

Integrated assessment of heavy metal contamination in water, sediments and marine organisms from Southeast coast of India

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The present investigation examined the bioaccumulation of toxic metals (Cu, Zn, Cd, Hg and Pb) in water, sediment and biota along the coastal regions of Parangipettai and Nagapattinam. The concentrations of heavy metals in water, sediment and biota were Zn>Pb>Cu>Hg>Cd, Cu>Zn>Pb>Cd>Hg and Zn>Cu>Pb>Hg>Cd, respectively. Statistical analysis, such as principal component analysis revealed that concentrations of Zn, Cu and Pb were found higher in water, sediments and biota at Parangipettai (St. 1). Geospatial analyses were made to study the spatial distribution of heavy metals and its sources in study sites observed. Accumulation factors of abiota and biota were identified by the domination of higher values than the average background values and followed by the comparison with the trace metals from other coastal regions in the southeast coast of India. The result of the present study shows that the Parangipettai region had higher pollutants than that of Nagapattinam.

[Keywords: Coastal pollution; Heavy metals; Box plots analysis; Southeast coast of India]

Introduction

Coastal regions form rapid growth in urbanization and industrialization; which leads to inflow of heavy metals into marine ecosystems and it has now become a major threat, in general, in aquatic ecosystem¹. Coastal ecosystems are highly affected by pollutants, such as, heavy metals, pesticides and antifoulants entering into the water column and sediments². The investigation of heavy metals in the marine environment is more important, because their consumption is highly harmful and results in poisoning³⁻⁶. The concentrations of different metals, like, Chromium (Cr), Manganese (Mn), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) are highly increasing in coastal areas due to the discharge of agricultural and domestic wastes; intrusion of wastes from industries like metal plating; entry of organic and inorganic chemicals; leaching of metals from solid waste; and use of metal and metal

components⁷⁻¹⁰. As a result of physio-chemical and biological interactions, these elements get accumulated in sediments and marine living organisms¹¹. Considering the determination of heavy metals, bioaccumulation, magnification and high toxicity characters, heavy metals are rated among the most serious pollutants in marine environments¹²⁻¹⁵. In recent years, marine organisms are highly exposed to trace elements which accumulate in their different tissues, and they are not essential to the metabolisms¹⁶⁻¹⁹. Further, there is also evidence of seasonal variations in different heavy metal contents within species^{3,20-21}. In addition, the spatial distribution of heavy metals in marine ecosystem impacted by natural and anthropogenic factors, such as, river runoff, industrial effluent, agriculture, and climate changes are the major sources to clarifying the pollution history of aquatic systems²²⁻²³. Hence, it is essential to distinguish between natural and anthropogenic impacts on the distribution of heavy

metals in the marine ecosystem. A bioaccumulation index and PCA have been applied to finding the source of heavy metals and the seasonal variations observed in India^{12-13,24-25}. However, few studies have combined GIS-based techniques used to generate spatial patterns of heavy metals at local scale maps at Tamirabarani, Lakshawep and Andaman Islands²⁴⁻²⁶. Present study consists the results of the investigation on the seasonal and temporal variations in the concentrations of heavy metals in water, sediment and biological samples, to predict the sources of pollution using multivariate statistical analysis and the spatial distribution pattern of total heavy metals in Parangipettai (St. 1) and Nagapattinam (St. 2) in the Southeast coast of India through GIS-based chemometric approach.

Materials and Methods

The sampling stations St. 1 and St. 2 were selected based on the prevailing environment and fast land use/land cover development conditions around the study sites. The St. 1 has been influenced by Vellar river runoff and with the presence of mangrove patches, followed by St. 2 with high population density and intensive fishing and shipping activities. The samples of surface water, sediment and marine organisms were collected from Parangipettai (St. 1) and Nagapattinam (St. 2) at a distance from nearshore (0.5 km) and offshore (5 km), in seasonal intervals from June 2009 to July 2010 (Fig.1).

Sampling was done for a year, covering four seasons *viz.*, pre-monsoon, monsoon, post-monsoon and summer, in 2 stations which include 4 sites.

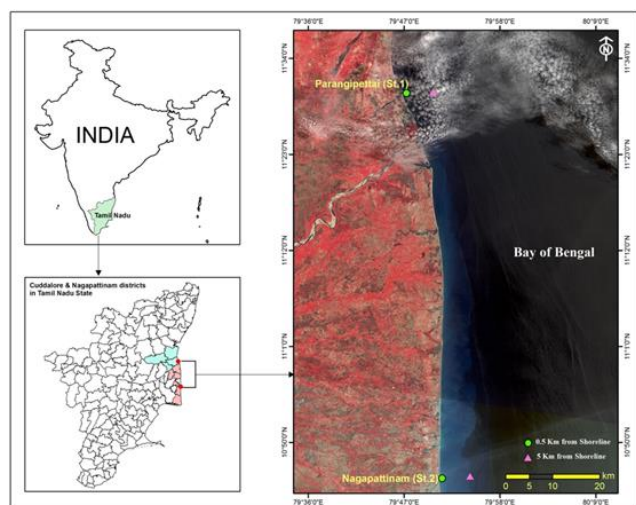


Fig. 1 — Study Area and Sampling stations

Triplicates of each sample, to arrive at the average values were collected and a total of 96 samples was obtained, each from surface water, sediment and biota.

Standards were prepared ranging from 1 $\mu\text{g/L}$ to 500 $\mu\text{g/L}$ with Certified Reference Materials (CRMs) (Sigma-Aldrich multi-element stock standard solution TraceCERT, in 10 % nitric acid) for calibration and aspirated into the ICP-OES as per the manual given by PerkinElmer Inc. standard procedures. For quality assurance/quality control (QA/QC) purposes, digestion of procedure blanks, duplicates of 10% sample and the standards were prepared using customary reference materials in the above-said procedure. Surface water samples were collected in LDPE bottles of 1L capacity, and filtered through Millipore filtering unit using 0.45 μm Whatman filter paper. The heavy metals were pre-concentrated and separated from the bulk matrix by complexation with ultrapure-grade Ammonium Pyrrolidine Dithio-Carbamate Methyl Iso-butyl Ketoneapdc (APDC-MIBK) extraction procedure²⁷. The organic layer containing metal chelates was collected back and extracted with 50% HNO_3 and diluted with metal-free double distilled water making up to 25 ml to analyze in Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (PerkinElmer Inc. Optima 2100TM DV).

To extract heavy metals, such as, Cd, Cu, Pb, Zn and Hg from the sediments, an acid digestion procedure was followed²⁸⁻²⁹. Sediment samples (1000g) were collected from the surface area of sediments and were placed into clean polyethylene cover and transported to the laboratory. The preserved sediment was dried at 110 $^{\circ}\text{C}$ for 5–6 hours, and stored in pre-cleaned polyethylene bags. To estimate the weight of metals, 25 mg of sample was re-dried with a Sigma-Trace-grade mixture of 1ml conc. H_2SO_4 , 5ml conc. HNO_3 and 2ml of conc. HClO_4 . A few drops of hydrofluoric acid were added to achieve complete dissolution of the materials. The mixture was boiled, evaporated to near dryness and suspended in 10ml 2N HCl. It was passed through a filter and made up to 25ml with metal-free double distilled water. The obtained solutions were stored in acid-washed glass vials for Hg analysis and polypropylene containers were used for other metals. The residue formed was dissolved in 10ml of 10% V/V nitric acid solution and the same was aspirated into ICP-OES (PerkinElmer

Inc.-Optima 2100TM DV). Finally, the concentration was quantified and expressed in $\mu\text{g/g}$.

Marine shell- and fin-fish samples, such as, *Penaeus indicus* (shrimp), *Sardinella longiceps*, *Rastrelliger kanagurta*, *Scomberomorus guttatus*, and *Parastromateus niger* (all fishes) and *Perna viridis* (mussel) were collected from two stations in different seasons. The samples were thoroughly washed using distilled water before analysis. The frozen samples were dried in an oven at 60°C for 24 hrs. Approximately, 2g was taken from the dried samples and 20ml of concentrated HNO_3 was added (Ultrapure-grade Sigma-Aldrich) and then they were kept 24 hrs for digestion. To separate the heavy metals from the samples, nitric and Perchloric acids were added in the ratio of 4:1 after incubation and were kept in the hot plate at 120°C until the residue turned from yellow to white. To dissolve the residues 10ml of 10 % nitric acid (TraceSELECT-grade Sigma-Aldrich) was added. This residual solution was transferred to 50ml LDPE vial and the mixture was allowed to stand for 2 hours towards settling. The supernatant liquid was filtered using Whatman No.1 filter paper. The filtered sample was directly aspirated for metals and analyzed by ICP-OES - Optima 2100 DV). Results were expressed in $\mu\text{g/g}$.

Data obtained from analytical methods were treated statistically using the commercial statistical software package of PRIMER version 7 for the Analysis of variance using one-way ANOVA in which three replications were carried out to observe the spatial variations of metal variables. Principal Component Analysis (PCA) was performed using PRIMER version 7 to classify the elements of the different seasons on the basis of their similarities using plots, to identify relative homogeneous groups of variables with similar properties.

