Assessing heavy metal toxicity in sediments of Chennai Coast of Tamil Nadu using Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) with statistical approach

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1. Introduction

Estuarine and coastal regions are often polluted by various anthropogenic contaminants ranging those resulting from industrial and agricultural activities, domestic wastes and vehicular emissions. Due to increasing toxicity and the persistence of heavy metal pollution, heavy metals research of estuarine and coastal areas are now becoming widespread. Human impacts on environment can be assessed by measuring concentration of heavy metals in soils, plants, animals and sediments because metal pollution can adversely affect the density and diversity of biotic communities including humans. Sediments are also sources of metals for aquatic organisms and therefore, play key role in assessing pollution levels in marine environment. They also provide basic information necessary for quantifying risks associated with environmental health issues. Consequently, all types of coastal sediments ranging from those in densely populated urban areas to those in highly industrialized regions are being intensely studied.

Environmental contamination arising from rapid urbanization and industrialization has recently become an issue of immense concern all over the world [1–3]. These contaminations are particularly significant in estuarine and coastal sediments, which usually act as a sink that receives the heavy metals through adsorption from suspended matter and subsequent sedimentation [4,5]. Sediment bound heavy metals have a tendency to adsorb and accumulate on fine-grained particles that eventually move into the depositional areas [6–9].

Sediment pollution by heavy metals has been regarded as a critical problem in marine environment because of their toxicity, persistence and bioaccumulation [5,10–12]. Many studies have shown that high...
concentration of heavy metals in sediments could have significant negative impact on the health of marine ecosystems [13–16]. Knowledge of the distribution and concentration of heavy metals in sediments will help in detecting their sources in aquatic systems [17]. Therefore, heavy metal distributions in sediments offer a more realistic approach of evaluating their actual environmental impact.

The concentration of trace elements in coastal sediment can be useful for baseline studies and also, in the assessment of sediment quality in future research. Multi-elemental analysis of sediment may reveal the presence of heavy metals and their concentrations, which sometimes are contaminants that may have toxic influence on ground and surface water resources, plants, animals and humans [18]. Energy dispersive X-ray fluorescence (EDXRF) is a nuclear analytical technique used in this study to determine the elemental composition of sediment samples. The EDXRF technique is a versatile tool commonly used in environmental research.

The study area, which spans from Pulicat Lake to Vadanemmeli of Chennai Coast, Tamil Nadu, India is located in one of the most populated regions of southeastern, India. The area is dominated by intensive industrial activities in which the discharge of their effluents into the river has been going on for a long time. This coast is a very important environmental, economical, commercial, agricultural and recreational location in southeastern India. This study was conducted to investigate the impacts of rapid economic development along the East Coast of Tamil Nadu on heavy metal deposition and to assess their potential ecological risk. Specifically, the objectives of this study were: (i) to determine the levels of heavy metals (Mg, Al, K, Ca, Ti, Fe, V, Cr, Mn, Co, Ni, and Zn) in the sediments and to identify the possible sources of these metals via statistical analysis; (ii) to quantify the extent of metal pollution using enrichment factor (EF), geo accumulation index (Igeo), contamination factor (CF) and pollution load index (PLI) and to indentify the possible sources of these heavy metals by multivariate statistical methods.

2. Materials and methods

2.1. Sample collection and preparation

22 sediment samples were collected from Chennai Coast along the Bay of Bengal Coastline (Pulicat Lake to Vadanemmeli) in Southeastern India using a Peterson grab sampler from 10 m water depths during the pre-monsoon season. All sampling points were located parallel to the shoreline as shown in Fig. 1. The grab sampler collects the samples at 10 cm below the seabed in all sampling points. Around 25 cm thick subsurface samples from the seabed were collected by the grab. From the grabbed samples, 10 cm thick sediment layer was sampled from the middle of the grab to avoid metal contamination by the jaws of the grab.

Table 1 shows the geographic coordinates (latitudes and longitudes) of the various sampling locations. A hand held Global Positioning System – Garmin Oregon 550, as used in measuring the coordinates of the sampling points. Inter station spacing was maintained at 3 NM (nautical mile). Coastal craft was utilized for collecting samples at each station. After travelling to the beach by road the sample collection team hires a boat from artisanal fishermen, who convey them to the sampling points after about 60 min of sailing. The Peterson grab sampler is suitable for sampling near-shore sea bed sediments particularly, in locations where the sea bed is dominted by sandy, silt and/or gravelly sediments. This technique is the conventional method of sampling shallow sea bottom sediments [19–21]. Each sediment sample was carefully taken from the central portion of the dredge with a plastic spatula previously washed with 2 M HCl and 2 M HNO3 [22].
samples were stored in plastic bags at 4 °C. The samples were oven dried at 105 °C for 24 h to a constant weight and sieved using a 63 μm sieve. The use of grain sizes of < 63 μm, in such analysis has several advantages including (1) heavy metals are mainly linked to silt and clay particles (2) this grain size is like that of suspended matter in water, and (3) it has been used in many studies on heavy metal contamination [23]. Then the samples were grinded to a fine powder using an agate mortar. All the pulverized samples were stored in desiccators until they were analyzed. One gram of the fine ground sample and 0.5 g of boric acid (H$_3$BO$_3$) were mixed. The mixture was thoroughly ground and pressed to a pellet of 25 mm diameter using a 20-ton hydraulic press [24].

### 2.2. EDXRF technique

The pellets were analyzed using EDXRF spectrometer (model EX-6600SD manufactured by Xenemetric, Israel). This instrument is available at Environmental and Safety Division, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, Tamil Nadu. This spectrometer is equipped with a side window X-ray tube (370 W) that has Rhodium as anode. The power specifications of the tube are 3–60 kV and 10–5833 μA. Selection of filters, tube voltage, sample position and current are fully computer controlled and having an energy resolution of 136 eV ± 5 eV Mn customizable. The silicon drift detector 25 mm X-ray and 10-sample turret enables the instrument to position and analyze 10 samples concurrently. Quantitative analysis was conducted with the help of an in-built NEXT software. A standard soil sample (NIST SRM 2709a) was used as reference material for standardizing the instrument [23]. This soil standard was obtained from a follow field in San Joaquin valley, central California. Results obtained from the analysis of soil standard (reference material) (NIST SRM 2709a) are given in Table 2. A typical EDXRF spectrum for sediment (CPL) is shown in Fig. 2.

