Risk of Sediments of East Coast of Tamilnadu by Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) and Sediment Quality Guidelines (SQGS)

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Abstract

The heavy metals inventory and the ecological risk of the coastal sediments from Periyakalapattu to Parangipettai coast along the Bay of Bengal coastline, Tamilnadu, India were investigated. The concentration of heavy metals like Mg, Al, Si, K, Ca, Ti, Fe, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Ba, La and Pb were determined in sediment using energy dispersive X-ray fluorescence (EDXRF) technique. The mean concentration of heavy metal found in the order of Mn> Ba > V > Cr > Zn > La > Ni > Si >Pb> Co > As > Cd > Cu > Al > Fe >Ca> Ti > K > Mg. The assessment of heavy metal enrichment as well as the contamination status in the sediments was determined by the pollution load index. Further the potential ecological risk of heavy metals in sediments studied by different sediment quality guidelines (SQGs).

Keywords: Sediment; Contaminant metals; EDXRF; Potential ecological risk; SQGs

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Introduction

Estuarine and coastal regions are often polluted by various contaminants arising from industrial processes, agricultural activities, domestic wastes and vehicles emission. The rapid industrialization in the coastal area increases the heavy metal contamination in sediments. Due to the toxicity and persistence of pollution, heavy metals research of estuarine and coastal area has attracted more public concerns recently. One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and bio-magnification, resulting in potential long-term implications on human health and ecosystem [1]. Heavy metals resulting from anthropogenic contamination associated with organic matter present in thin fraction of the sediments. Sediments are ecologically important components of the aquatic habitat and also a reservoir of contaminants in water body.

Sediments are source of metals for aquatic organisms and play a key role to assess pollution in the marine environment and provide basic information for the judgment of ecological health risks. Sediments have been widely shows as environmental indicators and their ability to trace contamination sources. Sediment pollution by heavy metals has been a critical problem in marine environment because of their toxicity and bioaccumulation. The coastal sediments provide useful information about environmental and geochemical nature of the marine environment.

Multi-elemental analysis of sediments may reveal the presence of heavy metals which are contaminants and may have toxic influence on ground water and surface water. A number of analytical methods had been used in elemental studies during the past 50 years. Among these, the most successful are instrumental

neutron activation analysis (INAA), XRF, and inductively coupled plasma-mass spectrometry (ICP-MS). INAA has a longer history and its advantages include: good precision, accuracy, and reliable bulk analysis of the sample. In the majority of cases, INAA is more sensitive than XRF. It is also more matrix independent and less susceptible to geometric effects than XRF. However, INAA, requires access to a nuclear reactor, a longer analytical time and additional sample preparation for irradiation. XRF has the advantage of non-destructive analysis for a given sample, but has limited detection capability compared to INAA. ICP-MS has the advantage of sensitivity but requires sample dissolution which is difficult for many inorganic materials, especially for those with high silica content like obsidian. In contrast, while laser ablation ICP-MS requires minimal sample preparation and the analysis is minimally invasive to the sample analysis is frequently semi-quantitative at best.

The EDXRF technique is chosen for the present work due to its advantages like non-requirement of chemical treatment of the samples; it is less time consuming non-destructive method and it is ideal for environmental research. It is short processing time, accurate, relatively cheap, low detection limits and easy to use and also rapid for multi-elemental analysis. The fundamental principle behind XRF is that when electrons of particular elements are excited by X-rays they emit or fluorescence a spectrum of X-rays that is specific to that element. ED-XRF is widely used as a non-destructive method for chemical analysis of environmental matrix [2-4].

Hence the objective of the present work is to (i) determine the accumulation, distribution of heavy metals in sediments of the east coast of Tamilnadu and (ii) assess the potential ecological risk of sediments using sediment quality guidelines viz., Threshold Effect Level (TEL), Probable Effect Level (PEL), Effect Range Low (ERL)/Effective Rage Median (ERM) and Sever Effect Level (SEL).

