ORIGINAL ARTICLE

A baseline study of trace metals in a coral reef sedimentary environment, Lakshadweep Archipelago

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Abstract Surficial and core samples collected from the sedimentary microenvironments of Lakshadweep Archipelago were analysed for their trace metal contents. The synoptical relations in spatial distributions with respect to environmental conditions such as pH, organic carbon and sediment texture were inter-correlated. Some of the metals exhibited good correlations with Fe/Mn, which reflect their similarity in distribution rather than anthropogenic enrichment. Inter-relating the variations in metal—pH relationships with metal—organic carbon, in general, those which exhibited positive correlations with pH, displayed negative interactions with organic carbon content and vice versa. Comparatively, higher values of Fe in the mangrove area of one of the islands highlight the possibility of pre-cipitation of Fe as iron sulphides, which are common in mangrove ecosystem. Based on the contamination factors for Pb, Zn and Cd, as well as the geo-accumulation index of Cd, it can be generalised that some of the islands remain polluted with respect to these elements. An evaluation based on pollution load index shows that none of the islands surveyed for this study posed a serious threat in trace metal pollution. Bray Curtis similarity index was computed to find out the similarity among metals/islands, using non-transformed data of metal concentrations. Group linkage clustering technique was used for drawing dendrograms to show the similarity among them.

Keywords Trace metals · Coral reef sediments · Lakshadweep · Indian Ocean · Dendrograms

Introduction

Modern society drives us to an increasing use of a wide range of chemicals in industrial and agricultural practice. These chemicals, their breakdown products and by-products generated as part of their production will often end up in the final reservoir, the sea. The issue that arises in these circumstances is whether the presence of residual concentrations of these compounds represents a risk to humans and to biota in the marine environment (Michael et al. 2002).

Sediments act as a sensitive indicator for the monitoring of contaminants in a marine environment and, as a result, are essential components in many international monitoring programmes. Trace metals are introduced into the marine environment in a number of ways. The impact of trace metal pollution on coastal and estuarine areas could be substantial because of the variety of inputs to these areas; potential sources include riverine inputs, land runoff (both include treated and untreated sewage), industrial effluents, atmospheric deposition and coastal waters (Zwolsman et al. 1996; David 2002; Gregory et al. 2002). They may also be deposited in the sea "naturally" as a consequence of

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erosion from ore-bearing rock, wind-blown dust, volcanic activity and forest fires. Further, the concentration of trace metals in sediments reflects both logical mineralogy and the origin and nature of the sediments (e.g. grain size, clay, organic content, etc.).

Coastal reef areas are being heavily impacted by increasing trace metals from terrestrial origin, including runoff and river inputs. The detrimental effect of trace metals on the structure of coral reef communities is well documented. However, these effects on specific coral species have been more variable depending on the type and size of the sediment, frequently on the load, clearing ability, colony morphology and species resistance (Esslemont 2000; Elizalde et al. 2002; Anu et al. 2007).

The biggest problems with trace metals are that they are persistent (remain in the environment unchanged for years) and they bioaccumulate (increase in concentration as they go up the food chain). So, in addition to posing a threat to the health of coral reefs around the world, toxic metals also pose a long-term public health risk, especially for the human population that relies on fish for proteins.

In an area like Lakshadweep (Fig. 1), where the lives of people depend on their primary links to the ecosystem and productivity pattern is not so energy-intensive, the concept of pollution is very new. An evaluation is necessary to assess whether pollution from different sources is taking its toll on the ecosystem, in spite of being declared as a "no industry zone".

This study is focuses on the pattern of enrichment of trace metals (Cu, Cr, Co, Ni, Pb, Zn, Cd, Mn and Fe) in the different sedimentary environments of six inhabited islands, namely, Kavaratti, Kadamath, Minicoy, Androth and Kiltan (Fig. 1), belonging to the Lakshadweep Archipelago. To assess the inter-environmental variations of trace metals, the study area of each island is geographically located into several compartments such as core profile, lagoon profile and seaside profile. An artificial mangrove ecosystem of the Minicoy Island is also selected for an inter-ecosystem comparison (i.e. between reefs and mangroves).

Materials and methods

Study area

Lakshadweep is an archipelago consisting of 12 atolls, 3 reefs and 5 submerged banks. It is located between 8°–12°13′′N latitude and 71°–74°E longitude. It is 220–440 km away from the coastal city of Kochi in Kerala, India (Fig. 1). Lakshadweep has an area of 32 km^2 and it has ten inhabited islands, viz. Kavaratti, Agathy, Amini,

Androth, Kiltan, Kalpeni, Kadamath, Chetlat, Bitra and Minicoy.

Sampling procedure

The concentration levels of trace metals and their spatial distributional characteristics were studied among the sediments of Kavaratti, Kadamath, Minicoy, Androth, Agathy and Kiltan islands (Fig. 1). The sampling locations in the six islands of Lakshadweep Archipelago are also schematically marked in the station map. Sediment samples were collected using a specially fabricated stainless steel coring device. Sub-samples were carefully skimmed (excluding shells and leafy materials) and packed in polythene containers. These were kept in icebox storage for transportation to the laboratory and stored in deep freezers till all the analyses were performed. Lagoon transect samples were collected from four islands (Kavaratti, Kiltan, Kadamath and Minicoy islands) and seaside transect samples were collected from three islands (Kiltan, Kadamath and Agathy). Core samples were also collected, leading to the possibility of discussion on the basis of inter-island and intra-island variations. In Kavaratti, two cores were collected: one from the northern end and the other from the southern part, and so also for Androth, in which one core was collected from the land and near the sea. In Kiltan, only one core was collected from up to 1.3 m depth within the central part of the island. In order to have an inter-comparison of coral/mangrove ecosystems, sediment samples were also collected from the mangrove area in the Minicoy Island, which is considered to be a "virgin island" with respect to human interference.

Analytical techniques

Measurement of pH of the sediment samples was carried out by following the procedure of Jackson (1963). Sedimentary organic carbon was determined by adopting the procedure of Gaudette et al. (1974) with some modifications as per APHA (1992) procedure for those sediment samples, which have chloride interference.

For the determination of textural characteristics of the sediments, two techniques were applied. For sediments having particle size less than 63 μm, a particle analyser (Sympatec, Germany) was used. For sandy sediments, dry sieving was made using a Ro-Tap sieve shaker. A representative portion, about 15−20 g, was sieved for 15 min using a standard set of ASTM sieves at half phi (1/2 Φ) intervals. The standard classification for particles into Wentworth size classes was accepted to classify the textural characteristics of sandy sediments as coarse sand, medium sand, fine sand and silt-clay (Folk 1974).
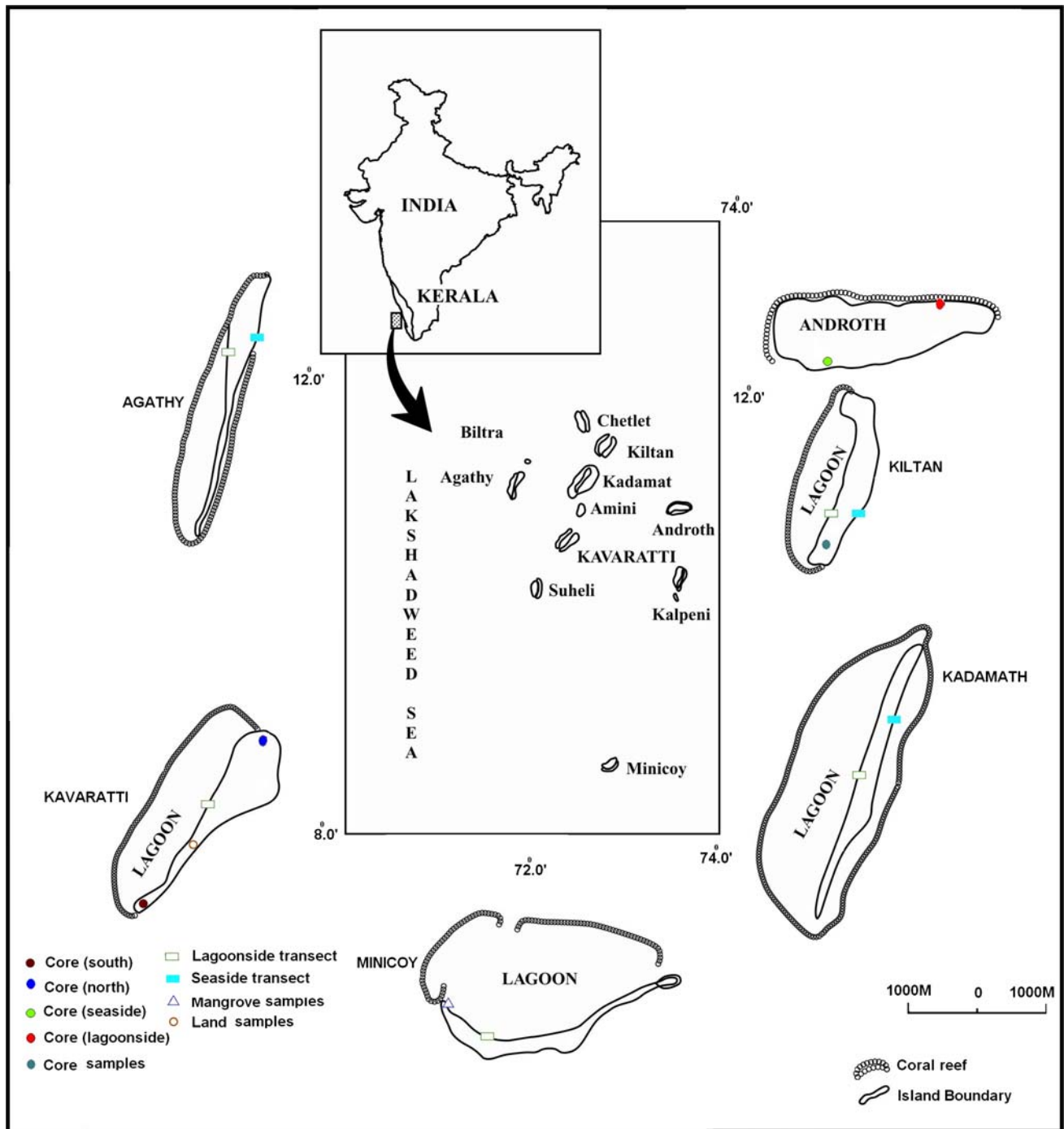
Fig. 1 Location map of Lakshadweep Archipelago and collection islands

For the determination of the total trace metals, the sediment was dried and powdered in an agate mortar. Approximately, 1 g of the homogenised sediment was digested with a mixture of concentrated HNO_3 and concentrated HCl in the ratio of 1:3 (aqua regia) at 95°C for 24 h (Johansson 1975; Young et al. 1992). The digest was dissolved in a minimum quantity of water and centrifuged

at 4,000 rpm. The supernatant liquid was filtered using a membrane filter of 0.45 μm pore size and the filtrate was made up to a definite volume. It was then analysed for trace metals, namely, Fe, Zn, Cu, Co, Cr, Cd, Mn, Pb and Ni using a graphite furnace atomic absorption spectrophotometer (Perkin Elmer: 3110). The precision of the analysis was performed by standard spiking technique of

quadruplicates and expressed as the coefficient of variation for each element: Cu 2.9%, Co 3.3%, Cr 3.1%, Cd 2.7%, Pb 3.9%, Zn 3.0%, Ni 2.0%, Mn 2.4% and Fe 2.5%.

