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Metals in Fish along the Southeast Coast of India

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Abstract Metal concentrations (cadmium, chromium, iron, lead, copper, manganese, zinc and mercury) in the muscle of five fish species (*Epinephelus chlorostigma*, *Lutjanus russelli*, *Terapon jarbua*, *Cynoglossus arel* and *Lagocephalus lunaris*) from the six fish landing centres along southeast coast of India were measured. In Cuddalore and Mudasalodai, the level of toxic metals cadmium, chromium and manganese were well above the permissible limits. Concentrations of cadmium, chromium, manganese and mercury in *C. arel* were above the permissible limit and it is consistent with their habitat and diet. The results showed a relationship between metal concentrations and pollution status of the areas.

Keywords Metals · Tissues · Fish · Southeast coast of India

Metal especially in coastal environment is common and prevalence due to the fast development of industries, urbanization and human population. There are essential and non essential metals, but when their limits exceed in the body of organism, they become more toxic. Metals like copper, zinc and iron are essential for fish metabolism while others such as mercury, cadmium and lead have no known role in biological systems. Excessive pollution in coastal environment could lead to health hazards in man, through consumption of fish. Among animal species, fish are prone to the detrimental effects of these pollutants because of the continuous exposure (Olaifa et al. 2004). Metals from natural and anthropogenic sources continuously enter the aquatic ecosystem where they pose serious threat because of their toxicity, long persistence, bioaccumulation and biomagnification in the food chain (Papagiannis et al. 2004).

Fish being at the higher level of the food chain accumulate large quantities of metals and the accumulation depends upon the intake and elimination from the body (Karadede et al. 2004). Pollution monitoring studies in the coastal regions showed that there are some elevated levels of metals (Henry et al. 2004). Comparative study regarding the metal accumulation in fishes along southeast coast region of India is limited. Hence, the present study is taken up to find out the metal concentrations (Cd, Cr, Fe, Pb, Cu, Mn, Zn and Hg) in muscle tissues of five commercially valuable fish species *Epinephelus chlorostigma*, *Lutjanus russelli*, *Terapon jarbua*, *Cynoglossus arel* and *Lagocephalus lunaris* from six fish landing centres viz. Chennai, Pondicherry, Cuddalore, Mudasalodai, Palayar and Karaikal along southeast coast of India.

Materials and Methods

The fish were collected from the fish markets of Chennai, Pondicherry, Cuddalore, Mudasalodai, Palayar and Karaikal (Fig. 1) during December, 2010–January, 2011. After collection, fish were immediately transported to the laboratory in an ice box. The specimens were thawed at room temperature and their total length and weight were recorded and no significant differences were found among same species (Table 1). Metal concentrations from the fish tissues were determined by following the method of Dhaneesh et al.

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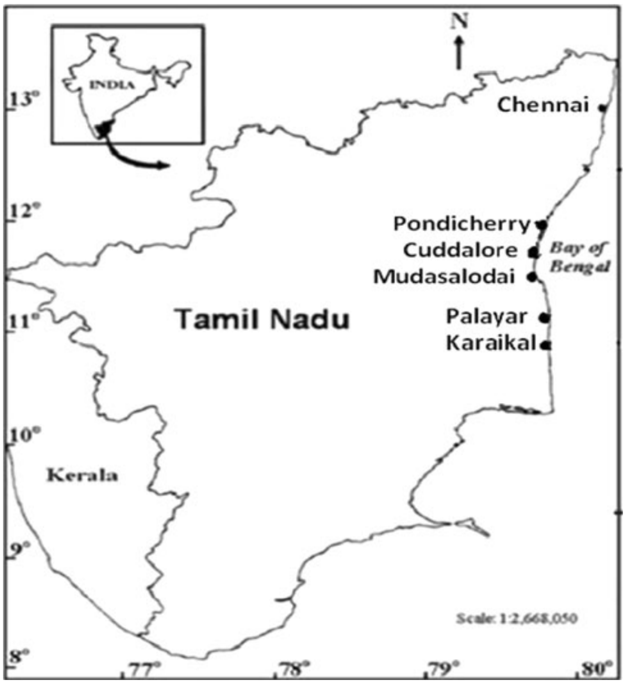

