Estimation of pollution indices and hazard evaluation from trace elements concentration in coastal sediments of Kerala, Southwest Coast of India

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Abstract

**Background:** The environment is always subjected to exposure from different natural and anthropogenic sources of trace elements. The excessive intake of these trace elements may become toxic and cause health disorders to the people when the concentration exceeds certain threshold limits. The measurement of trace elements concentration in general and toxic trace elements concentration in particular is important for the assessment and prediction of risk to the environment and public. Distribution of trace elements in various environmental matrices depends on the nature of the element itself and the site-specific characteristics such as type of the matrices and its physicochemical parameters. In view of these aspects, an attempt is made to assess the concentration of trace elements and pollution indices in the sediment samples collected from the coastal belt of Kerala and possible conclusions were drawn.

**Results:** The results of pollution indices clearly indicate the moderate level of trace elements contamination in the coastal belts of Kerala. Significant correlations were observed between the concentration of trace elements and physicochemical parameters of the sediments.

**Conclusion:** Most of the trace elements enrichment in the coastal belt is due the crustal materials or natural weathering process and atmospheric deposition. The investigation revealed the sources of most of the elements present in the coastal belt of Kerala are lithogenic such as weathering and atmospheric deposition.

**Keywords:** Trace elements, Pollution indices, ICP-MS, Coastal Kerala

Background

In recent years, the environment is highly polluted due to the increase in the population pressure on land, industrialization, use of fertilizers and other man-made activities on the ecosystem. The trace elements discharged by various human activities will contaminate the environmental matrices such as air, water, soil, sediment, etc., and further they settle down in soil and sediment. The trace elements accumulation and enrichment in soil and sediment increase enormously when time progresses and leads to contamination of the adjacent agricultural areas, food crops, and aquatic systems.

The quality of life can only be improved by the availability of good water, soil and air from the environment. However, undesired changes in the chemical, physical, and biological characteristics of the different environmental matrices have created a tremendous threat to the people. The impacts of trace elements accumulation and enrichment have been paid more attention because of their peculiar pollutant characteristics. Trace elements supposed to be present in trace levels play an important role in the human life cycle (Santos et al. 2005). The trace elements are natural constituents of the earth's crust, and
accumulation of trace elements in different environmental matrices depends on both natural and anthropogenic factors (Parth et al. 2011).

The distribution of elements depends on the weathering of parent rocks and pedogenesis. The elements such as Mn, Cr, and Ni are constituents of some rock types of volcanic and metamorphic origin (Alloway 1995). During the weathering process, the primary crystalline structures of some rock minerals are completely broken and the relevant chemical is thus either absorbed in the topsoil or transported toward surface water or groundwater targets. The behavior of trace elements in the environment depends on the enrichment level, origin and forms, and also properties of the environmental matrix. The environment is always subjected to exposure from different anthropogenic sources of trace elements, viz. industrial waste, mining activities, smelters, foundries, combustion processes, transportation, etc. (Tokman et al. 2004).

In the current scenario, the disposal of waste generated as a result of the various human activities is a matter of serious concern. The waste management of industrial effluents and municipal wastes is highly essential for the abatement of environmental pollution (Brar et al. 2000). The migration of elemental constituents from waste disposal sites to the ecosystem is a complex process and involves various geochemical activities. The elemental constituents can bio-magnify in animals and plants eventually making their way to humans through food chain (Abrahams 2002). The frequent use of fertilizers and pesticides in agricultural lands will result in the enrichment of trace metals such as Ni, Cu, Cd, and Zn in the topsoil. A clear understanding of the migration of trace elements from soil to plants is essential for producing the impact of spreading the metal-containing waste on agricultural lands. The adverse effects of trace elements are related to the soil’s ability to absorb and retain such elements (Elliot et al. 1986). The trace elements are essential for plants at certain levels and can also be toxic at certain threshold levels (Facchinelli et al. 2001). The trace elements do not decay with time, unlike radionuclides and many organics, and hence long-term monitoring is also needed. The elements such as Cd, As, and Pb are particularly important because they are not biodegradable and can accumulate in human vital organs, producing progressive toxicity (Alam et al. 2003).

The toxic elements can reduce soil fertility and increase input to the food chain which leads to accumulation of toxic elements in food stuffs and ultimately can endanger human health. The deficiency and excess concentration of certain elements can be toxic and cause abnormalities and health disorders to the biological ecosystem. The contamination due to trace elements in the biological system is of major concern because of its toxicity and threat to the human life cycle (Purves 1985). Hence, studies on trace elements accumulation in various environmental matrices due to natural and anthropogenic sources have been carried out by several investigators around the world.

In the earlier works, Lagermerff et al. (1970), Chao (1972), Kothny (1973), Mikkelson and Brandon (1975), Ito and Limura (1975), Kirkham (1975), Bingham et al. (1976), Jugsujinda and Patrick (1977), Reddy and Patrick (1977), Colbourn and Thornton (1978), Haines and Pocock (1980), Fergusson et al. (1980), Gibson and Farmer (1983), Forstner (1985); Purves (1985), Elliott (1986), and Xian (1987) have carried out assessment of the concentration of heavy metals through various anthropogenic sources such as industrial wastes, automobile emissions, mining and agricultural activities. The anthropogenic sources can easily accumulate in the soil and can lead to serious environmental issues.