Statistical analysis

Statistical method applied was three-way ANOVA: (1) for testing the difference in the concentration of trace metals with respect to south and north, among core depths and among metals at Kavaratti and Kiltan islands; (2) for testing the difference in the trace metal concentration with respect to south and north, among stations and among metals at Kiltan island; and (3) among islands, land lagoon variations and metals based on the trace metal concentration at Kavaratti, Minicoy, Agathy and Kiltan islands, using original data and standardised data. Having found these differences as significant, Student's *t* test was applied to determine the pairwise differences between core depths and stations and between lagoon types and land environments. Fromentin et al. (1993) have stated that the multivariate technique allows data sets to be summarised, but not designed to casually model the ecological phenomenon. In this study, the geographical space is described by the average distribution of the trace metals in the different media and their comparison through three-way ANOVA is mentioned. An ecological space is described by the step-up multiple regression technique (Anu et al. 2005), and the bioethological space is developed through the multivariate factor analysis by Q-mode and R-mode after row/column normalisation and varimax rotation to simple structure for uniqueness of the factor loadings obtained for grouping of locations/stations/depths and for grouping of metals in the various islands (dendrograms).

Results

The distributions of Cu, Cr, Co, Ni and Zn in the surface samples of the islands surveyed are given in Fig. 2a and b, whereas those of Pb, Mn, Cd and Fe are given in Fig. 3a and b. Depthwise distributions of Cu, Cr, Co, Ni and Pb in the core samples are represented in Fig. 4a and those of Zn, Mn, Cd and Fe are given in Fig. 4b. The mean values of quadruplet analyses are plotted in these figures.

In Kavaratti, distinct variations were observed in the behaviour of trace metals towards the northern as well as southern part of the island. In the northern side, Fe, Mn, Cu and Zn concentrations displayed maxima at the surface and the other metals (Cr, Co, Ni, Pb and Cd) showed maxima at

depth (~ 0.90 m). Whereas in the southern side, the surficial layer was capable of producing a maxima only for Fe and Mn, and for all other metals depthwise mobility was predominant. In Kiltan Island, Mn, Fe and Cd displayed maximum surface concentrations. For other elements, i.e. Cu, Cr, Co, Ni and Pb, surface minima were displayed followed by maximum enrichment at a deeper depth (1.30 cm). The core profiles of land and seaside samples of Androth Island also exhibited remarkable differences. In the land core, metals like Co, Ni, Pb, Fe, Zn and Mn exhibited maximum concentrations on the surface. Contrary to this behaviour, towards the seaside, except nickel, all other metals displayed minimum values towards the surface and their replenishment at various subsurface depths were very evident.

Justifying these observations, in Kavaratti, the surface samples are characterised by higher percentage of medium sand content and organic matter enrichment (22.27%). Compared to other depths, the pH was slightly decreased (Fig. 5), which can be a reason for the surface enrichment of redox-sensitive metals such as Fe and Mn. In Kiltan Island, organic carbon content at the surface as well as at 1.3 m depth was very high (28.69 and 31.33, respectively). Here also, the surface samples are characterised by high amount of iron and manganese, whereas, at 1.3 m depth maximum concentration of Cu, Cr, Co, Ni and Pb was found. Compared to other depths, the pH of the surface samples was slightly decreased. Regarding the textural characteristics, the surface samples were sandy (fine sand), whereas at 1.3 m depth, it was predominantly silty-clay. This pattern was reflected in the Androth Island also: Cu, Cr, Mn, Cd and Fe showed maximum enrichment at 1 m depths, which was characterised by high organic carbon content (14.10%) and a decreased pH.

Discussion

The redox-sensitive iron and manganese hydroxides and oxides under oxidation condition constitute a significant sink of heavy metals in aquatic systems (Wittmann 1983; Laluraj and Nair 2006). The distribution of some heavy metals studied was similar to that of Fe and Mn. This evidences the general feature that the hydroxides and oxides of Fe/Mn readily sorb or co-precipitate cations and anions; even a low percentage of $Fe(OH)_3$ has a controlling influence on the heavy metal distribution in an aquatic system. Iron oxide coating is an important factor responsible for the concentration of trace elements in the aquatic environment (David 2002; Komarek and Zeman 2004). Chemically, mobile elements are concentrated in fine particles than coarser bed sediments. Several investigations

Fig. 2 **a** Variability of Cu, Cr, Co, Ni and Zn in the surficial sediments of Kavaratti, Minicoy and Agathy islands. **b** Variability of Cu, Cr, Co, Ni and Zn in the surficial sediments of Kadamath and Kiltan islands
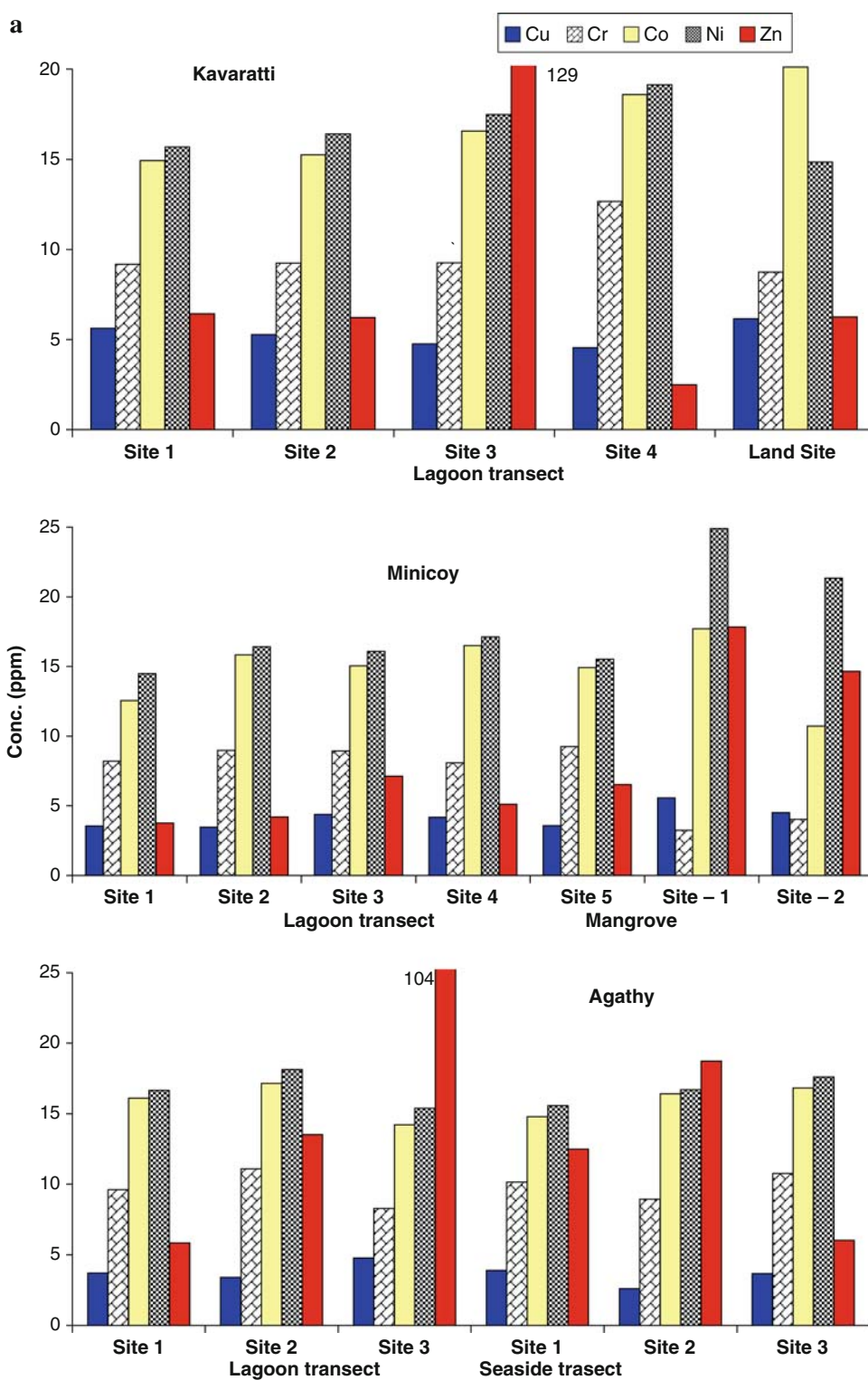
repeatedly advocate that the metal scavenging ability of sediments increases as the particle size decreases (Unni-krishnan and Nair 2004; Casey et al. 2007). Increased organic carbon levels in the fine particulates catalyse the metal scavenging ability.

Synoptic relations

The salient features of the spatial distributional character-istics of trace elements among the six islands can be inter-correlated as follows,

Fig. 2 continued
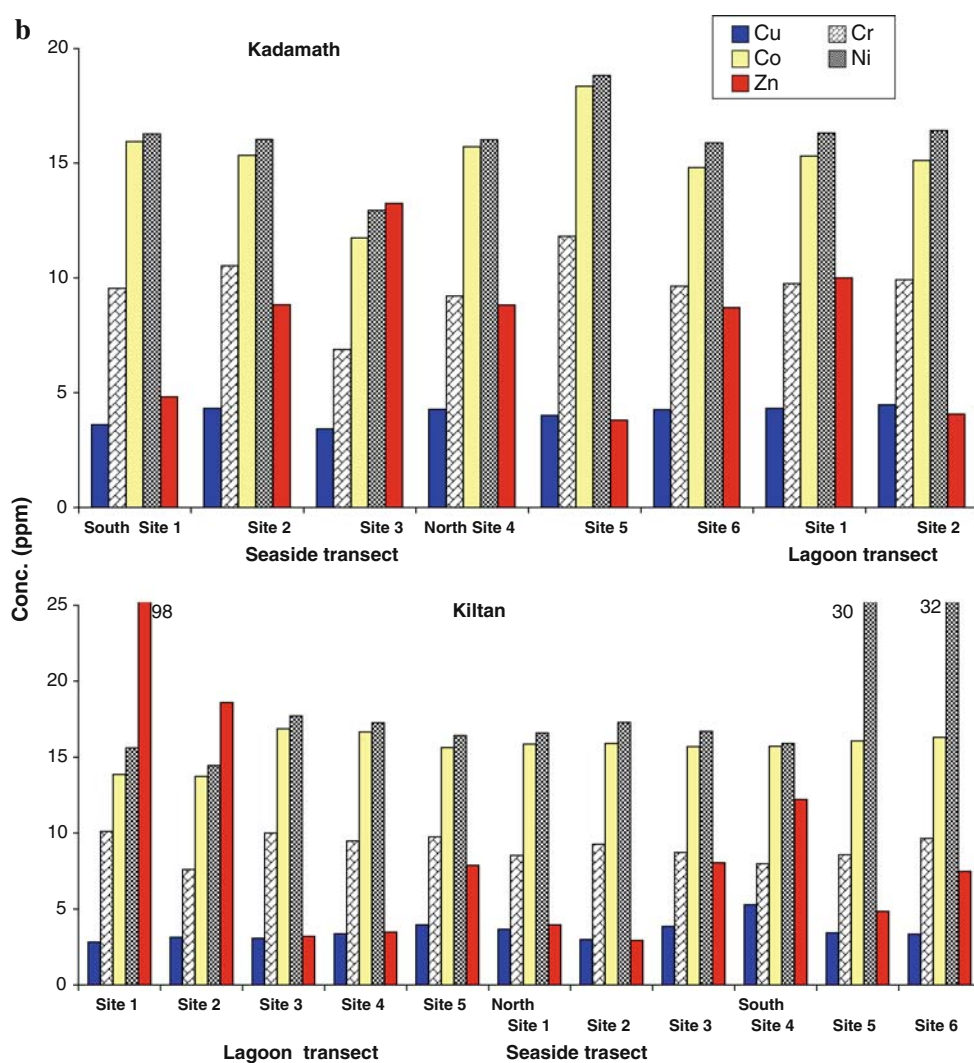
- Metal–metal inter-relation highlighting similar sources of input or chemo-behavioural pattern
- Metal–pH relationships reflecting redox-sensitive metal ad/desorption from sediments
- Metal–organic carbon co-variability focusing on metal webbing into biorhythm
- Metal–particle size/nature connectivity indicating the particle surface area/nature control on metal loading