Fig. 1 Fish sampling areas along the southeast coast of India

(2012a, b). Fish were dissected to muscle using stainless steel knife and dried in hot air oven at 70°C for 14 h. A porcelain mortar and pestle were employed to grind and homogenise the dry tissue and weighed to 1 g (±0.01 g) using an electronic weighing balance (Denver, USA). The weighed samples were digested in 100 mL glass beaker with concentrated nitric acid (20 mL) overnight. It is then mixed with 10 mL of concentrated nitric acid and perchloric acid (4:1) solution followed by hotplate heating at 120°C up to complete dryness. The residue was then dissolved and diluted with 20 ml of a solution of de-ionised water and conc. nitric acid (4:1) (v:v) and then this solution is filtered through No. 1 Whatman filter paper. Concentrations of metals except Hg were determined by using Inductively Coupled Plasma Optical Emission Spectrometer (Perkin Elmer, Optima 2100DV). Total mercury was determined by a Coleman Mercury Analyzer (MAS-50B) according to the method of cold vapour described by Hatch and Ott (1968). The precision of the analytical procedure was checked by analyzing standard reference materials of commercially available standards (Merck KGCA, 64271 Damstadt, Germany, ICP-Multielement standard solution IV, 23 elements in nitric acid). De-ionised water was obtained from a Millipore water system. All acids and chemicals used were of analytical reagent grade. Metal concentrations were calculated in microgrammes per gramme dry weight (μg metal g^{-1} d.w.). Laboratory glass wares were kept overnight in 10% nitric acid solution and rinsed with de-ionised water and air dried before use.

Table 1 Number of specimens (n), average length and total wet weight (Mean ± SD)

Species	*N*	Length (cm)	Total wet weight (g)	Concentration of metals (μg g^{-1})							
				Cd	Cr	Cu	Fe	Mn	Pb	Zn	Hg
E. chlorostigma	18	17.6 ± 7.09	95.5 ± 107.04	0.04 ± 0.03	0.13 ± 0.09	1.11 ± 1.87	1.72 ± 1.32	0.13 ± 0.08	0.27 ± 0.25	1.86 ± 0.79	0.03 ± 0.03
L. russelli	18	14.27 ± 2.32	48.5 ± 23.91	0.04 ± 0.03	0.16 ± 0.11	1.41 ± 2.06	1.87 ± 1.62	0.20 ± 0.13	0.21 ± 0.13	2.01 ± 0.88	0.09 ± 0.11
T. jarbua	18	16.1 ± 4.51	90.67 ± 82.76	0.01 ± 0.02	0.13 ± 0.15	1.49 ± 2.24	1.27 ± 1.11	0.16 ± 0.13	0.14 ± 0.10	2.23 ± 0.54	0.11 ± 0.12
C. arel	18	16.28 ± 1.94	58.33 ± 25.09	0.30 ± 0.65	0.32 ± 0.57	1.07 ± 1.72	1.46 ± 0.58	0.26 ± 0.24	0.09 ± 0.07	1.99 ± 0.61	0.11 ± 0.21
L. lunaris	18	15.82 ± 1.64	90.33 ± 27.05	0.00 ± 0.00	0.17 ± 0.25	1.43 ± 2.27	1.46 ± 0.99	0.11 ± 0.06	0.07 ± 0.02	1.92 ± 1.13	0.04 ± 0.10

Pearson Correlation Coefficient was employed for the better understanding of relationship between the concentrations of various metals using statistical package of SPSS 16.0 for windows. One way ANOVA was employed to understand the variation in the concentration of metals with respect to different species. Group linkage clustering technique was used for studying the similarities between metals at each station using statistical package of Primer 6.