### 2.3. Multivariate statistical analysis

Statistical technique involving principal component analysis (PCA) was employed to identify the main source of heavy metals (natural or anthropogenic) in the samples. In addition, cluster analysis (CA) was performed to obtain information about the similarities and dissimilarities in concentration of heavy metals present among the different sampling sites to ascertain the dominance influence of a particular pollution sources in the study area. A computer code Statistical Package for Social Science (SPSS, version 16.0) was used in performing the statistical analysis.

### 3. Results and discussion

#### 3.1. Metal contents in surface sediments

The concentration of elements in sediments from Pulicat Lake to Vadanemmeli, along the East Coast of Tamil Nadu, southeastern India is presented in Table 3. The elements Al, Ca, K, Fe, Ti, Mg, Mn, V, Cr, Zn, Ni and Co chosen for the present work may be due to toxicity when its level in higher than the crustal level. The elements like Al, Ca,K & Mg is included in the list of heavy metals may be due to their toxic in nature when it is higher than background levels. The concentration varies from 100 to 4200 mg kg$^{-1}$ for Mg; 16400–33500 mg kg$^{-1}$ for Al; 7900–11400 mg kg$^{-1}$ for K; 2400–15700 mg kg$^{-1}$ for Ca; 500–8300 mg kg$^{-1}$ for Ti; 4100–20000 mg kg$^{-1}$ for Fe; 23.70–129.00 mg kg$^{-1}$ for V; 16.20–93.00 mg kg$^{-1}$ for Cr; 68.40–381.10 mg kg$^{-1}$ for Mn; 1.20–7.10 mg kg$^{-1}$ for Co; 15.60–23.60 mg kg$^{-1}$ for Ni and from 18.60–45.30 mg kg$^{-1}$ for Zn.

Among the heavy metals detected, Aluminium (Al) is the most abundant metal in the sediments. The mean order of metal concentration decreases in the following order, Al > Ca > K > Fe > Ti > Mg > Mn > V > Cr > Zn > Ni > Co [19,25]. Comparatively the locations of Chennai Port (CPT) and Vadanemmeli (CVM) are characterized by higher concentrations of Co, Cr, Ni, V and Zn (Table 3). This may be due to the high tourists’ boat activities and other anthropogenic activities like shipping and harbour activities, industrial and urban wastage discharges, dredging, etc. Such findings are in agreement with results obtained by earlier workers like Millward and Moore [26], Nath et al. [27] and Santhiya et al. [28].

Amongst the elements obtained, Ti, Fe, V, Cr, Mn, Co, Ni and Zn have higher concentrations in locations such as Vadanemmeli (CVM) and Kovalam Beach (CKB). Mg, Al and K have high concentrations at Chennai Harbor (Nagooranthottam) (CCH) and Panaiyur (CPR) (Table 3). This may be due to recent increase in industrial (in the coastal areas) and harbor activities that involves movement of naval vessels throughout the year. Furthermore, the presence of heavy metals in coastal sediments can also be attributed to other sources like municipal waste waters, mine discharge, irrigation discharge, and erosion of rocks and parent soil materials [29–31]. Several studies have shown

#### Table 2

| Element | Certified values (mg kg$^{-1}$) | EDXRF values (mg kg$^{-1}$) | %error |
|---------|--------------------------------|----------------------------|--------|
| Mg      | 14600.0                        | 14900.0                    | +2.05  |
| Al      | 72100.0                        | 68400.0                    | −5.13  |
| K       | 20500.0                        | 19100.0                    | −6.83  |
| Ca      | 19100.0                        | 16500.0                    | −13.6  |
| Ti      | 3400.0                         | 3100.0                     | −8.82  |
| Fe      | 33600.0                        | 33900.0                    | +0.99  |
| V       | 110.0                          | 98.8                       | −10.18 |
| Cr      | 130.0                          | 112.1                      | −13.77 |
| Mn      | 529.0                          | 568.2                      | 7.41   |
| Co      | 12.8                           | 12.8                       | 0      |
| Ni      | 83.0                           | 69.3                       | −16.5  |
| Zn      | 107.0                          | 127.9                      | 19.53  |