The potentially toxic metals such as Cu, Cd, Cr, Pb, As, Hg, Se, Ni and Zn may accumulate in food crops or may leach through soils polluting water bodies and always pose a threat to the environment and health of the human beings (Hooda and Alloway 1998). Among these metals, Pb and Cd are the most hazardous from an environmental viewpoint. The accumulation and movement of trace elements in the soil are significantly affected by the physicochemical parameters associated with the soil (Li and Shuman 1996) and the adsorption process of the soil (Berti and Jacobs 1996). The mobility of the trace elements depends not only on their total concentration in soil but also on the soil properties, elemental properties, and environmental factors (He et al. 2004). The organic matter content, moisture content, pH, and redox potential of the soil considerably affect the solubility of metals (Bozkurt et al. 2000). Most of the soils are soluble in acidic soils, in slightly basic, neutral or nearly neutral soils (Schmitt and Sticker 1991). The texture, pH, organic matter content, moisture content, and cation exchange capacity are important with respect to the form of trace metal and its bioavailability. The elements Mn, Fe, and Pb can be enriched in soil because of their low mobility at acidic pH. However, the elements Zn, Cu, and Ni have higher mobility under acidic conditions.

Generally, the concentration and distribution of trace elements are influenced by the nature of parent materials, mobility, climate, mineralogy, texture, geological factors and the physicochemical parameters of the environmental matrices (Krishna and Govil 2007). The most important variables of soils which control the trace element availability are pH, mineral composition, organic matter quantity and quality, texture, temperature, and water regime. Mortved (1991) gave some models to predict the phytoavailability of trace elements, especially of Cu, Zn,
Cd, and Pb, but rather they are limited to a given plant and specific growth conditions. The discharge of a large amount of sewage and other waste from different outlets influences the concentration of the trace elements in the coastal area (Solai et al. 2010). The trace elements are present mainly in water, soil and sediment components of environmental matrix. The coastal marine sediments are largely governed by the physicochemical parameters of that environment and also the biogeochemical processes (Patil et al. 2012; Saravanakumar et al. 2008). Together with the quantification of trace elements concentration, the estimation of pollution indices in different environmental matrices can also be highly significant. The major pollution indices are enrichment factor (EF), contamination factor (CF), geo-accumulation index ($I_{geo}$), pollution load index (PLI), and modified degree of contamination ($mC_d$) (Shafie et al. 2013).

In view of all the above, the coastal environment of Kerala has been identified for the present investigation with the major objectives of understanding the dynamics of trace elements, estimating pollution indices and correlating physicochemical parameters with trace elements concentration, in the sediment samples collected from the region. The results are presented and discussed in detail in the light of literature and various studies conducted elsewhere.

**Methods**

In the present investigation, inductively coupled plasma-mass spectrometer (ICP-MS) (Model: iCAP RQ; Maker: Thermo Electron Corporation) is used for the quantification of trace elements in the sediment samples collected from the coastal belt of Kerala. The physicochemical parameters were measured using appropriate instruments and methods. ArcGIS10.5 version has been used for mapping and cartographical analysis.

**Study area**

Kerala has nine coastal districts, viz. Kasaragod, Kannur, Kozhikode, Malappuram, Thrissur, Ernakulam, Alappuzha, Kollam and Thiruvananthapuram, and the present study covers all the nine coastal districts having a total coastal stretch of about 560 km. The samples were collected from 18 different locations (Fig. 1) along the coastal belt of Kerala, viz. Bekal, Muzhappilangad, Kappad, Padinjarekkara, Akalad, Cheri, Mararikulam, Alappuzha, Thottapalli, Alappad, Parayakadavu, Chavara, Neendakara, Thangassery, Kollam, Mayyanad, Shankumugham, and Kovalam.

The latitude and longitude of these sampling stations are given in Table 1. The coastal environment of Kerala, especially the southern parts, is heavily industrialized and urbanized. Also, the industrial installations in the study area are very close to the costal belts. The rapid increase in population, large-scale development of manufacturing industries, and other man-made activities has contributed a large amount of waste disposal such as sewage water and solid discharges that contain a number of trace elements.

**Sample collection**

About 1m² of the area was marked, and the stones, pebbles, grass and the root mat on its surface were cleaned. The ‘V’-shaped cut was done first and then the sediment samples up to the desired depth (0–20 cm) were taken, and a uniformly 2-cm-thick slice was taken. The bulk sample was reduced to about 500 gm by quartering process. The samples which were collected were mixed thoroughly and divided into four equal parts, the two opposite ones were discarded, and the remaining two were mixed again. This process was repeated until about 500 gm of sediments sample was left, and this part was taken as the representative sample. All the samples were collected in a polythene bag and brought to the laboratory for further analysis.

**Sample digestion and mineral analysis**

The samples were dried at room temperature and ground to powder using an agate mortar and sieved through a 2 mm sieve. Then, the samples were digested using triacid method. For the triacid preparation, $\text{HNO}_3$, $\text{H}_2\text{SO}_4$, and $\text{HClO}_4$ were mixed in the ratio of 9:2:1, respectively. From the sieved sample, 1 gm of accurately weighted sample is transferred into a conical flask. Ten milliliters of triacid is added to this and then heated at 80 °C until the samples were completely digested. After digestion, the samples were made up to 100 mL using distilled water and used for mineral analysis of ten trace elements, viz. As, Cd, Cu, Cr, Mn, Zn, Ni, Pb, Ti, and Fe, using inductively coupled plasma-mass spectrometer (ICP-MS) (Del Mastro et al. 2015).

**Assessment of pollution indices**

Mainly five parameters are used for the assessment of degree of contamination in the environment due to the trace metal accumulation. They are enrichment factor (EF), contamination factor (CF), geo-accumulation index ($I_{geo}$), pollution load index (PLI), and modified degree of contamination ($mC_d$). These five parameters are the indicators of pollution level in the environment.