Results and Discussion

In the present study, concentrations of Cd, Cr, Fe, Pb, Cu, Mn, Zn and Hg (μg g^{-1} dry wt) were determined in the muscle tissues of five fish species (*Epinephelus chlorostigma*, *Lutjanus russelli*, *Terapon jarbua*, *Cynoglossus arel* and *Lagocephalus lunaris*) collected from six landing centers along southeast coast of India. The distribution of metal concentrations in tissue samples of different species collected from different areas is given in Table 1 and 2. Metals showed significant variations in concentration with respect to fish species and areas. According to Pearson Correlation Coefficient, the metals were significantly correlated to each other at each sampling area at 0.05 level. One way ANOVA revealed that the concentration of metals was significantly varied with respect to different species ($p < 0.05$).

Among the five fish species, high concentration of Cd, Cr, Mn and Hg were observed in *C. arel* and high concentration of Cu and Zn were in *T. jarbua* (Table 1). It is found that the fish collected from Chennai, Cuddalore, Mudasalodai and Palayar were highly accumulated with the toxic metals such as Hg (0.24 ± 0.22 μg g^{-1}); Cd (0.35 ± 0.71 μg g^{-1}); Cr (0.51 ± 0.58 μg g^{-1}) and Pb (0.22 ± 0.27 μg g^{-1}), respectively. Among them, concentration of Cd in fish of Cuddalore and Cr in Cuddalore and Mudasalodai were above the maximum permissible limits recommended by FAO/WHO (1976). The concentrations of Mn in all the study areas were above the maximum permissible limits (Table 2). The essential elements such as Fe, Zn and Cu were highly accumulated in Karaikal (2.56 ± 0.76 μg g^{-1}), Pondicherry (2.92 ± 0.49 μg g^{-1}) and Mudasalodai (4.56 ± 0.48 μg g^{-1}), respectively.

Dendrograms are drawn for studying the similarities between metals at each station using group linkage clustering technique based on Bray Curtis coefficient of similarity (Figs. 2, 3 and 4). Cd and Hg got grouped at the highest level of similarity (100%) at Pondicherry, Mudasalodai and Karaikal. Cr and Mn at Karaikal and Cr, Mn and Hg at Palayar, were successively grouped at 100% level similarity. Further at Mudasalodai, cluster of Cr and Fe were formed at the next level of similarity (99%) and at Cuddalore, cluster of Cr and Mn were successively grouped at next level of similarity (96%). Followed by this, Mn and Pb were grouped between 90 and 95% similarity at Chennai and Pondicherry.

Fish are considered as one of the most susceptible aquatic organisms to toxic substances present in water (Alibabic et al. 2007). Marine organisms, including fish, may accumulate metals through direct absorption or via food chain and pass them to human beings, by consumption, causing chronic or acute disorder. Numerous reports described the metal residues in wild fish from marine species (Storelli et al. 2006: Dhaneesh et al. 2012a, b). In the present study, the spatial distribution pattern of Cd, Cr, Mn and Hg showed comparatively higher concentrations in Chennai, Cuddalore and Mudasalodai and concentrations of Cd, Cr and Mn were above the maximum permissible limits. High population and industrial effluent are the prime sources of metal contamination in coastal waters of Chennai and Cuddalore. In Mudasalodai, the anticorrosive and antifouling paints applied on the boats are found to be the source of metals. Sivaperumal et al. (2007) stated that, under certain environmental conditions, metals might accumulate up to a toxic concentration and cause ecological damages. So in the near future, an immediate risk may

Table 2 Concentration of metals accumulated in the muscle tissues of fishes collected from fish landing centers along southeast coast of India