Geographical Information System (GIS) techniques were used to map the spatial variation of total heavy metals concentrations in water and sediments from nearshore and offshore regions of the study areas. The values of total concentration of heavy metals are attributed in ArcGIS 10.2. Interpolation by Kriging methods was used to produce *in-situ* digital spatial maps of available heavy metals³¹⁻³². Further, freshwater sources of the rivers were also digitized on screen for the comparison and support of multivariate data. Generally, Bioaccumulation factor (BAF) is used to quantify the bioaccumulation of environmental pollutants. It is based on the assumption that the

organisms achieve a certain level of chemical equilibrium with the particular medium with respect to the pollutants in question³⁰. BAF illustrates the importance between sediments and the water column, and its influence on exposure of all aquatic biota in two study stations. BAF predicts the toxic effects in aquatic organisms, especially when chemical residue-based dose-response relationships were analyzed.

$$\text{BAF} = C_B/C_W$$

Where,

C_B = Chemical concentration in organism

C_W = Chemical concentration in water (mass of chemical/L)

BAF defined "Ratio of the steady-state chemical concentrations in an aquatic water-respiring organism and the water determined from field data in which sampled organisms are exposed to a chemical in the water and in their diet". The BAF calculated using the method of Mountouris et al.³⁰.

$$\text{Bioaccumulation factor} = \frac{x_1}{x_2} \times 100$$

$$X_2 = \frac{(a_1 + a_2)}{2}$$

Where,

a_1 = water,

a_2 = sediment

x_1 = organisms (biota)

x_2 = water + Sediments/2 (abiota)

Results

Heavy metal analysis in seawater

The ranges of the heavy metals concentrations in seawater were as follows: Cd was recorded a maximum of $0.182 \mu\text{g L}^{-1}$ in St. 1 at the offshore (5 km) and a minimum of $0.16 \mu\text{g L}^{-1}$ in St. 2 at nearshore (0.5 km). Seasonal variation of Cd ranged $0.04\text{--}0.36 \mu\text{g L}^{-1}$ in both stations and was found to be the maximum during the monsoon (November) and the minimum in summer (May). Cu was observed to be the maximum of $0.56 \mu\text{g L}^{-1}$ in St. 1 at 0.5 km and a minimum of $0.37 \mu\text{g L}^{-1}$ in St. 2 at 5 km. It varied from 0.23 to 0.86mg l^{-1} in four different

Table 1 — Heavy metal concentrations in the water and surface sediments of the study stations [Parangipettai (St. 1) Nagapattinam (St. 2)] with transect intervals also shown; all values shown in means \pm Standard deviation. Near shore: 0.5 km; Offshore: 5 km.

Seasonal patterns	Location	Water									
		Cd ($\mu\text{g. L}^{-1}$)		Cu ($\mu\text{g. L}^{-1}$)		Pb ($\mu\text{g. L}^{-1}$)		Hg ($\mu\text{g. L}^{-1}$)		Zn ($\mu\text{g. L}^{-1}$)	
		0.5 km	5 km	0.5 km	5 km	0.5 km	5 km	0.5 km	5 km	0.5 km	5 km
Pre-monsoon (July–Sep)	(St.1)	0.15 \pm 0.01	0.26 \pm 0.04	0.24 \pm 0.10	0.23 \pm 0.06	0.34 \pm 0.01	0.28 \pm 0.02	0.38 \pm 0.01	0.05 \pm 0.01	2.65 \pm 1.40	4.20 \pm 1.33
	(St.2)	0.24 \pm 0.03	0.23 \pm 0.05	0.18 \pm 0.08	0.27 \pm 0.09	0.26 \pm 0.05	0.24 \pm 0.03	0.73 \pm 0.02	0.56 \pm 0.10	0.46 \pm 0.03	0.48 \pm 0.02
Monsoon (Oct–Dec)	(St.1)	0.33 \pm 0.07	0.45 \pm 0.06	0.43 \pm 0.15	0.24 \pm 0.10	0.33 \pm 0.09	0.29 \pm 0.02	0.74 \pm 0.06	0.60 \pm 0.03	3.28 \pm 0.91	2.67 \pm 0.99
	(St.2)	0.45 \pm 0.09	0.34 \pm 0.08	0.29 \pm 0.09	0.54 \pm 0.21	0.47 \pm 0.10	0.26 \pm 0.02	2.43 \pm 0.10	0.63 \pm 0.04	0.33 \pm 0.12	2.67 \pm 1.01
Post-monsoon (Jan–Mar)	(St.1)	0.02 \pm 0.01	0.07 \pm 0.02	0.13 \pm 0.05	0.31 \pm 0.14	1.55 \pm 0.40	0.64 \pm 0.06	0.01 \pm 0.01	0.26 \pm 0.04	57.26 \pm 4.7	11.54 \pm 3.8
	(St.2)	0.16 \pm 0.05	0.02 \pm 0.01	0.73 \pm 0.31	0.24 \pm 0.05	0.36 \pm 0.02	0.54 \pm 0.09	0.34 \pm 0.1	0.14 \pm 0.06	0.03 \pm 0.01	3.46 \pm 0.85
Summer (April–June)	(St.1)	0.02 \pm 0.01	0.03 \pm 0.02	2.64 \pm 0.41	0.26 \pm 0.09	2.15 \pm 0.17	2.84 \pm 0.10	0.15 \pm 0.01	0.56 \pm 0.09	59.36 \pm 5.32	48.87 \pm 3.5
	(St.2)	0.06 \pm 0.02	0.06 \pm 0.03	0.54 \pm 0.17	0.01 \pm 0.01	0.34 \pm 0.08	0.23 \pm 0.01	0.05 \pm 0.01	0.75 \pm 0.12	2.96 \pm 0.81	2.54 \pm 0.11
Seasonal patterns	Location	Sediment									
		Cd ($\mu\text{g. g}^{-1}$)		Cu ($\mu\text{g. g}^{-1}$)		Pb ($\mu\text{g. g}^{-1}$)		Hg* ($\mu\text{g. g}^{-1}$)		Zn ($\mu\text{g. g}^{-1}$)	
		0.5 km	5 km	0.5 km	5 km	0.5 km	5 km	0.5 km	5 km	0.5 km	5 km
Pre-monsoon (July–Sep)	(St.1)	0.45 \pm 0.35	0.91 \pm 0.28	1.54 \pm 1.21	2.26 \pm 2.28	12.54 \pm 8.36	0.87 \pm 0.43	0.35 \pm 0.27	0.26 \pm 0.17	1.28 \pm 1.0	1.54 \pm 1.23
	(St.2)	2.26 \pm .92	1.44 \pm 1.17	0.87 \pm 0.42	0.86 \pm 0.42	0.03 \pm 0.01	0.43 \pm 0.10	0.06 \pm 0.09	0.05 \pm 0.04	10.46 \pm 6.6	4.82 \pm 3.55
Monsoon (Oct–Dec)	(St.1)	0.94 \pm 0.37	0.87 \pm 0.42	0.85 \pm 0.38	1.46 \pm 1.05	11.96 \pm 6.38	7.54 \pm 3.14	0.65 \pm 0.31	0.74 \pm 0.28	9.34 \pm 6.37	11.96 \pm 5.98
	(St.2)	1.46 \pm 1.12	0.86 \pm 0.43	0.46 \pm 0.41	0.76 \pm 0.45	0.87 \pm 0.41	0.86 \pm 0.53	0.46 \pm 0.19	0.66 \pm 0.31	6.26 \pm 3.47	14.05 \pm 10.5
Post-monsoon (Jan–Mar)	(St.1)	0.50 \pm 0.31	2.67 \pm 1.27	47.54 \pm 6.38	36.06 \pm 8.33	14.84 \pm 8.39	11.26 \pm 10.10	0.26 \pm 0.16	0.07 \pm 0.09	29.09 \pm 12.66	12.85 \pm 10.0
	(St.2)	0.46 \pm 0.21	0.12 \pm 0.06	41.63 \pm 8.27	32.45 \pm 9.35	8.53 \pm 5.63	7.15 \pm 3.8	0.25 \pm 0.21	1.65 \pm 1.12	23.86 \pm 16.91	13.26 \pm 8.31
Summer (April–June)	(St.1)	0.35 \pm 0.10	0.14 \pm 0.08	35.34 \pm 9.37	41.63 \pm 10.81	11.36 \pm 6.21	12.64 \pm 5.34	0.26 \pm 0.21	0.06 \pm 0.09	12.86 \pm 6.68	24.86 \pm 12.3
	(St.2)	0.26 \pm 0.09	0.26 \pm 0.10	42.86 \pm 10.6	3.10 \pm 1.17	11.79 \pm 6.39	7.86 \pm 2.7	0.31 \pm 0.30	0.47 \pm 0.38	28.62 \pm 20.26	13.16 \pm 10.6

seasons; with a maximum value recorded during summer (May) and the minimum in pre-monsoon (August). The high median value and significant temporal and spatial variances were observed among the stations (Fig. 2; Table 1).

Pb was noticed the maximum ($1.05 \mu\text{g L}^{-1}$) in St. 1 at nearshore area and the minimum ($0.31 \mu\text{g L}^{-1}$) in St. 2 at offshore. It varied (0.28 – $1.39 \mu\text{g L}^{-1}$) in four different sampling seasons among which the maximum was recorded during the summer (May) and the minimum in pre-monsoon (August). Hg was recorded the maximum ($0.45 \mu\text{g L}^{-1}$) in 5 km at St.2, and the minimum ($0.33 \mu\text{g L}^{-1}$) in 0.5 km at St. 1. It ranged from 0.18 to $0.60 \mu\text{g L}^{-1}$ in different sampling seasons and its maximum was recorded during the monsoon (November) and the minimum in post-monsoon (Feb.). The concentration of Zn was recorded the maximum ($23.72 \mu\text{g L}^{-1}$) at St. 1 in nearshore and the minimum ($1.88 \mu\text{g L}^{-1}$) at St.2 in offshore water. It ranged from 1.94 to $28.43 \mu\text{g L}^{-1}$ in four different sampling seasons and recorded the maximum during summer (May) and the minimum in pre-monsoon (August). The concentrations of Cd, Cu, Pb, Hg and Zn were significant ($P > 0.01$) among the sampling stations, transects and also the seasons (Fig. 3 & 3a). The Box–Whisker plots, representing

seasonal variations in heavy metal concentrations, are given in Figs. 2, 3 and 3a.

From the graph (Fig.2c), it is observed that Cd values were higher in pre-monsoon and monsoon, but Cu values were higher in post-monsoon and summer in both the stations. In case of Hg, values were observed higher ($0.75 \mu\text{g L}^{-1}$) in a monsoon and summer season at St.1 and St. 2. Moreover, Pb and Zn showed high ($2.15 \mu\text{g L}^{-1}$ and $59.36 \mu\text{g L}^{-1}$) values in post-monsoon and summer seasons in both the stations, respectively. Seasonal variation of heavy metals was significant ($p > 0.01$).

PCA was used in this study to analyze the sources of pollutants in the study area. Metal concentration in different seasons, including near- and offshore waters are shown in Fig. 4.

