

Multivariate statistical and GIS-based approaches for toxic metals in tropical mangrove ecosystem, southeast coast of India

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Abstract The heavy metal concentrations in water and sediment samples were investigated in the tropical Muthupet mangrove ecosystem, southeast coast of India. The results demonstrated that, ranges of metals in water comprise of Cd—0.05 to 3.72; Cu—0.5 to 4.43; Pb—6.31 to 17.87; Zn—0.0 to 12.91 ppm and sediment comprises of Cd—0.06 to 0.57; Cu—4.46 to 20.59; Pb—2.90 to 21.35; Zn—4.41 to 39.18 ppm. In all the three sites, heavy metals in sediment exhibited significant higher concentrations compared to water, except Cd. The spatial distribution of metals in water and sediment samples followed a similar pattern except Cd with the preponderance of Zn (75% of total metals) followed by Cu and Pb. Muller's Geoaccumulation indexes (Igeo) showed Cd is a potent pollutant in the ecosystem and moderately contaminated the study area. The aquaculture and agricultural culture practices follow improper disposal of municipal wastages, and idol immersion activities are the potent metallic sources for heavy metal pollution were identified by performing principle component analysis. In order to protect the ecosystem from further contamination, regular monitoring is needed in order to control the anthropogenic discharges.

Keywords Heavy metals · Water and sediment samples · Spatial distribution · Geoaccumulation index

Introduction

Mangrove ecosystem is present across the tropics and sub-tropics region of the world. It acts as a natural barrier against cyclone, typhoons and tsunami, and also an effective natural buffering zone against storms, floods and stabilizes coastal zone from erosion. Along with mangrove ecosystem are the flourished nurseries for variety of aquatic animals, in addition they are the nesting and migratory sites for thousands of birds. The mangrove ecosystem covers approximately 1.7×10^5 km² of the tropical and subtropical regions of the world (Valiela et al. 2001; Krauss et al. 2008; Sandilyan and Kathiresan 2012). In India, mangrove forest covers 360×10^3 ha of coastal tracts to occupy 3% of the world's mangrove forest (Mastallar 1996; Badarudeen et al. 1996).

Metals plays vital role in both ancient and modern world because of their potent and unique properties. The level of metal pollution is increased enormously due to intense usage and improper disposal of wastes. Apart from the natural occurrences, metals enter in to the ecosystem through the man made activities such as sewage sludge disposal, application of pesticides such as copper oxychloride and copper hydroxide (Ramesh et al. 2008) and over usage of organic fertilizers. Dissolved form of metals in the ecosystem is mainly absorbed by mixture of organic materials and mineral with the presence of charged surface organic matters (Langston 1986). On the other hand, they are also present in ionized form in water. It could be attributed that, the metals present in the ecosystem cannot be

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metabolized by aquatic organism, thus resulting in increase of toxic substances in the aquatic environment. Sediments have huge capabilities to retain heavy metals from tidal waters, fresh water flow of rivers and storm water runoff (Tam and Wong 2000). Similar to other coastal zones, mangrove ecosystem receives a large amount of waste water from the drainages and rivers, and has become a massive pollution sink.

In India, improper and unauthenticated preparation of idols for various purposes is increasing over a decade. Idol immersion is a major anthropogenic activity which suddenly causes significant water pollution in different water bodies such as lakes, reservoirs, ponds, rivers, canals, and seas. Mainly in Muthupet, the idol immersion activity around the lagoon water bodies has become a major threat to the mangrove ecosystem along with other activities. Many researchers (Giripunje et al. 2014; Vyas et al. 2007; Bajpai et al. 2002) reported that heavy metal concentration in the water bodies has significantly increased after immersing the idols in certain water bodies in India.

In this study area, there are many reports (Balakrishnan et al. 2015; Usha Natesan et al. 2014; Priya et al. 2014; Thilagavathi et al. 2011; Ashok Kumar et al. 2011; Janaki Raman et al. 2007) on heavy metal concentration in either water or sediment, but no such report is available with the concern of heavy metal concentration in both water and sediment in the particular ecosystem. It is necessary to understand the current status of metal pollution level in Muthupet mangrove ecosystem to assess ecosystem quality. In the present study, the concentration of heavy metals in water and sediment of Muthupet mangrove to assess the status of mangrove ecosystem with reference to geochemical and nutrient cycling, the potent source of metal pollution was identified by Multivariate statistical analysis and sediment quality calculated using Geoaccumulation index with the background values.

Materials and methods

Study area

Muthupet mangrove ecosystem (Lat 10° 25' N: Long 79° 39' E) is situated at southernmost end of the Cauvery delta connected to Palk strait which opens to Bay of Bengal (Fig. 1). It has a gentle slope towards the Bay of Bengal. The distributaries of Cauvery viz., the

Paminiyar, Koraiyar, Kandankurichanar, Kilaithangiyar and Marakkakoraiyar discharges their water into the wetlands and formed a larger lagoon before reaching the Palk Strait. Besides the lagoon, the wetland includes many tidal creeks, channels, and small bays, bordered by thick mangroves; and a number of manmade canals dug across the mangrove wetlands particularly in their western part and fished intensively. The lagoon receives inflow of freshwater during northeast monsoon (October–December) through the above drainage arteries occupied by agricultural soils, mangrove swamps and aquaculture ponds. From February to September, freshwater discharge into the mangrove wetland is negligible. The soil in the lagoon is clayey silt and towards the landward side it is silty clay due to fresh silt deposits. The present study was carried out to collect the samples in ten different stations and the geological coordination of the sampling sites (Table 1). All these stations were categorized into three sites based on different environmental conditions. This mangrove system is characterized by tidal mudflats where geochemical gradients and potential metal mobility changes are likely to be more significant. The following are the study sites.

Site I—fresh water influenced area

Station 1 and Station 2 are highly fresh water influenced sites of this study area. There might be a chance to drain the sewage water to the lagoon. The depth of these stations is around 1–1.5 m, however it may varied according to the water flow. More than 100 aqua forms are located nearby this station.

Site II—river mouth

Site II consists of Stations 3, 4, 5, 6, and 10 and all these stations are river mouths. All the five stations receive the sewage from agriculture, aquaculture and salt pan activities. Depth of the site is below 1 m, due to intense flow of fresh water and plenty of sediment has loaded on it.

Site III—lagoon

It covers three different stations 7, 8, and 9 including the lagoon area and the sea mouth region. Minor amount of fishery activities enters through the sea mouth into the lagoon system and the average depth of lagoon is around 2 to 4 m.

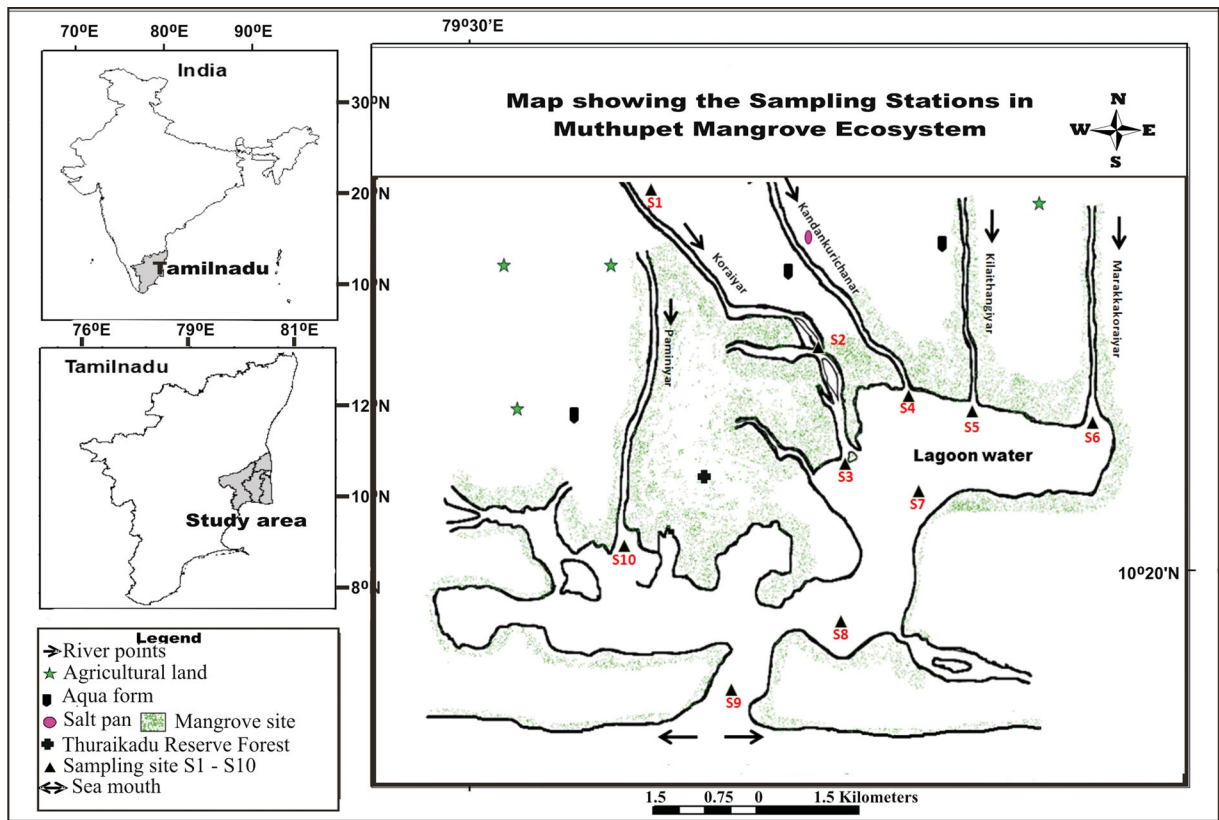


Fig. 1 Study area description and sampling stations

Collection and preservation of samples

The water and sediment samples were collected across the mangrove region for a period of 1 year during

Table 1 Station name and Geographical coordination of study area

Name of the Stations	Latitude	Longitude
S1- Azad Nagar	10°23.58.N	79° 30.09. E
S2- Jambuvanodai	10°21.90 N	79° 30.99 E
S3- Vavval Thottam	10°20.19.N	79° 32.38. E
S4- Kandankurichanar	10°20.46.N	79° 33.01. E
S5- Kilaithangi River	10°20.34.N	79° 33.47. E
S6- Karpaganadhar Kulam	10°20.16.N	79° 35.10. E
S7- Mayil Island	10°19.93 N	79° 33.23 E
S8- Mullipallam creek	10°19.35 N	79° 32.44 E
S9- Sea mouth	10°18.49.N	79° 31.17. E
S10- Pamini River end	10°19.12.N	79° 29.47. E

January 2015 to December 2015. Samples were collected at monthly interval and processed data was presented seasonal wise viz. Post monsoon (January–March), Summer (April–June), Premonsoon (July–September), and Monsoon (October–December). In all the stations, 2 cm depth of sediment samples were collected using the acid cleaned PVC pipes and stored in Zip lock covers for further analysis. One liter of water samples was collected for the heavy metal extraction and 250 ml of water samples collected in pre cleaned and polyethylene containers (Poly Lab, India) for physicochemical analysis. All the samplings were conducted at the time of forenoon session. One milliliter of chloroform was added in all the collected water samples to inhibit the biological processes for physico-chemical analysis (Sliwka-Kaszynska et al. 2003). One milliliter of concentrated HNO₃ was added to preserve the water samples for heavy metal extraction. Collected water samples were refrigerated and stored at 4 °C and the sediment samples were air dried at the room temperature in the laboratory.