#### Table 1

| S.No | Location                  | Sample ID | Latitude   | Longitude   |
|------|---------------------------|-----------|------------|-------------|
| 1    | Pulicat Lake              | CPL       | 13°34′8.2″N | 80°18′7.5″E |
| 2    | Pulicat (Koanangkuppam)   | CPK       | 13°25′31.42″N | 80°21′26.12″E |
| 3    | Kattupalli                | CKP       | 13°19′27.33″N | 80°22′51.77″E |
| 4    | Power Station             | CPS       | 13°15′35.37″N | 80°22′21.94″E |
| 5    | Nettukuppam               | CKN       | 13°14′10.50″N | 80°23′53.23″E |
| 6    | Ennore                    | CEE       | 13°12′41.88″N | 80°21′18.71″E |
| 7    | Tiruchinnakuppam          | CTK       | 13°9′36.02″N  | 80°20′32.34″E |
| 8    | Chennai Harbor            | CCH       | 13°8′20.61″N  | 80°29′0.82″E |
| 9    | Chennai Port (Kasimedu/Fishing Harbour) | OPT     | 13°6′5.45″N  | 80°19′44.78″E |
| 10   | Kanimedu-Tondiarpet       | CKU       | 13°7′14.61″N  | 80°19′44.04″E |
| 11   | Neppiar Bridge            | CNB       | 13°4′17.77″N  | 80°19′34.47″E |
| 12   | Marina Beach              | CMB       | 13°2′24.23″N  | 80°18′20.02″E |
| 13   | Broken Beach              | CBB       | 13°5′54.40″N  | 80°18′21.48″E |
| 14   | Besent Nagar              | CBN       | 13°0′8.21″N   | 80°18′17.37″E |
| 15   | Thiruvanniyur             | CTR       | 12°59′38.39″N | 80°18′99.98″E |
| 16   | Neelankarai               | CNI       | 12°57′2.18″N  | 80°17′29.61″E |
| 17   | Chennai Golden Beach      | CGG       | 12°55′3.90″N  | 80°17′16.44″E |
| 18   | Panaiyur                  | CPR       | 12°53′32.32″N | 80°17′4.18″E  |
| 19   | Kanathursunami, (Reddykuppam) | CGI     | 12°50′12.66″N | 80°16′34.01″E |
| 20   | Mutukkaudu (Karkattukuppam) | CMK     | 12°48′36.74″N | 80°16′40.72″E |
| 21   | Kovalam Beach             | CKB       | 12°47′24.36″N | 80°16′48.33″E |
| 22   | Vadanemmeli, (Puthiyakalpakkam) | CVM     | 12°44′59.05″N | 80°16′39.20″E |
that accumulations of heavy metals in sediments might be due to point sources such as direct discharge of large amounts of industrial and domestic sewages into rivers and/or seas [32,33]. There are many chemical and pharmaceutical factories located along the east coast of Tamil Nadu whose discharge can heavily pollute the soils with heavy metals. Additionally, these elevated metals concentration might have originated from non-point sources such as agricultural pollution (e.g. fertilizers and livestock manure), atmospheric transport and other industrial activities [16]. Overall, our data indicates that the elevated heavy metal levels in sediments resulted mainly from anthropogenic activities such as discharge of wastewaters, aquaculture and shipping activities.

3.2. Quantification of heavy metal pollution in the sediments

Many methods, suitable for assessing heavy metal pollution of sediments, exist. These pollution indicators, which were used to determine metal accumulation, distribution and their pollution status in order to obtain information suitable for quantitative ranking of different sampling sites, include enrichment factor (EF), geo-accumulation index \(I_{geo}\), contamination factor (CF) and pollution load index (PLI). For optimal interpretation of geochemical data, appropriate choice of background values are important. Many researchers use the average shale values or the average crustal abundance data as reference baselines [19,25,34,35] (Chadrasekaran et al., 2015). Absence of background values of metal concentrations in Indian estuarine systems made us to use the average concentration values of metal in sediments reported by Turekian and Wedepohl [36].

3.2.1. Enrichment factor (EF)

Enrichment factor (EF) is a normalization technique widely used to separate the metals of natural variability from those resulting from anthropogenic influences on heavy metals in sediments using Eq. (1) [37,38] as:

\[
EF = \left( \frac{C_{\text{sample}}}{C_{\text{UCC}}} \right)_{\text{sample}} \left( \frac{C_{\text{UCC}}}{C_{\text{UCC}}} \right)_{\text{UCC}}
\]  

(1)

Table 3

| S. No. | SampleID/Elements | Mg  | Al  | K   | Ca  | Ti  | Fe  | V   | Cr  | Mn  | Co  | Ni  | Zn  |
|-------|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.    | CPL               | 1700| 21200| 7900| 5700| 1700| 6500| 41.40| 27.30| 115.90| 2.30| 16.40| 22.40|
| 2.    | CPK               | 2500| 32200| 11000| 12300| 2700| 8100| 42.00| 21.70| 183.30| 2.70| 17.70| 26.30|
| 3.    | CKP               | 1400| 26900| 11100| 7200| 600| 4500| 24.60| 17.90| 70.70| 1.30| 16.60| 31.00|
| 4.    | CPS               | 1500| 16400| 8200| 5100| 600| 3800| 23.70| 21.30| 68.40| 1.20| 16.50| 25.70|
| 5.    | CNK               | 2100| 18800| 8500| 6000| 700| 4700| 26.30| 21.90| 84.90| 1.60| 16.70| 25.50|
| 6.    | CEE               | 2100| 25200| 8700| 2400| 1700| 9800| 37.00| 41.60| 213.60| 3.30| 18.90| 35.00|
| 7.    | CTK               | 3200| 27500| 11300| 15700| 500| 5500| 26.30| 22.10| 102.70| 1.80| 17.30| 34.20|
| 8.    | CCH               | 4200| 30200| 11200| 12600| 2400| 9600| 46.10| 34.00| 198.20| 3.50| 20.30| 28.80|
| 9.    | CPT               | 1300| 26900| 8600| 12300| 3900| 12800| 62.50| 41.90| 256.50| 4.60| 18.40| 45.30|
| 10.   | CKU               | 1200| 24900| 9900| 8100| 1400| 6000| 30.80| 24.60| 114.90| 2.10| 16.80| 24.30|
| 11.   | CNB               | 2200| 23800| 10100| 11400| 2400| 8800| 37.40| 39.00| 153.80| 3.00| 17.60| 26.60|
| 12.   | CMB               | 1200| 20100| 10000| 5500| 600| 4100| 24.10| 16.20| 76.90| 1.30| 15.60| 26.00|
| 13.   | CBB               | 1000| 25400| 10000| 10000| 1600| 6900| 31.70| 28.30| 149.00| 2.50| 17.00| 22.40|
| 14.   | CBN               | 3500| 28700| 11200| 11500| 1700| 7800| 34.70| 30.80| 152.50| 2.80| 22.10| 28.90|
| 15.   | CTR               | 2000| 23500| 9400| 9900| 800| 5100| 25.70| 26.80| 101.70| 1.70| 19.00| 18.60|
| 16.   | CNI               | 1900| 22100| 9100| 9200| 1200| 5900| 29.80| 27.50| 121.90| 2.10| 18.10| 21.10|
| 17.   | CCG               | 2200| 33500| 11400| 15300| 5300| 16000| 85.70| 59.30| 307.70| 5.70| 23.40| 37.70|
| 18.   | CFR               | 1400| 29200| 10600| 11600| 2400| 9800| 43.30| 40.20| 192.90| 3.40| 20.60| 27.60|
| 19.   | CRI               | 1500| 19200| 8300| 10100| 1600| 6600| 28.30| 32.60| 134.40| 2.20| 17.90| 20.10|
| 21.   | CKK               | 32900| 10900| 13600| 2700| 11400| 50.30| 44.40| 216.50| 4.00| 20.90| 44.90|
| 22.   | CVM               | 1400| 26600| 8100| 12300| 8500| 20000| 129.00| 93.00| 381.10| 7.10| 23.60| 43.40|