Five principle components were extracted, accounting for 100 % of the total variance. In the rotated component matrix, PC1 explains 72.2 % variance as contributed by Pb and Zn during summer at both study areas in nearshore waters. PC2 explains 17.7 % variance as contributed by Cu, Hg and Cd during pre-monsoon at Nagapattinam and during the monsoon at both the stations. Relationships among heavy metals and seasons in the nearshore waters are illustrated in Fig. 4 and Table 2. Moreover, in the

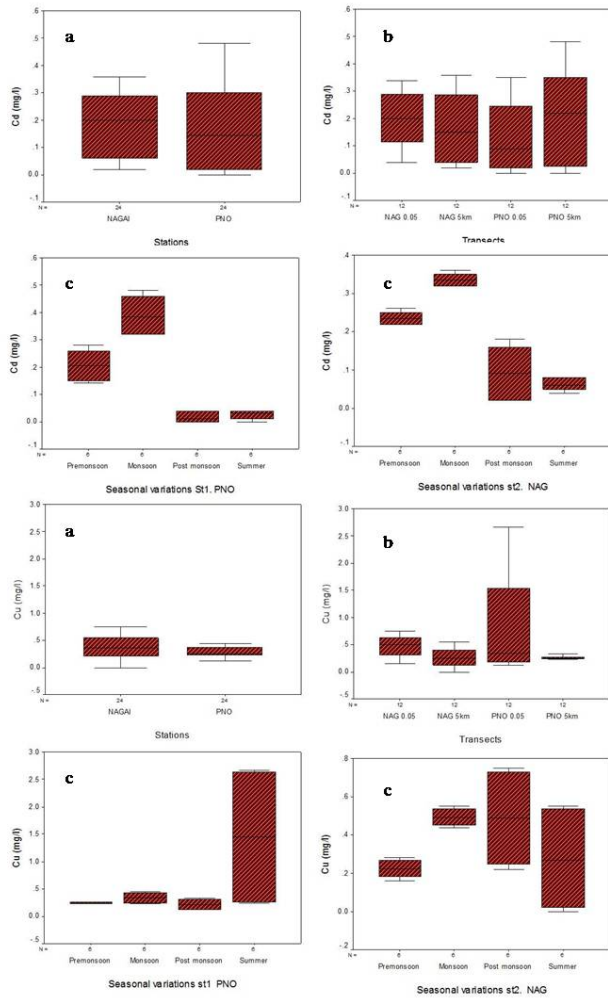


Fig. 2 — The variations of Cd and Cu in seawater at two stations (St.1: PNO = Parangipettai & St.2: NAG = Nagapattinam) (a), transects (nearshore [0.5 km] & offshore [5 km]) (b) and four seasons (c) during 2009–10. In each plot, the central point denoted the median, the interval between the 25% and 75% percentiles, standard deviation represented and the Whisker indicates the range.

rotated component matrix, there was a strong variability (PC1 explains 46.6 % variance), contributed by Pb, Zn and Hg during post-monsoon and summer at both the study areas from offshore waters (Fig. 4a& Table 2a).

It was also observed that the variability (PC2 explains 25.2 % variance) was contributed by Cu, Cd, Hg, Pb and Zn during pre-monsoon at Nagapattinam, Monsoon at both the stations and summer at Parangipettai station. In addition to the multivariate analysis, the visual map developed through geospatial analysis illustrated the dispersion pattern of total heavy metal concentration in a simplified manner compared between the study sites (Fig. 5). From this

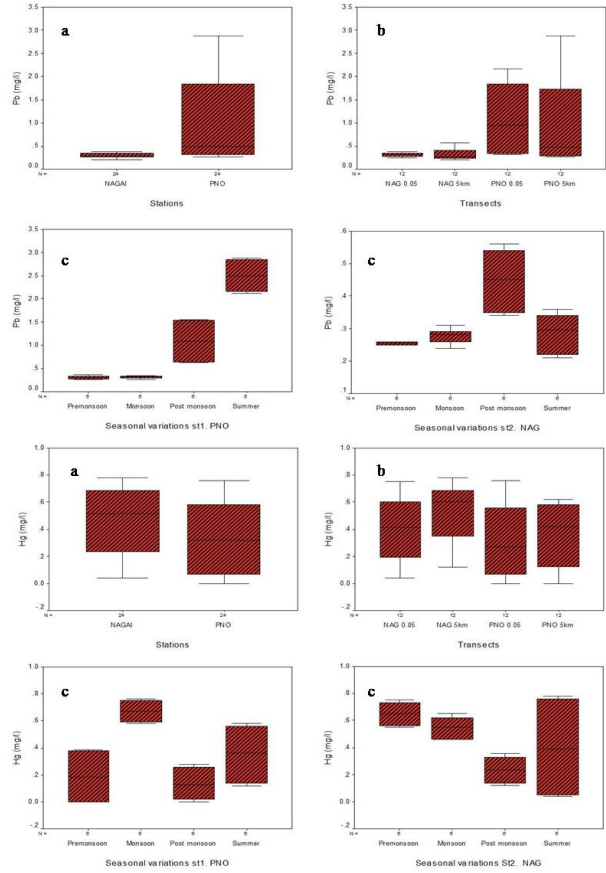


Fig. 3 — Seasonal variations of lead (Pb), mercury (Hg) in seawater at two stations (St.1: PNO = Parangipettai & St.2: NAG = Nagapattinam) (a), transects (nearshore [0.5 km] & offshore [5 km]) (b) and four seasons (c) during 2009–10. In each plot, the central point denoted the median, the interval between the 25% and 75% percentiles, standard deviation represented and the Whisker indicates the range.

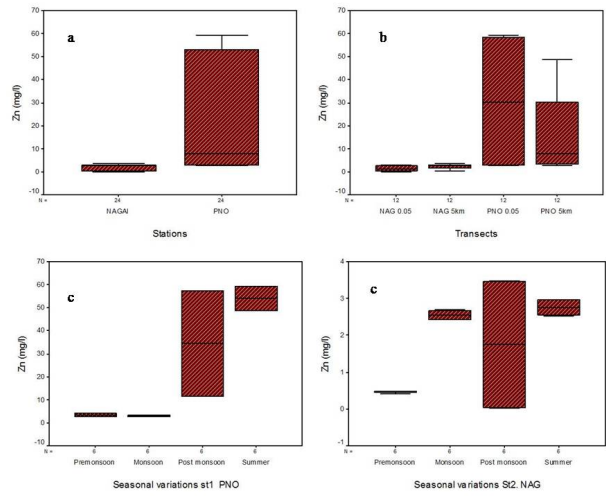


Fig. 3a — Seasonal variations of zinc (Zn) in seawater two different stations (St.1: PNO = Parangipettai & st.2: NAG = Nagapattinam). (a) transects (nearshore [0.5 km] & offshore [5 km]) (b) and four seasons (c) during 2009–10.

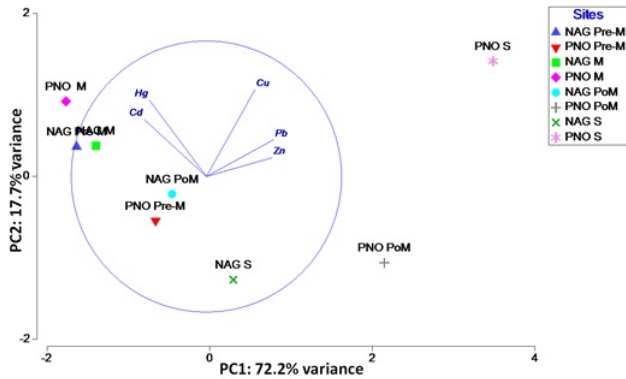


Fig. 4 — PCA results in the plot-loading of the nearshore water

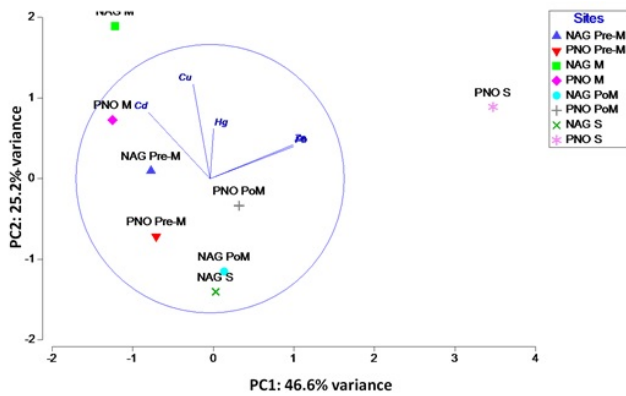


Fig. 4a — PCA results in the plot-loading of the offshore water

analysis, it is revealed that the total heavy metals concentration in nearshore waters of Parangipettai is comparatively high in all the four seasons (Fig. 5) *viz.*, pre-monsoon: 3.76 $\mu\text{g L}^{-1}$, Monsoon: 5.12 $\mu\text{g L}^{-1}$, post-monsoon: 58.97 $\mu\text{g L}^{-1}$ and summer: 64.32 $\mu\text{g L}^{-1}$, respectively. The multivariate analysis illustrates that heavy metals carried by river runoff influence the high concentration of metals in the study sites.

Heavy metal analysis in Sediments

Cd was found the maximum of 0.89 $\mu\text{g g}^{-1}$ at St. 2 and the minimum of 0.85 $\mu\text{g g}^{-1}$ at St. 1. The maximum of 0.90 $\mu\text{g g}^{-1}$ was noticed in 0.5 km at St. 2 and the minimum of 0.83 $\mu\text{g g}^{-1}$ was at 0.5 km at St. 1. It ranged from 0.25 to 1.26 $\mu\text{g g}^{-1}$ at different sampling seasons in the two stations and it was recorded a maximum during the monsoon (August) and the minimum in summer (May). In the case of Cu, the maximum of 20.83 $\mu\text{g g}^{-1}$ was observed at 0.5 km in St. 1 and the minimum of 15.37 $\mu\text{g g}^{-1}$ at 5 km in St. 2. It ranged from 0.88 to 39.42 $\mu\text{g g}^{-1}$ in different sampling seasons of the two stations and recorded a maximum in post-monsoon (Feb.) and the minimum in monsoon (November) (Fig. 6 & Table 1).