Study Area

Sediment samples were collected along the Bay of Bengal coastline, from Periyakalapattu to Parangipettai 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. Recent industry developments during the last two decades in Cuddalore, Auroville, Thazhankuda and Sitheripettai coastal towns include offshore oil production, chemical, fertilizer processing plants and more than 150 small scale industries, all located 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., rivers Puravandayanar, Uppanar pass through the agricultural belt of Tamilnadu state and finally drain into the Bay of Bengal in this coastal sector.
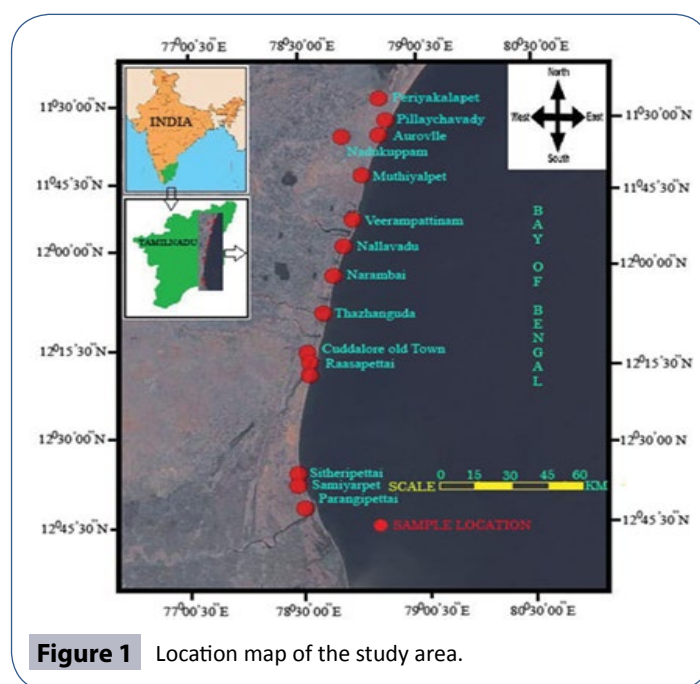
Figure 1 Location map of the study area.

Table 1 Geographical latitude and longitude for the sampling locations.

S. No	Name of the Location	Location ID	Latitude	Longitude
1	Periyakalapet	PP1	12° 1' 46.6320'' N	79° 51' 49.0032'' E
2	Ellaipillaichavady	PP2	11° 55' 54.0228'' N	79° 48' 19.1268'' E
3	Auroville	PP3	11°59'2.8422"N	79°50'55.5334"E
4	Nadukuppam	PP4	11°58'1.7401"N	79°38'35.5103"E
5	Muthialpet	PP5	11° 57' 18.2556'' N	79° 50' 4.1712'' E
6	Veerampattinam	PP6	11° 54' 5.6160'' N	79° 49' 36.7428'' E
7	Nallavadu	PP7	11° 51' 27.6014'' N	79°34'27.46"E
8	Narambai	PP8	11° 49' 3.2520'' N	79° 48' 0.9216'' E
9	Thazhankuda	PP9	11°46'14.2020"N	79°47'40.5605"E
10	Cuddalore OT	PP10	11° 45' 0.0000'' N	79° 45' 0.0000'' E
11	Raasapettai	PP11	11° 40' 56.2692'' N	79° 46' 17.5008'' E
12	Sitheripettai	PP12	10° 30' 31.6944'' N	77° 13' 17.7600'' E
13	Betlodai	PP13	11° 21' 45.2300'' N	79° 32' 21.8544'' E
14	Samiyarpettai	PP14	11° 32' 57.2100'' N	79° 45' 31.8744'' E
15	Parangaipettai	PP15	11° 30' 0.0000'' N	79° 46' 0.0012'' E

Materials and Methods

Sample collection and preparation

Sediment sample were collected by a Peterson grab sampler from parallel to the shoreline. The grab sampler collects 10 cm thick bottom sediment layer from the seabed along the 15 locations **(Figure 1).** Uniform quantity of sediment samples were collected from all the sampling stations. 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 -4°C until analysis. The samples were air dried at 105°C for 24 h to a constant weight and sieved using a 63 μm sieve in order to identify the geochemical concentrations. The grain size <63 μm, which presents several advantages: (1) heavy metals are mainly linked to silt and clay; (2) this grain size is like that of the suspended matter in water; and (3) it has been used in many studies on heavy metal contamination. Then samples were ground into a fine powder for 10-15 min, using an agate martor. 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) [3]. The **Figure 1** shows the sampling location map of the Study area.

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

EDXRF technique

The prepared pellets were analyses 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 (370 W) that has Rhodium as anode. The power specifications of the tube are 3-60 kV; 10-5833 μA. Selection of filters, tube voltage, sample position and current are fully customizable. The detector SDD 25 mm2 has an energy resolution of 136 eV ± 5 eV at 5.9 keVMn X-ray and 10- sample turret enables keeping and analyzing 10 samples at a time. The quantitative analysis is carried out by the In-built software nEXT.