Discussing the above facts, significant correlations were formulated by evaluating Pearson correlation coefficients for the dependent variables (Tables 1, 2, 3). Some of the metals exhibited good correlations with Fe, the values being less than that of Mn and vice versa, which may reflect their distribution rather than anthropogenic enrichment. Cobalt displayed significant positive correlations with Fe and Mn, attesting that cobalt occurs in association with Fe–Mn oxides, which are believed to be its common carriers (Neaman et al. 2004). The levels of significance of correlations exhibited were different for different metals, in

which low correlations indicate that these two metals behave differently from Fe and Mn, which are most strongly influenced by redox conditions (Griffin et al. 1989; Zwolsman et al. 1996). Considering the positive correlations exhibited by Ni with Fe and Mn in some islands, it was found to be (1) co-varying more strongly with manganese than with iron; (2) precipitated by sulphide ions in local regions of low oxidation potentials; (3) adsorbed by materials such as ferrous sulphide, hydrated ferric oxide and hydrated manganese.

Inter-relating the metal distribution with organic carbon content, except with some anomalies, metals were negatively correlated with organic carbon content. This attests the fact that organic carbon content alone cannot be a decisive factor in the mechanism of metal accumulation in sediments. The nature/texture of the sediments i.e. clay, silt or sand (since particle size relates to surface area), presence or absence of reducing environment, etc. are all equally important with respect to the metal enrichment capacity of

Fig. 3 a Variability of Pb, Mn, Cd and Fe in the surficial sediments of Kavaratti, Minicoy and Agathy islands.
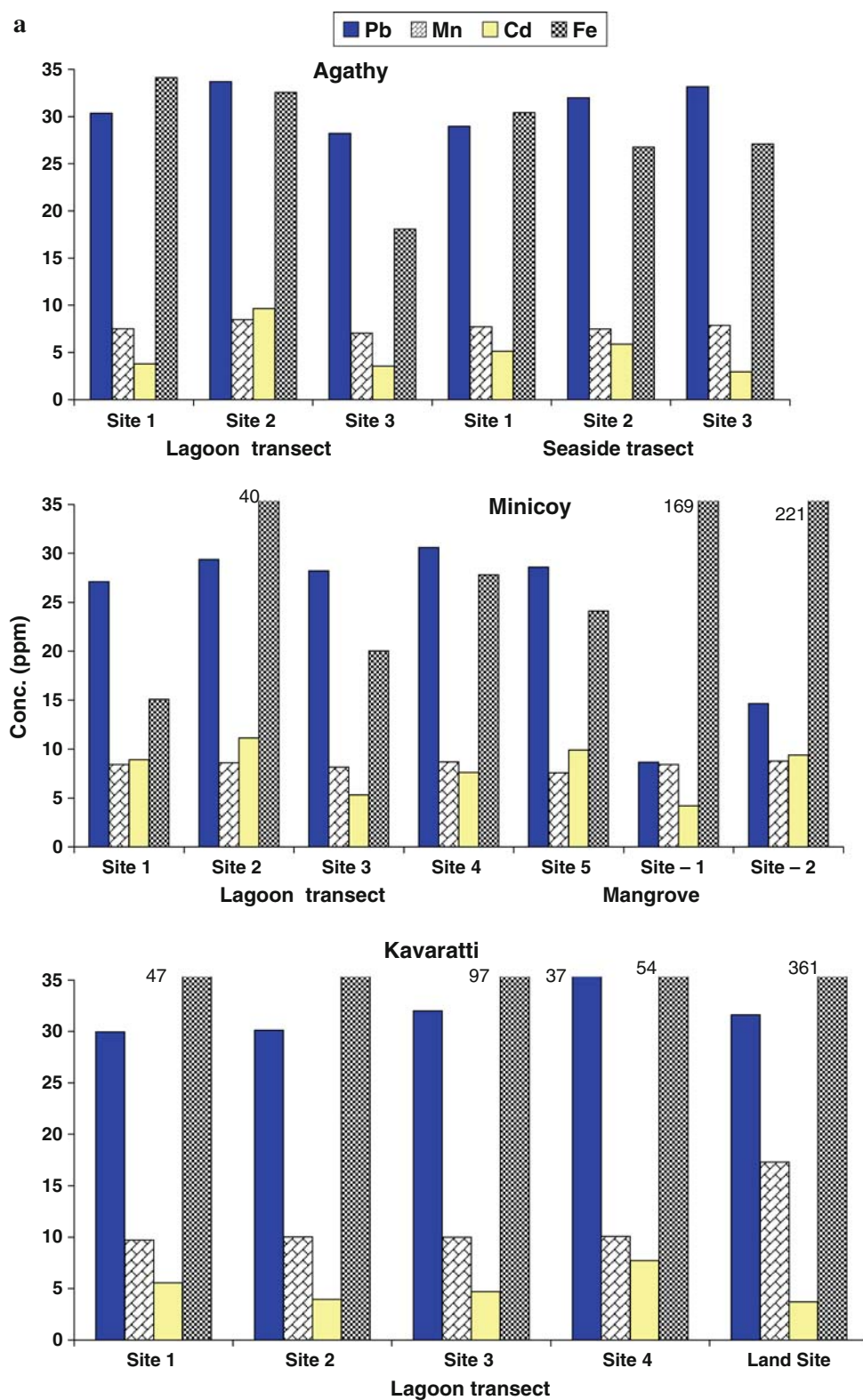**b** Variability of Pb, Mn, Cd and Fe in the surficial sediments of Kadamath and Kiltan islands

sediments. Generally, considering the variations of organic carbon content among the islands, enrichments were found only at some selected stations. Mangrove samples of Minicoy and soil surface samples of various islands showed organic carbon enrichment compared with the lagoon and seaside profiles. The higher organic carbon content of the surface soils corresponds to decrease in the content of $CaCO_3$ due to its dissolution by organic acids.

Fig. 3 continued
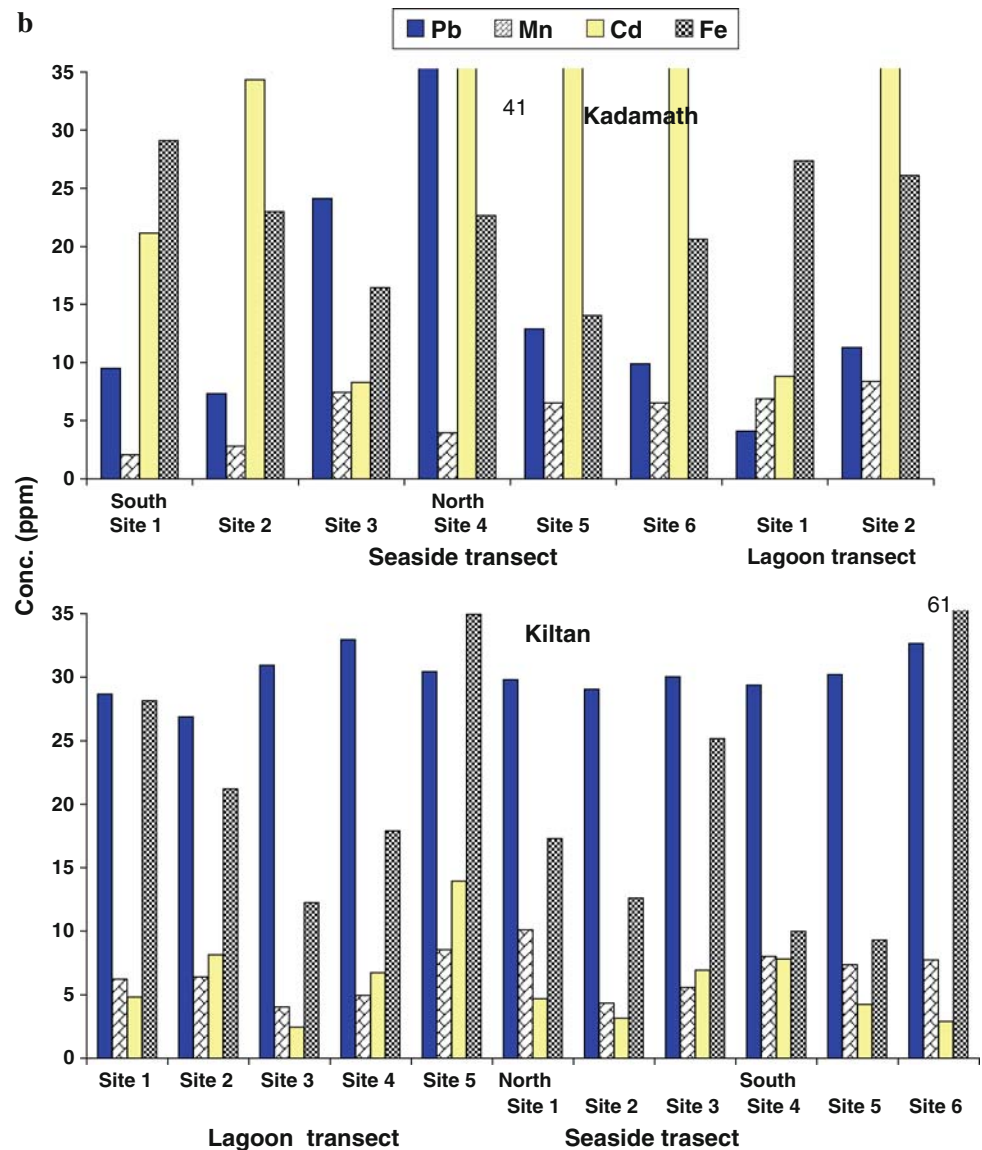
The difference in organic carbon content with depth may be considered as due to the variation in accumulation rates in these zones. The variations of pH with the organic carbon content are characterised by a decrease in pH. The lowering of pH is due to the acids released during the decomposition of accumulated organic matter. The chemical nature of bottom sediments and organic matter associated with sediments, play a major role in the cycling and concentration of many trace elements.

On comparing the metal–pH relationships with variations in organic carbon, it is viewed that those which exhibited positive correlations with pH displayed negative interactions with organic carbon content and vice versa, with some exceptions. Iron may be the most redox-sensitive element in aquatic systems to pH changes, forming new solid phases capable of scavenging other trace elements from solution with a rise in pH (Ranville et al. 2004). The redox-sensitive iron and manganese hydroxides under oxidising conditions constitute significant sinks of heavy metals in aquatic systems. These hydroxides readily adsorb or co-precipitate cations and anions. The reactivity of manganese in aquatic systems exhibits a complex behaviour with conservative and non-conservative nature depending upon the number of factors, such as the concentration in sediment, water and suspended particles, ionic strength, pH and Eh (Bucciarelli et al. 2001; Watmough et al. 2007). The major portion of copper in tropical seawater has been found to be associated with organic matter. Some of the characteristic observations regarding the behaviour of Ni in Minicoy were the significant positive correlation exhibited with organic carbon and a negative correlation with pH.