**Enrichment factor (EF)**

The parameter used for the estimation of degree of contamination due to trace elements in the soil or sediment samples is called the enrichment factor (Salah et al. 2012). The estimation of the presence and intensity of
the anthropogenic contaminant deposition can also be done from the enrichment factor. There is a reference element concentration which is stable in the soil with the normalization of one metal concentration of topsoil in the calculation (Barbieri 2016). The Fe and Al are used for most of the studies as the reference element.

**Fig. 1** Sampling locations along the coastal belt of Kerala
The investigators working on the coastal and marine sediments use Fe as the reference element in several studies (Emmerson et al. 1997; Lee et al. 1998). From these observations, in the present study of enrichment factor, Fe is taken as the reference element. The enrichment factor can be calculated by the following relation:

\[
EF = \left( \frac{C_x}{C_{Fe}} \right)_{\text{sediment}} \div \left( \frac{C_x}{C_{Fe}} \right)_{\text{reference}}
\]

where \((C_x/C_{Fe})_{\text{sediment}}\) is the ratio of the concentration of the element \(x\) to that of Fe in the sediment sample and \((C_x/C_{Fe})_{\text{reference value}}\) is the ratio of the concentration of the element \(x\) to that of Fe in an unpolluted reference baseline. Table 2 gives the classification of enrichment factor. The reference value is chosen as the upper continental crust (UCC)/continental crust (CC) value from the literature (Taylor et al. 1964; Bowen 1979; Wedepohl 1995; Rudnick and Gao 2004, Elias et al. 2018). The same method was used by Birch (2017) and Rudnick and Gao (2004) to estimate the upper continental crust values of the metals. The upper continental crust values of trace elements chosen for the present investigation are summarized in Table 7.

**Contamination factor (CF)**

The contamination factor is the ratio of metal concentration in the sediment sample to the reference value of that metal (Barbieri 2016). The sediment sample contamination can be assessed using the contamination factor and can be calculated using the following relation:

\[
CF = \frac{(C_x)_{\text{sediment}}}{(C_x)_{\text{reference}}}
\]

where \((C_x)_{\text{sediment}}\) is the concentration of the element \(x\) in the sample and \((C_x)_{\text{reference}}\) is the concentration of the reference element. The classification of contamination factor is given in Table 3.

**Geo-accumulation index (I\(_{\text{geo}}\))**

The concentration of metal accumulation in sediment above the baseline concentration is estimated by the geo-accumulation index and was proposed by Mullar. It is classified into seven classes and is a quantitative measure of the degree of pollution in aquatic sediments. The seven classes are classified from unpolluted to very strongly polluted (Rubio et al. 2000; Praveena et al. 2008). The geo-accumulation index can be calculated by the following relation:

\[
I_{\text{geo}} = \log_2 \left( \frac{C_x}{1.5 \times B_x} \right)
\]

where \(C_x\) is the concentration of metal \(x\) in the sediment sample and \(B_x\) is the background or reference value of metal \(x\). In order to compensate for the variations due to the lithogenic effects, a 1.5 background matrix factor is used (Haris et al. 2017). The classification of geo-accumulation index is given in Table 4.

### Table 1 Latitude and longitude of the sampling stations

| Sampling station | Latitude (decimal degree) | Longitude (decimal degree) |
|------------------|---------------------------|---------------------------|
| Bekal            | 12.4181                   | 75.015091                 |
| Muzhappilangad   | 11.7955                   | 75.442607                 |
| Kappad           | 11.3877                   | 75.720291                 |
| Padinjarekkara   | 10.7949                   | 75.909124                 |
| Akadal           | 10.6383                   | 75.977784                 |
| Cherai           | 10.1416                   | 76.178283                 |
| Mararikulam      | 9.59964                   | 76.298573                 |
| Alappuzha        | 9.49131                   | 76.330254                 |
| Thottapalli      | 9.30743                   | 76.385715                 |
| Alappad          | 9.11571                   | 76.472256                 |
| Parayakadavu     | 9.08442                   | 76.487435                 |
| Chavara          | 8.99078                   | 76.523178                 |
| Neendakara       | 8.94180                   | 76.535753                 |
| Thangassery      | 8.88178                   | 76.570237                 |
| Kollam           | 8.88002                   | 76.599373                 |
| Mayyanad         | 8.84601                   | 76.623282                 |
| Shankumukham     | 8.47548                   | 76.912888                 |
| Kovalam          | 8.39935                   | 76.971584                 |

### Table 2 Classification of enrichment factor

| Enrichment factor | Sediment quality                  |
|-------------------|-----------------------------------|
| EF < 2            | Deficiency to minimal enrichment  |
| 2 < EF < 5        | Moderate enrichment               |
| 5 < EF < 20       | Significant enrichment            |
| 20 < EF < 40      | Very high enrichment              |
| EF > 40           | Extremely high enrichment         |

Barbieri (2016), Abdulqaderismaeel and Kusag (2015), Mei et al. (2011), Salah et al. (2012)

### Table 3 Classification of contamination factor

| Contamination factor | Contamination level  |
|----------------------|----------------------|
| CF < 1               | Low contamination    |
| 1 ≤ CF < 3           | Moderate contamination|
| 3 ≤ CF < 6           | Considerable contamination|
| CF > 6               | Very high contamination|

Rudnick and Gao (2003), Salah et al. (2012)
Pollution load index (PLI)
Pollution load index is used for the determination of entire pollution level of a specific area. It is also explained as the assessment of overall sediment toxicity. The pollution load index can be calculated using the following relation:

\[
\text{PLI} = \left[ \prod_{i=1}^{n} C_{F_i} \right]^{1/n}
\]

where \( C_{F_i} \) is the contamination factor of \( i \)-th metal and \( n \) is the number of metals assessing. The classification of pollution load index is given in Table 5.