Physico-chemical analysis of water samples

The common water quality parameters such as surface water temperature, pH, and salinity were measured using the PCSTestr-35. The nutrients such as nitrite, nitrate, phosphate, and ammonia were analyzed using the standard method (APHA et al. 1998).

Analysis of heavy metals in water and sediment samples

The preserved water samples were filtered with millipore filtration unit (0.45 μ). The filtrated water was transferred into 2 l separating funnel and added 10 ml of 1% APDC solution (Ammonium Pyrrolidine Dithio Carbamate). The chelates were extracted by adding MIBK (Methyl Iso-Butyl Ketone) with vigorous shaking for 15 min. The aqueous phase was removed and the organic layer was collected separately. The same procedure was repeated to extract the organic layer. The collected organic layer was extracted with 50% HNO₃ and finally made up into 25 ml with Millipore filtered water (Jonathan et al. 2008). The dried sediment samples were grounded as a fine powder with the agate mortar and pestle. About 1 g of the fine powdered sediment samples were weighed in an analytical balance (Shimadzu Corporation, Japan). The heavy metal extraction was carried out by the modified method (Karbassi et al. 2008). Finely grounded 1 g of sediment samples was digested with 10 ml of acid mixture HNO₃, H₂SO₄ and HClO₄ in the ratio of 5:2:1 at 60 °C in the hot plate. A few drops of hydrochloric acid were added to allow the complete digestion of sample. Finally, the dried and digested samples were made up into 25 ml with Millipore water and filtered using Whatman No.1 paper for analysis of heavy metals.

The extracted samples of water and sediment were analyzed with the Atomic Absorption Spectrophotometer (AA7000-Shimadzu Corporation, Japan). The working wavelength of the heavy metals was 213.85 nm for Zn, 324.75 nm for Cu, 228.80 nm for Cd, and 217.00 nm for Pb. Quality assurance testing was relied on the control of blanks and yield for chemical procedure. For acquired quantification, triplicate the samples, blanks and standardized reference materials were used during analysis. The metal standards were prepared by

(MERCK Genei, Bangalore) analytical grade chemicals with double distilled water in the range of 0.5 to 3 ppm concentration and were run to check the precision of the instrument throughout the analysis.

Statistical approaches

The Pearson correlation (PC) was conducted to find the relationship between the physico-chemical parameters and heavy metal concentrations in water and sediments. Two-way ANOVA method was used to find the significant variation in heavy metal concentrations between water and sediment with regards to sampling sites and seasons at 0.05% levels. The principal component analysis (PCA) and the cluster analysis (CA) tests were conducted to identify the source of pollutants in Muthupet Mangrove ecosystem (Prasanna et al. 2012). The statistical methods like PC and ANOVA were performed with Origin 8.0; PCA and Cluster Analysis were performed by PAST (3.0 Windows) and SPSS (16.0 Windows).

Spatial distribution

Degrees of metal concentration in the study area and their spatial distribution at different depths were mapped using geographical information system (GIS). Data processing and spatial interpolation analysis were performed using ArcGIS 10.2 method. Inverse distance weighting (IDW) technique was applied in the present study. The degree of phenomenal (weight) was dependent on the distance of the point to another unknown point.

Geo accumulation index

Geoaccumulation index (*I_{geo}*) was proposed by (Muller 1979) to assess the pollution levels in surface sediments of the study area. The following formula was used for calculation of Geo accumulation index

$$I_{geo} = \log_2 \left(C_n / 1.5B_n \right)$$

where C_n represents the concentration of trace metals in the sediment samples and B_n represents the geochemical background of particular element during the earth crust. Due to unavailability of background

values for these metals in our study area, the Bn values were considered according to (Taylor and McLennan 1985) and the factor 1.5 is introduced to compensate the background content due to lithogenic effects.

The *Igeo* is classified into 5 grades to evaluate contamination level:

Class	Value	Classification
0	<0	Uncontaminated
1	0–1	Uncontaminated to moderately contaminated
2	1–2	Moderately contaminated
3	2–3	Moderately to strongly contaminated
4	3–4	Strongly contaminated
5	4–5	Strongly to extremely strongly contaminated
6	>5	Extremely contaminated

Results and discussion

Physico-chemical parameters

Seasonal variation in physico-chemical parameter of Muthupet Mangrove Ecosystem is shown in Fig. 2a–g. As shown in Table 2, the surface water temperature varied between 28 and 34 °C in the study area, maximum in summer and minimal in post monsoon. Seasonal variation of the surface water temperature is mainly due to weather conditions. Probably the highest range of water temperature in summer is related to bright sunshine, longer photo period, dry wind and high evaporation rate. The obtained results were correlated with the previous report (Ashok Kumar et al. 2011; Paramasivam and Kannan 2005; Kannan et al. 2003) in this study area. The lower temperature was due to cloudy sky, subsequent freshwater input through streams and channels and rainfall which has brought down the temperature to a minimum level in Muthupet (Ajithkumar et al. 2006) and Cuddalore (Mathivanan and Rajaram 2014).

The minor variation in water pH may affect the chemical processes and physiological functioning of biological organisms. Table 2 reveals the pH value of the study area and its ranging between 6.31 and 7.87. The maximum level was recorded in monsoon as 7.87 which might be due to direct mixing of sewage and aqua farm waste water from the nearby areas, while minimum 6.31 in post monsoon. Higher value of pH could be

attributed to enhance the growth of algal population to enhance the utilization of CO₂ for photosynthesis (Chaterjee and Raziuddin 2006; Paramasivam and Kannan 2005; Ajithkumar et al. 2006). The lowest pH in the study area during post monsoon season due to direct influence of fresh water, lowering of primary productivity, reduction of salinity, temperature and decomposition of organic matter (Kumar et al. 2013; Govindasamy et al. 2000; Sankar et al. 2010).

Salinity of the study area varied between 0 to 32 ppt was shown in the Table 2. The higher salinity was recorded during summer at station 10 were attributed to higher intense of solar radiation, high evaporation rate and lower rain fall (Sridhar et al. 2006; Balasubramanian and Kannan 2005) whereas, lower salinity in all the seasons of station 1 may due to mixing fresh water into lagoon. However, water salinity was mainly regulated by rate of rain fall, influence of fresh water and strong solar radiation (Balasubramanian and Kannan 2005; Ajithkumar et al. 2006). Salinity of the study area shows strong positive correlation with Nitrite ($r = 0.784, p < 0.01$), followed by ammonia, Cu and Zn in sediment ($r = 0.745, 0.650, 0.702$, respectively) with respect of significance $p < 0.05$ (Table 5). Thus, the positive correlation of the above parameters is directly linked with salinity. However, phosphate has given negative correlation with the same.

Nitrite concentration varied between 0.10 and 7.86 µg/l in site 1, 0.10–8.73 in site 2 and 0.53–6.57 µg/l in site 3 (Table 2). At site 1, the highest concentration of nitrite was found at station 1 which has been loaded with direct discharge of nitrite containing wastages (Ramesh et al. 2008) of phytoplankton excretion, bacterial decomposition of Planktonic detritus (Rajasegar 2003; Govindasamy et al. 2000; Asha and Diwakar 2007) whereas, lowest in the same site of post monsoon. In site 2, elevated level of nitrite was recorded as 8.73 µg/l, which was due to the influence of aquaculture wastages containing excessive feed materials and the fecal matter of aquatic organisms (Ramesh et al. 2008). Maximum level of nitrate 6.57 µg/l was noted at site 3 of monsoon season thus high tidal influence may attribute to interchanging of fresh and sea water. The earlier studies (Paramasivam and Kannan 2005; Ajithkumar et al. 2006) reported that Muthupet mangrove was loaded with higher concentration of nitrite.

Concentration of nitrate ranges from 0.017 to 0.86 µg/l in site 1, 0.091–1.08 µg/l in site 2, and 0.09–

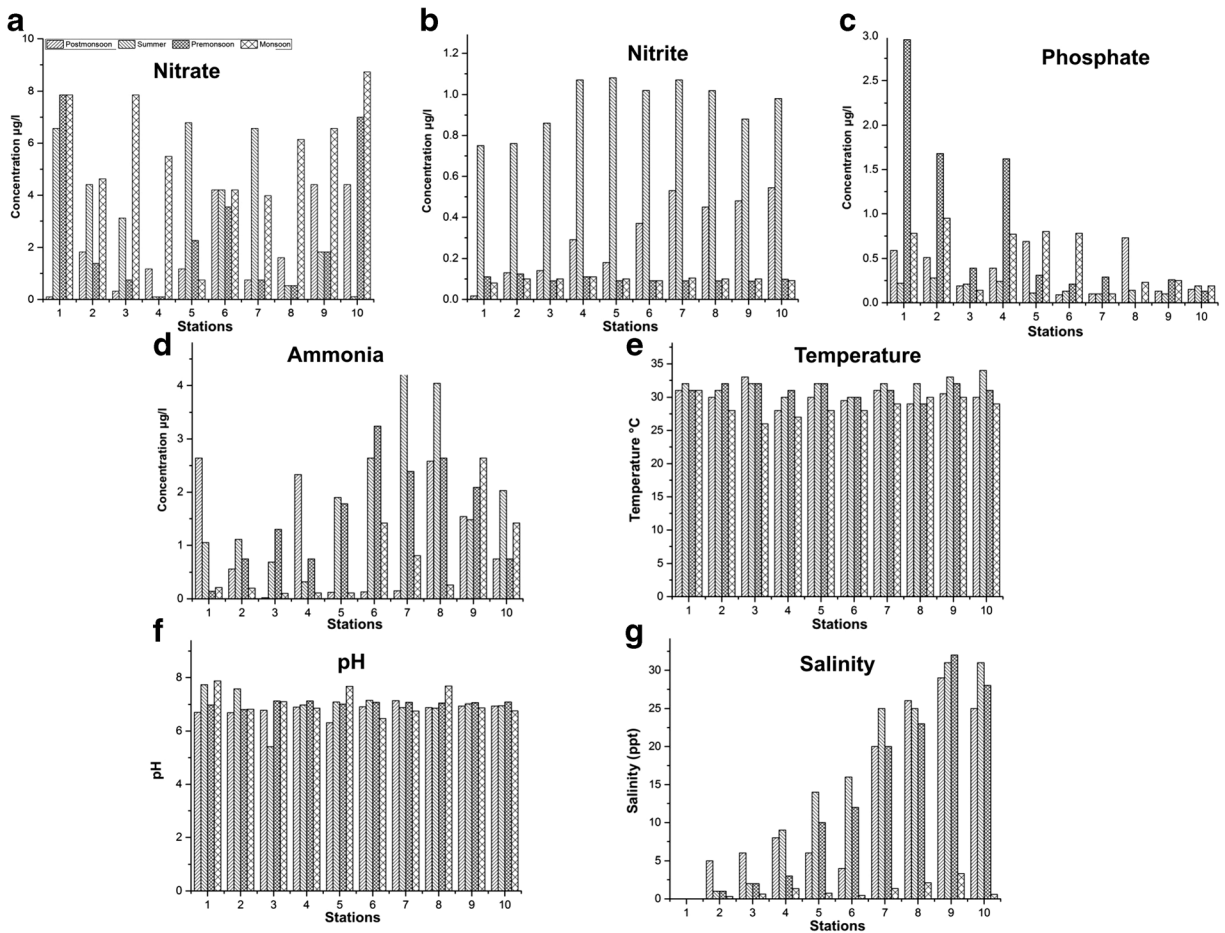


Fig. 2 a–g Seasonal variation of physico-chemical parameters of water samples recorded in different stations of the study area