Table 2 — Rotated component matrix for the heavy metal concentration of nearshore water of Parangipettai and Nagapattinam. Bold values are statistically significant at $p > 0.5$. Pre-M: Pre-monsoon; M: Monsoon; PoM: Post-monsoon; S: Summer

Heavy metals variable	Component				
	PC1	PC2	PC3	PC4	PC5
Cd	-0.46	0.421	-0.219	0.748	-0.061
Cu	0.359	0.641	0.65	0.065	0.179
Pb	0.517	0.271	-0.334	-0.006	-0.754
Hg	-0.422	0.564	-0.271	-0.653	0.051
Zn	0.580	0.138	-0.586	0.099	0.627
Monsoonal Variable					
NAG Pre-M	-1.64	0.367	-0.321	-0.506	0.00852
PNO Pre-M	-0.665	-0.543	0.132	-0.212	-0.0287
NAG M	-1.4	0.377	-0.0705	0.654	-0.0064
PNO M	-1.77	0.921	-0.384	0.0294	0.0168
NAG PoM	-0.462	-0.214	0.591	-0.0314	-0.0177
PNO PoM	2.15	-1.06	-1.16	0.0694	7.14
NAG S	0.291	-1.27	0.836	0.049	0.0277
PNO S	3.49	1.42	0.373	-0.0521	-0.0003
Eigen values	3.61	0.885	0.4	0.106	0.00033
%Variation	72.2	17.7	8	2.1	0
Cum. %Variation	72.2	89.9	97.9	100	100

Table 2a — Rotated component matrix for the heavy metal concentration of offshore water of Parangipettai and Nagapattinam. Bold values are statistically significant at $p > 0.5$. Pre-M: Pre-monsoon; M: Monsoon; PoM: Post-monsoon; S: Summer

Heavy metals variable	Component				
	PC1	PC2	PC3	PC4	PC5
Cd	-0.46	0.504	-0.08	0.733	-0.024
Cu	-0.126	0.704	0.488	-0.5	0.008
Pb	0.623	0.241	0.041	0.209	-0.713
Hg	0.026	0.372	-0.868	-0.328	0.003
Zn	0.619	0.252	0.036	0.245	0.701
Monsoonal Variable					
NAG Pre-M	-0.773	0.966	-0.434	-0.197	-0.0582
PNO Pre-M	-0.709	-0.717	1.24	0.83	0.0583
NAG M	-1.22	1.89	0.205	-0.682	0.0197
PNO M	-1.25	0.727	-0.767	0.904	-0.0381
NAG PoM	0.134	-1.15	0.948	-0.418	-0.143
PNO PoM	0.32	-0.335	0.795	-0.435	0.124
NAG S	0.299	-1.4	-1.84	-0.271	0.0518
PNO S	3.47	0.889	-0.143	0.27	-0.0142
Eigen values	2.33	1.26	1.04	0.36	0.00676
%Variation	46.6	25.2	20.9	7.2	0.1
Cum.%Variation	46.6	71.8	92.7	99.9	100

Pb was observed to be the maximum of 10.37 $\mu\text{g g}^{-1}$ in St. 1 at 0.5 km and the minimum of 4.68 $\mu\text{g g}^{-1}$ in St. 2 at 5 km, respectively. It was ranged from 3.47 to 10.91 $\mu\text{g g}^{-1}$ in different seasons at both the stations

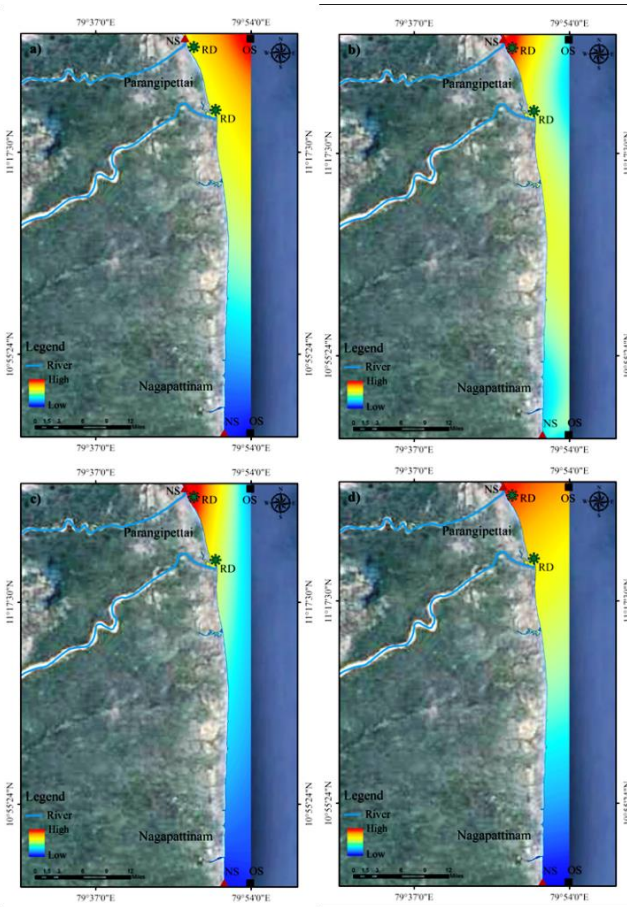


Fig. 5 — Spatial distribution of total heavy metal concentration in seawater in the study areas; a) pre-monsoon; b) monsoon; c) post-monsoon; d) summer: NS- Nearshore; OS- Offshore; RD-River Discharge.

and recorded the maximum during summer (May) and the minimum in the pre-monsoon (August). In case of Hg the maximum of $0.48 \mu\text{g g}^{-1}$ was recorded at offshore in St. 2 and the minimum of $0.33 \mu\text{g g}^{-1}$ was in St. 1 at nearshore (Fig.7). It ranged from 0.17 to $0.55 \mu\text{g g}^{-1}$ in different sampling seasons at both the stations and recorded the maximum during the monsoon (November) and the minimum in pre-monsoon (August).

Zn was recorded the maximum of $14.31 \mu\text{g g}^{-1}$ in St. 2 at nearshore and the minimum of $12.97 \mu\text{g g}^{-1}$ in St. 1 at offshore. It ranged from 4.52 to $19.87 \mu\text{g g}^{-1}$ in four seasons in the two stations and the maximum was observed during summer (May) followed by the minimum in pre-monsoon (August) (Fig.7a).

The Box-Whisker plots for seasonal variations in heavy metals concentration are given in Figs. 6 and 7, 7a. From the graph, it is observed that Cd and Cu values were higher in pre-monsoon and post-monsoon in both the stations. In case of Hg, higher

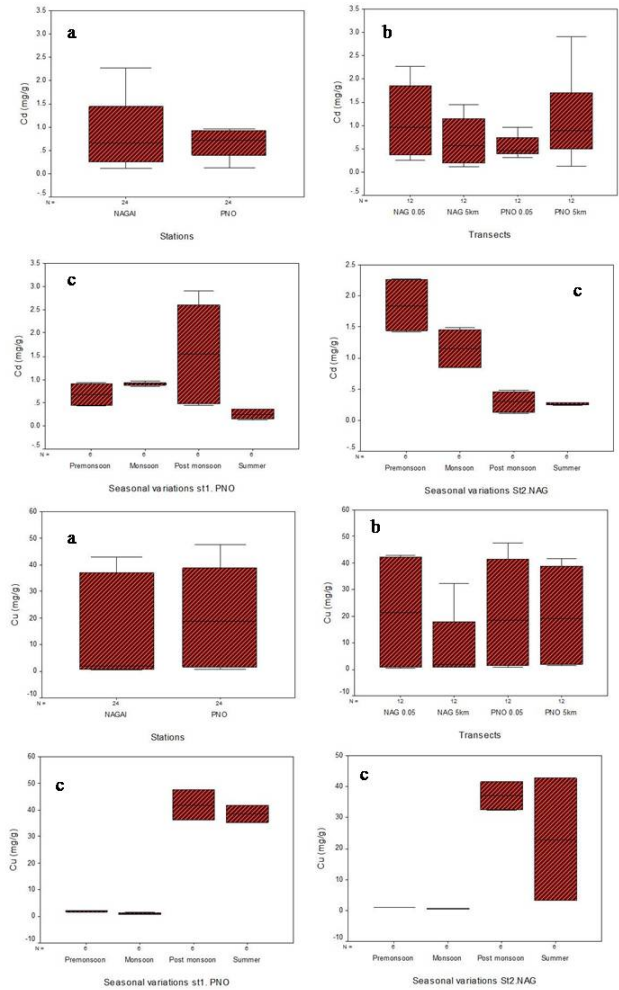


Fig. 6 — Seasonal variations of Cd and Cu in sediment at two stations (St.1: PNO = Paragipettai & St.2: NAG = Nagapattinam) (a) transects (near shore [0.5 km] & off shore [5 km]) (b) and four seasons (c) during 2009–10. In each plot the central point denoted the median, the interval between the 25% and 75% percentiles, standard deviation represented and the Whisker indicates the range.

values ($0.26 \mu\text{g g}^{-1}$) were observed during monsoon season at St.1 and the St.2 had higher ($0.47 \mu\text{g g}^{-1}$) values in post-monsoon. Moreover, Pb and Zn showed high values of 11.79 to $14.84 \mu\text{g g}^{-1}$ and 12.86 to $29.09 \mu\text{g g}^{-1}$, respectively, in post-monsoon and summer seasons in both the stations.

Multivariate analysis

PCA was applied in this study to analyze the sources of pollutants in the study areas. Variations in metal concentration in nearshore and offshore sediment samples collected in four seasons are shown in Fig. 8 along with factor loadings, varimax rotation, as well as Eigenvalues and communalities in Table 3.