A reference material standard soil (NIST SRM 2709a) was used for standardizing the instrument. This soil standard obtained from a follow field in the central California San Joaquin valley. **Table 2** reports the certified values with measured EDXRF and its shows that they are well agreement with each other.

Results and Discussions

Heavy metal distribution in the sediments of east coast of Tamil Nadu

The determined heavy metal concentration for 15 coastal locations of east coast of Tamilnadu using energy dispersive X-ray fluorescence (EDXRF) is given in **Table 3.** The heavy metal concentration varies from 25-6007 mg kg^{-1} for Mg; from 13532-37425 mg kg^{-1} for Al; from 129139-226500 mg kg^{-1}; from 4468-9350 mg kg^{-1} for K; from 4592-21679 mg kg^{-1} for Ca; from 530-51434 mg kg^{-1} for Ti; from 3647-57902 mg kg^{-1} for Fe; from 23.4-711 mg kg^{-1} for V; from 12.5-207.3 mg kg^{-1} for Cr; from 68.1-1387.6 mg kg^{-1} for Mn; from 1.1-19 mg kg^{-1} for Co;from 15.2-33.63 mg kg^{-1} for Ni; from BDL-3.60 mg kg^{-1} for Cu; from 14-89 mg kg^{-1} for Zn; from 4-6.9 mg kg^{-1} for As; from BDL-10.2 mg kg^{-1} for Cd; from 152.3-416.8 mg kg^{-1} for Ba; from BDL-216.7 mg kg^{-1} for La and from BDL-35.7 mg kg^{-1} for Pb. As can be seen from **Table 2**, the mean concentrations of heavy metal found in the following order of Mn> Ba > V > Cr > Zn > La > Ni > Si >Pb> Co > As > Cd > Cu > Al > Fe >Ca> Ti > K > Mg. The heavy metal concentration of the present work is compared with results of the other countries

**Table 3** Comparison of heavy metal (mgkg^{-1}) concentration of present work with other countries.

S. No.	Location	Cr	Mn	Co	Ni	Zn	References
1	Coastal shandong, Penninsula	35-99.6	-	-	19-56.8	37-181.1	[1]
2	Izmit Bay, Turkey	74.3	-	-	-	930	[6]
3	Danube River, Europa	26.5-556.5	442-1655	-	17.5-173.3	78-2010	[7]
4	Bohai Bay, Bohai Sea China.	33.5	-	-	30.5	71.7	[8]
5	Bremen Bay, Germany	131	-	-	60	790	[9]
6	Tinto River, Spain	11-151	-	6.8-42	1.6-36	68-5280	[10]
7	Pearl river estuary	89	-	-	41.7	150	[11]
8	Kafrain Dam, Jordan	160	730	60	100	120	[12]
9	Masan Bay, Korea	67.1	-	-	28.8	206.3	[13]
10	**East Coast of Tamilnadu, India**	**80.03**	**367.65**	**6.68**	**24.80**	**39.79**	**Present Study**

Table 4 Heavy metal concentration (mg kg⁻¹) of sediment samples of east coast of Tamilnadu, India.