Stations	Metal concentration (μg g^{-1})							
	Cd	Cr	Cu	Fe	Mn	Pb	Zn	Hg
Chennai	0.04 ± 0.04	0.09 ± 0.07	0.07 ± 0.06	2.46 ± 0.89	0.16 ± 0.09	0.18 ± 0.16	1.77 ± 0.49	0.24 ± 0.22
Pondicherry	0.02 ± 0.01	0.05 ± 0.03	0.03 ± 0.0	1.14 ± 0.54	0.10 ± 0.02	0.12 ± 0.12	2.92 ± 0.49	0.02 ± 0.03
Cuddalore	0.35 ± 0.71	0.30 ± 0.09	3.26 ± 0.87	0.24 ± 0.42	0.28 ± 0.19	0.07 ± 0.01	1.83 ± 0.44	0.08 ± 0.12
Mudasalodai	0.05 ± 0.07	0.51 ± 0.58	4.56 ± 0.48	0.50 ± 0.55	0.35 ± 0.10	0.14 ± 0.06	2.81 ± 0.53	0.05 ± 0.05
Palayar	0.01 ± 0	0.05 ± 0.01	0.06 ± 0.02	2.09 ± 0.26	0.05 ± 0.01	0.22 ± 0.27	1.22 ± 0.42	0.05 ± 0.05
Karaikal	0.01 ± 0.03	0.09 ± 0.06	0.06 ± 0.03	2.56 ± 0.76	0.09 ± 0.04	0.18 ± 0.16	1.55 ± 0.47	0.01 ± 0.03
WHO reference Standard	0.0–0.2	0.1–0.15	4–10	4–48	0.0025–0.005	0–1.5	58–150	0.50

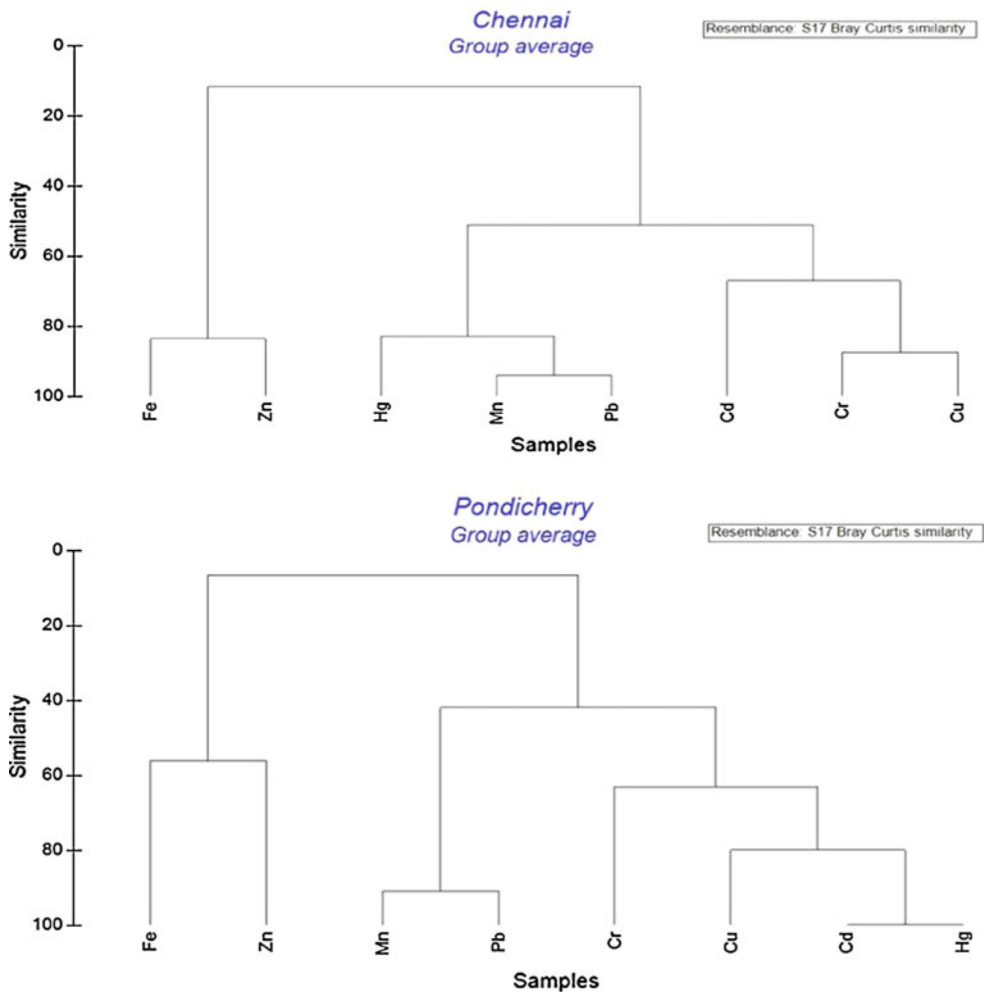

Fig. 2 Bray Curtis similarity index versus trace metals in Chennai and Pondicherry