1.07 µg/l in site 3 was shown in the Table 2. The highest concentration of nitrate in the study area during summer is due to discharging of nitrate based products from the

branching rivers. The lowest concentration of nitrate is recorded in post monsoon; however, the nitrate concentration in the aquatic environment is mainly regulated by

Table 2 Annual mean levels of physico-chemical parameters along with standard deviation

Station	Temp	pH	Salinity	Nitrite	Nitrate	Phosphate	Ammonia
St-1	31.25 ± 1.29	7.32 ± 0.57	0	5.60 ± 3.72	0.23 ± 0.34	1.14 ± 1.24	1.01 ± 1.16
St-2	30.25 ± 2.75	6.97 ± 0.40	1.83 ± 2.14	3.07 ± 1.69	0.27 ± 0.32	0.86 ± 0.62	0.66 ± 0.38
St-3	30.75 ± 2.28	6.60 ± 0.81	2.66 ± 2.32	3.01 ± 2.46	0.29 ± 0.38	0.23 ± 0.11	0.53 ± 0.60
St-4	29.00 ± 2.89	6.97 ± 0.11	5.34 ± 3.74	1.72 ± 2.57	0.39 ± 0.46	0.76 ± 0.62	0.88 ± 1.00
St-5	30.50 ± 3.00	7.02 ± 0.56	7.69 ± 5.66	2.75 ± 2.77	0.36 ± 0.48	0.48 ± 0.32	0.98 ± 1.00
St-6	29.38 ± 2.75	6.90 ± 0.30	8.12 ± 7.14	4.04 ± 0.33	0.39 ± 0.44	0.30 ± 0.32	1.86 ± 1.38
St-7	30.75 ± 2.58	6.69 ± 0.17	16.59 ± 10.42	3.01 ± 2.82	0.44 ± 0.46	0.15 ± 0.10	1.96 ± 1.92
St-8	30.00 ± 2.75	7.12 ± 0.39	19.03 ± 11.35	2.20 ± 2.67	0.41 ± 0.44	0.28 ± 0.32	2.38 ± 1.57
St-9	31.38 ± 2.14	6.97 ± 0.08	23.83 ± 13.73	3.66 ± 2.29	0.38 ± 0.38	0.19 ± 0.08	1.94 ± 0.54
St-10	31.00 ± 2.36	6.93 ± 0.13	21.15 ± 13.92	5.06 ± 3.75	0.42 ± 0.42	0.17 ± 0.03	1.24 ± 0.62

± indicated standard deviation

certain factors such as utilization by planktonic communities, production of nitrate by oxidizing ammonia releasing of nitrate containing effluents (Rajaram et al. 2005; Rajasegar 2003). Nitrate shows strong positive correlation (Table 5) with Zn in sediment ($r = 0.899$; $p < 0.01$) followed by ammonia, Cu and Pb in the sediment ($r = 0.666, 0.840, 0.803$; $p < 0.05$).

Table 2 shows the ammonia concentration ranges (0.02–4.47 $\mu\text{g/l}$) in this study area. From Table 2, the elevated level of ammonia is found to be 4.47 $\mu\text{g/l}$ at summer and lesser of 0.15 $\mu\text{g/l}$ was noticed in post monsoon. Ammonia level was varied between 0.11 and 2.64 $\mu\text{g/l}$ at site 2 followed by 0.02–2.64 $\mu\text{g/l}$ in site 1. Table 5 shows positive correlation of ammonia (Table 5) with salinity, nitrate, and Cu in sediment ($r = 0.745, 0.666, 0.649$; $p < 0.05$). Generally, concentrations of ammonia in aquatic ecosystems were regulated by wastewaters discharged from sewage treatment plants or industries, runoff from fertilized agricultural fields, decomposition dead phytoplankton and also due to excretion of ammonia by planktonic organisms (Rajasegar 2003).

Dissolved phosphates are major nutrient for marine phytoplankton (Mackey et al. 2007). Concentration of phosphate varied between 0.09 and 2.96 $\mu\text{g/l}$ (Table 2). The phosphate concentration in site 1 was 0.14–2.96 $\mu\text{g/l}$, followed by 0.09–1.62 $\mu\text{g/l}$ and 0.10–0.17 $\mu\text{g/l}$ in site 2 and 3, respectively. Maximum level of phosphate was recorded as 2.29 mg/l at site 1. However, the increased concentration might be due to waste water release and post harvesting practice from shrimp form leading to increased level of nitrogen (0.03–5.06 mg/l) and (0.05–2.02 mg/l) phosphorus (Ramesh et al. 2008). Phosphate shows the negative correlation with Zn in sediment and it confirms that phosphate does not have origin from the natural sources.

Heavy metal concentration

The concentration of heavy metals in sediment and surface water of all the ten stations at different seasons has varied seasonally and spatially was shown in the Tables 3 and 4. Sediment has higher metal concentration when compared to surface water samples. Thus sediments have a mixture of organic materials as well as minerals with the presence of charged surface organic matters (Langston 1986) which could be the possible factor for absorption and accumulation of heavy metals (Gibbs 1973; Luoma and Bryan 1981; Bettinetti et al.

2003; Hollert et al. 2003). Among the metals in water, Pb poses the higher concentration compared to other metals followed by Zn, Cu and Cd.

The mean concentration of Cu in water and sediment samples of study area varied between 0.50–4.43 mg/l and 4.46–20.59 mg/kg , respectively. The highest concentration of Cu was recorded in the water and sediment samples of site 1 as 2.94 mg/l (St-3) and 17.91 mg/kg (St-1) (Tables 3 and 4). The highest concentration is due to drain/dumping of domestic wastages, agricultural based drainages, increased boating activities, recurrent usage of antifouling paints, oil dropping from boats and fishing activities (Ashok Kumar et al. 2011). The lowest concentration of Cu in site 1 was 1.09 mg/l (St-2) in water and 4.46 mg/kg (St-2) in sediment. At site 2, the Cu concentration ranges between 0.79 and 4.35 mg/l in water, 10.10–20.59 mg/kg in sediment samples. In the site 3, the Cu concentration ranges between 0.50 and 4.43 mg/l in water, 9.89–19.20 mg/kg in sediment samples. The concentration of Cu in the sediment shows a significant positive correlation ($P < 0.01$) with CuS/PbS ($r = 0.886$) followed by CuS/salinity ($r = 0.650$), CuS/nitrate ($r = 0.840$), CuS/ammonia ($r = 0.649$), and CuS/ZnS ($r = 0.973$) with the Significant of ($P < 0.05$) (Table 5). Two-way ANOVA data revealed that Cu concentrations in sediment samples of different stations and seasons does not differ significantly at 5% significant level. There is no significant difference in the seasons and station as far as a lead concentration is concerned at 5% significant level. While, the water samples shows 5% significant level with season and non significant variation with station. Two-way ANOVA result shows both significant as well as non-significant variations between seasons ($p < 0.05$) and stations ($p < 0.05$).

The Cd concentration in water and sediment samples of study area varied between 0.05–3.72 mg/l and 0.06–0.57 mg/kg , respectively (Tables 3 and 4). The highest and lowest mean concentration of Cd in water samples of site 1 was 0.06 mg/l (St-1) and 3.51 mg/l (St-2). The highest and lowest mean concentration of Cd in water and sediment samples of site 2 was 3.54 mg/l (St-10) and 0.05 mg/l (St-10), 0.57 mg/kg (St-6) and 0.22 mg/kg (St-6), respectively. Increased concentration of Cd in the study area primarily with municipal waste waters and plating and galvanizing (Machine tools and metal products) (Ramesh et al. 2008) followed by industrial activities such as fossil fuel combustion, iron, steel and cement production, phosphate fertilizer are the potential

Table 3 Seasonal variations of heavy metal concentrations (mg/l) in water samples of study area (mean ± SD)