Modified degree of contamination (mCd)
The modified degree of contamination helps in the assessment of overall heavy metal contamination in the sediment samples. The degree of contamination is a cumulative index calculated by the sum of individual contamination factors (\( C_{d} \)). The modified degree of contamination can be used for better assessment value. The modified degree of contamination can be calculated using the following relation:

\[
m_{Cd} = \frac{\sum CF}{n}
\]

where \( CF \) is the contamination factor and \( n \) is the number of analyzed trace elements. The classification of modified degree of contamination is given in Tables 6, 7.

Results
The concentration of trace elements, viz. As, Cd, Cu, Cr, Mn, Zn, Ni, Pb, Ti and Fe, in the sediment samples collected from the coastal environment of Kerala is summarized in Table 8. The spatial distribution of important toxic trace elements along the Kerala coastal belt is shown in Figs. 2, 3.

The statistical data of the enrichment factor derived from the concentration of trace elements are given in Table 9. The enrichment factor value of As is higher, and a lower value for Ti is observed when compared with other elements in the sediment samples. The distribution of enrichment factor due to trace elements is under minimal and moderate condition, and most of the trace elements enrichment in the sediments of coastal Kerala may be due to the natural weathering processes.

The statistical parameters of the contamination factor are summarized in Table 10. The higher value of contamination factor is observed for Zn and lower value for As. The contamination factor values corresponding to each element for all the collected samples were less than one. It indicates that the present study area is under low contamination due to the accumulation of trace elements.

The statistical data of the geo-accumulation index are given in Table 11. The geo-accumulation index value corresponding to the trace elements for all the collected samples was negative. It indicates that present study area is practically unpolluted due to the accumulation of trace elements.

The statistical parameters of pollution load index and modified degree of contamination are shown in Table 12. Pollution load index varies from 0.0006 (Akalad, Cherai, and Shankumukham) to 0.0047 (Thottapalli) with a mean value of 0.0021. The pollution load index was less than one in all the sampling stations, which indicates that there is no overall pollution in the coastal belt of Kerala due to trace elements enrichment. Modified degree of

### Table 4 Classification of geo-accumulation index

| Geo-accumulation index | \( I_{geo} \) class | Pollution intensity         |
|------------------------|---------------------|------------------------------|
| >5                     | 6                   | Very strongly polluted      |
| >4–5                   | 5                   | Strong to very strongly polluted |
| >3–4                   | 4                   | Strongly polluted            |
| >2–3                   | 3                   | Moderately to strongly polluted |
| >1–2                   | 2                   | Moderately polluted         |
| >0–1                   | 1                   | Unpolluted to moderate polluted |
| <0                     | 0                   | Practically unpolluted      |

Müller (1979)

### Table 5 Classification of pollution load index

| Pollution load index | Pollution level       |
|----------------------|-----------------------|
| \( \leq 1 \)         | No metal pollution    |
| >1                   | Metal pollution exists |

Tomlinson et al. (1980), Bramha et al. (2014)

### Table 6 Classification of modified degree of contamination

| Modified degree of contamination | Contamination status                        |
|----------------------------------|---------------------------------------------|
| \( m_{Cd} < 1.5 \)              | Nil to a very low degree of contamination    |
| \( 1.5 \leq m_{Cd} < 2 \)       | Low degree of contamination                  |
| \( 2 \leq m_{Cd} < 4 \)         | A moderate degree of contamination           |
| \( 4 \leq m_{Cd} < 8 \)         | A high degree of contamination               |
| \( 8 \leq m_{Cd} < 16 \)        | A very high degree of contamination          |
| \( 16 \leq m_{Cd} < 32 \)       | An extremely high degree of contamination    |
| \( m_{Cd} \leq 32 \)            | Ultrahigh degree of contamination            |

Abrahim and Parker (2008), Bramha et al. (2014), Mazurek et al. (2017), Sivakumar et al. (2016)
contamination ranges from 0.013 (Shankumukham) to 0.129 (Parayakadavu) with a mean value of 0.066. The modified degree of contamination for all the sampling stations was less than 1.5 indicating that the coastal belts are under the category of nil to a very low degree of contamination.

The statistical data of the physicochemical parameters of sediment samples collected from the coastal belts are as follows:

Table 7 Upper continental crust values of trace elements from previous studies

| Trace elements | References |
|----------------|------------|
| As            | 4.8        |
| Cd            | 0.09       |
| Cu            | 28         |
| Cr            | 92         |
| Mn            | 1000       |
| Zn            | 67         |
| Ni            | 47         |
| Pb            | 17         |
| Ti            | 6400       |
| Fe            | 50,400     |
| Rudnick and Gao (2004) |
| Kemp and Hawkesworth (2004) |
| Gao et al. (1998) |
| Borodin (1999) |
| Taylor and McLennan (1995) |
| Wedepohl (1995) |
| Condie (1993) |
| Sims et al. (1990) |
| Shaw et al. (1986) |
| Taylor and McLennan (1985) |
| Weaver and Tarney (1984) |
| Taylor and McLennan (1981) |
| Ronov and Yaroshevsky (1976) |
| Shaw et al. (1976) |
| Eade and Fahrig (1973) |
| Fahrig and Eade (1968) |
| Shaw et al. (1967) |