be raised at Chennai, Cuddalore and Mudasalodai from metal pollution. While all the metal concentrations were accumulated comparatively low in the fish collected from Palayar, because of the absence of industrial effluents.

Metals are the source for common contaminations in the near shore marine environment adjacent to industrial activities and are ubiquitous in sewage discharge from urban areas. Among the five fish, the toxic metals Cd (0.30 ± 0.65 μg g^{-1}), Cr (0.32 ± 0.57 μg g^{-1}), Mn (0.26 ± 0.24 μg g^{-1}) and Hg (0.11 ± 0.21 μg g^{-1}) were highly accumulated in *C. arel* (Table 1). Another toxic metal Pb (0.27 ± 0.25 μg g^{-1}) was highly accumulated in *E. chlorostigma* collected from Palayar. Accumulation of chromium in fish is not a serious problem since the fish are able to eliminate it from the body. Chromium readily penetrates gill membranes by passive diffusion and concentrates at high levels in various organs and tissues. Flatfish are sensitive to pollution because they reside in bottom sediments where chemical contaminants are trapped. Flatfish utilize near shore habitats, where environmental degradation is likely to be the greatest, as nursery grounds. Since *C. arel* is dwelling in the benthic region, it may be a reason for the high accumulation of the metals obtained from the present study.

Cadmium is a serious contaminant, a highly toxic element, which is transported in the air. The proposed limit values for human consumption of fish reach approximately 0.2 μg Cd g^{-1} dry wt (FAO/WHO, 1976). In the present study, the highest value of cadmium was documented from Cuddalore (0.35 ± 0.71 μg g^{-1}) and it was above permissible limit. Manganese is an essential element for both animals and plants and its deficiency result in severe skeletal and reproductive abnormalities in mammals (Sivaperumal et al. 2007). Mn concentration was higher in fish collected from Mudasalodai (0.35 ± 0.10 μg g^{-1}) and lower level was shown in Palayar (0.05 ± 0.01 μg g^{-1}). As copper is an essential part of several enzymes and necessary for the synthesis of haemoglobin, most marine organisms have evolved mechanisms to regulate concentrations of this metal in their tissues. High concentration of Cu was in Mudasalodai (4.56 ± 0.48 μg g^{-1}) but it is within the permissible limits.

Zinc, an essential micronutrient for both animals and humans, has been a cofactor for nearly 300 enzymes in all marine organisms. As a constituent of many enzymes, Zn is