Fig. 4 **a** Variability of Cu, Cr, Co, Ni and Pb in the core samples of Kavaratti, Androth and Kiltan islands. **b** Variability of Zn, Mn, Cd and Fe in the core samples of Kavaratti, Androth and Kiltan islands
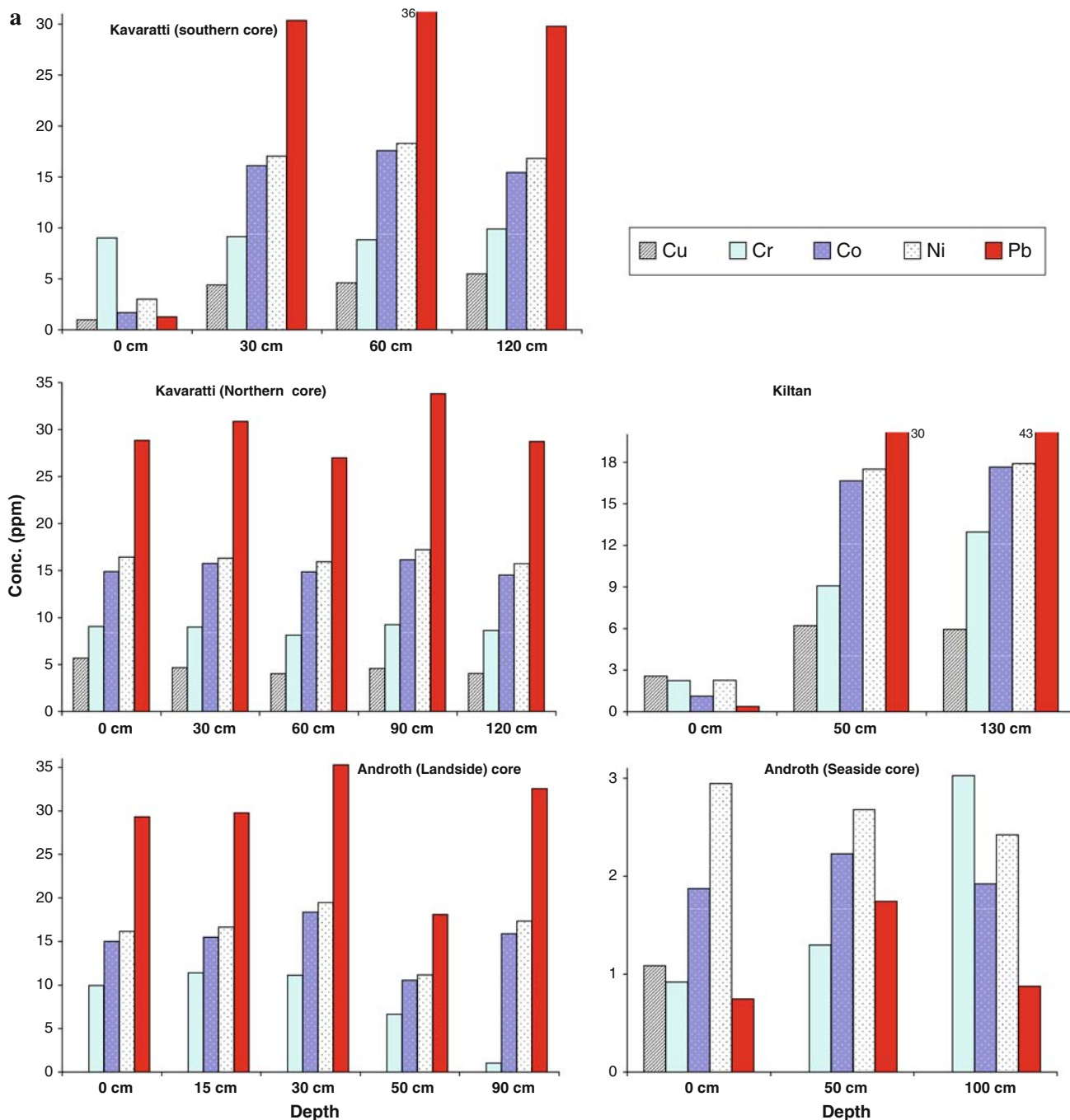
The seasonal production of biogenic particles only tends to influence particle composition and partitioning when suspended loads are low and for those metals with a tendency to concentrate in organic phases e.g. Cd and Cu. The Fe enrichment most likely results from reduction of Fe in the sediments during the oxidation of organic matter. In Lakshadweep Archipelago, most of the elements showed an increase in accumulative pattern with decrease in particle size (Table 3). This is evidenced by the fact that most of the metals exhibited affinity towards <63 μm-size fractions (Fig. 6), followed by very fine and fine sand fractions. This is well characterised in Androth in which all the metals displayed moderate negative correlations with sand fractions ranging from very coarse sand to fine sand. In Kadamath, Co, Cu, Mn and Fe were found to be associated with silt + clay fraction (<63 μm), as evidenced by
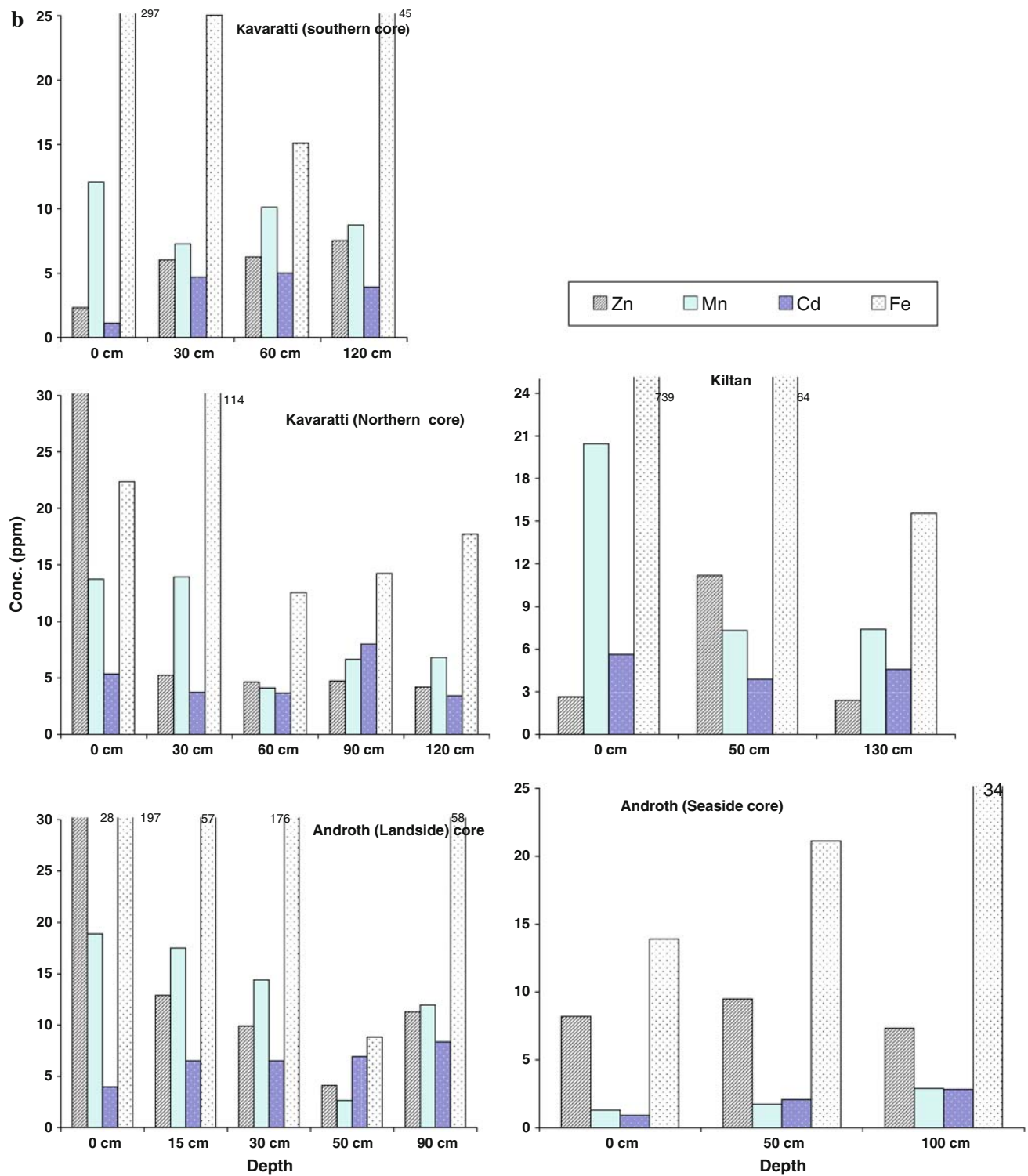
Fig. 4 continued

the positive value of Pearson correlation coefficients between the metals and silt + clay fraction of the sediment. Metals like Cr, Ni, Zn and Cd showed association with the fine sand fraction (250−125 μm). Zn and Cd

displayed an affinity towards very coarse sand in the Kadamath island, whereas Fe was associated with fine sand ($r = 0.683$). In Agathy, Cu and Zn correlated with the very coarse sand fractions. In addition to medium sand, Cr, Co,
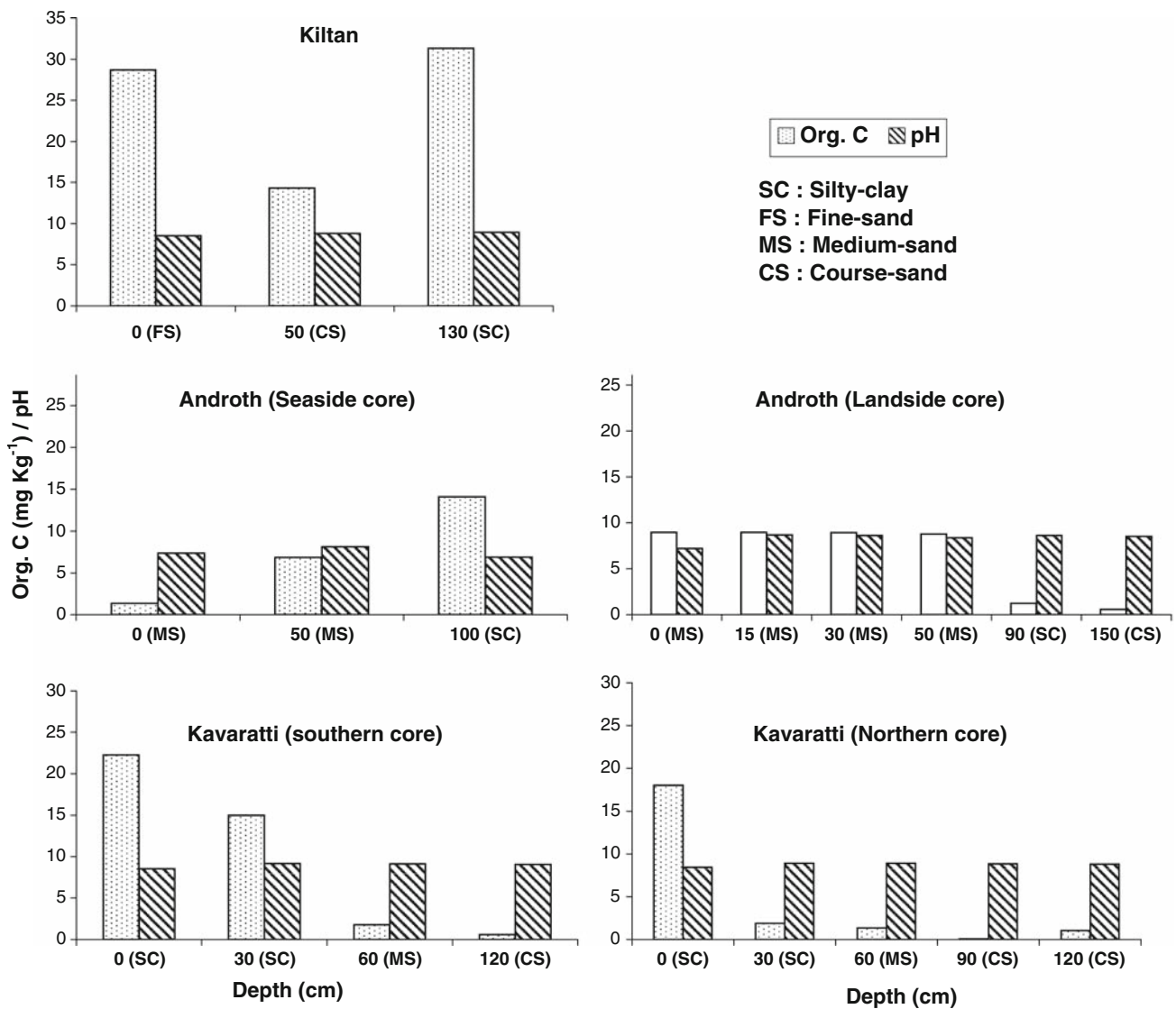
Fig. 5 Depthwise variability of organic carbon, pH and sediment nature in core samples