Element	Station	Season				ANOVA					
		Post monsoon	Summer	Premonsoon	Monsoon	Factor	DF	SS	MS	F value	P value
Cu	St-1	1.87 ± 0.83	1.66 ± 0.62	1.65 ± 0.76	1.59 ± 0.50						
	St-2	1.17 ± 1.25	1.14 ± 0.72	1.09 ± 0.51	1.81 ± 0.86						
	St-3	2.90 ± 3.70	1.85 ± 0.30	1.14 ± 0.38	1.60 ± 0.62						
	St-4	2.11 ± 1.00	1.39 ± 0.85	1.24 ± 0.37	1.26 ± 0.15						
	St-5	4.21 ± 4.21	1.26 ± 0.59	1.48 ± 0.18	1.54 ± 0.02	Station	9	5.26	0.58	0.86	0.569
	St-6	4.35 ± 2.70	1.16 ± 0.25	1.41 ± 0.33	0.91 ± 0.15	Season	3	14.48	4.82	7.10	0.001
	St-7	4.43 ± 0.60	1.09 ± 0.40	1.18 ± 0.31	1.30 ± 0.35						
	St-8	0.50 ± 0.40	0.81 ± 0.17	1.01 ± 0.35	1.34 ± 0.51						
	St-9	1.05 ± 1.12	1.31 ± 0.22	1.51 ± 1.05	1.52 ± 0.15						
	St-10	4.32 ± 2.23	0.79 ± 0.29	1.03 ± 0.52	1.34 ± 0.48						
Cd	St-1	0.05 ± 0.04	1.41 ± 1.63	0.35 ± 0.33	0.13 ± 0.07						
	St-2	0.12 ± 0.11	3.50 ± 5.47	0.21 ± 0.27	0.20 ± 0.05						
	St-3	0.18 ± 0.19	0.67 ± 0.28	0.13 ± 0.11	0.12 ± 0.08						
	St-4	0.07 ± 0.06	0.37 ± 0.04	0.13 ± 0.11	0.10 ± 0.12						
	St-5	0.13 ± 0.06	0.59 ± 0.43	0.12 ± 0.14	0.13 ± 0.10	Station	9	4.69	0.52	0.835	0.59
	St-6	0.09 ± 0.06	3.34 ± 4.98	0.07 ± 0.11	0.11 ± 0.13	Season	3	29.9	9.96	15.97	0.036
	St-7	0.18 ± 0.13	3.71 ± 2.93	0.13 ± 0.06	0.11 ± 0.10						
	St-8	0.36 ± 0.44	3.55 ± 4.94	0.06 ± 0.07	0.09 ± 0.15						
	St-9	1.80 ± 2.49	1.12 ± 0.32	0.08 ± 0.12	0.10 ± 0.20						
	St-10	0.43 ± 0.47	3.53 ± 5.33	0.05 ± 0.09	0.08 ± 0.21						
Pb	St-1	12.49 ± 0.64	13.78 ± 0.51	8.09 ± 6.68	8.02 ± 5.22						
	St-2	11.81 ± 1.60	16.46 ± 2.78	8.12 ± 6.77	7.73 ± 5.30						
	St-3	12.72 ± 3.20	14.76 ± 0.39	7.44 ± 6.17	7.96 ± 5.14						
	St-4	12.15 ± 1.12	17.86 ± 6.36	7.36 ± 6.06	7.67 ± 5.22						
	St-5	14.53 ± 3.20	14.61 ± 0.57	7.51 ± 6.20	8.19 ± 5.14	Station	9	3.76	0.41	0.427	0.908
	St-6	13.46 ± 1.84	15.37 ± 1.51	7.24 ± 5.96	7.62 ± 4.81	Season	3	499.67	166.55	170.44	0
	St-7	15.16 ± 0.08	15.25 ± 1.41	7.10 ± 5.82	7.62 ± 4.81						
	St-8	12.10 ± 0.72	14.91 ± 1.24	6.91 ± 5.66	7.22 ± 5.22						
	St-9	13.85 ± 2.88	16.31 ± 3.20	6.84 ± 5.58	7.39 ± 4.17						
	St-10	14.99 ± 1.76	14.88 ± 1.11	6.31 ± 5.13	7.11 ± 4.09						
Zn	St-1	ND	3.58 ± 1.46	3.18 ± 0.41	ND						
	St-2	1.37 ± 2.49	2.90 ± 2.23	2.58 ± 2.38	ND						
	St-3	2.95 ± 4.60	4.58 ± 3.38	2.16 ± 3.11	ND						
	St-4	ND	8.06 ± 10.73	2.19 ± 3.15	ND						
	St-5	0.20 ± 0.34	12.91 ± 13.58	8.94 ± 10.73	ND	Station	9	31.35	3.48	0.569	0.809
	St-6	ND	4.36 ± 5.63	2.09 ± 3.31	ND	Season	3	215.26	71.75	11.72	0.042
	St-7	ND	6.49 ± 3.59	2.13 ± 3.21	ND						
	St-8	0.41 ± 1.45	3.29 ± 2.50	2.11 ± 3.36	0.20 ± 0.00						
	St-9	9.78 ± 14.64	4.59 ± 2.95	0.73 ± 0.98	ND						
	St-10	ND	2.29 ± 1.53	1.97 ± 3.21	0.04 ± 0.00						

MS mean square, df degree of freedom, significance level 0.05, ND not Detectable

Table 4 Seasonal variations of heavy metal concentrations (mg/kg) in sediment samples of study area (mean ± SD)

Element	Station	Season				ANOVA					
		Post monsoon	Summer	Premonsoon	Monsoon	Factor	DF	SS	MS	F value	P value
Cu	St-1	6.14 ± 5.68	8.94 ± 2.17	7.92 ± 9.13	17.91 ± 7.78						
	St-2	8.82 ± 2.96	7.19 ± 2.28	4.46 ± 4.44	11.22 ± 0.89						
	St-3	8.20 ± 1.15	8.98 ± 3.33	8.09 ± 4.89	14.15 ± 3.14						
	St-4	14.73 ± 4.76	16.71 ± 5.93	10.33 ± 7.54	18.47 ± 1.63						
	St-5	13.65 ± 1.80	19.90 ± 0.30	10.10 ± 2.98	20.59 ± 0.45	Station	9	316.22	35.13	6.61	0.059
	St-6	11.19 ± 1.38	15.89 ± 4.10	15.68 ± 4.13	18.54 ± 2.13	Season	3	234.43	78.14	14.71	0.071
	St-7	17.52 ± 5.11	15.93 ± 2.45	14.04 ± 6.53	15.22 ± 4.70						
	St-8	9.86 ± 4.67	15.40 ± 5.16	14.67 ± 4.41	18.94 ± 1.06						
	St-9	12.70 ± 5.84	19.20 ± 3.17	13.46 ± 5.08	17.64 ± 0.01						
	St-10	11.46 ± 5.38	15.67 ± 5.75	11.70 ± 5.91	17.46 ± 2.25						
Cd	St-1	0.06 ± 0.05	0.53 ± 0.17	0.55 ± 0.53	ND						
	St-2	0.45 ± 0.03	0.57 ± 0.17	0.53 ± 0.46	ND						
	St-3	0.33 ± 0.08	0.55 ± 0.22	0.48 ± 0.28	ND						
	St-4	0.25 ± 0.11	0.48 ± 0.20	0.30 ± 0.13	ND						
	St-5	0.24 ± 0.12	0.51 ± 0.29	0.43 ± 0.35	ND	Station	9	0.07	0.007	1.24	0.312
	St-6	0.22 ± 0.15	0.37 ± 0.05	0.57 ± 0.61	ND	Season	3	1.43	0.47	75.05	0.032
	St-7	0.24 ± 0.19	0.36 ± 0.24	0.38 ± 0.58	ND						
	St-8	0.20 ± 0.10	0.35 ± 0.06	0.55 ± 0.61	ND						
	St-9	0.24 ± 0.13	0.51 ± 0.21	0.47 ± 0.56	ND						
	St-10	0.27 ± 0.17	0.40 ± 0.02	0.30 ± 0.37	ND						
Pb	St-1	15.67 ± 0.32	16.66 ± 1.16	4.64 ± 7.29	9.09 ± 4.49						
	St-2	16.75 ± 1.84	17.57 ± 0.68	2.90 ± 4.29	8.97 ± 3.36						
	St-3	17.83 ± 3.04	17.72 ± 1.38	3.77 ± 5.70	10.34 ± 3.20						
	St-4	21.12 ± 0.16	21.35 ± 2.07	4.19 ± 6.41	12.49 ± 3.85						
	St-5	19.25 ± 1.52	20.21 ± 1.97	3.93 ± 5.94	11.87 ± 2.80	Station	9	40.93	4.54	4.91	0.059
	St-6	18.62 ± 1.92	20.67 ± 2.35	4.59 ± 7.05	11.53 ± 3.77	Season	3	1573.25	524.41	566.39	0
	St-7	19.70 ± 0.88	20.29 ± 1.95	3.57 ± 5.37	9.60 ± 4.25						
	St-8	18.74 ± 1.12	20.82 ± 2.27	4.28 ± 6.53	10.51 ± 3.93						
	St-9	18.40 ± 0.32	20.82 ± 1.61	4.11 ± 6.28	12.10 ± 2.96						
	St-10	17.04 ± 1.28	20.74 ± 2.04	4.59 ± 7.14	11.93 ± 6.09						
Zn	St-1	11.32 ± 10.03	15.01 ± 1.97	18.84 ± 18.51	17.76 ± 1.82						
	St-2	17.96 ± 1.50	15.47 ± 2.73	4.41 ± 3.11	14.32 ± 6.05						
	St-3	21.22 ± 1.94	18.23 ± 7.30	19.95 ± 5.92	21.67 ± 18.05						
	St-4	36.59 ± 4.04	34.77 ± 6.39	29.41 ± 10.55	32.36 ± 11.37						
	St-5	33.86 ± 1.16	35.12 ± 4.61	30.16 ± 3.35	32.51 ± 12.86	Station	9	2430.4	270.04	20.76	0.062
	St-6	30.96 ± 4.82	32.37 ± 6.32	39.18 ± 2.34	31.14 ± 12.36	Season	3	9.12	3.04	0.23	0.872
	St-7	34.14 ± 8.96	32.19 ± 8.43	36.72 ± 6.56	26.00 ± 1.40						
	St-8	28.79 ± 4.49	31.14 ± 12.14	37.95 ± 2.90	32.71 ± 7.93						
	St-9	33.54 ± 6.34	33.85 ± 10.05	36.35 ± 5.36	32.52 ± 10.43						
	St-10	29.47 ± 5.54	32.80 ± 7.24	33.44 ± 7.36	32.23 ± 11.36						

MS mean square, df degree of freedom, significance level 0.05, ND not Detectable

Table 5 Pearson correlation coefficient among various physico-chemical parameters and heavy metals

Parameter	Temp	pH	Salinity	NO ²⁻	NO ³⁻	PO ₄ ³⁻	NH ₃	CuW	CdW	PbW	ZnW	CuS	CdS	PbS	ZnS
Temp	1														
pH	0.123	1													
Salinity	0.279	0.003	1												
NO ²⁻	0.590	0.304	0.003	1											
NO ³⁻	-0.244	-0.153	0.784**	-0.310	1										
PO ₄ ³⁻	-0.120	0.578	-0.740*	0.165	-0.737*	1									
NH ₃	-0.013	0.274	0.745**	-0.050	0.666*	-0.528	1								
CuW	0.134	-0.311	-0.208	0.309	0.056	-0.177	-0.294	1							
CdW	0.148	0.131	0.547	0.247	0.375	-0.353	0.606	-0.286	1						
PbW	-0.145	-0.227	-0.020	-0.269	0.251	-0.034	-0.209	0.450	-0.226	1					
ZnW	-0.025	-0.313	0.124	-0.548	0.210	-0.287	-0.050	0.223	-0.529	0.590	1				
CuS	-0.201	0.073	0.650*	-0.243	0.840*	-0.548	0.649*	0.181	0.032	0.328	0.480	1			
CdS	0.062	-0.305	-0.481	-0.140	-0.661*	0.271	-0.476	-0.202	-0.076	0.025	0.131	-0.682*	1		
PbS	-0.474	-0.156	0.515	-0.450	0.803*	-0.487	0.411	0.058	-0.144	0.362	0.502	0.886**	-0.568	1	
ZnS	-0.266	-0.080	0.702*	-0.299	0.899**	-0.652*	0.631	0.117	0.069	0.269	0.445	0.973*	-0.661*	0.939**	1

**Correlation is significant at the 0.01 level (2-tailed).

*Correlation is significant at the 0.05 level (2-tailed).

sources of Cd and Zn exposure (Manju et al. 2014). The lowest mean concentration of Cd in water and sediment samples of site 2 was 0.05 mg/l (St-10) and 0.22 mg/kg (St-6), respectively. In the site 3, the highest and lowest mean concentration of Cd was recorded as 3.72 and 0.06 mg/l. Two-way ANOVA data shows that Cd concentrations in water samples of different stations do not differ at 5% significant level. There is no significant difference in the seasons as far as Cd concentration is concerned at 5% significant level. Two-way ANOVA results of Cd in sediment show non-significant variation in seasons ($p < 0.05$), whereas significant variations in stations ($p < 0.05$).