Table 8 Concentration of trace elements in the sediment samples collected from the coastal belt of Kerala

| Sampling station | As (ppb) | Cd (ppb) | Cu (ppb) | Cr (ppb) | Mn (ppm) | Zn (ppm) | Ni (ppb) | Pb (ppb) | Ti (ppb) | Fe (ppm) |
|------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Bekal            | 5.2      | 0.08     | 13.10    | 0.06     | 1.76     | 0.25     | 18.60    | 16.80    | 0.13     | 16.10    |
| Muzhappilangad  | 1.80     | 0.13     | 11.20    | 0.11     | 0.58     | 0.26     | 16.60    | 4.70     | 0.11     | 16.87    |
| Kappad           | 5.70     | 0.11     | 12.40    | 0.17     | 1.33     | 0.16     | 15.40    | 30.30    | 0.27     | 45.18    |
| Padinjarekkara   | 4.50     | 0.16     | 14.50    | 0.12     | 1.25     | 0.12     | 12.30    | 24.60    | 0.23     | 41.38    |
| Akalad           | 1.90     | 0.21     | 6.10     | 0.04     | 1.01     | 0.09     | 7.30     | 9.90     | 0.09     | 18.42    |
| Cheri            | 1.10     | 0.07     | 5.20     | 0.03     | 0.20     | 0.10     | 5.20     | 10.40    | 1.36     | 5.05     |
| Mararikulam      | 2.40     | 0.10     | 7.70     | 0.14     | 0.73     | 0.10     | 6.70     | 35.80    | 0.27     | 18.36    |
| Alappuzha        | 6.30     | 0.17     | 15.40    | 0.40     | 1.80     | 0.19     | 15.50    | 95.50    | 0.61     | 60.19    |
| Thottapalli      | 46.50    | 0.16     | 24.80    | 0.57     | 3.78     | 3.39     | 32.50    | 49.90    | 2.89     | 203.58   |
| Alappad          | 9.10     | 0.12     | 8.50     | 0.13     | 0.92     | 0.24     | 10.50    | 27.50    | 0.90     | 34.37    |
| Parayakadavu     | 20.20    | 0.27     | 29.30    | 0.56     | 3.51     | 0.78     | 35.70    | 70.60    | 2.93     | 201.22   |
| Chavara          | 43.50    | 0.19     | 30.80    | 0.31     | 1.83     | 0.46     | 30.20    | 24.10    | 1.02     | 122.19   |
| Neendakara       | 33.50    | 0.18     | 33.40    | 0.27     | 4.20     | 0.54     | 34.70    | 64.50    | 1.21     | 248.62   |
| Thangassery      | 30.40    | 0.16     | 25.40    | 0.21     | 3.33     | 0.71     | 28.30    | 56.50    | 1.06     | 195.70   |
| Kollam           | 102.8    | 0.08     | 15.60    | 0.09     | 1.64     | 0.26     | 17.20    | 30.50    | 0.20     | 64.80    |
| Mayyanad         | 6.40     | 0.27     | 19.60    | 0.11     | 2.32     | 0.29     | 23.00    | 19.80    | 0.47     | 34.70    |
| Shankumukham     | 0.06     | 0.08     | 6.20     | 0.06     | 0.12     | 0.21     | 3.40     | 5.20     | 0.54     | 7.82     |
| Kovalam          | 171.4    | 0.08     | 14.30    | 0.11     | 1.30     | 0.30     | 14.20    | 9.20     | 0.51     | 75.95    |
| Mean             | 27.83    | 0.15     | 16.31    | 0.19     | 1.76     | 0.47     | 18.18    | 32.54    | 0.82     | 78.36    |

Reference value for this study
belt of Kerala are shown in Table 13. The dependence of physicochemical parameters of sediments samples on the concentration of trace element has been studied using Pearson's correlation matrix and is given in Table 14.

In the Pearson's correlation analysis (Table 14), the values were taken from −1 to +1, where −1 indicates the perfect negative correlation; 0 indicates no correlation; and +1 indicates a perfect positive correlation. In the present study, correlation coefficient values between −0.5 and 0.5 were considered. A significant positive correlation is observed between most of the trace elements. Arsenic did not show any significant correlation with any of the elements or physicochemical parameters. The physicochemical parameters, viz. organic matter content and silt + clay (%), show a significant positive correlation with the concentration of Fe. A good positive correlation is observed between electrical conductivity and concentration of Cu. The physicochemical parameters, viz. moisture content, pH, and sand (%), did not possess any impact on the trace elements accumulation in the beach sediments of coastal Kerala.

Discussion
The results of trace elements concentration in sediment samples indicate that arsenic concentration varies in the range from 0.06 ppb (Shankumukham) to 171.4 ppb (Kovalam) with a mean value of 27.83 ppb. The enrichment factor of arsenic varies from 0.10 (Shankumukham) to 28.83 (Kovalam) with a mean value of 4.61. Minimal enrichment was observed for arsenic in most of the coastal areas by the natural means, i.e., through crustal materials or natural weathering process. There are only a few coastal regions having moderate or significant enrichment of arsenic. This indicates that the anthropogenic sources like disposal of sewage, industrial activities, domestic and urban wastes contribute more to the enrichment in these regions rather than natural means. The geo-accumulation index of arsenic for all the sampling stations was less than zero, indicating coastal belts.

![Spatial distribution of As and Cd concentration](image-url)
are practically unpolluted due to the presence of arsenic. The contamination factor was less than one in all the sampling stations, which indicates that the coastal belts are less contaminated with arsenic.

The concentration of cadmium ranges from 0.07 ppb (Cherai) to 0.27 ppb (Mayyanad) with a mean value of 0.15 ppb. The enrichment factor of cadmium ranges from 0.37 (Neendakara) to 7.01 (Cherai) with a mean value of 2.19. The results indicate that most of the sampling sites have minimal enrichment by the nature. Moderate and significant enrichment of cadmium in a few coastal regions is the result of contribution of unnatural sources like industrial or manmade activities. The geo-accumulation index of cadmium for all the selected sampling stations was less than zero indicating that the coastal belts are practically unpolluted due to the presence of arsenic.