Ni, Pb and Mn in this island showed affinity towards the silt + clay faction. Iron was strongly correlated with the fine sand fraction ($r = 0.925$), whereas for Cd the affinity was towards coarse sand as well as very fine sand fractions. In Androth, all the metals displayed association with silt + clay as well as very fine sand fractions, whereas negative correlations were displayed by other fractions (very coarse sand–fine sand).

Higher concentrations of Fe and Mn in the clay fraction compared to that in the bulk fractions were found because these elements get precipitated on the surface area of silt + clay, which is comparatively flat, and also flocculate along with organic carbon, which can hold more of the precipitate (Mohan 1997). The fine size silt + clay particles are held in the precipitates, form as a floc in the alkaline

environment and get deposited (Gustafsson et al. 2000). Comparison of the enrichment pattern of different elements with that of Fe and Mn in different size fractions (Table 3) highlights that similarity in metal enrichments is controlled by Fe and Mn hydroxide phases in the alkaline environment. Fine-grained sediments with low carbonate content are characterised by higher concentrations of trace elements than coarse-grained sediments with higher carbonate.

Mangrove variability in the Minicoy Island

In the Minicoy Island, an artificial mangrove habitat is created, which is considered to be a virgin area. This is in the formative stage and is free from serious human interaction. Mangrove ecosystems are one of the major types of

Table 1 Summary of correlation coefficients among the metals, organic carbon and pH in Kavaratti, Kadamath and Minicoy islands

Island	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	Org. C	pH
Kavaratii											
Cu	1.000										
Cr	0.066	1.000									
Co	0.843	0.209	1.000								
Ni	0.760	0.268	0.914	1.000							
Pb	0.783	0.287	0.958	0.975	1.000						
Zn	0.120	−0.038	0.107	0.159	0.103	1.000					
Mn	0.225	0.043	0.025	−0.212	−0.123	0.103	1.000				
Cd	0.460	0.537	0.589	0.683	0.697	0.060	−0.108	1.000			
Fe	−0.220	−0.103	−0.301	−0.636	−0.515	0.010	0.708	−0.463	1.000		
Org.C	−0.345	−0.194	−0.511	−0.644	−0.640	−0.036	0.487	−0.377	0.568	1.000	
pH	−0.266	−0.166	0.294	0.310	0.365	0.141	−0.368	0.063	−0.404	–	1.000
Kadamath											
Cu	1.000										
Cr	0.552	1.000									
Co	0.414	0.932	1.000								
Ni	0.459	0.957	0.988	1.000							
Pb	0.255	0.864	0.921	0.937	1.000						
Zn	−0.077	−0.799	−0.904	−0.870	−0.820	1.000					
Mn	−0.075	0.543	0.584	0.655	0.794	−0.578	1.000				
Cd	0.034	−0.327	−0.397	−0.316	−0.332	0.310	0.069	1.000			
Fe	0.180	−0.030	0.018	−0.028	−0.337	−0.067	−0.420	−0.069	1.000		
Org.C	−0.252	−0.400	−0.423	−0.363	−0.434	0.211	0.068	0.837	0.294	1.000	
pH	0.110	−0.010	0.173	0.110	−0.060	−0.066	−0.196	−0.444	0.713	–	1.000
Minicoy											
Cu	1.000										
Cr	−0.829	1.000									
Co	0.311	0.091	1.000								
Ni	0.902	−0.945	0.194	1.000							
Pb	−0.836	0.969	0.040	−0.940	1.000						
Zn	0.889	−0.939	0.025	0.958	−0.968	1.000					
Mn	0.244	−0.454	−0.188	0.356	−0.275	0.193	1.000				
Cd	−0.824	0.418	−0.461	−0.510	0.459	−0.519	0.009	1.000			
Fe	0.690	−0.941	−0.268	0.882	−0.908	0.908	0.444	−0.192	1.000		
Org.C	0.876	−0.964	0.096	0.976	−0.987	0.975	0.262	−0.499	0.887	1.000	
pH	−0.487	0.809	0.417	−0.737	0.817	−0.807	−0.011	0.025	−0.456	–	1.000

natural wetlands in tropical and subtropical regions, flooded by fresh river water as well as by salty oceanic water. Salt marshes, particularly those located near or along estuaries such as mangrove forests, are often polluted by river-borne and marine-derived particles and pollutants (Tam and Wong 1995). As in other coastal marshes, mangrove sediments are reduced and act either as sources or sinks of heavy metals (Thomas and Fernandez 1997).

On comparing the trace element concentrations reported for these mangrove samples with the lagoon profile of the Minicoy, except for Fe, Ni and Zn, lower values or more or less equal concentrations as that of lagoon samples were recorded. Higher values of Fe in the mangroves highlight the possibility of precipitation of Fe as iron sulphides, which are common in mangrove ecosystem. It is generally described as the principal metal that precipitates with sulphide compounds in anaerobic sediments and these sulphides form a major sink for heavy metals in the mangrove area. Comparing the trace elemental levels in the mangrove of the Minicoy Island with other mangrove

Table 2 Summary of correlation coefficients among the metals, organic carbon and pH in Apathy, Androth and Kiltan islands

Island	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	Org. C	pH
Agathy											
Cu	1.000										
Cr	−0.274	1.000									
Co	−0.730	0.670	1.000								
Ni	−0.547	0.743	0.964	1.000							
Pb	−0.674	0.693	0.970	0.971	1.000						
Zn	0.698	−0.727	−0.713	−0.590	−0.610	1.000					
Mn	−0.418	0.925	0.746	0.820	0.782	−0.645	1.000				
Cd	−0.435	0.430	0.450	0.497	0.489	−0.246	0.730	1.000			
Fe	−0.037	−0.303	−0.284	−0.469	−0.416	−0.232	−0.565	−0.769	1.000		
Org. C	0.002	−0.151	0.090	0.013	−0.139	−0.180	−0.184	−0.176	0.335	1.000	
pH	0.089	0.521	0.249	0.293	0.315	−0.343	0.215	−0.471	0.278	–	1.000
Androth											
Cu	1.000										
Cr	0.608	1.000									
Co	0.940	0.716	1.000								
Ni	0.945	0.703	0.999	1.000							
Pb	0.954	0.685	0.998	0.999	1.000						
Zn	0.302	0.378	0.287	0.291	0.298	1.000					
Mn	0.921	0.753	0.865	0.870	0.874	0.552	1.000				
Cd	0.784	0.420	0.833	0.826	0.832	−0.115	0.527	1.000			
Fe	0.621	0.680	0.724	0.723	0.719	0.458	0.762	0.323	1.000		
Org. C	−0.113	0.193	−0.257	−0.269	−0.256	0.268	0.100	−0.310	−0.007	1.000	
pH	0.666	0.405	0.731	0.725	0.725	−0.231	0.454	0.793	0.285	–	1.000
Kiltan											
Cu	1.000										
Cr	0.419	1.000									
Co	0.430	0.881	1.000								
Ni	0.094	0.541	0.668	1.000							
Pb	0.498	0.959	0.950	0.618	1.000						
Zn	−0.209	0.136	−0.048	−0.084	−0.004	1.000					
Mn	−0.138	−0.777	−0.881	−0.525	−0.803	−0.138	1.000				
Cd	0.065	−0.103	−0.077	−0.291	−0.066	−0.012	0.119	1.000			
Fe	−0.294	−0.826	−0.961	−0.612	−0.898	−0.115	0.914	−0.012	1.000		
Org. C	0.358	−0.165	−0.473	−0.466	−0.252	−0.178	0.577	−0.146	0.607	1.000	
pH	−0.404	0.041	0.523	0.412	0.448	−0.533	−0.687	−0.434	−0.304	–	1.000

ecosystems, it can be attested that the Minicoy Island remains virgin with regard to trace metal pollution.

Pollution indices

Metal pollution in estuarine, harbour and coastal environment is usually caused by land runoff, mining activities, stripping and dredging activities and anthropogenic inputs. Sediments in such affected domain not only record its history, but also indicate the degree of pollution. The extent of contamination of aquatic sediments has been earlier quantified by comparing with an uncontaminated natural background for a specific constituent (Turekian and Wedephol 1961; Forstner and Muller 1973). An assessment based on pollution load index (PLI) has been employed to assess the extent of pollution by metals in sediments as suggested by Tomlinson et al. (1980).