At site 1, the mean concentration of Pb ranges from 7.44 to 16.47 mg/l in water and 2.90–17.83 mg/kg in sediment (Tables 3 and 4). The highest and lowest mean concentration of Pb in water samples of site 1 was 16.47 mg/l (St-2) and 7.44 mg/l (St-3), respectively. The highest concentration of Pb was recorded in St-3, due to discharging of lead containing industrial waste. At site 2, the mean concentration of Pb in the water and sediment samples varied between 6.31–17.87 mg/l and 3.93–21.35 mg/kg, respectively. In the site 3, the mean concentration of Pb in water and sediment samples varied between 6.84–16.32 mg/l and 3.57–20.82 mg/kg, respectively. Pb shows positive correlation with CuS ($r = 0.886$; $p < 0.01$) and nitrate ($r = 0.803$; $p < 0.05$) and the results indicated that both the metal might have the same origin (Table 5). Pb concentration in water samples of different season do not differ significantly at 5% significant level. Two-way ANOVA result indicates that there is no significant difference in the seasons as far as lead concentration is concerned at 5% significant level. Two-way ANOVA data on the Pb in sediment results shows significant variations between stations ($p < 0.05$) and seasons ($p < 0.05$).

The mean concentration of Zn in the water and sediment samples of study area varied between ND–12.91 mg/l and 4.41–39.18 mg/kg, respectively (Tables 3 and 4). The highest mean concentration of Zn in the study area was recorded during premonsoon, whereas the lowest during post monsoon. The mean concentration of Zn in the study area varied spatially and seasonally. Results shows that Zn concentration was highest in St-4 and St-6 could be attributed with discharging of wastage from Zn consuming industries such as electroplating, tyre manufacturing, and paint preparing industries along with agricultural and aqua farm wastages. Zn posses strong positive correlation

with nitrate ($r = 0.899$) and PbS ($r = 0.939$) by means of 0.01 significant (Table 5) followed by 0.05 significant correlation with salinity ($r = 0.702$). Zinc concentration in water and sediment samples of different stations differ significantly at 5% significant level. There are no significant differences of Zn concentration in water and sediment with respect to season at 5% significant level.

The present study has compared (Table 6) with other mangrove ecosystem in the world; the mean concentrations of heavy metals in Muthupet mangrove sediment are higher with other mangroves like Futian mangrove (Chai et al. 2015), Huanghe Estuary (Wu et al. 2007), Sungei Buloh, Singapore (Cuong et al. 2005) and Fadiouth Senegal (Bodin et al. 2013). The mean concentration was lower than Pearl River, South China (Bai et al. 2011), Gulf of Kachchh, India (Goutam et al. 2015), Nansha, China (Wu et al. 2014) and Shenzhen Bay (Li et al. 2015). The sources of contamination in various mangroves are compared with this study, mainly aquaculture activities, preparation and storage of food (Tam and Wong 2000; Behera et al. 2013), release of agricultural input products (Behera et al. 2013), pulp, paper, fertilizer (Caeiro et al. 2005).

Principle component analysis

Four PCs are extracted from given data set of heavy metal concentration in water. PC 1, PC 2, PC 3, and PC 4 represent about 43.92, 34.40, 17.15, and 4.51 of total variance, respectively. PC 1 and PC 2 furnishes the Eigen value >1 explaining with 78.33% of total variance, whereas PC 3 and PC 4 results with Eigen value <1 and are consider to be lesser important compared to other two (Mathivanan and Rajaram 2014). Therefore, the first two PCs alone need to be considered for further analysis. In PC1 Cd and Pb shows strong positive loadings, Zn moderate positive loading, and Cu negative loading. Cd and Pb metals are strongly correlated and clearly indicated that they are from external sources (Table 7). PC1 values correspond to the study area which might be loaded with Cd due to manmade activities such as dumping of municipal wastages and plating and galvanizing of mechanical tools (Ramesh et al. 2008) followed by Pb and Zn. Primarily, elevated level of Pb was originated through extended boating activities for recreational and commercial purposes and the Secondary sources were mainly derived from idol immersion activities, loading of Zn in the study area from dumping of tyre based wastages nearer to or into the water bodies. The second most

Table 6 Comparative account on the distribution of heavy metals in Muthupet mangrove with available literature

Location	Cd	Cu	Pb	Zn	Reference
Shenzhen Bay, South China	2.30	31.7	47.8	296.3	Li et al. 2015
Nansha, China	0.80	113.0	55.3	159.0	Wu et al. 2014
Sungei Buloh, Singapore.	0.20	07.10	12.3	51.20	Cuong et al. 2005
Fadiouth, Senegal	0.03	03.50	2.40	5.40	Bodin et al. 2013
Gulf of Kachchh, India	0.41	84.0	20.0	107.0	Goutam et al. 2015
Muthupettai, India	–	11.35	30.0	15.89	Janaki Raman et al. 2007
Maryut lagoon, Egyptian	0.98	0.01	0.34	2.65	Younis et al., 2014
Futian mangrove	0.01	0.13	0.17	2.06	Chai et al. 2015
Huanghe Estuary	0.02	0.28	0.23	0.76	Wu et al. 2007
Pearl River, South China	1.18	51.52	32.33	127.41	Bai et al. 2011
<i>Muthupet Mangrove</i>	<i>0.57</i>	<i>20.59</i>	<i>21.35</i>	<i>39.18</i>	<i>Present study</i>

Inorder to highlighted the present study we have make the differentiation (italicized)

important for the presence of Zn in the environment is galvanized products followed by roof and façade materials. The summarized data of PC 2 shows variance around 34.40% with the Eigen value of 1.376 and it indicates that Cu shows strong positive loading of 0.729 (>0.6) with active participation of boating activities, usage of copper-based paints, agricultural fungicides as copper oxychloride and copper hydroxide, fertilizer and electro plating wastages from nearby branching rivers, whereas Pb shows moderate positive loading of 0.562 (<0.6); Pb is typically coupled with coal combustion and fuel combustion and fly ash from coal-fired power plants (Dahl et al. 2008).

In addition, the biplot analysis of the PCA shows the inter-relationship between seasons, metal level and the stations (Fig. 3a). Biplot clearly indicates that the first upper quadrant was strongly loaded with Cd and which

was occupied mostly by summer samples, followed by Pb with few stations shared from Cd. Second upper quadrant was filled by Cu with respect to most of the post monsoon samples. Zn has very lesser importance when compared with other elements which occupies the first lowered quadrant with only two stations from summer and post monsoon. Finally, second lowered quadrant was engaged with most of the monsoon and pre monsoon samples with negative loading.

The results of PCA for heavy metal contents in sediment of Muthupet mangrove ecosystem are shown in Table 8. Unlike surface water, sediment possesses more capacity to accumulate metals with the presence of organic matters and other possible absorbents thus it could be the right choice by many authors (Qiao et al. 2010; Gu et al. 2012; Zhang 2006) to assess environmental pollution of particular area. Meanwhile PCA was performed for sediment too. According to these results, PC1 and PC2 have Eigen values are greater than one with total cumulative percentage of 72.67. PC1 includes Cu has strong positive loading 0.685(>0.6) followed by Zn and Pb with moderate loading points of 0.599 and 0.249 respectively (<0.6). The results indicated that PC1 was strongly influenced by Cu due to broad spectrum of anthropogenic influence such as application of Cu containing agrochemicals related to specialized agricultural practices. However, Zn and its components are also used in various manufacturing goods like paint, batteries, electrical apparatus, cosmetic, automobile tires, and fertilizers. PC 2 was extracted with Eigen value of 1.026 and 25.64% of variance along with Cd performs strong

Table 7 Loading and parameters of four heavy metals on the four rotated principle components (PC) for water samples

Element	PC 1	PC 2	PC 3	PC 4
Cu	-0.264	<i>0.729</i>	0.381	0.503
Cd	<i>0.657</i>	0.112	-0.496	0.557
Pb	0.525	0.562	0.118	-0.628
Zn	0.472	-0.374	<i>0.772</i>	0.205
Eigen value	1.757	1.376	0.686	0.181
% variance	43.922	34.409	17.155	4.5137
<i>Cumulative</i>	<i>43.92%</i>	<i>78.33%</i>	<i>95.49%</i>	<i>100.00%</i>

Italicized values are strong positive loading (0.60)