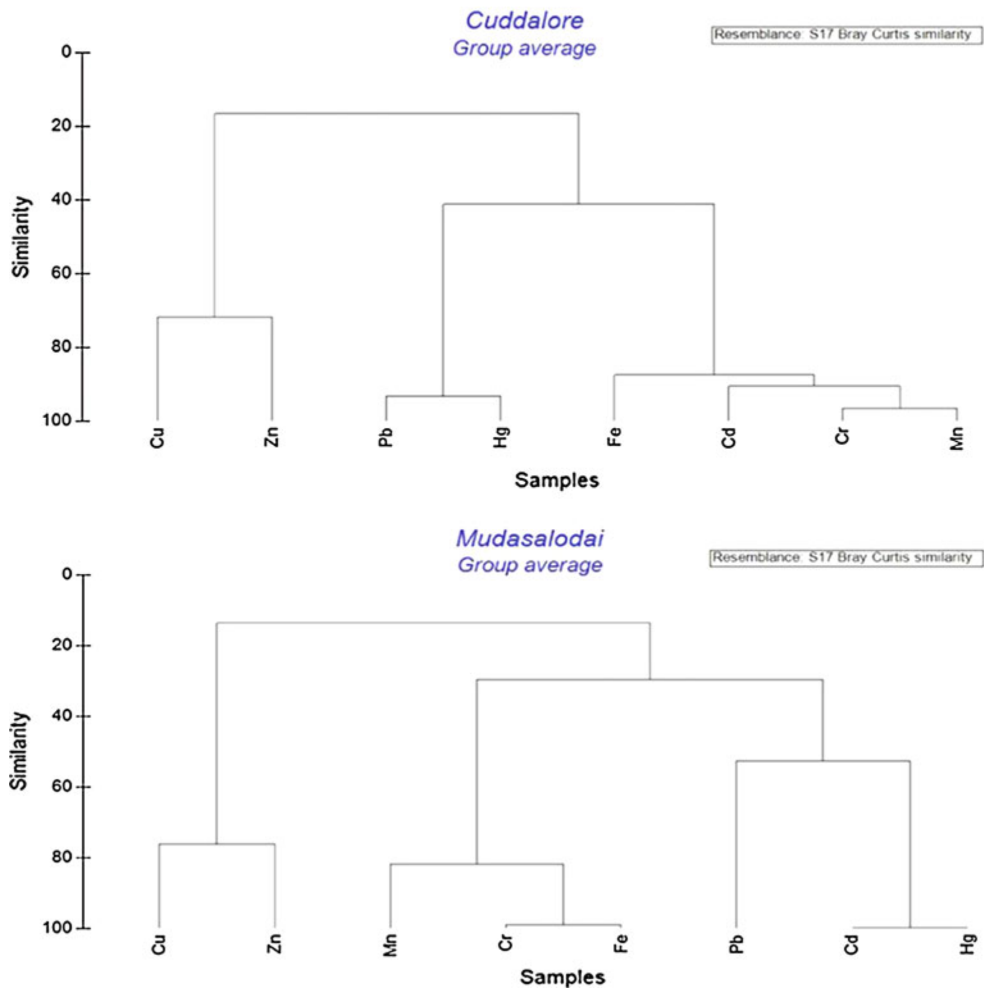

Fig. 3 Bray Curtis similarity index versus trace metals in Cuddalore and Mudasalodai

responsible for certain biological functions, for which a relatively high level is required to maintain them (Heath 2000). The recommended daily allowance is 10 mg/day in growing children and 15 mg/day for adults (NAS-NRC 1974). A deficiency of zinc is marked by retarded growth, loss of taste and hypogonadism, leading to decreased fertility. Zinc toxicity is rare but, the concentrations in water up to 40 mg/kg, may induce toxicity, characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite, and nausea (NAS-NRC 1974). In the present study, Zn concentration was higher in Pondicherry (2.92 ± 0.49 μg g^{-1}) and lower in Palayar (1.22 ± 0.42 μg g^{-1}). The highest Fe concentration (2.56 ± 0.76 μg g^{-1}) was observed in fish collected from Karaikal and this value is below the RDA (Recommended Dietary Allowance) recommended limit (NRC 1989).

Lead is a non-essential toxic metal that can affect humans when ingested or inhaled in high doses. In fish, it can cause deficits or decreases in survival, growth rates, development and metabolism, in addition to increased mucus formation (Burger et al. 2002). In the present study, the maximum accumulated level of lead was 0.22 ± 0.27 μg g^{-1} in Palayar and it is within the limits. Among the species taken for the analysis, mercury values (maximum 0.24 ± 0.22 μg g^{-1} in Chennai) are much below the proposed limit value for human consumption (approx. 2.5 μg g^{-1} dry wt, CSHPF 1995).