According to this, PLI can be evaluated using the equation

Table 3 Correlations between metals and sediment particle sizes

Sediment particle size	Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe
Kavaratti									
>1,000 mm	−0.365	−0.114	−0.316	−0.305	−0.266	−0.202	−0.529	−0.478	−0.075
1,000−500 mm	−0.418	−0.227	−0.325	−0.274	−0.225	−0.269	−0.457	−0.421	−0.163
500−250 mm	−0.220	−0.150	−0.285	−0.124	−0.112	−0.132	−0.195	−0.013	−0.309
250−125 mm	0.120	0.554	0.091	0.279	0.190	0.472	−0.041	0.477	−0.269
125−63 mm	−0.070	−0.162	0.023	0.011	−0.055	−0.137	−0.080	−0.055	0.002
<63 mm	0.318	−0.279	0.313	0.007	0.071	−0.173	0.528	−0.129	0.545
Kadamath									
>1,000 mm	−0.398	−0.559	−0.620	−0.583	−0.396	0.548	0.033	0.797	−0.520
1,000−500mm	−0.287	−0.283	−0.401	−0.442	−0.275	0.551	−0.239	0.314	−0.589
500−250 mm	0.049	0.358	0.596	0.512	0.446	−0.291	0.264	−0.483	0.372
250−125 mm	0.074	0.225	0.164	0.212	0.008	−0.236	0.157	−0.183	0.683
125−63 mm	0.407	0.052	−0.059	0.061	−0.080	−0.445	−0.110	−0.053	0.288
<63 mm	0.421	0.076	−0.037	0.085	−0.057	−0.456	−0.089	−0.064	0.284
Agathy									
>1,000 mm	0.714	−0.773	−0.786	−0.692	−0.683	0.998	−0.881	−0.196	−0.871
1,000−500 mm	0.189	−0.800	−0.686	−0.824	−0.789	0.498	−0.758	0.514	−0.175
500−250 mm	−0.415	0.893	0.804	0.870	0.848	−0.748	0.906	−0.295	0.450
250−125 mm	−0.394	0.404	0.513	0.411	0.263	−0.738	0.421	0.023	0.925
125−63 mm	−0.687	−0.362	0.311	0.183	0.409	0.021	−0.105	0.627	−0.298
<63 mm	−0.045	0.693	0.578	0.751	0.715	−0.311	0.623	−0.613	−0.018
Androth									
>1,000 mm	−0.623	−0.714	−0.549	−0.523	−0.548	−0.547	−0.613	−0.926	−0.674
1,000−500mm	−0.631	−0.732	−0.565	−0.554	−0.562	−0.570	−0.633	−0.813	−0.683
500−250 mm	−0.630	−0.731	−0.565	−0.554	−0.561	−0.570	−0.633	−0.811	−0.682
250−125 mm	−0.640	−0.740	−0.570	−0.553	−0.568	−0.573	−0.638	−0.870	−0.693
125−63 mm	0.538	0.649	0.463	0.446	0.460	0.466	0.537	0.807	0.596
<63 mm	0.645	0.744	0.577	0.562	0.574	0.580	0.645	0.856	0.697
Kiltan									
>1,000 mm	0.330	0.101	0.305	0.324	0.153	0.453	−0.495	−0.149	−0.362
1,000−500 mm	−0.309	0.244	0.309	0.373	0.188	0.848	−0.545	0.079	−0.490
500−250 mm	−0.314	−0.142	0.020	0.018	−0.103	−0.385	0.167	0.587	−0.035
250−125 mm	−0.601	−0.846	−0.813	−0.823	−0.835	−0.403	0.930	−0.012	0.826
125−63 mm	−0.385	−0.861	−0.883	−0.891	−0.891	−0.340	0.902	0.013	0.939
<63 mm	0.388	0.401	0.093	0.056	0.359	−0.277	−0.004	−0.280	0.029

$$\mathrm{PLI} = n\sqrt{\text{product of n number of CF values}}$$

where CF = contamination factor, N = number of metals.

The contamination factor (CF)

$$= \frac{\text{metal concentration in sediment}}{\text{background value of the metal}}$$

Geo-accumulation index (I_{geo}), a pollution indicator, which takes into account natural background as well as variation with rock types (lithogenic effect), is calculated using the equation (Muller 1979)

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

where C_n = the measured concentration, B_n = the background value (world shale average) of element "n".

In an attempt to summarise the results of this study, contamination factors (CF), PLI and geo-accumulation index (I_{geo}) have been evaluated for all the metals studied both in the lowest and highest ranges of concentrations. The values of various pollution indices, CF, PLI and I_{geo}, calculated for the trace metals Cu, Cr, Co, Ni, Pb, Zn, Mn, Cd and Fe along the six islands are given in Table 4. The

Fig. 6 Regression plots between metal concentrations and sediments having <63 (m fraction)
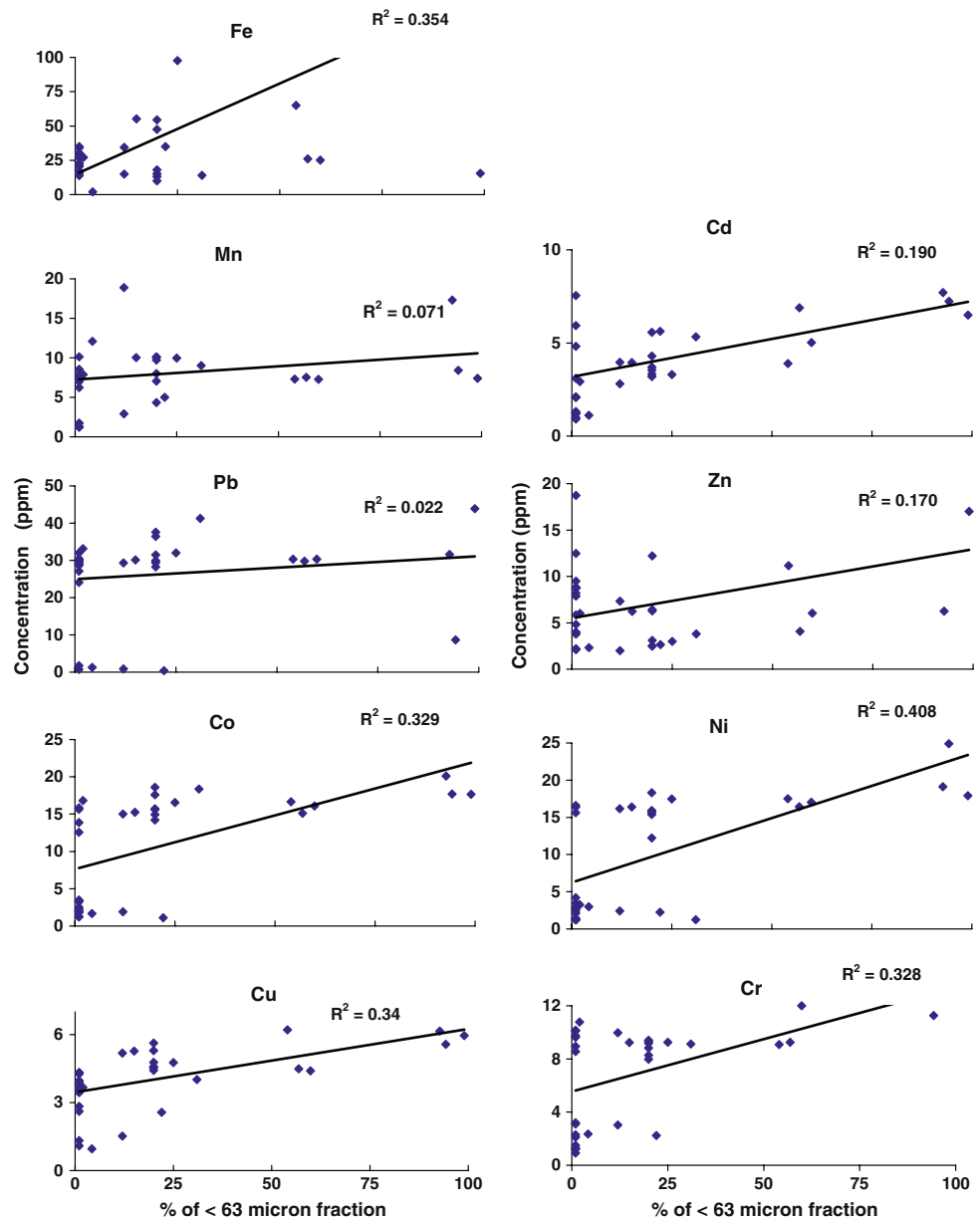
range of values of CF, PLI and I_{geo} of each trace metal is tabulated on the basis of islands surveyed, so as to project the data on a location/pollutant scale.

An evaluation based on PLI formulates the fact that the values of PLI recorded for all these islands were less than one. The geo-accumulation index (I_{geo}) was also in agreement with contamination factors recorded for the elements. Regarding the geo-accumulation index of heavy metals in the study area, elements except Cd can be included in the I_{geo} class zero (Muller 1979); the geo-accumulation index of cadmium was fond to be very high, ranging from 0.30 to 8.75. A contamination factor of less than one indicates the insignificant role of anthropogenic inputs such as industrial effluents, domestic sewage,

mining activities and land runoff towards the metal incorporation in sediments. Relatively, higher values of PLI have been reported for Vishakhapatnam harbour (1.45–1.78: Panigrahy et al. 1997), Vishakhapatnam inner harbour (PLI = 3.82, Satyanarayana et al. 1994), indicating gross pollution.

Statistical approach

At Kavaratti Island, on comparing the south and north, and core depths and trace metals, after standardizing the data for row and columns, it is observed that there is great difference between the north and the south ($F_{(1,32)} = 11{,}651.4$, $P < 0.01$) ($F_{(4,32)} = 2.1346$, $P < 0.05$) and also

**Table 4** Various pollution indices calculated for the six islands

Islands	Pollution indices	Trace metals									Pollution load index (PLI)
		Cu	Cr	Co	Ni	Pb	Zn	Mn	Cd	Fe	
Kavaratti	CF	0.02–0.23	0.09–0.14	0.09–1.06	0.04–0.28	0.06–1.88	0.02–1.37	0.005–0.153	3.7–26.7	0.00027–0.0353	1.7×10^{-6}–0.536
	I_{geo}	–0.001	0.022	0.026	0.015	0.011	0.009	0.002	0.335	0.0000520	
		0.051	0.027	0.152	0.042	0.174	0.049	0.006	6.671	0.0001546	
Kadamath	CF	0.08–0.10	0.08–0.13	0.62–0.97	0.19–0.28	1.21–2.06	0.04–0.14	0.009–0.011	15.37–45.03	0.00031–0.00063	3.6×10^{-4}–5.1×10^{-3}
	I_{geo}	0.026	0.021	0.125	0.036	0.153	0.014	0.002	4.899	0.0000552	
		0.032	0.026	0.147	0.042	0.179	0.026	0.003	8.347	0.0000704	
Minicoy	CF	0.08–0.12	0.03–0.10	0.57–0.93	0.21–0.37	0.43–1.53	0.04–0.19	0.009–0.012	14.03–37.1	.00033–0.0.0095	1.3×10^{-4}–2.03×10^{-2}
	I_{geo}	0.027	0.013	0.120	0.038	0.104	0.013	0.002	4.608	0.0000566	
		0.037	0.024	0.145	0.045	0.165	0.029	0.003	7.725	0.0001270	
Agathy	CF	0.06–0.11	0.09–0.12	0.75–0.90	0.23–0.27	1.41–1.69	0.06–1.09	0.009–0.011	9.77–32.16	0.00039–0.00074	4.6×10^{-4}–1.11×10^{-2}
	I_{geo}	0.021	0.023	0.134	0.039	0.161	0.018	0.002	3.446	0.0000604	
		0.033	0.026	0.144	0.041	0.169	0.047	0.003	7.268	0.0000737	
Androth	CF	0.02–0.14	0.01–0.13	0.09–0.97	0.04–0.29	0.04–1.76	0.04–3.02	0.002–0.024	3.03–27.87	0.00019–0.0038	3.2×10^{-7}–7.4×10^{-2}
	I_{geo}	0.002	–0.001	0.032	0.013	–0.014	0.014	0.000	–0.302	0.0000435	
		0.039	0.026	0.147	0.042	0.171	0.057	0.004	6.808	0.0001081	
Kiltan	CF	0.02–0.21	0.01–0.14	0.06–0.93	0.03–0.48	0.02–2.20	0.02–1.04	0.005–0.026	3.7–51.03	0.00020–0.0160	2.1×10^{-6}–0.227
	I_{geo}	–0.001	0.002	0.005	0.012	–0.048	0.009	0.002	0.335	0.0000459	
		0.048	0.027	0.145	0.049	0.182	0.046	0.004	8.748	0.0001381	