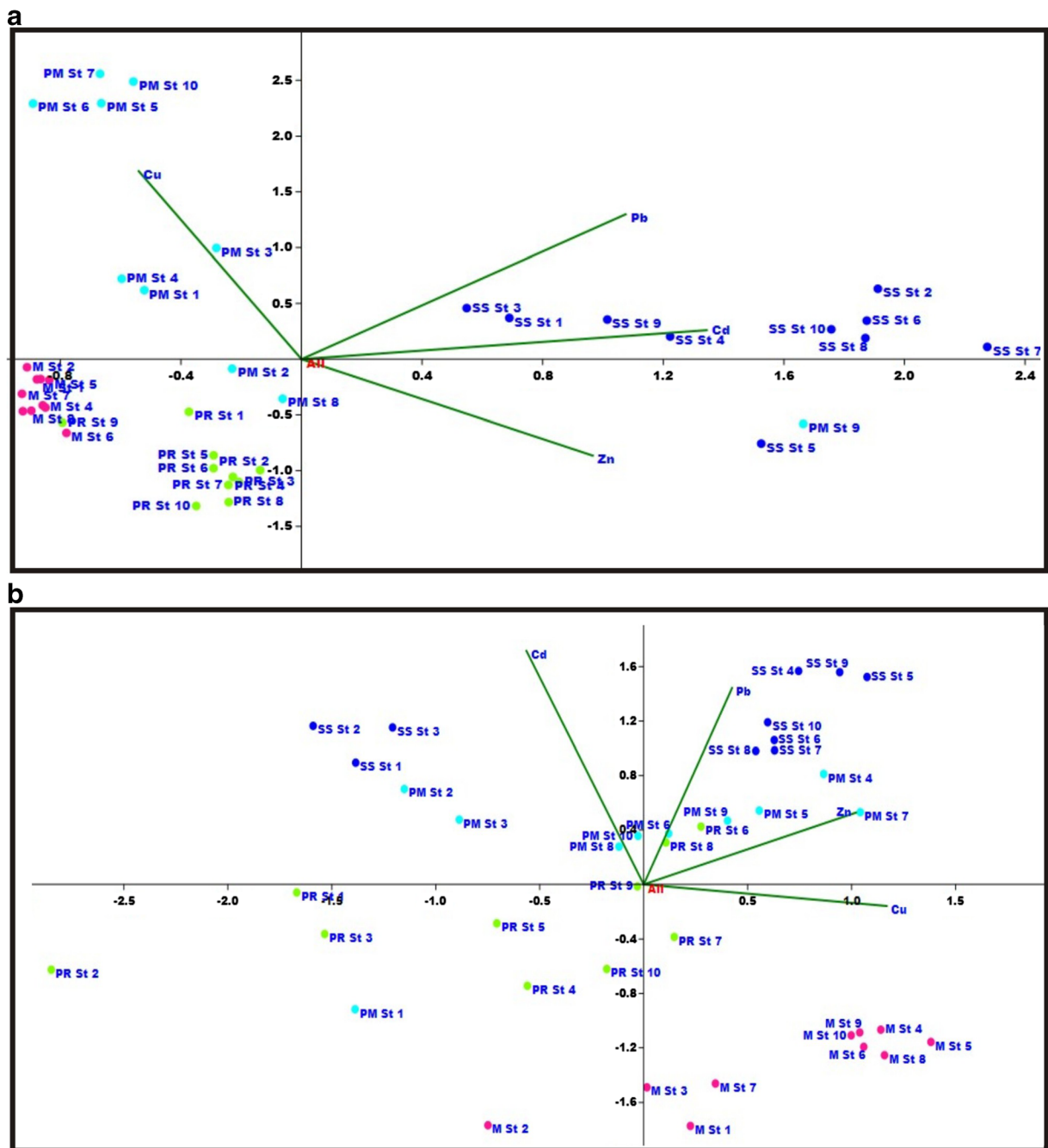


Fig. 3 a Biplot for metals in water samples of different stations of Muthupet Mangrove in four seasons. b Biplot for metals in sediment samples of different stations of Muthupet mangrove in four seasons

positive loading of 0.743 followed by Pb and Zn. Facchinelli et al. 2001 have reported the possible heavy metal sources as anthropogenic component where Cu and Zn have been associated with specific agronomic practices were Pb was derived from car exhaust and all the three metals were due to anthropogenic activity.

Therefore, it seems reasonable to infer that, PC2 is related to both natural and anthropogenic sources at the regional scale.

Biplot clearly indicates that Cu, Pb, and Zn have strong inter-relationship when compared to Cd. Moreover, Cd shows unique and strong loading points

Table 8 Loading and parameters of four heavy metals on the four rotated principle components (PC) for sediment samples

Element	PC 1	PC 2	PC 3	PC 4
Cu	<i>0.685</i>	-0.069	0.088	<i>0.720</i>
Cd	-0.331	<i>0.743</i>	0.481	0.327
Pb	0.249	<i>0.625</i>	-0.734	-0.088
Zn	0.599	0.229	0.471	-0.606
Eigen value	1.881	1.026	0.891	0.202
% variance	47.021	25.641	22.286	5.052
Cumulative	47.01%	72.67%	94.95%	100.00%

Italicized values are strong positive loading (0.60)

(Fig. 3b). The first upper quadrant was mostly occupied by Pb and Zn with perfect correlation among the metals thus around five more station from summer and few from post and premonsoon have been loaded with both metals. Second upper quadrant was filled with Cd mostly with post monsoon followed by summer; there has been no relationship of Cd with other metals. The first lower quadrant is engaged with Cu and most of monsoon samples. Second lower quadrant was filled with most of the premonsoon samples with negative loading points.

Cluster analysis

The cluster dendrogram was generated by ward method, wherein two main clusters nodes are generated namely cluster A and B, that contains numerous sub-clusters in water samples of the study area (Fig. 4a). The cluster A was mainly occupied by summer and post monsoon samples of all the stations. While cluster B have two sub nodes, with alternative seasons of cluster A. However, the dendrogram confirmed that the seasonal variation is influenced in heavy metals concentration.

Cluster analysis identified two clusters among the studied heavy metals in Muthupet sediments (Fig. 4b). The heavy metal concentration in cluster A reveals the similarity in freshwater influenced station 1, 2 and 3 in all the seasons. Unlike cluster A, the two sub clusters of B (B1—post monsoon and summer; B2—premonsoon and monsoon) shows fluctuation in heavy metal concentration. Statistical investigations revealed that Muthupet mangrove ecosystem shows seasonal influence in heavy metal concentration.

Spatial distribution patterns of Cu, Cd, Pb, and Zn in Muthupet mangrove ecosystem were shown in (Fig. 5) using contour maps based on IDW method. These maps

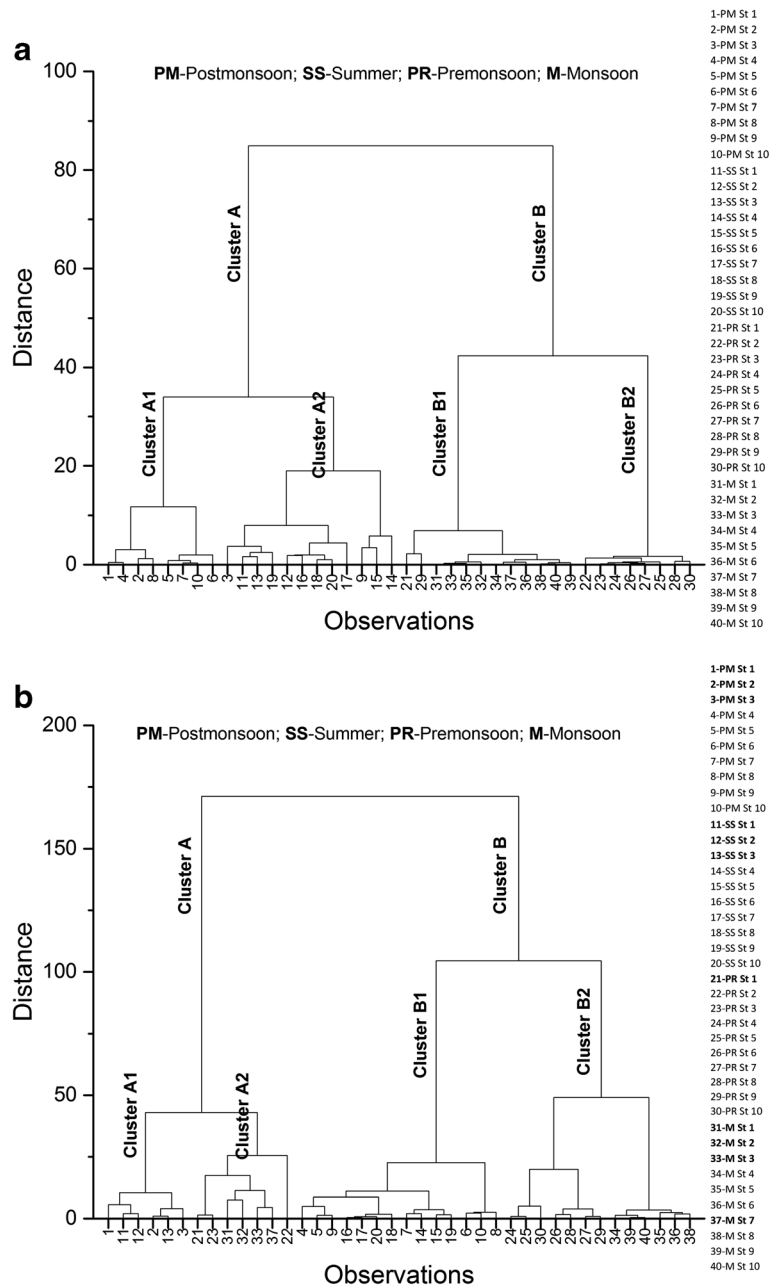
demonstrate the diverse zone of lower or higher concentrations in the ecosystem. In order to characterize the spatial distributions of heavy metals in study area effectively, it was divided into site 1 (S1, S2, and S3), site2 (including S4, S5, S6, and S10), and site 3 (S7, S8, and S9). According to Fig. 5, average concentration of Cd from each sampling site decreases in the order of site 1 < (max 0.24) site 3(max 0.19) < site 2(max 0.18). The site 1 (station 2) of the study area was highly enriched with Cd being proved as carcinogen. Cd has health risk to human being and has potential ecological damage to the environment (Hall et al. 1997).

Cu and Zn are two essential nutrients for both human and aquatic life, which has abundant natural resources found in the environment. However, both of them are needed at low concentrations, when the levels exceed it can become toxic to aquatic life (Hall et al. 1997). Spatial distribution of the Cu and Zn found in (Fig. 5) has a similar pattern between them in study area however, average concentration of metals varied station to the station. Average concentration of each sampling site of Cu concentration decreases in the order of site 2 (max 17.76) < site 3(max 16.46) < site 1(max 13.11). By comparison, average concentrations of Zn in each sampling site have decreased in the following trend of site 2(max 33.49) < site 3(max 32.94) < site 1(max 20.08).

According to Sadip et al. 2003, lower concentration of Pb poses a threat to existence in a marine environment when compared with other heavy metals. Spatial distribution of Pb shows unique pattern which is not similar with Cd, Cu, and Zn, namely their concentrations decrease in the order of site 2 (max 13.93) < site 3 (max 12.43) < site 1(max 13.20). The similar spatial distribution pattern of the concerned heavy metals in site might be closely related to the similar geological enrichment characteristics, which also shows that they might come from the same input sources.