Chromium is a hazardous metal notified by the USFDA (1993), even though not covered by EC regulations for fish and other aquatic products. Chromium was detected in almost all the samples and the highest concentration was detected in Mudasalodai (0.51 ± 0.58 μg g^{-1}) but the values were above the limits of 12–13 mg/kg (USFDA 1993). The biologically usable form of chromium plays an essential role in glucose metabolism and it has been estimated that the average human requires nearly 1 μg/day. Deficiency of chromium results in impaired growth and disturbances in glucose, lipid and protein metabolism (Calabrese et al. 1985). The results presented on metal contents in the examined species gives an indication of the environmental conditions along southeast coast of India.

Among the six areas selected for study, three areas (Chennai, Cuddalore and Mudasalodai) were highly polluted with Hg, Cd, Cr and Mn. In addition to the industrial

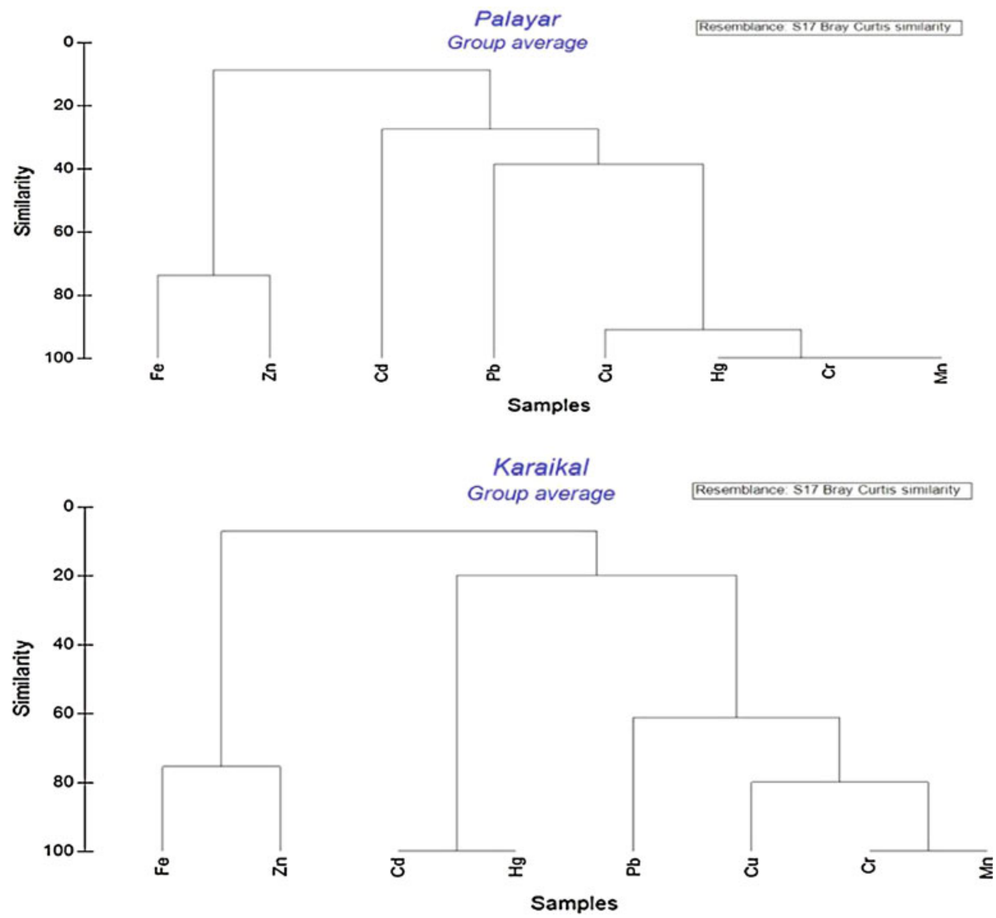

Fig. 4 Bray Curtis similarity index versus trace metals in Palayar and Karaikal

activities, anthropogenic introduction of pollution also resulted from local people. This study has enlightened the fact that persistent pollutants like metals should be regularly monitored and any variation from the normal distributional pattern can furnish an idea about the proper management of the coastal area. A competent monitoring programme is an essential adjunct to any attempt of managing the coastal areas in an ecologically sound and sustainable manner.

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