CF contamination facor, I_{geo} geo-accumulation index, *PLI* pollution load index
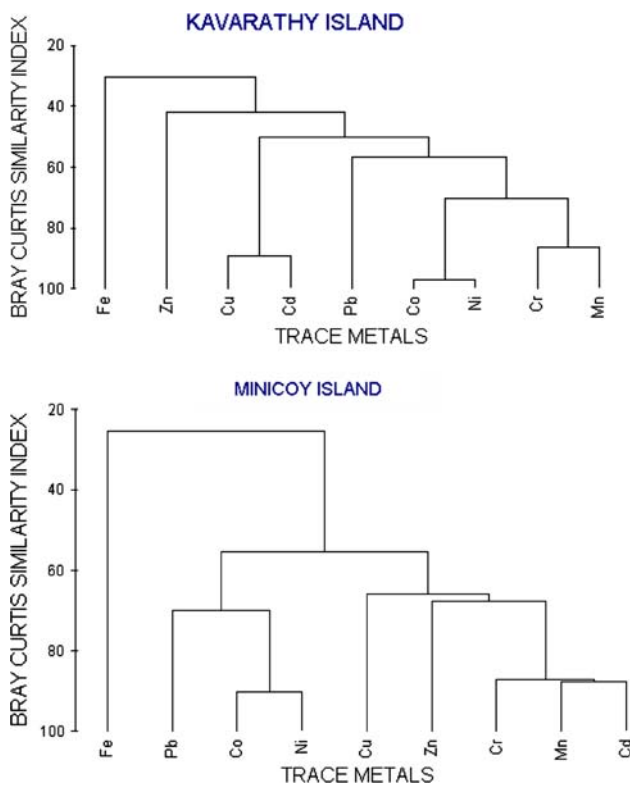
Fig. 7 Bray Curtis similarity index versus trace metals in Kavaratti and Minicoy islands
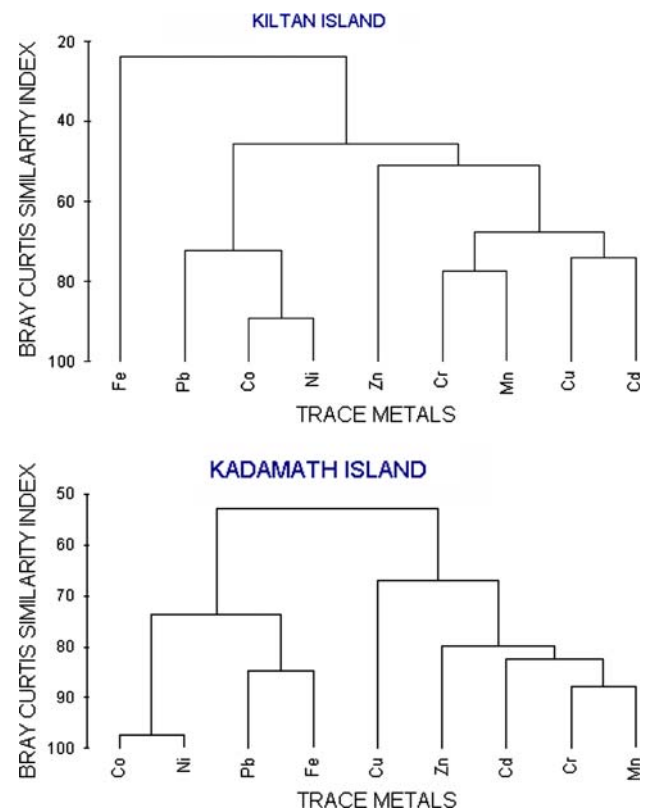
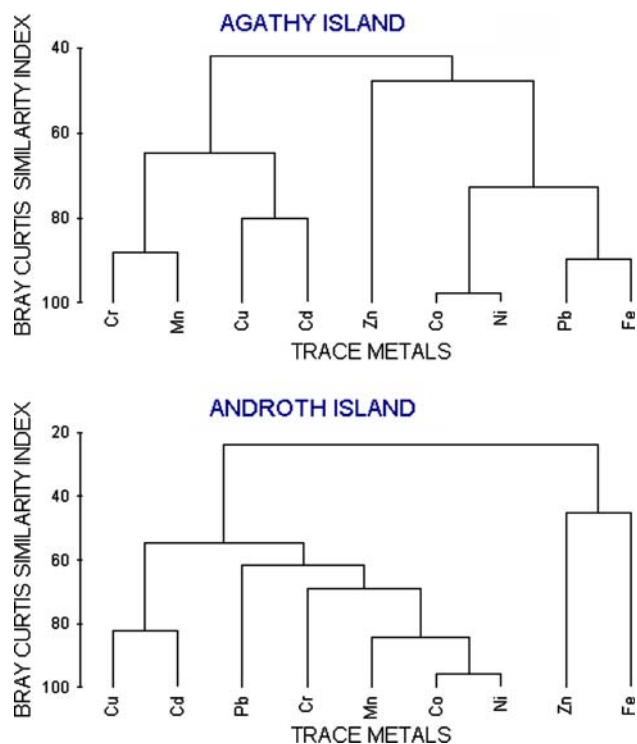Fig. 8 Bray Curtis similarity index versus trace metals in Kiltan and Kadamath islands

between core depths and metals ($F_{(8,32)} = 7{,}715.9$, $P < 0.01$). The distribution with respect to core depth showed that in the north, at the surface, the average metal concentration was only 50% of that in the south, whereas at 30 cm depth in the south, it was nearly 50% of that in the north. But at greater depths (core depths >60 cm), not much difference was observed between the north and the south for the average metal concentration as well as for the variation in the distribution. With respect to metals, great difference was observed between iron and other metals. On the basis of statistical analysis, the order of abundance of metals found was iron $>$ lead $>$ nickel $>$ cobalt $>$ chromium $>$ manganese $>$ zinc $>$ copper $>$ cadmium in the south, with a lead for zinc and manganese over chromium in the north. This reflects both natural and pollution aspects. Distribution was more stable for copper, cobalt, nickel, lead, cadmium and iron in the north than that at south.

Q-mode factor analysis based on row normalisation and varimax rotation to simple structure grouped the core depths of >60 cm at the south and north together as factor 1, with high negative factor loading. Factor 1 explains 64.25% of the spatial variations and it forms the differential factor group, indicating that this factor gives sufficient information on the trace metal distribution in this island. R-mode factor analysis based on column normalisation and

varimax rotation to simple structure has grouped the metals, copper, chromium, cobalt, nickel, lead, manganese and cadmium, together into group 1, which explains about 62.99% of the spatial variations. This factor forms the differential factor group indicating that additional metals considered do not add significantly to the information on the trace metal distribution in this island with regard to pollution aspects.

Manganese and iron are grouped together in second factor groups and zinc in the third, solving the difference in the distribution of the latter two group elements and association of manganese with iron.

At the Kadamath Island, the three-way ANOVA applied showed significant differences between south and north ($F_{(1,17)} = 394.465$, $P < 0.01$), among metal concentrations ($F_{(8,17)} = 3{,}757.58$, $P < 0.01$) and also to some extent among tidal levels ($F_{(1,32)} = 2.8492$, $P < 0.05$). Since the tidal level differences were not very great, only the interactions between the directions and the metals were highly significant ($F_{(1,32)} = 2{,}121.78$, $P < 0.01$). The average distribution of metals showed not much north−south differences, and also not much tidal differences, even though individual metals showed north−south differences with highest variation during high tide in the north (CV% = 78.45). During low tide (CV% <51.81), the

Fig. 9 Bray Curtis similarity index versus trace metals dendrograms in Androth and Agathy islands

variation was less than that at the surface and that during high tide. Based on the average distribution, the metals could be arranged as lead > iron > nickel > cobalt > chromium > zinc > manganese > cadmium > copper with the maximum spatial variation for zinc (38.38%) and the least for manganese (3.88%) in the south and the same ranking follows for the north also with zinc > Manganese > cadmium following the reverse order.

Q-mode factor analysis grouped the spatial locations into three factor groups, metal distribution at the surface and low tide in the south being similar to that during low tide in the north, forming the differential factor group (VE = 50.74%). The distribution of metal at the surface soil in the north is similar to that during high tide in the south and forms the factor group 2. These two distributions are highly different from that during high tide in the north. R-mode factor analysis grouped the metals into four factor groups: lead, zinc and manganese forming factor group 1; nickel showing a unique distribution, constituting factor group 2; copper, chromium and cadmium linked with high positive factor loading, factor group 3; and these three together extract the maximum information about the trace metal distribution (differential factor group) with respect to tidal influence at this island. Cobalt and iron distributions show similar pattern with respect to tidal variation.

At the Kiltan Island, three-way ANOVA applied after row and column standardisation showed that there was

significant difference between stations as well as between metals ($P < 0.001$). All the first order interactions are also highly significant ($P < 0.05$). Average distribution of the trace metals in the south are all higher than that in north at all the stations. There is an increasing trend towards the sea side from the land side irrespective of the directions. At the south, there is less heterogeneity in the metal distribution, landward than seaward, whereas in the north more or less the same pattern of variation was observed at all the stations. Regarding the spatial distribution of the metals, the average metallic content in the south was greater than that in the north, with the highest value for iron in the south and for lead in the north. The average concentration ranks the metals in the form: iron > lead > nickel > cobalt > chromium > zinc > manganese > cadmium > copper in the south, whereas the order is lead > iron > nickel > cobalt > chromium > manganese > zinc > cadmium > copper in the north. In the south, iron is most affected by spatial variations, whereas cobalt the least. In the north, spatial variations affects the metal distribution in such a manner that iron is replaced by zinc.

Q-mode factor analysis applied for grouping of stations delineated three distinct factor groups. The first constituted stations at 50 and 100 m, and at the seaside in both south and north, with high negative factor loadings. The second factor group is unique with the only land station in the south. Factor group 3 contains stations mostly in the north, but with moderate positive factor loading. The grouping shows that north seaward stations have characteristics of both factor group 1 and that of the stations in factor group 3. The factor groups 1 and 2 form the differential factor groups. This again statistically designates the stations of factors 1 and 2 as sufficient in the sense that these provide maximum information on the trace metal concentration in this island.

R-mode factor analysis grouped the metals into three distinct factor groups containing the metals, copper, chromium, cobalt, nickel, lead and iron with high negative factor loading. Factor group 2 is formed by zinc and manganese, again with high negative factor loading. Cadmium and iron are distinct from the factor groups 1 and 2, as well as from each other forming factor groups 3 and 4, respectively. Moderate factor loading for iron in factor 1 shows its resemblance in distribution to that of other metals in group 1, and its high loading for factor 4 spells out its unique characteristic of being moderately abundant in the north and highly abundant in the south. Factors 1 and 2 (VE = 47.17 + 28.04 = 75.21, >50%) being the differential factor groups show that all the metals except cadmium are important in the study of pollution effect in this island.