S. No	Element	Mg	Al	Si	K	Ca	Ti	Fe	V	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Ba	La	Pb	PLI
1	PP1	2223	20696	223285	6615	8943	2039	9534	50.11	42.38	192.26	3.38	20.86	0.0	30.54	4.7	5.5	312.4	12.9	4.4	0.3490
2	PP2	25	20255	216248	6202	7239	2340	8458	50.9	30.3	180.1	2.8	19.8	0.0	23.0	4.7	2.1	306.1	29.1	1.5	0.2820
3	PP3	1800	37425	226500	5484	8070	51434	57902	711.0	207.3	1387.6	19.0	24.4	0.0	89.0	6.9	0.0	180.2	216.7	35.7	0.9520
4	PP4	300	13532	210618	6800	4592	530	3647	23.4	12.5	68.1	1.1	15.2	0.0	14.0	4.0	0.0	411.9	0.0	0.0	0.2410
5	PP5	1028	19066	189935	7869	7406	1216	5520	26.37	21.21	110.05	1.88	16.48	0.0	20.16	4.8	10.2	385.4	0.0	1.4	0.2800
6	PP6	6007	30893	161332	5044	20809	15464	35269	234.71	127.00	750.16	12.51	33.63	0.0	62.31	6.5	3.4	209.0	47.0	17.0	0.8310
7	PP7	3022	26895	133697	4468	21176	11689	33771	204.56	123.33	748.38	11.95	33.30	0.0	65.67	5.8	0.0	152.3	31.0	19.8	0.6470
8	PP8	5051	31132	150205	4850	21679	19539	40489	310.87	155.77	869.09	14.35	30.23	3.60	65.94	7.4	0.0	176.0	51.2	25.5	0.7830
9	PP9	816	21212	147446	6085	12057	3357	13407	64.94	54.52	243.11	5.01	23.21	0.0	30.78	5.2	1.4	256.7	19.1	9.1	0.3860
10	PP10	1608	19866	129139	5392	11628	3776	13137	71.38	55.33	263.74	4.61	24.59	0.0	29.00	4.7	3.6	236.1	6.4	6.1	0.3640
11	PP11	795	23554	178547	7286	11363	931	8308	31.85	43.85	157.81	3.10	22.84	0.0	22.47	4.8	2.3	308.2	0.0	6.8	0.3450
12	PP12	1773	22928	202630	9350	11586	724	6693	28.12	30.32	128.35	2.40	21.67	0.0	36.02	5.6	1.8	416.8	1.0	7.6	0.3110
13	PP13	2072	20975	179547	7147	9403	1583	9530	40.01	66.16	185.61	3.42	23.16	0.0	25.08	4.9	3.8	302.5	3.1	5.5	0.3690
14	PP14	3440	21775	136994	4859	13169	3469	19281	86.6	112.3	112.3	6.5	32.1	0.0	37.8	4.4	5.1	250.4	18.0	5.0	0.4260
15	PP15	4612	25167	134370	5232	12027	8814	24594	151.9	118.1	118.1	8.3	30.4	0.0	45.0	5.0	2.8	224.0	6.0	9.4	0.4770
	Average	2305	23691	174699	6179	12076	8460	19302	139.11	80.03	367.65	6.68	24.80	3.60	39.79	5.3	3.8	275.2	36.8	11.1	0.4695

Table 5 Comparison between sediment quality guidelines (SQGs) and heavy metals concentration (mg kg⁻¹) in the present study with percentage of sample in each guideline.

Sediment quality guidelines	Mg	Al	K	Ca	Ti	Fe	V	Cr	Mn	Co	Ni	Zn
Threshold Effect Level (TEL)	n.a	n.a	n.a	n.a	n.a	n.a	n.a	52	n.a	n.a	15.9	124
Probable Effect Level (PEL)	n.a	n.a	n.a	n.a	n.a	n.a	n.a	160	n.a	n.a	42.8	271
Effect Range Low (ERL)	n.a	n.a	n.a	n.a	n.a	n.a	n.a	81	n.a	n.a	20.9	150
Effective Range Median (ERM)	n.a	n.a	n.a	n.a	n.a	n.a	n.a	370	n.a	n.a	51.6	410
Sever Effect Level (SEL)	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	1100	n.a	50	270
Measured values in present study	2305	23691	6179	12076	8460	19302	139.11	80.03	367.65	6.68	24.80	39.79
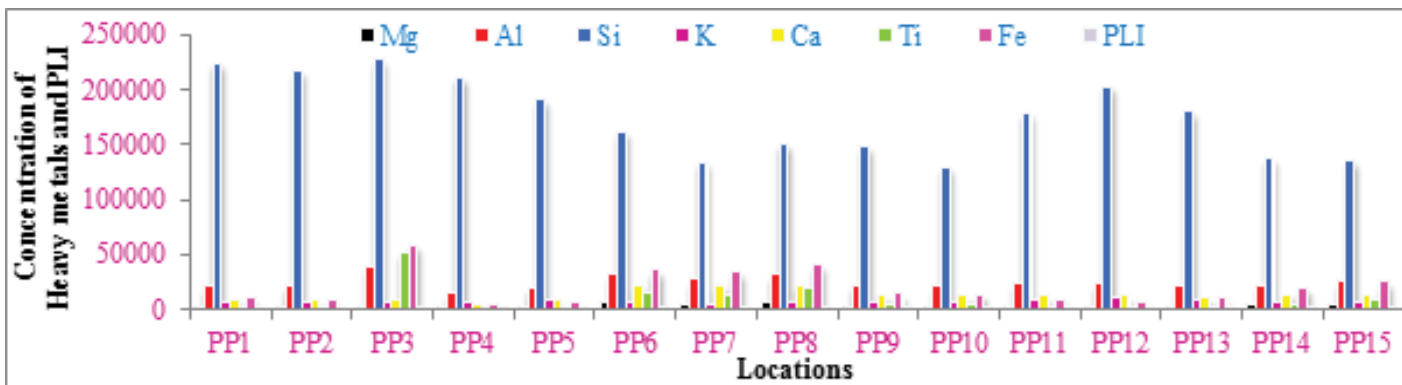
Figure 2 Heavy metal distribution and PLI in the sediments with different location.