Mean 1918 25436 9832 9859 2109 8209 41.58 34.14 160.80 2.85 18.79 29.12

Crustal Average (Turekien and Wedepohl 1961) 15000 80000 26600 22100 4600 47200 130 90 850 19 68 95

Fig. 2. A typical EDXRF spectrum for CPL sample.
where \( C_X \) and \( C_{AI} \) denote the concentrations of elements X and Al respectively in the samples and average shale obtained from Turekian and Wedepohl [36]. Some common ranges of EF categories are: < 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) [39]. Generally, an EF value of about 1 suggests that such levels of metal enrichment might have originated entirely from crustal materials or natural weathering processes [40]. An EF value > 1.5 suggests that a significant portion of metal is delivered from non-crustal materials, or non-natural weathering processes, so anthropogenic sources become an important contributor [41]. 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 [19]. The enrichment factor levels of sediments in the study area are given in Table 4.

Variations in EF levels for heavy metals were: 0.03–0.82 (mean of 0.44) for Mg, 1.02–1.67 (mean of 1.31) for K, 0.53–3.17 (mean of 2.13) for Ca, 0.35–6.00 (mean of 1.53) for Ti, 0.31–1.39 (mean of 0.59) for Fe, 0.62–3.28 (mean of 1.09) for V, 0.65–3.42 (mean of 1.31) for Cr, 0.27–1.48 (mean of 0.64) for Mn, 0.22–1.24 (mean of 0.51) for Co, 0.97–1.77 (mean of 1.33) for Ni and 0.73–1.56 (mean of 1.07) for Zn (Table 4). Minimum EFs served in some elements (e.g., Mg, Fe, Mn and Co) are less than unity implying that such elements are depleted in some phases relative to crustal abundance in the area [42].

The EF values for Mg, K, Fe, V, Cr, Mn, Co, Ni and Zn were less than 1.5, which indicate dominant metal enrichments from natural sources (Table 4). EF values greater than 1.5 that were obtained for V (CPT, CPR and CVM), Cr (CEE, CPT, CNB, CPR, CMK and CVM), Ni (CPS, CTR, CMK and CVM), Zn (CPT and CVM), suggest that these levels of enrichment might have originated from sources that are of non-crustal origin. These results suggest that sediments in these areas are contaminated with heavy metals (V, Cr, Ni and Zn), whose major source is anthropogenic inputs from industrial activities [43]. However, sediments from some stations outside these locations were either slightly or not contaminated with these heavy metals.

Finally, the levels of heavy metal enrichment served in sediments in the East Coast of Tamil Nadu are "minimal to moderate." The order of total EF are Ca > Ti > Ni > K > Cr > V > Zn > Mn > Fe > Co > Mg. The enrichment of Ca and Ti may be due to anthropogenic sources of non crustal origin. The variational pattern of heavy metal EF along the east coast of Tamil Nadu is shown in Fig. 3.

### Table 4

| Elements | Mg  | K   | Ca  | Ti  | Fe  | V   | Cr  | Mn  | Co  | Ni  | Zn  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| CPL      | 0.47| 1.24| 1.49| 1.54| 0.57| 1.32| 1.26| 0.57| 0.50| 1.36| 0.98|
| CPR      | 0.46| 1.14| 2.12| 1.61| 0.47| 1.07| 0.50| 1.27| 0.39| 0.97| 0.76|
| CKP      | 0.31| 1.38| 1.49| 0.43| 0.31| 0.62| 0.65| 0.65| 0.72| 0.77| 1.09|
| CPS      | 0.54| 1.67| 1.73| 0.70| 0.43| 0.98| 1.27| 0.43| 0.34| 1.77| 1.45|
| CNK      | 0.66| 1.51| 1.77| 0.72| 0.46| 0.95| 1.14| 0.37| 0.39| 1.56| 1.26|
| CEE      | 0.49| 1.15| 0.53| 1.30| 0.72| 0.99| 1.61| 0.88| 0.61| 1.32| 1.29|
| CTK      | 0.68| 1.37| 3.17| 0.35| 0.37| 0.65| 0.99| 0.99| 0.30| 1.11| 1.15|
| CCH      | 0.82| 1.24| 2.32| 1.53| 0.59| 1.03| 1.10| 0.68| 0.54| 1.18| 0.88|
| CPT      | 0.28| 1.07| 2.54| 2.79| 0.88| 1.57| 1.52| 0.99| 0.79| 1.20| 1.56|
| CKU      | 0.28| 1.33| 1.81| 1.08| 0.45| 0.84| 1.04| 0.48| 0.39| 1.19| 0.90|
| CNB      | 0.54| 1.41| 2.66| 1.94| 0.68| 1.06| 1.60| 0.67| 0.58| 1.30| 1.04|
| CMB      | 0.35| 1.66| 1.52| 0.57| 0.38| 0.81| 0.79| 0.40| 0.30| 1.37| 1.20|
| CBB      | 0.23| 1.31| 2.19| 1.52| 0.50| 0.84| 1.09| 0.61| 0.46| 1.24| 0.82|
| CBN      | 0.72| 1.30| 2.23| 1.14| 0.50| 0.82| 1.05| 0.55| 0.45| 1.36| 0.93|
| CTR      | 0.46| 1.48| 2.07| 1.26| 0.52| 0.95| 1.47| 0.59| 0.47| 1.51| 0.94|
| CNI      | 0.63| 1.33| 2.34| 0.65| 0.40| 0.74| 1.12| 0.45| 0.34| 1.42| 0.73|
| CCG      | 0.03| 1.37| 2.31| 1.04| 0.49| 0.91| 1.22| 0.57| 0.44| 1.44| 0.88|
| CPR      | 0.39| 1.13| 2.54| 3.04| 0.88| 1.73| 1.73| 0.95| 0.79| 1.23| 1.04|
| CRI      | 0.28| 1.21| 2.21| 1.58| 0.62| 1.00| 1.35| 0.68| 0.54| 1.24| 0.88|
| CMK      | 0.46| 1.44| 2.92| 1.60| 0.64| 1.00| 1.66| 0.72| 0.53| 1.64| 0.97|
| CKB      | 0.36| 1.10| 2.30| 1.58| 0.64| 1.03| 1.32| 0.68| 0.56| 1.12| 1.26|
| CVM      | 0.31| 1.02| 2.57| 6.00| 1.39| 3.28| 3.42| 1.48| 1.24| 1.56| 1.51|
| Mean     | 0.44| 1.31| 2.13| 1.53| 0.59| 1.09| 1.31| 0.64| 0.51| 1.33| 1.07|