![Fig. 3 Spatial distribution of Ni and Pb concentration](image_url)

**Table 9 Statistical parameters of the enrichment factor**

| Statistical parameter | As  | Cd  | Cu  | Cr  | Mn  | Zn  | Ni  | Pb  | Ti  |
|-----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Minimum               | 0.10| 0.37| 0.23| 0.72| 0.84| 1.61| 0.20| 0.32| 0.01|
| Maximum               | 28.83| 7.01| 1.98| 5.21| 6.12| 19.89| 1.66| 5.44| 2.12|
| Mean                  | 4.61| 2.19| 0.74| 2.52| 1.88| 6.21| 0.60| 1.86| 0.21|
| Median                | 1.89| 1.6 | 0.51| 2.07| 1.57| 3.30| 0.44| 1.47| 0.06|
| Std. deviation        | 7.48| 2.03| 0.52| 1.50| 1.33| 5.35| 0.46| 1.56| 0.49|
| Skewness              | 2.79| 1.27| 1.18| 0.67| 2.24| 1.39| 1.44| 1.43| 3.86|
| Kurtosis              | 7.24| 0.66| 0.43| −0.82| 5.75| 1.0 | 0.88| 1.09| 15.47|
The contamination factor was less than one in all the sampling stations, which indicates that the coastal belts are less contaminated with cadmium. The concentration of copper ranges from 5.20 ppb (Cherai) to 33.4 ppb (Neendakara) with a mean value of 16.31 ppb. The enrichment factor of copper varies in the range from 0.23 (Thottapalli) to 1.98 (Cherai) with a mean value of 0.74. It indicates that all the sampling stations have deficiency to minimal enrichment of copper by the nature. The geo-accumulation index of copper in all the sampling stations was less than zero, which shows that the coastal belts are practically unpolluted with the presence of copper. The contamination factor was

| Statistical parameters | As   | Cd   | Cu   | Cr   | Mn   | Zn   | Ni   | Pb   | Ti   |
|------------------------|------|------|------|------|------|------|------|------|------|
| Minimum                | 0.0001 | 0.00080 | 0.00022 | 0.00040 | 0.00010 | 0.00100 | 0.00011 | 0.00030 | 0.00002 |
| Maximum                | 0.0022 | 0.003 | 0.0026 | 0.0085 | 0.008 | 0.055 | 0.0011 | 0.0055 | 0.0005 |
| Mean                   | 0.00034 | 0.0016 | 0.0008 | 0.0028 | 0.0025 | 0.0076 | 0.00057 | 0.0019 | 0.00014 |
| Median                 | 0.00013 | 0.00165 | 0.00063 | 0.00185 | 0.0021 | 0.004 | 0.00051 | 0.0015 | 0.00009 |
| Std. deviation         | 0.00059 | 0.0007 | 0.00057 | 0.0025 | 0.002 | 0.0123 | 0.0003 | 0.0015 | 0.00015 |
| Skewness               | 2.710 | 0.686 | 1.915 | 1.365 | 1.289 | 3.798 | 0.373 | 1.086 | 1.812 |
| Kurtosis               | 6.750 | −0.256 | 4.823 | 0.939 | 1.816 | 15.227 | −1.039 | 0.606 | 2.741 |

| Statistical parameter | Al | Cd | Cu | Cr | Mn | Zn | Ni | Pb | Ti |
|-----------------------|---|---|---|---|---|---|---|---|---|
| Minimum               | −16.44 | −10.89 | −12.70 | −11.75 | −13.31 | −10.00 | −13.78 | −12.43 | −16.54 |
| Maximum               | −4.96 | −8.94 | −10.05 | −7.48 | 11.04 | −4.79 | 11.70 | −6.74 | −11.51 |
| Mean                  | −9.38 | −9.96 | −11.30 | −9.50 | −4.57 | −8.37 | −9.16 | −9.91 | −14.05 |
| Median                | −9.715 | −9.85 | −11.26 | −9.65 | −9.39 | −8.51 | −11.46 | −9.81 | −13.99 |
| Std. deviation        | −2.73 | 0.62 | 0.84 | 1.21 | 9.12 | 1.28 | 7.42 | 1.50 | 1.51 |
| Skewness              | −0.705 | 0.059 | −0.139 | 0.024 | 1.029 | 1.229 | 2.626 | 0.121 | 0.019 |
| Kurtosis              | 1.336 | −1.135 | −1.025 | −0.470 | −0.910 | 2.341 | 5.732 | −0.165 | −0.833 |

The concentration of copper ranges from 5.20 ppb (Cherai) to 33.4 ppb (Neendakara) with a mean value of 16.31 ppb. The enrichment factor of copper varies in the range from 0.23 (Thottapalli) to 1.98 (Cherai) with a mean value of 0.74. It indicates that all the sampling stations have deficiency to minimal enrichment of copper by the nature. The geo-accumulation index of copper in all the sampling stations was less than zero, which shows that the coastal belts are practically unpolluted with the presence of copper. The contamination factor was
Table 14  Pearson's correlation matrix