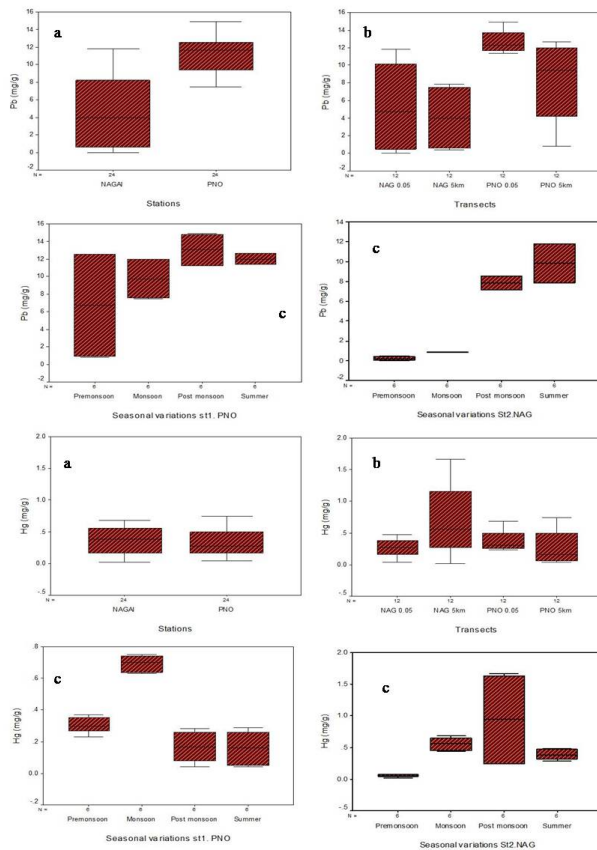


Fig. 7 — Seasonal variations of Pb and Hg in sediment at two stations (St.1: PNO = Paragipettai & St.2: NAG = Nagapattinam) (a), transects (nearshore [0.5 km] & off shore [5 km]) (b) and four seasons (c) during 2009–10.

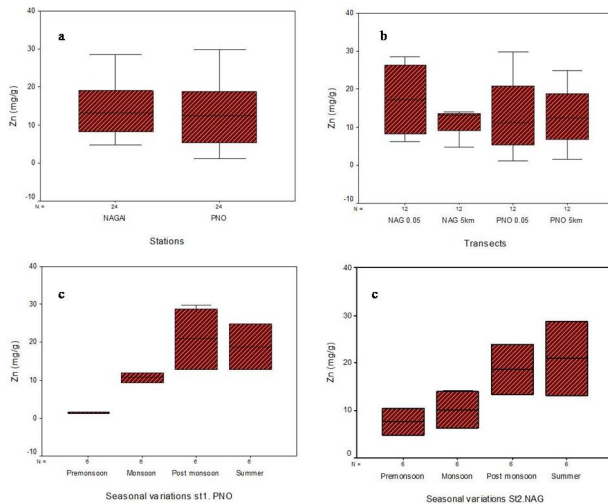


Fig. 7a — Seasonal variations of Zn in sediment at two stations (St.1: PNO = Paragipettai & St.2: NAG = Nagapattinam) (a) transects (nearshore [0.5 km] & off shore [5 km]) (b) and four seasons (c) during 2009–10.

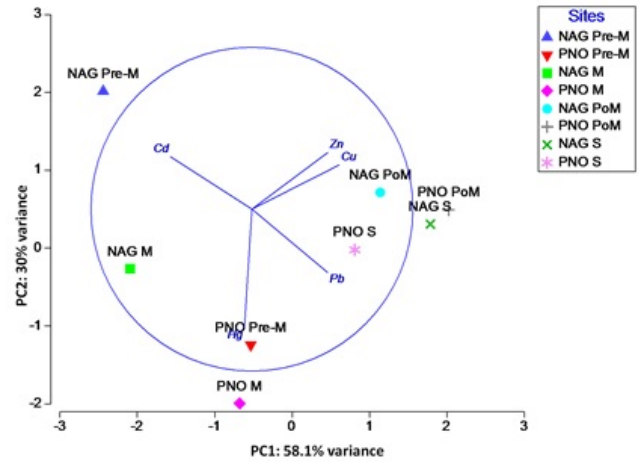


Fig. 8 — PCA results in the plot-loading of the nearshore Sediment

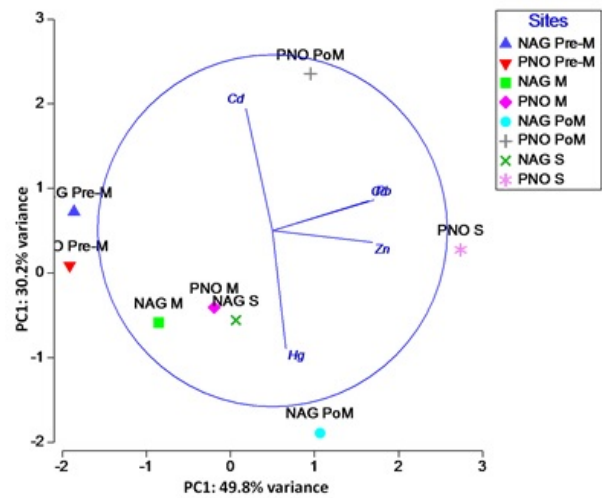


Fig. 8a — PCA results in the plot-loading of the offshore sediment

Five principle components were extracted, accounting for 100 percentage of the total variance. In the rotated component matrix, there was a strong variability (PC1 explains 58.1 % variance), contributed by Cu, Zn and Pb during post monsoon and summer at both the stations. Similarly, it was also observed that a considerable variability (PC2 explains 30 % variance) was contributed by Cd, Cu and Zn during post-monsoon at both the stations and summer at Nagapattinam station.

In the rotated component matrix for offshore sediment samples, it was observed that a strong variance (PC1 explains 49.8 % variance) was contributed by Pb, Zn, Cu and Hg, during post monsoon and summer in both the study areas (Fig. 8a & Table 3a).

Table 3 — Rotated component matrix for the heavy metal concentration of near shore sediment of Parangipettai and Nagapattinam.

Heavy metal variable	Component				
	PC1	PC2	PC3	PC4	PC5
Cd	-0.507	0.324	-0.312	0.579	-0.454
Cu	0.543	0.273	-0.122	-0.309	-0.721
Pb	0.502	-0.392	0.338	0.698	-0.15
Hg	-0.047	-0.737	-0.646	-0.103	-0.161
Zn	0.563	0.351	-0.596	0.269	0.475
Monsoonal Variable					
NAG Pre-M	-2.44	2.02	0.189	0.381	0.0167
PNO Pre-M	-0.535	-1.24	1.19	0.0351	0.154
NAG M	-2.1	-0.267	-0.66	-0.518	-0.0338
PNO M	-0.68	-2	-0.637	0.404	-0.0462
NAG PoM	1.14	0.715	-0.178	-0.388	0.054
PNO PoM	2.02	0.501	-0.176	0.483	-0.11
NAG S	1.79	0.308	-0.389	-0.0764	0.214
PNO S	0.809	-0.0219	0.661	-0.321	-0.248
Eigen values	2.9	1.5	0.421	0.153	0.0213
% of Variation	58.1	30	8.4	3.1	0.4
Cum.%Variation	58.1	88.1	96.5	99.6	100

Table 3a — Rotated component matrix for the heavy metal concentration of off shore sediment of Parangipettai and Nagapattinam. Bold values are statistically significant at $p>0.5$

Heavy metal variable	Component				
	PC1	PC2	PC3	PC4	PC5
Cd	-0.152	0.696	-0.521	0.368	-0.292
Cu	0.552	0.17	-0.37	-0.717	-0.125
Pb	0.581	0.175	-0.046	0.392	0.69
Hg	0.077	-0.672	-0.681	0.266	-0.092
Zn	0.573	-0.066	0.356	0.355	-0.644
Monsoonal Variable					
NAG Pre-M	-1.86	0.725	0.197	-0.274	-0.145
PNO Pre-M	-1.91	0.883	0.0571	-0.588	0.361
NAG M	-0.856	-0.584	0.259	0.288	-0.847
PNO M	-0.193	-0.407	-0.0341	0.741	0.282
NAG PoM	1.07	-1.89	-1.27	-0.314	-0.003
PNO PoM	0.953	2.35	-0.987	0.187	-0.0119
NAG S	0.0657	-0.557	0.707	0.366	0.461
PNO S	2.74	0.274	1.07	-0.406	-0.0974
Eigen values	2.49	1.51	0.623	0.212	0.167
%Variation	49.8	30.1	12.5	4.2	3.3
Cum.%Variation	49.8	80	92.4	96.7	100

Likewise, PC2 explains 30.1 % variance, contributed by Cd, Pb and Cu during pre-monsoon at both the stations and post-monsoon during summer at Parangipettai station.

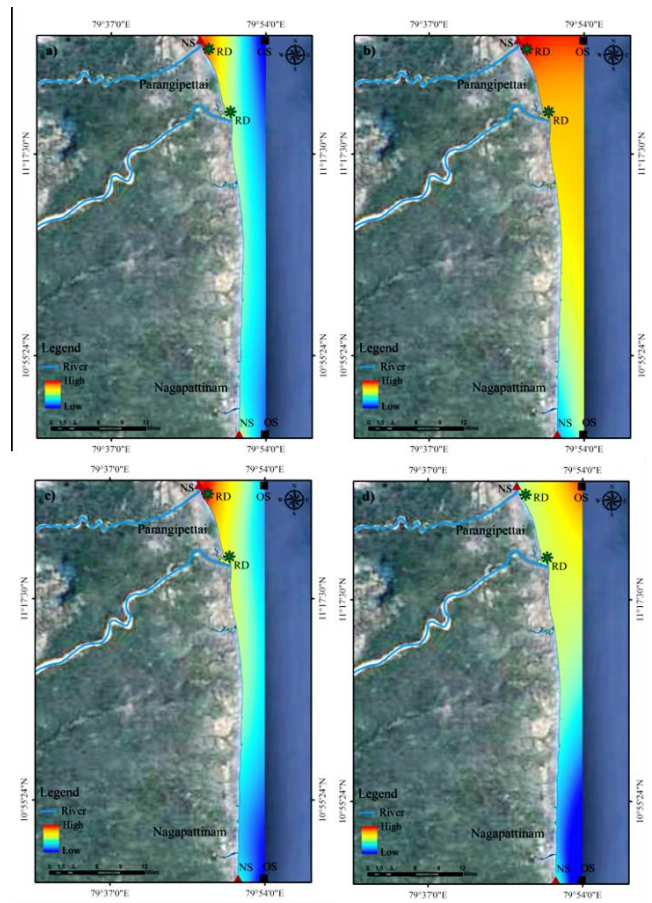


Fig. 9 — Spatial distribution of total heavy metal concentration in sediments in the study areas; a) pre-monsoon; b) monsoon; c) post-monsoon; d) summer: NS-Nearshore; OS-offshore; RD-River Discharge.