The geo-accumulation index (I\(_{geo}\))

Possible metal enrichments in aquatic sediments was evaluated using geoaccumulation index (I\(_{geo}\)) (Eq. (2)) of Muller [44]. The formula used for calculating I\(_{geo}\) is expressed in Eq. (2):

\[
I_{geo} = \log_2 \left( \frac{C_n}{1.5 \times B_n} \right)
\]

Fig. 3. Plot of locations versus EF values of heavy metals.
where, \( C_n \) is the concentration of metal n in the sediments, \( B_n \) is the background concentration value for metal n [36], and the factor 1.5 is used because of possible variations of background data due to lithological variations. The Igeo parameter was successfully calculated using the global average shale data from Turekian and Wedepohl [36].

According to a scale established by Muller [44], sediments can be classified as non polluted (Igeo < 1), very slightly polluted (1 < Igeo < 2), moderately polluted (2 < Igeo < 3), highly polluted (4 < Igeo < 5) and very highly polluted (Igeo > 5). The Igeo values for each element at the various sampling sites were calculated using background values. Igeo values from all the locations are given in Table 5.

The Igeo values of coastal sediments are -2.42 to -7.81 (average -3.78) for Mg, -1.81 to -2.34 (average -2.03) for K, -0.61 to -3.32 (average -1.40) for Ca, 0.27 to -3.79 (average -2.10) for Ti, -1.82 to -4.22 (average -3.25) for Fe, -0.60 to -3.04 (average -2.38) for V and -0.54 to 3.06 (average -2.11) for Cr. Others were -1.74 to 4.22 (average -3.14) for Mn, -2.01 to -4.57 (average -3.48) for Co, -1.67 to -2.19 (average -2.01) for Ni and -1.65 to -2.94 (average -2.34) for Zn (Table 5). The average pollution degree of these metals decreases in the order: Si > Ca > Mn > Fe > Co > Mg. Variation in Igeo indices values with locations is shown in Fig. 4.

According to Muller [44] scale, these Igeo indices, which are generally < 1 indicate the investigated area is not polluted. Thus, the range of Igeo values from heavy metals suggests that the investigated sediments are not seriously polluted.

### Table 5

| Elements | Mg    | K     | Ca    | Ti     | Fe    | V     | Cr    | Mn    | Co    | Ni    | Zn     |
|----------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|--------|
| CPL      | -3.73 | -2.34 | -2.07 | -2.02  | -3.45 | -2.24 | -2.31 | -3.46 | -3.63 | -2.19 | -2.67  |
| CRI      | -3.17 | -1.86 | -0.96 | -1.35  | -3.13 | -2.22 | -2.64 | -2.80 | -3.40 | -2.08 | -2.44  |
| CKP      | -4.01 | -1.85 | -1.74 | -3.52  | -3.98 | -2.99 | -2.91 | -4.17 | -4.45 | -2.18 | -2.20  |
| CPS      | -3.91 | -2.28 | -2.23 | -3.52  | -4.22 | -3.04 | -2.66 | -4.22 | -4.57 | -2.18 | -2.47  |
| CNK      | -3.42 | -2.23 | -2.00 | -3.30  | -3.91 | -2.89 | -2.62 | -3.91 | -4.15 | -2.17 | -2.48  |
| CEE      | -3.42 | -2.20 | -3.32 | -2.02  | -2.85 | -2.49 | -1.70 | -2.58 | -3.11 | -1.99 | -2.03  |
| CTK      | -2.81 | -1.82 | -0.61 | -3.79  | -3.69 | -2.89 | -2.61 | -3.63 | -3.98 | -2.12 | -2.06  |
| CCH      | -2.42 | -1.83 | -0.93 | -1.52  | -2.88 | -2.08 | -1.99 | -2.69 | -3.03 | -1.89 | -2.31  |
| CPT      | -4.11 | -2.21 | -0.96 | -0.82  | -2.47 | -1.64 | -1.69 | -2.31 | -2.63 | -2.03 | -1.65  |
| CKB      | -4.23 | -2.01 | -1.57 | -2.30  | -3.56 | -2.66 | -2.35 | -3.47 | -3.76 | -2.16 | -2.55  |
| CNB      | -3.35 | -1.98 | -1.07 | -1.52  | -3.01 | -2.38 | -1.79 | -3.05 | -3.25 | -2.09 | -2.42  |
| CMG      | -4.23 | -2.00 | -2.13 | -3.52  | -4.11 | -3.02 | -3.06 | -4.05 | -4.45 | -2.27 | -2.45  |
| CBB      | -4.49 | -2.00 | -1.26 | -2.11  | -3.36 | -2.62 | -2.25 | -3.10 | -3.51 | -2.07 | -2.67  |
| CBN      | -2.68 | -1.83 | -1.06 | -2.02  | -3.18 | -2.49 | -2.13 | -3.06 | -3.35 | -1.76 | -2.30  |
| CTR      | -3.49 | -1.89 | -1.40 | -2.11  | -3.36 | -2.52 | -1.88 | -3.19 | -3.51 | -1.84 | -2.52  |
| CNI      | -3.17 | -2.09 | -1.28 | -3.11  | -3.80 | -2.92 | -2.33 | -3.65 | -4.07 | -1.98 | -2.94  |
| CCG      | -7.81 | -2.13 | -1.38 | -2.52  | -3.58 | -2.71 | -2.30 | -3.39 | -3.76 | -2.05 | -2.76  |
| CPR      | -3.35 | -1.81 | -0.65 | -0.38  | -2.15 | -1.19 | -1.19 | -2.05 | -2.32 | -1.68 | -1.92  |
| CKI      | -4.01 | -1.91 | -1.05 | -1.52  | -2.85 | -2.17 | -1.75 | -2.72 | -3.07 | -1.86 | -2.37  |
| CKM      | -3.91 | -2.27 | -1.25 | -2.11  | -3.42 | -2.78 | -2.05 | -3.25 | -3.70 | -2.07 | -2.67  |
| CKB      | -3.49 | -1.87 | -0.82 | -1.35  | -2.63 | -1.95 | -1.60 | -2.56 | -2.83 | -1.84 | -1.67  |
| CVM      | -4.01 | -2.30 | -0.96 | -0.27  | -1.82 | -0.60 | -0.54 | -1.74 | -2.01 | -1.67 | -1.72  |
| Mean     | -3.78 | -2.03 | -1.40 | -2.10  | -3.25 | -2.38 | -2.11 | -3.14 | -3.48 | -2.01 | -2.34  |