|     | As  | Cd  | Cu  | Cr  | Mn  | Zn  | Ni  | Pb  | Ti  | Fe  | MC  | pH  | EC (µS/m) | OM  | Silt + clay (%) | Sand (%) |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------|-----|-----------------|----------|
| As  | 1.0 |     |     |     |     |     |     |     |     |     |     |     |           |     |                 |          |
| Cd  | -0.236 | 1.0 |     |     |     |     |     |     |     |     |     |     |           |     |                 |          |
| Cu  | 0.231 | 0.578* | 1.0 |     |     |     |     |     |     |     |     |     |           |     |                 |          |
| Cr  | 0.049 | 0.515* | 0.699** | 1.0 |     |     |     |     |     |     |     |     |           |     |                 |          |
| Mn  | 0.170 | 0.567* | 0.889** | 0.718** | 1.0 |     |     |     |     |     |     |     |           |     |                 |          |
| Zn  | 0.156 | 0.185 | 0.447 | 0.694** | 0.598** | 1.0 |     |     |     |     |     |     |           |     |                 |          |
| Ni  | 0.187 | 0.588* | 0.963** | 0.738** | 0.922** | 0.552* | 1.0 |     |     |     |     |     |           |     |                 |          |
| Pb  | -0.062 | 0.410 | 0.573* | 0.760** | 0.679** | 0.295 | 0.555* | 1.0 |     |     |     |     |           |     |                 |          |
| Ti  | 0.053 | 0.385 | 0.570* | 0.818** | 0.633** | 0.736** | 0.632** | 0.484* | 1.0 |     |     |     |           |     |                 |          |
| Fe  | 0.264 | 0.444 | 0.898** | 0.745** | 0.925** | 0.597** | 0.866** | 0.647** | 0.717** | 1.0 |     |     |           |     |                 |          |
| MC  | 0.269 | -0.079 | 0.102 | 0.072 | 0.086 | 0.016 | 0.129 | 0.107 | -0.083 | 0.212 | 1.0 |     |           |     |                 |          |
| pH  | 0.110 | -0.064 | -0.268 | 0.073 | -0.085 | 0.090 | -0.206 | 0.075 | 0.015 | -0.005 | 0.110 | 1.0 |           |     |                 |          |
| EC (µS/m) | 0.301 | 0.175 | 0.513* | 0.238 | 0.346 | 0.051 | 0.467 | 0.121 | 0.109 | 0.496 | 0.705** | -0.072 | 1.0 |           |     |                 |          |
| OM  | -0.119 | 0.280 | 0.489 | 0.209 | 0.410 | 0.004 | 0.431 | 0.310 | 0.305 | 0.529* | 0.035 | 0.037 | 0.244 | 1.0 |           |     |                 |          |
| Silt + Clay (%) | 0.032 | 0.230 | 0.574* | 0.362 | 0.477 | 0.221 | 0.460 | 0.374 | 0.342 | 0.604** | 0.190 | -0.249 | 0.522* | 0.577* | 1.0 |           |     |                 |          |
| Sand (%) | 0.134 | 0.133 | 0.125 | 0.006 | 0.114 | 0.078 | 0.184 | -0.111 | 0.093 | 0.069 | -0.154 | 0.084 | 0.056 | -0.056 | -0.184 | 1.0 |           |     |                 |          |

MC: moisture content; EC: electrical conductivity; OM: organic matter content

*Correlation is significant at the 0.05 level (two-tailed)

**Correlation is significant at the 0.01 level (two-tailed)
less than one in all the sampling stations indicating that coastal belts are less contaminated with copper.

The concentration of chromium ranges from 0.03 ppm (Cherai) to 0.57 ppm (Thottapalli) with a mean value of 0.19 ppm. The enrichment factor of chromium varies in the range from 0.72 (Thangassery) to 5.21 (Shankumukham) with a mean value of 2.52. It indicates that most of the sampling sites have minimal enrichment by the nature. Significant enrichment of chromium was found in the coastal areas of Mararikulam and Shankumukham. The geo-accumulation index in all the sampling stations was less than zero, indicating that the coastal belts are practically unpolluted with the presence of chromium. The contamination factor was less than one in all the sampling stations, indicating that the coastal belt of Kerala is less contaminated with chromium.

The concentration of manganese varies from 0.12 ppm (Shankumukham) to 4.20 ppm (Neendakara) with a mean value of 1.76 ppm. The enrichment factor ranges from 0.84 (Chavara) to 6.12 (Bekal) with a mean value of 1.88. The results indicate that most of the sampling sites have minimal enrichment by the nature. A moderate enrichment was observed in Bekal, and it may be due to the waste disposal from the nearby urban environment or use of fertilizers from the nearby agricultural fields. The geo-accumulation index of manganese for all the sampling stations was less than zero, indicating that the coastal belts are practically unpolluted due to the presence of manganese. The contamination factor was less than one in all the sampling stations, indicating that coastal belts are less contaminated with manganese.

The concentration of zinc ranges from 0.09 ppm (Akalad) to 3.39 ppm (Thottapalli) with a mean value of 0.47 ppm. The enrichment factor ranges from 1.61 (Neendakara) to 19.89 (Shankumukham) with a mean value of 6.21. It indicates that all the sampling sites have moderate enrichment of zinc through unnatural means except Neendakara. Neendakara coast has the minimal enrichment of zinc by the nature. The geo-accumulation index of zinc for all the sampling sites was less than zero, indicating that the coastal belts are practically unpolluted due to the presence of zinc. The contamination value of zinc is less than one in all the sampling sites, indicating that the coastal belts of Kerala are less contaminated with zinc.

The concentration of nickel varies from 3.40 ppb (Shankumukham) to 35.70 ppb (Parayakadavu) with a mean value of 18.18 ppb. The enrichment factor varies from 0.20 (Neendakara) to 1.66 (Bekal) with a mean value of 0.60. It indicates that all the sampling sites have minimal enrichment of nickel by the nature. The geo-accumulation index of nickel for all the samples was less than zero, which indicates that the coastal belts are practically unpolluted with the presence of nickel. The contamination values of nickel are less than one in all the sampling sites, indicating that the coastal belts of Kerala are less contaminated with nickel.