Geospatial analysis of total heavy metals distribution in sediment and the visual map developed through geospatial analysis, which illustrated the dispersion pattern of total heavy metal concentration in a simplified manner, were compared between the study sites (Fig. 9).

This analysis revealed that total heavy metals concentration in nearshore of Parangipettai prevailed as the maximum except in the pre-monsoon (Fig. 9). However, fresh water flow determines the distribution of heavy metals in Parangipettai coast. From this data, it is observed that in the sediments, heavy metals are dispersed from Parangipettai to Nagapattinam coast during the monsoon (Fig. 9) by the sediment transport of freshwater runoff and it may result in upwelling in these study sites.

Heavy metal analysis in Biota

The concentrations of Cd, Cu, Pb, Hg and Zn in different marine organisms, like, *P. indicus*, *S. longiceps*, *R. kanagurta*, *S. guttatus*, *P. niger* and *P. viridis* were determined in two stations. The maximum Cd accumulation of $0.36 \mu\text{g g}^{-1}$ was observed in *P. indicus* tissue at St. 1 and the minimum of $0.26 \mu\text{g g}^{-1}$ in *R. kanagurta* in St. 2. It ranged from 0.17 to $0.45 \mu\text{g g}^{-1}$ in four different seasons and the maximum was during the pre-monsoon (August) and the minimum in monsoon (November).

The maximum Cu concentration of $5.51 \mu\text{g g}^{-1}$ was observed in *P. viridis* at St.2 and the minimum of $4.03 \mu\text{g g}^{-1}$ was recorded in *S. guttatus* at St. 1. It ranged from 3.71 to $5.03 \mu\text{g g}^{-1}$ in four different seasons and the maximum was recorded during the monsoon (November) and the minimum in summer (May) (Fig. 10 & Table 4). The Pb was recorded the maximum of $5.34 \mu\text{g g}^{-1}$ in *P. viridis* at St. 1 and the minimum of $0.83 \mu\text{g g}^{-1}$ in *S. guttatus* in St. 2, respectively. It ranged from 1.32 to $4.08 \mu\text{g g}^{-1}$ in different sampling seasons and the maximum was

during the monsoon (November) and the minimum in pre-monsoon (August). The concentration of Hg was recorded the maximum of $0.45 \mu\text{g g}^{-1}$ in *R. kanagurta* at St. 2 and the minimum of $0.12 \mu\text{g g}^{-1}$ in *P. viridis* at St. 1. It ranged from 0.12 to $0.45 \mu\text{g g}^{-1}$ in four different seasons and the maximum was recorded during the monsoon (November) and the minimum during summer (May).

The Zn was recorded a maximum of $59.76 \mu\text{g g}^{-1}$ in *P. viridis* at St. 2 and the minimum of $37.44 \mu\text{g g}^{-1}$ in *S. longiceps* at St. 1.

It ranged between 44.15 and $56.87 \mu\text{g g}^{-1}$ in different sampling seasons and recorded the maximum during the monsoon (November) and the minimum in summer (May) (Figs.11 and 11a Table 2). The Box-Whisker plots for seasonal variations in heavy metals concentration in marine organisms are given in Figs. 10 and 11. From the graph, it is observed that Cd, Cu and Hg values were higher in pre-monsoon and monsoon. Moreover, other metals Pb and Zn did not show much noticeable variation between the different seasons. This might be due to the rain water flow from the landward side and river runoff discharges bringing the pollutants into the coastal areas, and it is clearly noticed from the analysis.

The pollution of aquatic ecosystems by heavy metals from anthropogenic origin is one of the great ecological impacts. Heavy metal bioavailability results in high concentrations in water column and sediment, and correspondingly to biota, through the bio-concentration process.

Bio-concentration is referred to as the process by which a chemical species are accumulated into biota from its surrounding phases³⁰. The amount of bioaccumulation of metals is dependent on the total amount, the bioavailability of each metal in the environmental medium and the route of uptake, storage and excretion mechanisms.

BAFs analysis data:

BAFs analysis of the data in the present study revealed (Figs. 12, 13, & 14) that Parangipettai study site had higher concentration of lead, copper and zinc transferred from aquatic to biotic when compared to the Nagapattinam coastal region.

Discussion

Heavy metal accumulation affects the ecosystem, by imbibing the toxic chemicals into aquatic biota. The accumulation of the metals affects the life cycle

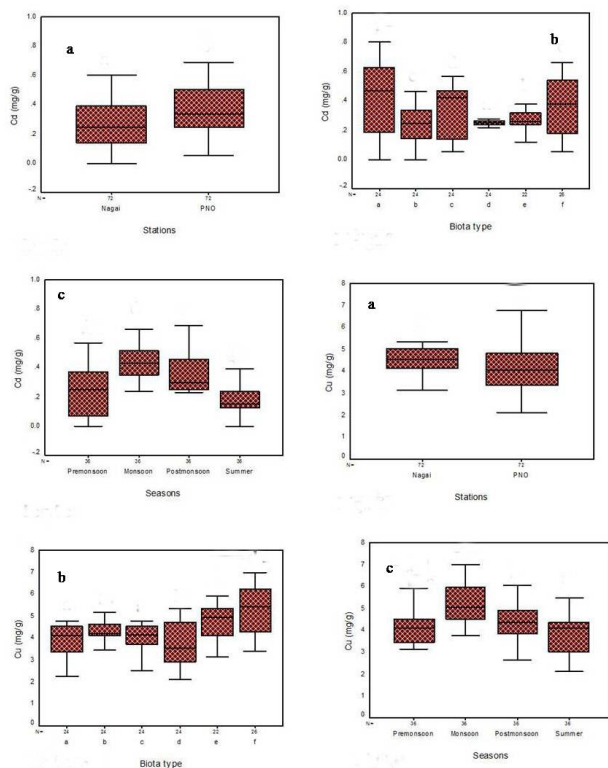


Fig. 10 — Seasonal variations of Cd and Cu in organisms at two stations (St. 1: PNO=Parangipettai & St. 2: NAGAI=Nagapattinam). (a) transects (nearshore [0.5 km] & offshore [5 km]) (b) and four seasons (c) during 2009–10. (a) *P. indicus*; (b) *S. longiceps*; (c) *R. kanagurta*; (d) *S. guttatus*; (e) *P. niger*; (f) *P. viridis*

Table 4 — Variation of heavy metals (Mean \pm SD) variables in different organisms collected from Parangipettai (st.1) and Nagapattinam (st.2).