in the world and given in **Table 4** and **Figure 2** shows the Heavy metal distribution in the sediment with different location.

Pollution load index (PLI)

The pollution load index (PLI) provides a simple, comparative means for assessing the level of heavy metal pollution [5]. PLI is determined as the nth root of the product of nCf

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \cdots \times CF_n)^{1/n} \quad \text{---------- (1)}$$

where Cf is the contamination factor and n is the number of metals. CF is considered to be an effective tool in monitoring the pollution over a period of time. CF is the ratio between the sediment metal concentration at a given site and the background value of the metal and it is given by the formula,

$$CF = \frac{C_{heavy metal}}{C_{background}} \quad - - - - - - - -(2)$$

According to Tomlinson et al. (1980) [5] PLI>1 means that pollution is present; otherwise, if it is below 1, there is no metal pollution. The pollution load index (PLI) ranged from 0.24 to 0.95 **(Table 3)**. The minimum and maximum value of the PLI noticed in PP4 (0.2410) and PP3 (0.9520) respectively. According to the mean PLI value (0.4696), the east coast of sediments was practically not polluted. The variation of PLI show in **Figure 2.**

Potential ecological risk by sediment quality guidelines (SQGs)

Sediment quality guidelines (SQGs) can be used to evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and can be designed to aid in the interpretation of sediment quality [14]. These guidelines have been widely used to screen sediment contamination by comparing sediment contaminant concentrations with the corresponding quality guidelines in aquatic ecosystems [15, 16]. This guideline was used correctly classifying sediments as either toxic or non-toxic. SQGs developed for sediments ecosystems [17, 18]. The SQGs the effect range low (ERL)/ effect range median (ERM), Threshold Effect Level (TEL), Probable Effect Level (PEL), Sever Effect Level (SEL) was applied in this study, to assess the eco-toxicological sense of heavy metal concentrations in

sediment samples. The comparison between sediment quality guideline (SQGs) and heavy metals concentration (mg kg^{-1}) in the present study in each guideline is given in **Table 5**.

The concentration of Ni is greater than threshold effect level (TEL) and effect range low (ERL) for all the sampling locations but less than the sever effect level (SEL) and effective range medium (ERM). Similarly the concentration of Zn in all the sampling locations less than the Threshold effect level (TEL), Probable Effect Level (PEL), effect range low (ERL), effect range median (ERM) and Sever Effect Level (SEL).

The contaminate by metal greater than threshold effect level (TEL) for Cr and less than the Probable Effect Level (PEL) and slightly less than the effect range median (ERM). These SQGs results indicate that the concentrations of Cr and Ni are likely to result in harmful effects on sediment-dwelling organisms due to human activities in the coastal area. But other heavy metals normally occur in the sediments due to natural origin.

Conclusion

◊ Distribution of Mg, Al, Si, K, Ca, Ti, Fe, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Ba, La, and Pb in sediment samples were determined along the east coast of Tamilnadu.

◊ 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.

◊ The mean concentration of heavy metals compared with other results of other countries.

◊ The sediment quality guidelines (SQGs) indicates that the average concentration of Cr is greater than probable effect level (PEL), and effective rage median (ERM) while average concentration of Zn is greater than threshold effective level (TEL) and effective rage median (ERM). This shows that sediment samples are polluted by Cr and Zn.

◊ The results of the present investigation and actual knowledge about the metal distribution in these sediment indicate that continuous monitoring and efforts of remediation are required to improve the coastal environment near industrialized areas.

Acknowledgement

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