**Fig. 4.** Plot of locations versus Igeo values of heavy metals.

3.2.3. Contamination factor

Contamination factor (CF) was used to assess the level of contamination by the various metals in the sediments. CF was computed using Eq. (3)

\[
CF = \frac{C_{\text{heavy metal}}}{C_{\text{background}}}
\]

where \( C_{\text{background}} \) refers to the concentration of metal of interest in the sediments when there is no anthropogenic input. Where interpreting CF data if CF < 1, then the level of contamination is low, For 1 < CF < 3 then we have moderate contamination, for 3 < CF < 6 then the level of contamination is said to be considerable and for CF > 6, then we have high contamination [45]. The contamination factors obtained at all the studied locations are given in Table 6.

The range of CF results are 0.007–0.280 (average 0.128) for Mg, 0.186–0.381 (average 0.289) for Al, 0.297–0.429 (average 0.370) for K, 0.150–0.981 (average 0.616) for Ca, 0.109–1.804 (average 0.458) for Ti, 0.081–0.424 (average 0.174) for Fe, 0.182–0.992 (average 0.320) for V, 0.180–1.033 (average 0.379) for Cr, 0.080–0.448 (average 0.189)
for Mn, 0.063–0.374 (average 0.150) for Co, 0.312–0.472 (average 0.376) for Zn (Table 6). The concentrational trend, just like EF and Igeo, were Ca > Ti > Cr > Ni > K > V > Zn > Al > Mn > Fe > Co > Mg. Values of CF on all the samples are less than 1, thus, suggesting that the beach sediments are lowly contaminated with these elements. Fig. 5 shows the pattern of variation in CF of heavy metals with spatial locations.

### 3.2.4. Pollution load index

Since heavy metals always occur in sediments as complex mixtures with large variations in concentrations, then pollution load index (PLI) was used in determining the integrated pollution status of combined toxicant groups at sampling stations by calculating the nth root of the product of the n CF for the tested metals according equation 4

$$PLI = \left( \prod_{n} CF_n \right)^{1/n}$$

where $CF_n$ is value of the CF for metal n. The PLI values were interpreted in two levels as polluted (PLI > 1) and unpolluted (PLI < 1) [46]. A PLI value of zero indicates no pollution. The PLI results range from 0.164 to 0.489 with a mean of 0.271, thus indicating that the area is practically not polluted (Table 6). A criteria of all the pollution indicators in sediment based on pollution indices are given in Table 7.