Seasonal patterns	Heavy metal symbol ($\mu\text{g g}^{-1}$)	Name of the Organisms											
		<i>P. indicus</i>		<i>S. longiceps</i>		<i>R. kanagurta</i>		<i>S. guttatus</i>		<i>P. niger</i>		<i>P. viridis</i>	
		St.1	St. 2	St.1	St. 2	St.1	St. 2	St.1	St. 2	St.1	St. 2	St.1	St. 2
Pre-monsoon (July–Sep)	Cd	0.48 \pm 0.06	0.06 \pm 0.01	0.24 \pm 0.03	0.15 \pm 0.2	0.52 \pm 0.09	0.06 \pm 0.02	0.22 \pm 0.08	0.24 \pm 0.08	0.28 \pm 0.10	0.26 \pm 0.06	0.56 \pm 0.13	0.08 \pm 0.02
	Cu	3.58 \pm 0.03	4.77 \pm 0.05	4.28 \pm 0.04	4.18 \pm 0.3	3.76 \pm 0.02	4.03 \pm 0.06	3.34 \pm 0.07	1.3 \pm 0.10	5.92 \pm 0.09	2.08 \pm 0.04	0.22 \pm 0.10	104.27 \pm 0.08
	Pb	3.18 \pm 0.17	0.64 \pm 0.03	1.28 \pm 0.21	0.32 \pm 0.5	1.64 \pm 0.11	1.09 \pm 0.09	0.08 \pm 0.06	0.36 \pm 0.4	0.98 \pm 0.05	0.45 \pm 0.01	3.52 \pm 0.17	2.32 \pm 0.11
	Zn	41.92 \pm 3.72	57.22 \pm 1.6	34.28 \pm 1.83	37.1 \pm 3.2	49.98 \pm 3.8	41.08 \pm 3.5	53.12 \pm 7.1	159.17 \pm 6.2	35.44 \pm 2.7	42 \pm 4.5	55.78 \pm 6.2	252.02 \pm 4.7
	Hg	0.34 \pm 0.12	0.02 \pm 0.01	0.32 \pm 0.02	0.14 \pm 0.3	0.56 \pm 0.01	0.28 \pm 0.04	0.24 \pm 0.09	0.28 \pm 0.01	0.32 \pm 0.04	0.38 \pm 0.06	0.06 \pm 0.01	0.01 \pm 0.02
Monsoon (Oct–Dec)	Cd	0.66 \pm 0.25	0.6 \pm 0.01	0.31 \pm 0.6	0.43 \pm 0.4	0.42 \pm 0.06	0.52 \pm 0.25	0.28 \pm 0.05	0.38 \pm 0.3	0.32 \pm 0.12	0.44 \pm 0.03	0.66 \pm 0.20	0.46 \pm 0.12
	Cu	4.18 \pm 0.81	4.78 \pm 0.06	4.68 \pm 0.17	5.18 \pm 0.53	4.36 \pm 0.43	6.56 \pm 0.03	3.74 \pm 0.09	5.34 \pm 0.12	4.92 \pm 0.7	5.22 \pm 0.4	6.72 \pm 1.2	6.97 \pm 0.25
	Pb	3.58 \pm 0.12	3.78 \pm 0.91	2.28 \pm 1.2	3.28 \pm 0.87	2.14 \pm 0.64	2.64 \pm 1.93	1.08 \pm 0.35	1.46 \pm 0.05	1.68 \pm 0.12	2.38 \pm 0.11	4.32 \pm 0.27	5.32 \pm 0.47
	Zn	52.42 \pm 3.89	72.22 \pm 4.1	39.58 \pm 3.5	45.4 \pm 4.8	52.18 \pm 5.2	57.28 \pm 5.9	59.3 \pm 4.3	762.3 \pm 6.12	37.74 \pm 3.9	57.14 \pm 4.9	65.28 \pm 6.97	76.28 \pm 6.9
	Hg	0.38 \pm 0.10	0.48 \pm 0.11	0.32 \pm 0.09	0.32 \pm 0.10	0.64 \pm 0.31	0.69 \pm 0.42	0.34 \pm 0.21	0.48 \pm 0.35	0.39 \pm 0.26	0.56 \pm 0.53	0.11 \pm 0.86	0.31 \pm 0.19
Post-monsoon (Jan–Mar)	Cd	0.68 \pm 0.05	0.4 \pm 0.21	0.33 \pm 0.11	0.23 \pm 0.1	0.42 \pm 0.13	0.44 \pm 0.12	0.26 \pm 0.9	0.26 \pm 0.8	0.26 \pm 0.9	0.54 \pm 0.12	0.56 \pm 0.13	0.23 \pm 0.07
	Cu	3.38 \pm 0.19	4.12 \pm 0.21	4.08 \pm 0.18	4.6 \pm 0.19	3.66 \pm 0.17	4.76 \pm 0.21	2.64 \pm 0.09	5.01 \pm 0.21	4.12 \pm 0.15	4.02 \pm 0.18	6.02 \pm 0.23	4.77 \pm 0.19
	Pb	2.48 \pm 0.54	3.08 \pm 0.31	2.18 \pm 0.29	2.2 \pm 0.26	2.14 \pm 0.21	2.14 \pm 0.18	1.18 \pm 0.10	0.96 \pm 0.09	1.08 \pm 0.10	1.32 \pm 0.15	4.04 \pm 0.20	3.42 \pm 0.25
	Zn	47.12 \pm 4.26	67 \pm 3.95	33.58 \pm 2.81	45 \pm 3.9	48.15 \pm 4.3	51.08 \pm 4.7	52.12 \pm 5.1	162.43 \pm 6.3	28.72 \pm 4.8	52.1 \pm 5.8	55.18 \pm 6.0	72.18 \pm 6.2
	Hg	0.28 \pm 0.06	0.32 \pm 0.12	0.12 \pm 0.03	0.26 \pm 0.08	0.44 \pm 0.14	0.44 \pm 0.23	0.14 \pm 0.03	0.45 \pm 0.40	0.19 \pm 0.10	0.56 \pm 0.48	0.11 \pm 0.05	0.18 \pm 0.08
Summer (April–June)	Cd	0.38 \pm 0.17	0.02 \pm 0.01	0.13 \pm 0.09	0.13 \pm 0.6	0.12 \pm 0.06	0.11 \pm 0.03	0.06 \pm 0.02	0.22 \pm 0.09	0.12 \pm 0.05	0.34 \pm 0.16	0.37 \pm 0.09	0.18 \pm 0.13
	Cu	2.28 \pm 0.18	4.32 \pm 0.31	4.18 \pm 0.21	3.48 \pm 0.9	2.54 \pm 0.32	4.26 \pm 0.52	2.12 \pm 0.46	4.43 \pm 0.81	3.44 \pm 0.63	2.72 \pm 0.29	5.42 \pm 0.94	0.7 \pm 0.81
	Pb	2.18 \pm 0.61	2.11 \pm 0.20	1.18 \pm 0.16	0.42 \pm 0.09	2.28 \pm 0.15	1.34 \pm 0.96	1.08 \pm 0.08	0.57 \pm 0.05	0.38 \pm 0.08	1.11 \pm 0.09	2.54 \pm 0.18	2.02 \pm 0.21
	Zn	57.12 \pm 6.1	60.02 \pm 6.7	23.59 \pm 3.8	41.2 \pm 4.52	41.58 \pm 4.12	45.58 \pm 5.21	42.52 \pm 5.78	61.05 \pm 6.34	12.52 \pm 0.9	48.12 \pm 1.79	55.02 \pm 4.38	55.76 \pm 5.28
	Hg	0.22 \pm 0.04	0.12 \pm 0.03	0.06 \pm 0.02	0.26 \pm 0.6	0.24 \pm 0.09	0.34 \pm 0.16	0.17 \pm 0.09	0.36 \pm 0.18	0.12 \pm 0.82	0.52 \pm 0.19	0.02 \pm 0.01	0.09 \pm 0.02

and food chain³³⁻³⁴. The concentrations of heavy metals demonstrate seasonal fluctuations in an environment and in resident organisms³⁵⁻³⁶. Heavy metals such as Pb, Cd and Hg observed higher in water samples in St. 1 nearshore and offshore sites than those in St. 2. The Zn and Cu contents showed very high values in the nearshore water samples of Parangipettai and were poorly observed in Nagapattinam nearshore and offshore sites, and hence it is clear that the river runoff brings in high concentrations of elements from landside. The enrichment elements, such as, Pb and Cd in the study sites, are probably due to the anthropogenic activities

and is associated with river runoff from agricultural and shipping activities. This might be due to prolonged rain and river runoff into the coastal waters. The surrounding land areas support heavy agricultural and fishing activities which might be among the reasons to find slightly higher values of heavy metal presence in Parangipettai than in Nagapattinam.

In sediment sample, high concentrations of Cd have been observed in both the study sites. More than 50 % of sediment samples have mean values between 0.45–2.67 and 0.26–2.26 $\mu\text{g g}^{-1}$ in four seasons observed from Parangipettai and Nagapattinam,

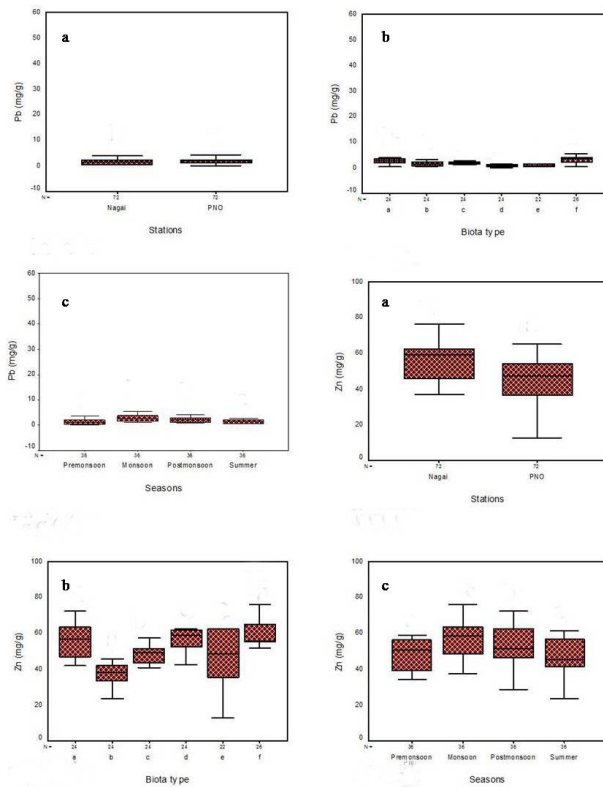


Fig. 11 — Seasonal variations of Pb and Zn accumulated in organisms at two stations (st.1: PNO=Parangipettai & st.2: NAGAI=Nagapattinam) (a) transects (near shore [0.5 km] & offshore [5 km]) (b) and four seasons (c) during 2009–10. In each plot, the central point denoted the median, the interval between the 25% and 75% percentiles, standard deviation represented and the Whisker indicates the range.

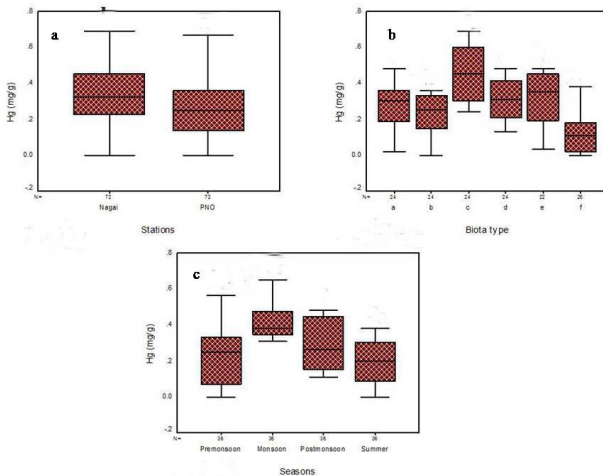


Fig. 11a — Seasonal variations of Hg accumulated in organisms at two stations (St.1: PNO = Parangipettai & St.2: NAGAI = Nagapattinam) (a) transects (nearshore [0.5 km] & offshore [5 km]) (b) and four seasons (c) during 2009–10.

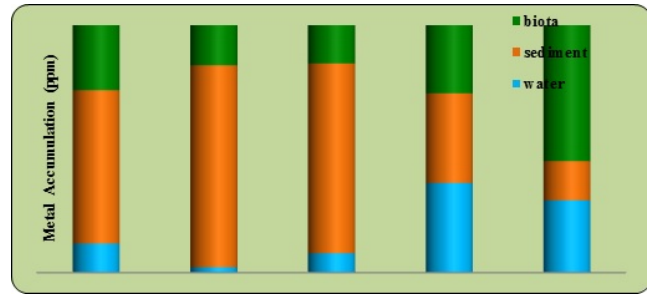


Fig. 12 — Heavy metals accumulation in the sediments, waters and animal tissues in Parangipettai.

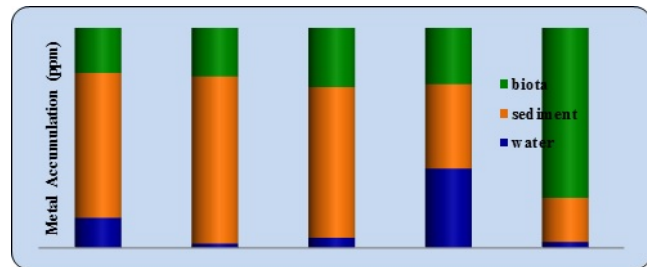


Fig. 13 — Heavy metals accumulation in the sediments, waters and animal tissues in Nagapattinam.