The result of Igeo shown in Table 9 indicates that all the four metals furnished with class values below 0 except Cd. However, Cd shows class value between 0.88 and 1.61 which indicates that the study area was uncontaminated to moderately contaminate and also the average values of the Cd provides the same pattern from the above results that the study area was moderately contaminated with Cd compared to other elements. Thus, the average class values Cu, Pb, and Zn come under uncontaminated category in the study area. So that the study area might not be contaminated by Cu, Pb, and Zn with reference to background values. The

Fig. 4 **a** Cluster analysis of sampling stations for different season based on their heavy metal concentrations in water (Ward’s method). **b** Cluster analysis of sampling stations for different season based on their heavy metal concentrations in sediment (Ward’s method)



overall conclusion of indexed class values indicates that the study area was uncontaminated to moderately contaminated by Cd due to extended anthropogenic activities of the mangrove ecosystem. Usha Natesan et al. 2014 reported that the sediments of the Muthupet mangrove ecosystem were uncontaminated for all the metals except for Cr in the surface sediment which falls under +the category uncontaminated to moderately contaminated. These sources mainly include fertilizers and

pesticides used in agricultural activities, the effluent of the nearby aqua farm and the City even with lack of major industrialized regions. Meanwhile, the Cu, Zn, and Pb indicates that all the sampling stations are classified in Class 0, which is practically uncontaminated, as observed in Fig. 5 where the overall profiles are below 0. Both the elements Cu and Zn indicate that they originated from the natural weathering process (Amin et al. 2009) and designated that still it is not being

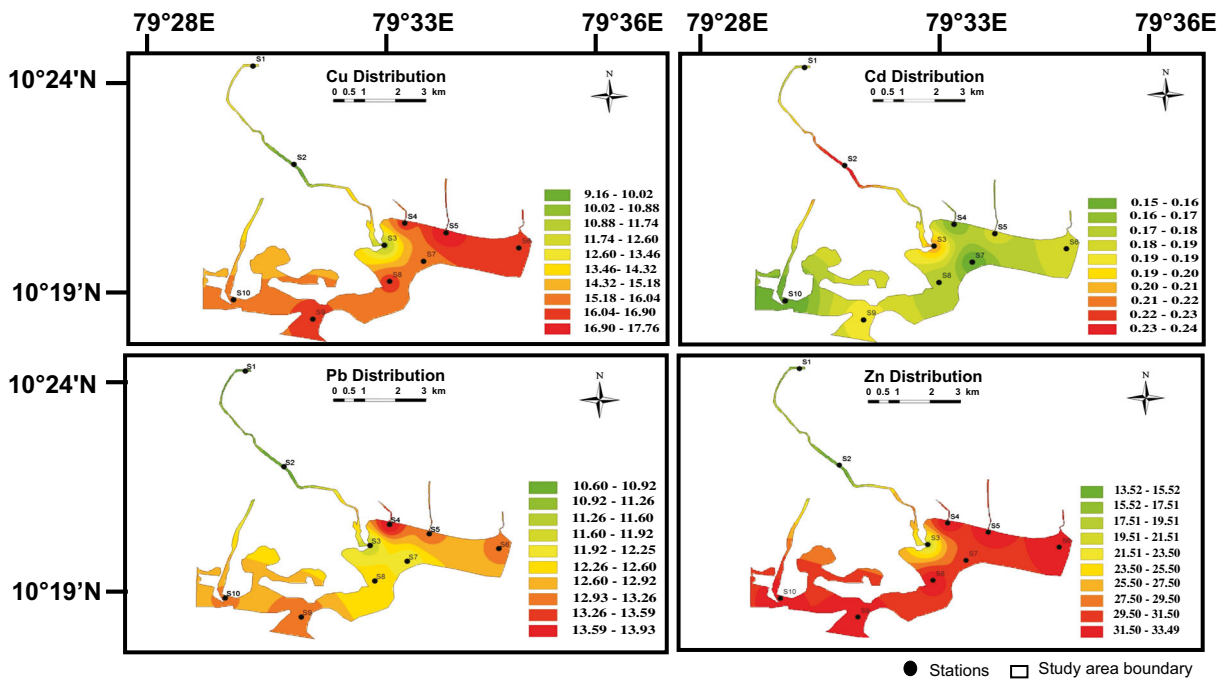


Fig. 5 Spatial distribution of metals in Muthupet mangrove ecosystem

contaminated by trace metals with reference to background values. The similar result was reported by (Cevik et al. 2009) geoaccumulation index reveal that sediments of the Seyhan dam weremoderately polluted with Cd whereas sediments were unpolluted with Cu, Cr and Zn.

Conclusion

A comprehensive analysis of heavy metal pollution was assessed in the Mangrove ecosystems of Southeast India, which was subjected to various socio economic and developmental activities. Based on the obtained results,

Table 9 Results of Geo-accumulation index for four metals at different station

Station	Cu	Cd	Pb	Zn	Class	Sediment grade
St-1	-2.06	1.21	-0.70	-3.03	0-2	Uncontaminated to moderately contaminated
St-2	-2.40	1.61	-0.64	-3.01	0-2	Uncontaminated to moderately contaminated
St-3	-2.00	1.37	-0.55	-2.42	0-2	Uncontaminated to moderately contaminated
St-4	-1.43	0.88	-0.29	-1.74	0-2	Uncontaminated to moderately contaminated
St-5	-1.25	1.21	-0.39	-1.70	0-2	Uncontaminated to moderately contaminated
St-6	-1.36	1.37	-0.40	-1.69	0-2	Uncontaminated to moderately contaminated
St-7	-1.36	1.12	-0.44	-1.76	0-2	Uncontaminated to moderately contaminated
St-8	-1.40	1.29	-0.43	-1.72	0-2	Uncontaminated to moderately contaminated
St-9	-1.32	1.37	-0.39	-1.67	0-2	Uncontaminated to moderately contaminated
St-10	-1.51	0.98	-0.44	-1.78	0-2	Uncontaminated to moderately contaminated
Average	-1.61	1.24	-0.47	-2.05	0-2	Uncontaminated to moderately contaminated

the Muthupet Mangrove ecosystem is classified as moderately polluted environment due to the influence of natural weathering processes along with other manmade activities. The investigation clearly depicts that the ecosystem receives metal load by anthropogenic activities which was confirmed by PCA and seasonal influence of heavy metal concentration was identified by Cluster analysis. The main anthropogenic activities in the study area include sewage disposal, wastages from salt pans, aquaculture and agriculture activities, fisheries activity, and idol immersion activity. The Muthupet lagoon was totally fresh water dominated during northeast monsoon when the drainage basins bring all terrestrial materials that were accumulated during dry period. In addition, regarding the sediment quality, Cd was considered to be moderately polluted, and remaining metals were classified as unpolluted. In summary, the present study provides excellent baseline data for the long-term monitoring of heavy metal pollution in Muthupet Mangrove Ecosystem. However, continuous monitoring and care should be taken to maintain healthy ecosystem.

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References

- Ajithkumar, T. T., Thangaradjou, T., & Kannan, L. (2006). Physico-chemical and biological properties of the Muthupettai mangrove in Tamil Nadu. *Journal Marine Biological Association of India*, *48*, 131–138.
- Amin, B., Ismail, A., Arshad, A., Yap, C. K., & Kamarudin, M. H. (2009). Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environment Monitor Assessment*, *148*, 291–305. doi:10.1007/s10661-008-0159-z.
- APHA, Clescerl, L. S., Greenberg, A. E., & Eaton, A. D. (1998). *Standard methods for examination of water & wastewater* (20th ed.). Washington, DC: American Public Health Association.
- Asha, P. S., & Diwakar, K. (2007). Recent trends in the hydrobiology of coastal and inshore waters off Tuticorin in the Gulf of Mannar, India. *Journal of the Marine Biological Association of India*, *49*, 7–11.
- Ashok Kumar, S., Rajaram, G., Manivasagan, P., Ramesh, S., Sampathkumar, P., & Mayavu, P. (2011). Studies on hydrographical parameters, nutrients and microbial populations of Mullipallam Creek in Muthupettai mangroves (southeast coast of India). *Research Journal of Microbiology*, *6*, 71–86. doi:10.3923/jm.2011.71.86.
- Badarudeen, A., Damodaran, K. T., Sajan, K., & Padmalal, D. (1996). Texture and geochemistry of the sediments of a tropical mangrove ecosystem, south west of India. *Environmental Geology*, *27*, 164–169. doi:10.1007/BF00770428.
- Bai, J., Xiao, R., Cui, B., Zhang, K., Wang, Q., Liu, X., & Gao, H. (2011). Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River estuary, South China. *Environmental Pollution*, *159*, 817–824. doi:10.1016/j.envpol.2010.11.004.
- Bajpai, A., Pani, S., Jain, R. K., & Mishra, S. M. (2002). Heavy metal contamination through idol immersion in a tropical lake. *Ecology and Environmental Conservation*, *8*, 157–159.
- Balakrishnan, T., Sundaramanickam, A., Shekhar, S., & Balasubramanian, T. (2015). Distribution and seasonal variation of heavy metals in sediments of muthupet lagoon, Southeast Coast of India. *Journal of Ecological Engineering*, *16*, 49–60.
- Balasubramanian, R., & Kannan, L. (2005). Physico-chemical characteristics of the coral reef environs of the Gulf of Mannar biosphere reserve, India. *International Journal of Ecology and Environmental Sciences*, *31*, 265–271.
- Behera, B. C., Mishra, R. R., Patra, J. K., Sarangi, K., Dutta, S. K., & Thatoi, H. N. (2013). Impact of heavy metals on bacterial communities from mangrove soils of the Mahanadi Delta (India). *Chemistry and Ecology*, *29*, 604–619. doi:10.1080/02757540.2013.810719.
- Bettinetti, R., Giarei, C., & Provini, A. (2003). A chemical analysis and sediment toxicity bioassays to assess the contamination of the river Lambro (northern Italy). *Archives of Environmental Contamination and Toxicology*, *45*, 72–80. doi:10.1007/s00244-002-0126-6.
- Bodin, N., Gom-Ka, R., Thiaw, O. T., Tito de Morais, L., Le Loch, F., Rozuel-Chartier, E., Auger, D., & Chiffolleau, J. F. (2013). Assessment of trace metal contamination in mangrove ecosystems from Senegal West Africa. *Chemosphere*, *90*, 150–157. doi:10.1016/j.chemosphere.2012.06.019.
- Caieiro, S., Costa, M. H., Ramos, T. B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G., & Painho, M. (2005). Assessing heavy metal contamination in Sado estuary sediment: an index analysis approach. *Ecological Indicators*, *5*, 151–169. doi:10.1016/j.ecolind.2005.02.001.
- Cevik, F., Göksu, M. Z., Derici, O. B., & Findik, O. (2009). An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geo accumulation index and statistical analyses. *Environmental Monitoring and Assessment*, *152*(4), 309–317. doi:10.1007/s10661-008-0317-3.
- Chai, M., Shen, X., Li, R., & Qiu, G. (2015). The risk assessment of heavy metals in Futian mangrove forest sediment in Shenzhen Bay (South China) based on SEM-AVS analysis. *Marine Pollution Bulletin*, *97*(1–2), 431–439. doi:10.1016/j.marpolbul.2015.05.057.
- Chaterjee, G., & Raziuddin, M. (2006). Status of water body in relation to some physico-chemical parameters in Asansol town, West Bengal. *Proc. Zool. Soc. India*, *5*(2), 41–48.
- Cuong, D. T., Bayen, S., Wurl, O., Subramanian, K., Wong, K. K. S., Sivasothi, N., & Obbard, J. P. (2005). Heavy metal contamination in mangrove habitats of Singapore. *Marine*