### Table 6

| Elements | Mg   | Al   | K    | Ca   | Ti   | Fe   | V    | Cr   | Mn   | Co   | Ni   | Zn   | PLI  |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| CPL      | 0.113| 0.241| 0.297| 0.356| 0.370| 0.138| 0.318| 0.303| 0.136| 0.121| 0.328| 0.236| 0.226|
| CPK      | 0.167| 0.366| 0.414| 0.769| 0.587| 0.172| 0.323| 0.241| 0.216| 0.142| 0.354| 0.277| 0.296|
| CHP      | 0.093| 0.306| 0.417| 0.450| 0.130| 0.095| 0.189| 0.199| 0.083| 0.068| 0.332| 0.326| 0.184|
| CPS      | 0.100| 0.186| 0.308| 0.319| 0.130| 0.081| 0.182| 0.237| 0.080| 0.063| 0.330| 0.271| 0.164|
| CNK      | 0.140| 0.214| 0.320| 0.575| 0.152| 0.100| 0.202| 0.243| 0.100| 0.084| 0.334| 0.268| 0.189|
| CEE      | 0.140| 0.286| 0.327| 0.150| 0.370| 0.208| 0.285| 0.462| 0.251| 0.174| 0.378| 0.368| 0.365|
| CTK      | 0.213| 0.313| 0.425| 0.981| 0.109| 0.117| 0.202| 0.246| 0.121| 0.095| 0.346| 0.360| 0.232|
| CCH      | 0.280| 0.343| 0.421| 0.788| 0.522| 0.203| 0.355| 0.378| 0.233| 0.184| 0.406| 0.303| 0.340|
| CPT      | 0.087| 0.306| 0.323| 0.769| 0.848| 0.271| 0.481| 0.466| 0.302| 0.242| 0.368| 0.477| 0.357|
| CKU      | 0.080| 0.283| 0.372| 0.506| 0.304| 0.127| 0.237| 0.293| 0.135| 0.111| 0.336| 0.256| 0.223|
| CNB      | 0.147| 0.270| 0.380| 0.713| 0.522| 0.186| 0.288| 0.433| 0.181| 0.158| 0.352| 0.280| 0.291|
| CMB      | 0.080| 0.228| 0.376| 0.344| 0.130| 0.087| 0.185| 0.180| 0.090| 0.068| 0.312| 0.274| 0.167|
| CBB      | 0.067| 0.289| 0.376| 0.625| 0.348| 0.146| 0.244| 0.314| 0.175| 0.132| 0.358| 0.236| 0.239|
| CNB      | 0.233| 0.326| 0.421| 0.719| 0.370| 0.165| 0.267| 0.342| 0.179| 0.147| 0.442| 0.304| 0.296|
| CTR      | 0.133| 0.277| 0.406| 0.569| 0.348| 0.146| 0.262| 0.409| 0.165| 0.132| 0.420| 0.261| 0.263|
| CNI      | 0.167| 0.267| 0.353| 0.619| 0.174| 0.108| 0.198| 0.298| 0.120| 0.089| 0.380| 0.196| 0.213|
| CCG      | 0.007| 0.251| 0.342| 0.575| 0.261| 0.125| 0.229| 0.306| 0.143| 0.111| 0.362| 0.222| 0.177|
| CPR      | 0.147| 0.381| 0.429| 0.956| 1.152| 0.339| 0.659| 0.659| 0.362| 0.300| 0.468| 0.397| 0.455|
| CKI      | 0.093| 0.352| 0.398| 0.725| 0.522| 0.208| 0.333| 0.447| 0.227| 0.179| 0.412| 0.291| 0.307|
| CMK      | 0.100| 0.218| 0.312| 0.631| 0.348| 0.146| 0.218| 0.362| 0.158| 0.116| 0.358| 0.212| 0.231|
| CKB      | 0.133| 0.374| 0.410| 0.850| 0.587| 0.242| 0.387| 0.493| 0.255| 0.211| 0.418| 0.473| 0.361|
| CVM      | 0.093| 0.302| 0.305| 0.769| 1.804| 0.424| 0.992| 1.033| 0.448| 0.374| 0.472| 0.457| 0.489|
| Mean     | 0.128| 0.289| 0.370| 0.616| 0.458| 0.174| 0.320| 0.379| 0.189| 0.150| 0.376| 0.307| 0.271|

### Table 7

| EF | Pollution status | CF | Pollution status | Igeo | Pollution status | PLI | Pollution status |
|----|------------------|----|------------------|------|------------------|-----|------------------|
| > 1| With anthropogenic sources | > 6 | Very high | > 5 | Extreme | > 1 | Polluted |
|   |                    | > 3 and < 6 | Considerable | 4–5 | Strong to extremely strong |       |                  |
|   |                    | > 1 and < 3 | Moderate | 3–4 | Strong |       |                  |
| < 1| Without anthropogenic sources | < 1 | Low | 2–3 | Moderate to strong | < 1 | Unpolluted |
|   |                          | < 0 | Unpolluted to moderate | 1–2 | Moderate |       |                  |

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Fig. 5. Plot of locations versus CF values of heavy metals.
3.3. Statistical analysis

Pearson correlation analysis was performed to determine the relationship between the various heavy metals. Another statistical technique—principal component analysis, was performed by evaluating the principal components and computing their eigenvectors to determine the main sources of the pollutants. The rotation of the principal components was carried out using Varimax method. Finally, cluster analysis was also carried out to identify the pollution sources. All the statistical analysis were performed using the commercial statistics software SPSS (Statistical Package for Social Science) version 16.0 for windows.

3.3.1. Pearson correlation analysis

The correlation analysis is a bivariant method which is usually applied in determining the relationship between two different parameters. Correlation analyses have been widely applied in environmental studies [47,48]. They provide an effective way of revealing the relationships between multiple variables thereby, enhancing the understanding of the various influencing factors as well as the main sources of the different chemical components. The relationship between heavy metal concentrations were analyzed using Pearson’s correlation coefficient.

Results obtained from the Pearson’s correlation analysis and their significance levels are shown in Table 8. Aluminum (Al) has a significant correlation with K (r = 0.723 p < 0.01) and Ca (r = 0.707 p < 0.01). Similarly, Ti correlated significantly with Fe (r = 0.967 p < 0.01), V (r = 0.987 p < 0.01), Cr (r = 0.938 p < 0.01), Mn (r = 0.949 p < 0.01), Co (r = 0.965 p < 0.01) and Ni (r < 0.01). According to reports from Lu et al. [49] and Saeddi et al. [50], if the correlation coefficient between the heavy metal factors is positive, then these factors may have a common source, mutual dependence and identical behavior during transportation. But potassium (K) negatively correlates with Ti (r = −0.087), V (r = −0.107) and Cr (r = −0.146). This shows that Ti, V and Cr originate from different sources.

3.3.2. Principal component analysis

PCA was used to identify the heavy metal sources in the sediments, and results obtained are presented in Table 9. The cumulative percentages of the variations inferred from the first two components, and the values of the first two principal components (PCs) after rotation for the maximum variance are shown in Table 9. These PCs were chosen based on their eigenvalues, which were both greater than 1.0. The total variance obtained from the first two PCs was greater than 81.41%.