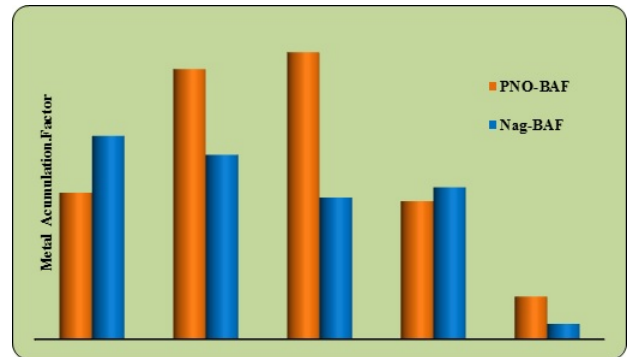


Fig. 14 — Bioaccumulation factor of the metals in the two different sampling stations of PNO-Parangipettai and Nag-Nagapattinam. (BAF-Bio-Accumulation Factor).

respectively, which are considerably above the natural background values. When comparing these results with other coastal ecosystems, Pichavaram and Tamirabarani have been reported with higher contamination²⁶. This high concentration of Cd is mainly caused due to the mix of chemicals from the painting of fishing boats by local inhabitants²⁵. Multivariate techniques can help to simplify and organize large data sets to make a useful generalization that can lead to meaningful insight²⁴⁻²⁵. A large number of researchers³⁷⁻³⁸ have used PCA in the evaluation of environmental data. Five principal components have been identified, explaining c. 100%

of the total variance. In seawater PCA, PC1 is found highly polluted with heavy metals due to the higher concentrations of Pb and Zn in summer season in nearshore water samples at both study sites. PC2 is loaded with metals, such as, Cu, Hg and Cd during pre-monsoon at Nagapattinam and monsoon in both the stations, whereas PC3 by Cu during pre-monsoon at Parangipettai, post-monsoon at Nagapattinam and summer in both the stations. Finally, PC4 is characterized by the loading of Cd, Cu and Zn during post-monsoon in Parangipettai, summer in Nagapattinam and monsoon in both the stations. In offshore water samples PCA data varied as follows: PC1 is loaded with Pb, Zn and Hg during post-monsoon and summer in both the study stations. PC2 expressed pollutant signal due to high concentration of Cu, Cd, Hg, Pb and Zn during pre-monsoon and monsoon in both the study areas. PC3 is characterized by the loading of Cu, Pb and Zn during pre-monsoon, monsoon and post-monsoon in Parangipettai and in Nagapattinam, respectively. The main sources of Pb, Cd and Hg in marine environment were storm water runoff from hinterland and sewage input³⁹ due to anthropogenic activities. Generally, in the coastal region, the anthropogenic activities are high including terrigenous inputs through terrestrial runoff, metal from minerals, forming basement and sedimentary rocks all over the coastline, increase in land traffic, agriculture activities, oil spills and discharges from landwards, as well as fishing boat operation, dumping of soft-waste and shipments of mineral products⁴⁰. Seasonal cyclones and heavy fishing boat trafficking might have contributed to the external source of metal contamination in the region. In sediment PCA analysis, PC1 is found with pollutants with higher concentrations of Cu, Zn and Pb during post-monsoon and summer in both the stations from nearshore sediments. Likewise, PC2 is loaded with metals, such as, Cd, Cu and Zn during post-monsoon in both the stations and summer in Nagapattinam station, whereas PC3 is with Cd during pre-monsoon season which had higher values in both the study sites. PC4 is characterized by the loading of Pb, Cd and Zn during pre-monsoon in both the study stations, monsoon followed by post-monsoon at Parangipettai, respectively. In offshore sediment samples PCA, PC1 is loaded with elements such as Pb, Zn, Cu and Hg during post-monsoon and summer at both the study areas. PC2 showed pollution effect due to the significant values of Cd, Pb and Cu during pre-monsoon in both the study stations and the post-monsoon samples showed

significant values at Parangipettai. This analysis revealed that pre-monsoon, monsoon and post-monsoon are correlated with pollutant loads in Parangipettai, due to the freshwater discharge from Vellar estuary. However, some of the elements like Pb, Cu and Zn show positive correlation in summer season in both the study stations, which might be due to the influence of upwelling or circulation pattern of water current. Geospatial analysis of total heavy metals distribution in seawater and sediment from nearshore and offshore and the data showing visual map developed through geospatial analysis illustrated the dispersion pattern of total heavy metals concentration and comparisons between the study sites in a simplified manner. This analysis revealed that total heavy metals concentration in Parangipettai was higher than in Nagapattinam. In the present study, significant seasonal variations of heavy metals concentrations in water, sediments and organisms at two sampling sites in south-east cost of India were

Table 5a — Concentration of heavy metal (mean values) in water reported from various marine environs of the India and compared standard values.

Location	Seawater (µg L ⁻¹) Heavy metals					Reference
	Cd	Cu	Pb	Hg	Zn	
Parangipettai (St. 1)	0.13	0.86	1.09	0.32	30.63	Present study
Nagapattinam (St. 2)	0.22	0.43	0.35	0.88	0.945	
Uppanar estuary	1.75-17.21	2.45-18.25	-	0.012-0.103	29.45-101	Sarkar et al., (2010)
East coast of Chennai	0.5	8.13	18.25	-	-	Arunkumar & Achuthan (2007)
Coromandel coast	0.30	0.31	-	0-0.12	9-130	Govindasamy & Azariah (1999)
Bay of Bengal	0.30-2.90	1.20-17.50	-	0.05-0.30	1.90-174.00	Qasim & Gupta (1983)
Andaman Island	0.22	3.89	1.8	-	0	Kaladharan et al., (2006)
Kerala coast	0.35	1.60	2.2	-	17.1	
Southwest coast of India	0.14	1.65	1.87	0.03	8.20	Robin et al., (2012)
WHO (1987)	0.00-0.5	3-5	0.01-1.0	0-0.01	5-40	WHO (1987)

Table 5b — Concentration of heavy metal in sediment and organism reported from various marine environs of the India and compared standard values.

Location	Organism (µg g ⁻¹) Heavy metals					Reference
	Cd	Cu	Pb	Hg	Zn	
Parangipettai (St. 1)	0.54	6.205	3.0	0.25	67.14	Present study
Nagapattinam (St. 2)	0.41	6.69	2.78	0.48	82.55	
Vellar Estuary	0.042	0.295	0.327	-	2.374	Ponnusamy et al., (2014)
Andaman Island	0.0	0.0	0.0	-	14.9	Kaladharan et al., (2006)
Kochi (Kerala coast)	0.0	0.0	0.0	-	33.3	Raja et al., (2009)
South east coast, India	0.18-0.54	0.1-0.3	-	-	14.1-35.5	
South east coast, India	4.35-6.38	3.09-3.62	-	-	79.3-84.3	Rejomon et al., 2010
NE Coast, India	0.33	3.9	-	0.48	19.9	Kumar et al., 2012.
Southwest coast of India	0.04	1.31	2.57	0.02	2.77	Robin et al., (2012)
Sediment (µg g ⁻¹)						
Parangipettai (St. 1)	0.56	21.31	12.67	0.38	13.14	Present study
Nagapattinam (St. 2)	0.61	22	7.26	0.36	17.97	
Vellar Estuary	0.135	0.38	2.05	-	9.48	Ponnusamy et al., (2014)
Uppanar estuary	2.25-9.21	5.2-81.27	-	0.16-0.115	27.6-75.42	Sarkar et al., 2010
Andaman Island	3.78	5.53	59.8	-	6.5	Kaladharan et al., 2006)
Kochi (Kerala coast)	5.33	19.0	7.5	-	97.8	
Southwest coast of India	0.28	-	27.80	0.19	-	Robin et al., (2012)
WHO/EPA standard	0.50-1.00	0.1-30	0-0.15	0.2-0.6	40-150	WHO (1989) FAO, 1983

recorded and compared with standard values and several other studies⁴¹⁻⁴⁵ (Tables 5a& 5b).

The concentrations of Cd, Cu, Pb, Hg and Zn significantly varied in seawater between the sampling stations due to the difference in distances among the study sites, difference in seasons and sediment characteristics in Parangipettai. Seasonal variations in concentrations of heavy metals in water and sediments were reflected in the coastal organisms. The maximum accumulations were observed in the sediments as compared to the water and organisms. The accumulation was the maximum in Nagapattinam and the minimum in Parangipettai area. The industrial and agricultural activities and also the river run-off are the sources of the heavy metals from landward side and its vicinity^{10,46-47}. The people living in Parangipettai and Nagapattinam region are exposed to the heavy metals by consuming the contaminated fishes⁴⁸. Although the total contents of heavy metals in the sediments are much higher, the bio-available quantities of a few heavy metals are low, which may tend to increase if no measures are taken to check the contamination of waters through anthropogenic interactions⁴⁹. The quantities of Zn, Cu and Pb are very high in total, as well as, in a number of residual fractions, which lead to their bioaccumulation in fish in the studied sites. The relatively large contents of Zn, Cu, Pb and Cd in fishes may be attributed to the association of these metals to the bioavailable fraction. Though the amount of Cd associated with the labile fraction is high, the concentration of Cd in fishes was low which could be due to the relatively low concentration of Cd in the sediments. The results indicated that the fishes from Parangipettai and Nagapattinam coasts were quite heavily contaminated with heavy metals. Mitigating the heavy metal contaminations from sediments and waters and also avoiding the discharge of contaminated effluents into the coastal environments is the best remedies to ensure the quality of fishes and other aquatic animals which are being used for human consumption^{40,44,50}. The present study clearly depicts that the maximum accumulation of Cu and Pb was found in mussel, *P. viridis* and the similar result was observed by Sakai *et al.*⁵¹. Agriculture, aquaculture and fishing are the primary activities of the people living in the Parangipettai and Nagapattinam^{45,52-53}. The results showed that the heavy metal concentrations in six different fishes of Parangipettai and Nagapattinam were found within the permissible

limits as proposed by FAO (1983) (Table 4&5a, b). Copper-contaminated paints and high organic matter might be the sources of Cu in the sediments⁵⁴, as it is well known that a major portion of copper in tropical seawater has been found to be associated with organic matter^{12,14,52}. Knowledge on the concentration and distribution of heavy metals in marine environment leads to better understanding of their behavior in the aquatic environment and in detecting pollution²⁵. In this concern, the future study would need continuous monitoring and evaluation of the metal accumulation in the coastal environments. Also, it is important for the better sanitation of aquatic meat used for human consumption. The marine ecosystem conservation and sustainable management of coastal activities are very essential for the wellbeing of the local coastal communities depending on the coastal resources along the southeast coast of India.

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