- Pollution Bulletin*, 50, 1713–1744. doi:10.1016/j.marpolbul.2005.09.008.
- Dahl, O., Pöykiö, R., & Nurmesniemi, H. (2008). Concentrations of heavy metals in fly ash from a coal-fired power plant with respect to the new Finnish limit values. *Journal of Material Cycles and Waste Management*, 10, 87–92. doi:10.1007/s10163-007-0189-6.
- Facchinelli, A., Sacchi, E., & Mallen, L. (2001). Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environmental Pollution*, 114, 313–324.
- Gibbs, R. J. (1973). Water chemistry of the Amazon River. *Geochimica Cosmochimica Acta*, 36, 1006–1066.
- Giripunje, M. D., Fulke, A. B., & Meshram, P. U. (2014). Effect of idol immersion on water quality and tilapia fish in Futala, Gandhisagar and Ambazari lakes of Nagpur, India. *SpringerPlus*, 3, 669. doi:10.1186/2193-1801-3-669.
- Goutam, K., Manoj, K., & Ramanathan, A. L. (2015). Assessment of heavy metal contamination in the surface sediments in the mangrove ecosystem of Gulf of Kachchh, west coast of India. *Environment and Earth Science*, 74, 545–556. doi:10.1007/s12665-015-4062-y.
- Govindasamy, C., Kannan, L., & Jayapaul, A. (2000). Seasonal variation in physico-chemical properties and primary production in the coastal water biotopes of Coromandel coast, India. *Journal of Environmental Biology*, 21, 1–7.
- Gu, Y., Wang, Z., Lu, S., Jiang, S., Mu, D., & Shu, Y. (2012). Multivariate statistical and GIS-based approach to identify source of anthropogenic impacts on metallic elements in sediments from the mid Guangdong coasts, China. *Environmental Pollution*, 163, 248–255. doi:10.1016/j.envpol.2011.12.041.
- Hall, L. W. J., Scott, M. C., & Killen, W. D. (1997). *A screening level probabilistic ecological risk assessment of copper and cadmium in the Chesapeake Bay watershed*. Annapolis, MD: Chesapeake Bay Program. USEPA.
- Hollert, H., Keiter, S., König, N., Rudolf, M., Ulrich, M., & Braunbeck, T. (2003). A new sediment contact assay to assess particulate bound pollutants using zebrafish (*Danio rerio*) embryos. *Journal of Soil Sediments*, 3, 197–207 http://tnenvis.nic.in/tnenvis_old/coastal%20data.pdf.
- Janaki Raman, D., Jonathan, M. P., Srinivasalu, S., Armstrong-Altrin, J. S., Mohan, S. P., & Ram-Mohan, V. (2007). Trace metal enrichments in core sediments in Muthupet mangroves, SE coast of India: application of acid leachable technique. *Environmental Pollution*, 145, 245–257.
- Jonathan, M. P., Srinivasalu, S., Thangadurai, N., Armstrong-Altrin, J. S., Ayyamperumal, T., & Ram-Mohan, V. (2008). Contamination of Uppanar River and coastal waters off Cuddalore, southeast coast of India. *Environmental Geology*, 53, 1391–1404. doi:10.1007/s00254-007-0748-0.
- Kannan, L., Paramasivam, S., Seenivasan, R., & Nadimuthu, N. (2003). Impact of shrimp farm activities on the water quality of Muthupettai mangrove environment, southeast coast of India. In A. L. Ramanathan & R. Ramesh (Eds.), *Recent trends in hydrogeochemistry* (pp. 87–92). New Delhi: Capital Publishing Company.
- Karbassi, A. R., Monavari, S. M., Nabi Bidhendi, G. H. R., Nouri, J., & Nematpour, K. (2008). Metal pollution assessment of sediment and water in the Shur River. *Environmental Monitoring and Assessment*, 147, 107–116. doi:10.1007/s10661-007-0102-8.
- Krauss, K. W., Lovelock, C. E., & McKee, K. L. (2008). Environmental drivers in mangrove establishment and early development: a review. *Aquatic Botany*, 89, 105–127. doi:10.1016/j.aquabot.2007.12.014.
- Kumar, R. N., Solanki, R., & Kumar, J. (2013). Seasonal variation in heavy metal contamination in water and sediments of river Sabarmati and Kharicut canal at Ahmedabad, Gujarat. *Environmental Monitoring and Assessment*, 185, 359–368. doi:10.1007/s10661-012-2558-4.
- Langston, W. J. (1986). Metals in sediments and benthic organisms in the Mersey estuary. *East. Coast. Shelf Sci.*, 23, 239–261. doi:10.1016/0269-7491(92)90099-V.
- Li, R., Li, R., Chai, M., Shen, X., Xu, H., & Qiu, G. (2015). Heavy metal contamination and ecological risk in Futian mangrove forest sediment in Shenzhen Bay South China. *Marine Pollution Bulletin*, 101(1), 448–456. doi:10.1016/j.marpolbul.2015.09.048.
- Luoma, S. N., & Bryan, G. W. (1981). A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *Science of the Total Environment*, 17, 165–196. doi:10.1016/0048-9697(81)90182-0.
- Mackey, K., Labiosa, R., Calhoun, M., Street, J., Post, A., & Paytan, A. (2007). Phosphorus availability, phytoplankton community dynamics, and taxon-specific phosphorus status in the Gulf of Aqaba, Red Sea. *Limnol. Oceanogr.*, 52(2), 873–885. doi:10.4319/lo.2007.52.2.0873.
- Manju, P., Nair, Akhil, P. S., & Sujatha, C. H. (2014). Toxic metal distribution in the core sediment of Cochin Estuarine System (CES). *Int. J. Environ. Res.*, 8(1), 133–138.
- Mastallar, M. C. (1996). Destruction of mangrove wetlands—causes and consequences. *Natural. Res. Dev.*, 43, 37–57.
- Mathivanan, K., & Rajaram, R. (2014). Anthropogenic influences on toxic metals in water and sediment samples collected from industrially polluted Cuddalore coast, southeast coast of India. *Environment and Earth Science*, 72, 997–1010. doi:10.1007/s12665-013-3017-4.
- Muller, G. (1979). Schwermetalle in den Sedimenten des Rheins Veränderungen seit. *Umschau*, 79(24), 778–783.
- Paramasivam, S., & Kannan, L. (2005). Physico-chemical characteristics of muthupettai mangrove environment southeast coast of India. *International Journal of Ecology and Environmental Sciences*, 31, 273–278.
- Prasanna, M. V., Praveena, S. M., Chidambaram, S., Nagarajan, R., & Elayaraja, A. (2012). Evaluation of water quality pollution indices for heavy metal contamination monitoring: a case study from Curtin Lake, Miri City, East Malaysia. *Environment and Earth Science*, 67, 1987–2001. doi:10.1007/s12665-012-1639-6.
- Priya, K. L., Jegathambal, P., James, E. J. (2014). Trace metal distribution in a shallow estuary. *Toxicological and Environmental Chemistry*, 96, 579–593.
- Qiao, M., Cai, C., Huang, Y., Liu, Y., Lin, A., & Zheng, Y. (2010). Characterization of soil heavy metal contamination and potential health risk in metropolitan region of northern China. *Environmental Monitoring and Assessment*, 172, 353–365. doi:10.1007/s10661-010-1339-1.
- Rajaram, R., Srinivasan, M., & Rajasegar, M. (2005). Seasonal distribution of physico-chemical parameters in effluent discharge area of Uppanar estuary, Cuddalore, south-east coast of India. *Journal of Environmental Biology*, 26, 291–297.

- Rajasegar, M. (2003). Physico-chemical characteristics of the Vellar estuary in relation to shrimp farming. *Journal of Environmental Biology*, 24, 95–101.
- Ramesh, R., Nammalwar, P., Gowri, V.S., 2008. Database on Coastal Information of Tamilnadu.
- Sadip, R., Husain, T., Bose, N., & Veitch, B. (2003). Distribution of heavy metals in sediment pore water due to offshore discharges: an ecological risk assessment. *Environmental Modelling & Software*, 18, 451–461.
- Sandilyan, S., & Kathiresan, K. (2012). Mangrove conservation: a global perspective. *Biodiversity and Conservation*, 21, 3523–3542. doi:10.1007/s10531-012-0388-x.
- Sankar, R., Ramkumar, L., Rajkumar, M., Sun, J., & Ananthan, G. (2010). Seasonal variations in physico-chemical parameters and heavy metals in water and sediments of Uppanar estuary, Nagapattinam, India. *Journal of Environmental Biology*, 31(5), 681–686.
- Sliwka-Kaszynska, M., Kot-Wasik, A., & Namiesnik, J. (2003). Preservation and storage of water samples. *Crit. Rev. Env. Sci. Tec.*, 33(1), 31–44. doi:10.1080/10643380390814442.
- Sridhar, R., Thangaradjou, T., Senthil Kumar, S., & Kannan, L. (2006). Water quality and phytoplankton characteristics in the Palk Bay, southeast coast of India. *Journal of Environmental Biology*, 27, 561–566.
- Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution*, 110, 195–205. doi:10.1016/S0269-7491(99)00310-3.
- Taylor, S. R., & McLennan, S. M. (1985). *The continental crust: Its composition and evolution*. Oxford: Blackwell.
- Thilagavathi, B., Raja, K., Bandana Das, K., Saravanakumar, A., Vijayalakshmi, S., & Balasubramanian, T. (2011). Heavy metal distribution in sediments of Muthupettai mangroves, South East Coast of India. *Journal of Ocean University of China*, 10, 385–390.
- Usha Natesan, M., Kumar, M., & Deepthi, K. (2014). Mangrove sediments a sink for heavy metals? An assessment of Muthupet mangroves of Tamil Nadu, southeast coast of India. *Environmental Earth Sciences*, 72(4), 1255–1270. doi:10.1007/s12665-014-3043-x.
- Valiela, I., Bowen, J. L., & York, J. K. (2001). Mangrove forests: one of the world's threatened major in tropical environments. *Bioscience*, 10, 807–815 (doi: 10.1641/00063568(2001)051[0807:MFOOTW]2.0.CO;2)10.1641/00063568(2001)051[0807:MFOOTW]2.0.CO;2).
- Vyas, A., Bajpai, A., Verma, N., & Dixit, S. (2007). Heavy metal contamination cause of idol immersion activities in urban lake Bhopal, India. *Journal Application Science Environmental Management*, 11, 37–39.
- Wu, Q. Q., Ma, Q. M., Wang, J. G., Jiang, Z. H., & Wang, X. L. (2007). The AVS in surface sediment of near sea area of Huanghe estuary. *Marine Environmental Science*, 26, 126–129.
- Wu, Q. H., Tam, N. F. Y., Leung, J. Y. S., Zhou, X. Z., Fu, J., Yao, B., Huang, X. X., & Xia, L. H. (2014). Ecological risk and pollution history of heavy metals in Nansha mangrove, South China. *Ecotoxicology and Environmental Safety*, 104, 143–151. doi:10.1016/j.ecoenv.2014.02.017.
- Younis, A.M., El-Zokm, G.M., & Okbah, M.A. (2014). Spatial variation of acid-volatile sulfide and simultaneously extracted metals in Egyptian Mediterranean Sea lagoon sediments. *Environmental Monitoring and Assessment*, 186, 3567–3579.
- Zhang, C. (2006). Using multivariate analyses and GIS to identify pollutants and their spatial patterns in urban soils in Galway, Ireland. *Environmental Pollution*, 501–511. doi:10.1016/j.envpol.2005.10.028.