Based on the results obtained from PCA, associations of heavy metal concentrations of Mg, Al, K, Ca, Ti, Fe, V, Cr, Mn, Co, Ni and Zn metals, which perhaps, originated from anthropogenic sources, accumulate in the sediments [19]. Factor-2 was dominated by Mg, Al, K and Ca with a variance of 21. 60%. These results show that the high concentrations of Mg, Al, K and Ca present in the sediments originate from parent rock materials.

3.3.3. Cluster analysis

Cluster analysis [19,25] of metals in the sediments was conducted in order to identify heavy metals associated with major elements and the results obtained are shown in the dendrogram (Fig. 6). The elements are hierarchically clustered and based on the total metal concentrations in the sediments, 2 distinct clusters were identified.

Cluster I contains Co, Ni, V, Cr, Mn, Mg, Ti, K, Ca, Fe and Zn suggesting that these elements probably originated from a common anthropogenic source. Cluster II contains Al only, which may be geochemically associated in nature due to its terrigenous source [27], and also immobile nature in marine environment [51]. Clustering of heavy metals Cr, V, Co, Ni and Zn with major elements Mg, Ti, Ca, Fe and K indicate that these elements might have originated from anthropogenic sources. The results of cluster analysis (CA) were consistent with those obtained from the principal component analysis thus, reflecting that these trace elements originated from a common source.

4. Conclusion

The levels of heavy metal pollution and their possible sources in coastal sediments have been investigated. Results show that the average concentrations of heavy metals in sediments along Chennai Coast do not exceed environmental background values suggesting that the sediments are not polluted. The mean concentration of metals decreases in the following order of Al > Ca > K > Fe > Ti > Mg > Mn > V > Cr > Zn > Ni > Co. The concentrations of Co, Cr, Ni, V and Zn

| Variables | Mg | Al | K | Ca | Ti | Fe | V | Cr | Mn | Co | Ni | Zn |
|-----------|----|----|---|----|----|----|---|----|----|----|----|----|
| Mg        | 1  | 0.409 | 0.365 | 0.057 | -0.017 | 0.071 | 0.062 | 0.294 | 0.110 | 1  | 1  | 1  |
| Al        |    | 0.409 | 0.723 | 0.707 | 0.463 | 0.437 | 0.596 | 0.618 | 0.557 |    |    |    |
| K         |    |    | 0.723 | 0.707 | 0.037 | -0.133 | 0.965 | 0.122 | 0.406 |    |    |    |
| Ca        |    |    |    | 0.707 | 0.037 | -0.133 | 0.965 | 0.122 | 0.406 |    |    |    |
| Ti        |    |    |    |    | -0.017 | 0.987 | 0.990 | 0.990 | 0.739 | 0.110 | 1  | 1  |
| Fe        |    |    |    |    |    | 0.987 | 0.990 | 0.990 | 0.739 | 0.110 | 1  | 1  |
| V         |    |    |    |    |    |    | 0.990 | 0.990 | 0.739 | 0.110 | 1  | 1  |
| Cr        |    |    |    |    |    |    |    | 0.990 | 0.990 | 0.739 | 0.110 | 1  |
| Mn        |    |    |    |    |    |    |    |    | 0.990 | 0.990 | 0.739 | 0.110 |
| Co        |    |    |    |    |    |    |    |    |    | 0.990 | 0.990 | 0.739 |
| Ni        |    |    |    |    |    |    |    |    |    |    | 0.990 | 0.739 |
| Zn        |    |    |    |    |    |    |    |    |    |    |    | 0.990 |

| Variables | Factor-1 | Factor-2 |
|-----------|-----------|-----------|
| Mg        | -0.0292   | 0.514     |
| Al        | 0.4543    | 0.858     |
| K         | 0.1332    | 0.899     |
| Ca        | 0.4310    | 0.738     |
| Ti        | 0.9808    | 0.035     |
| Fe        | 0.9892    | 0.135     |
| V         | 0.9711    | 0.004     |
| Cr        | 0.9609    | -0.066    |
| Mn        | 0.9754    | 0.157     |
| Co        | 0.9871    | 0.138     |
| Ni        | 0.7384    | 0.335     |
| Zn        | 0.6996    | 0.240     |

% of variance explained 59.81 21.60
reveal the impact of industrial and anthropogenic activities on heavy metal accumulation in the sediment. The metals (Co, Cr, Ni & V) are mainly of natural origin with the exception of some local anomalies for Zn. This anomaly may be directly associated with point discharges from municipal, dock and industrial activities. The concentrations of Co, Cr, V and Zn are high at some locations (e.g., CTK, CPT, CKU, CPR, CKI, CKB and CVM) probably because of high tourists, boating and other anthropogenic activities in such areas. Sediment contamination was assessed on the basis of enrichment factor (EF), geoaccumulation index (Igeo), contamination factor and pollution load index (PLI). The mean EF values for all metals, except V, Cr and Zn, were > 1.5 in CPT, CPR and CVM areas, thus suggesting that their enhanced levels are anthropogenic origin. CF values for the studied metals are < 1 which indicate that the sediments are not contaminated. Igeo values of heavy metals show that the sediments are not seriously polluted from anthropogenic inputs. The PLI capture that study area as being practically unpolluted. The location CVM showed concentration of high concentrations of Co, Cr, Ni, V in sediments whose major source might be from anthropogenic inputs for industrial activities. Results obtained from the pollution indicators (EF, CF, Igeo, and PLI) show that the sediments do not pose significant ecological risk.

Pearson correlation results show significant correlation between Ti and Fe, V, Cr, Mn, Ni and Co, which suggest that these elements probably originated from a common source. A good correlation between the overall metal contaminants determined by multivariate analysis and computed metal pollutant indices in all the sampling stations. The PCA and CA analysis technique have proved to be useful tools for the identification of contamination levels. We recommended that it is necessary to formulate and implement effective and efficient waste management policies to control metals discharged into the harbor areas and therefore minimise their associated adverse influences on the environment, ecosystem, and public health.

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