The concentration of lead in the samples chosen ranges from 4.70 ppb (Muzhappilangad) and 95.5 ppb (Alappuzha) with a mean value of 32.54 ppb. The enrichment factor varies from 0.32 (Kovalam) to 5.44 (Cherai) with a mean value of 1.86. The results indicate that most of the sampling sites have minimal enrichment by the nature. The geo-accumulation index of lead for all the sampling stations was less than zero, indicating that the coastal belts are practically unpolluted due to the presence of lead. The contamination factor was less than one in all the sampling stations, indicating that the coastal belts are less contaminated with lead.

The concentration of titanium in the collected sediment samples varies from 0.09 ppm (Akalad) to 2.93 ppm (Parayakadavu) with a mean value of 0.82 ppm. The enrichment factor varies from 0.01 (Mararikulam) to 2.12 (Cherai) with a mean value of 0.21. It indicates that most of the sampling sites have minimal enrichment of titanium by the nature. The geo-accumulation index of titanium for all the sampling sites was less than zero, indicating that the coastal belts are practically unpolluted with the presence of titanium. The contamination factor was less than one in all the sampling stations, indicating that the coastal belts of Kerala are less contaminated with titanium.

The trace elements concentration and pollution indices are compared with the literature values. The comparison of trace elements concentration, pollution load index, and modified degree of contamination with other regions of the world is summarized in Tables 15 and 16, respectively. From the comparison study, it is clear that the concentrations of the trace elements, pollution load index, and modified degree of contamination obtained from the present investigation were comparable with the reported values of the concentration of trace elements, pollution load index, and modified degree of contamination of other regions of the world.

**Conclusion**

The study indicates that the distribution and enrichment of trace elements in the coastal environment of Kerala depend on the lithogenic factors. Most of the trace elements enrichment in the coastal belt is due to the crustal materials or natural weathering process and atmospheric deposition. Trace elements, viz. zinc and arsenic, are found to be highly enriched, and nickel and titanium are less enriched in the coastal belt of Kerala. The anthropogenic sources, viz. industrial activities, disposal of sewage, use of fertilizers from the agricultural
Table 15 Comparison of trace elements concentration with other regions

| Region      | Trace elements concentration (ppm) | Reference               |
|-------------|------------------------------------|-------------------------|
|             | As       | Cd          | Cu          | Cr          | Mn         | Zn         | Ni         | Pb         | Ti         | Fe         |
| Coastal Kerala | 0.00006–0.171 | 0.00007–0.00027 | 0.0052–0.0334 | 0.03–0.57 | 0.12–42 | 0.09–3.39 | 0.0034–0.0357 | 0.0047–0.096 | 0.09–2.93 | 5.05–248.62 | Present study |
| China       | 8–23     | –           | 41–173     | –           | –         | 54–1040   | –           | 27–74      | –          | 2.10–2.95 | Mei et al. (2011) |
| Iraq        | –        | 0.87–2.35  | 1035–30.52 | 36.45–120.11 | 136.05–312.11 | 14.96–130.25 | 39.98–103.98 | 802–32.69 | –          | 928.7–3441.05 | Salah et al. (2012) |
| Madurai     | –        | 1.24–4.32  | 104–18.16  | 13.6–34.50 | –         | 22.24–45.6 | 11.52–14.80 | 2042–42.37 | –          | –          | Sarala and Vdya (2013) |
| Malaysia    | 3.6–65.9 | 0.09–1.1   | 1.5–66.2   | 1.7–126.0 | –         | 12.4–430  | 1.8–56.0    | 82–39.0    | –          | 5160–43,200 | Elias et al. (2018) |
| Jordan      | –        | 7.51–17.22 | 7.51–5021  | 23.85–124.23 | –         | 113.30–325.22 | 225.57–1711.84 | 1851–79.99 | –          | –          | Odat (2013) |
| Jharkhand   | –        | 0.2–0.7   | 21.6–93.2  | 17–67     | 353–993 | 78–188    | 27.4–98.3   | 17.1–384   | –          | 23,947–50,691 | Pandey et al. (2016) |
| Ghaziabad   | –        | 0.11–1.1  | 4.05–67.6  | 3.6–111.7 | 41.6–677.5 | 206–282  | 12.8–165   | 5.6–69.6   | –          | 10,865–24,873 | Chabukdhara et al. (2016) |
| Iran        | 2.89–5.02 | 9.67–16.65 | –          | –         | –       | 40–87.50   | 47–124.75  | 17.36–32.13 | –          | 3.74–5.24 | Vaezi et al. (2015) |
fields, domestic and urban wastes, might also influence the enrichment of trace elements in the coastal environments of Kerala. None of the trace elements concentration exceeded the permissible limits, and the pollution indices clearly indicate the quality of sediment samples in the coastal environment of Kerala is not very toxic in nature. The physicochemical parameters have influenced the concentration of the trace elements in the sediment samples. Periodic monitoring of the sediment samples is needed to evaluate the impact of toxic trace elements in the study area.

Table 16 Comparison of pollution load index and modified degree of contamination with other regions

| Region                  | Pollution load index | Modified degree of contamination | References                        |
|-------------------------|----------------------|----------------------------------|-----------------------------------|
| Coastal Kerala          | 0.0006–0.0047        | 0.013–0.129                      | Present study                     |
| Iraq, Euphrates River   | 0.45–1.15            | –                                | Salah et al. (2012)               |
| Jharkhand, India        | 0.97–1.14            | –                                | Pandey et al. (2016)              |
| Bay of Bengal           | 0.24–1.25            | 0.61–2.01                        | Sivakumar et al. (2016)           |
| Bangladesh              | <1                   | 1.5–3.34                         | Fahima and Rafizul Islam (2019)   |
| Iran                    | 1.2–1.56             | 5.07–8.02                        | Vaezi et al. (2015)               |
| Tamil Nadu              | 0.49–1.4             | 0.247–11.75                      | Devanesan et al. (2018)           |

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