Three-way ANOVA applied for the lagoon features at Kavarathy, Minicoy, Agathy and Kiltan islands showed

**Fig. 10** Bray Curtis similarity index versus lagoon characters dendrograms in Kavaratti and Kadamath islands
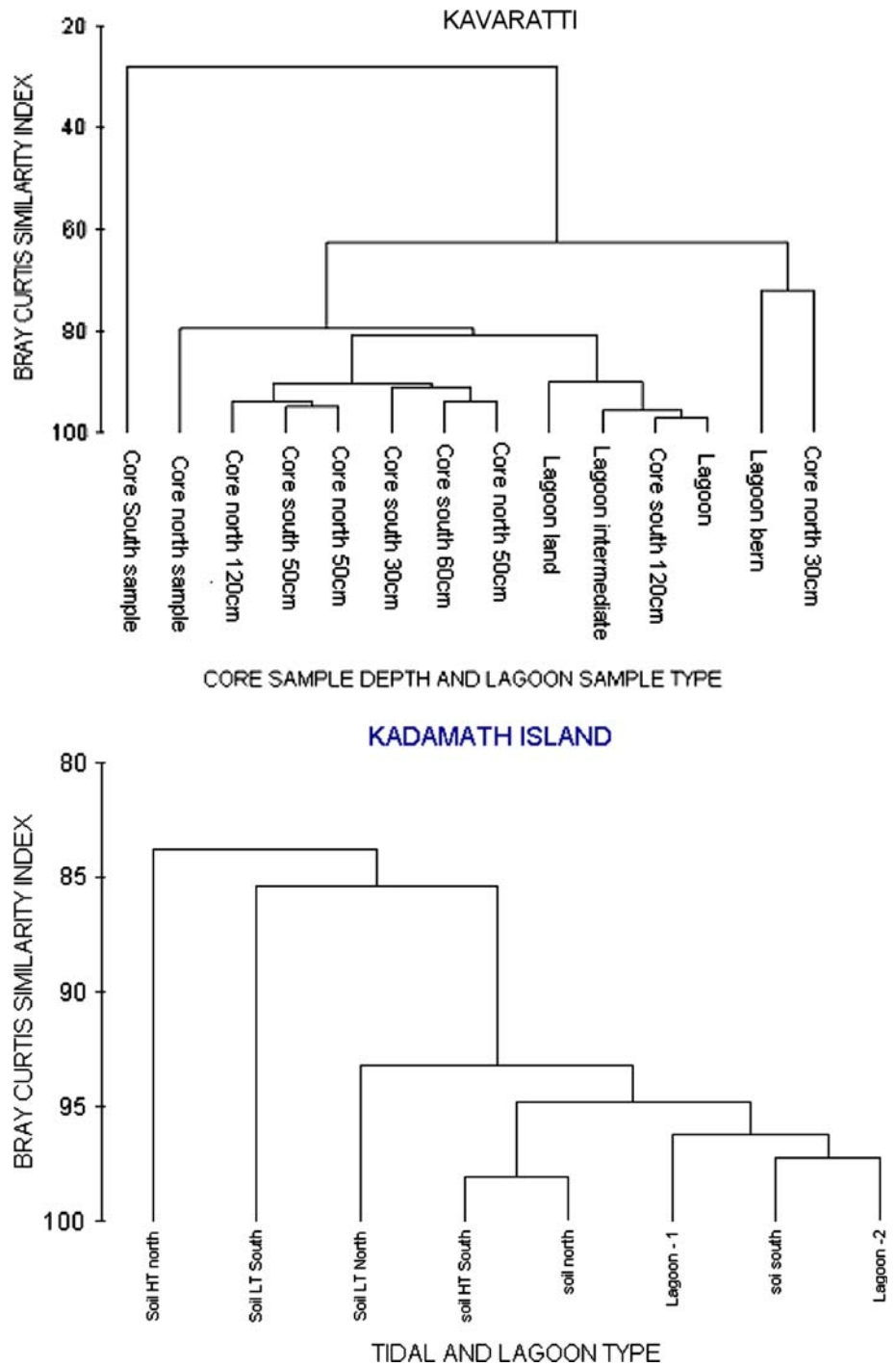
significant island-wise differences ($F_{(3,72)} = 2{,}377.26$, $P < 0.001$) and metal-wise differences ($F_{(8,72)} = 28{,}033.7$, $P < 0.001$). Lagoon feature–station interaction was moderately high ($P < 0.05$). So also station−metal interaction ($P < 0.001$), indicating that the distribution of metals differs with respect to island characteristics.

Q-mode factor analysis applied for grouping of lagoon features at the four islands showed that of the three factor groups, the first two are statistically significant (Eigen value, $\lambda > 1$). The first factor is the differential factor group explaining 50.02% of the spatial variability in the lagoon area. The factor 1 group contains invariably the intermediate area, berm area and the land area of the four islands, with all factor loadings being moderately highly negative. Factor group 2 contains lagoon 1 of Agathy and Kiltan islands and berm area of Kavarathy showing the similarity in the metal concentration of these spots, with high positive factor loadings. Factor group 3 is exclusively

Fig. 11 Bray Curtis similarity index versus lagoon characters dendrograms in Minicoy and Kiltan islands
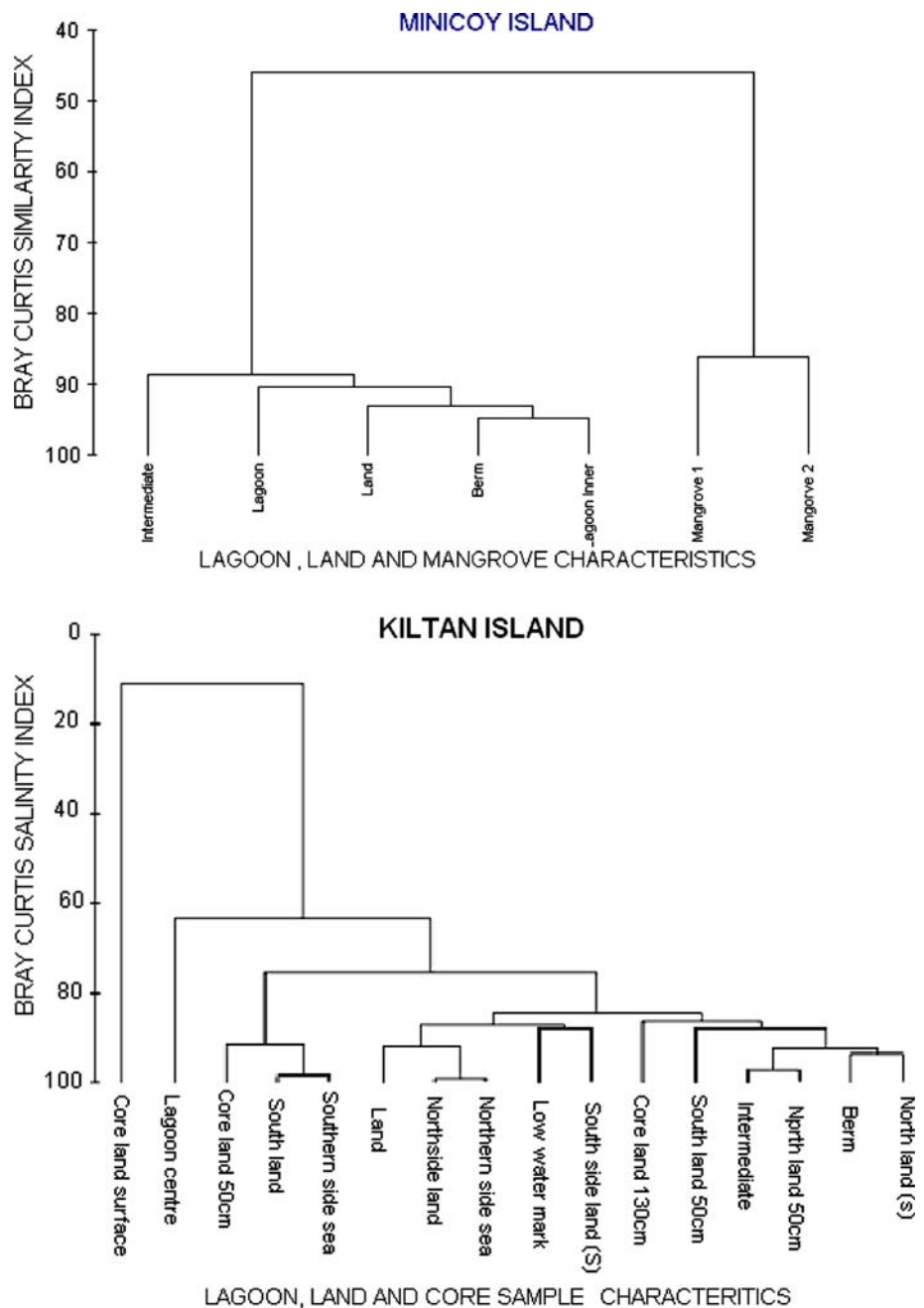
of the Kavarathy Island (except the berm); Minicoy intermediate area and Kiltan land area also show some characteristics common to these areas.

R-mode analysis applied for grouping trace metals in the lagoon area delineated three significant factor groups with factor 1 containing all the metals except zinc (factor group 2) and manganese (factor group 3). It is the differential factor group that explains 63.01% of the spatial variations. This analysis further indicates that factor group 1 provides almost all the information on pollution of the lagoon area of these islands.

Dendrograms are drawn for studying the similarities between: (1) metals at each island (2) station characteristics at each island (3) metals at different lagoons of the four islands and (4) lagoon features at the four islands using group linkage clustering technique based on Bray Curtis coefficient of similarity calculated on the normalised data (Figs. 7, 8, 9, 10, 11). At the Minicoy Island, two clusters of lagoon features are obtained, which clusters together the mangrove area and the lagoon area separately each with 85−90% similarity. At the Kiltan Island, three distinct and highly similar clusters are obtained with 85−100%

similarity. These clusters depict the differences between the north and the south and also landward and seaward differences as obtained under factor analysis. Dendrograms in this study show that, even though a non-parametric method, these can be used to replace exactly the results obtained with factor analysis, which is a parametric method with test of significance.

Conclusion

On summarizing the results, the following points can be abstracted,

- The six islands selected for study in Lakshadweep Archipelago remain unpolluted with respect to the six metals, viz. Cu, Cr, Co, Ni, Mn and Fe.
- Based on the contamination factors for Pb, Zn and Cd, as well as the geo-accumulation index of Cd, it can be generalised that these islands remain polluted with respect to these elements. The severe effect is from cadmium, as evidenced by high values of contamination factors and geo-accumulation index of this element.

Looking into the justification for this observation, one important factor is the oil-based power generation prevailing in these islands. For this, a large quantity of crude oil is used as a fuel source, which contributes to a large proportion of associated pollutants like Pb, Cd and Zn. Another factor is shipping activity, which contributes in two ways: one is contamination of these metals through oil and another is from antifouling coatings of ships, the major ingredient of which is lead. The major contribution towards pollution is from cadmium, compared to that of Pb and Zn, and this is very high in Kiltan. Lead is known to form colloids in seawater and such colloids could have settled down after gaining weight by adsorbing onto the surface of planktonic debris, which consequently resulted in higher concentration in the sediment.

Kiltan Island lies along the international shipping route. In September 1974, an American oil tanker "Transhuron", owned by Hudson Waterways Corporation and chartered by the US Navy, ran aground on Kiltan (NIO 1974). The tanker was badly damaged and its oil began to spill. It was carrying about 18,500 tonne of furnace oil from Bahrain to the Philippines. Nearly 3,000 tonne of oil leaked from the tanker into the sea creating oil pollution in a wide area. This incident might also have contributed to the enrichment of persistent inorganic pollutants such as Pb, Zn and Cd.

In terms of the population size of the islands, Androth is the most populated island (17.6%), followed by Kavaratti (16.8%). The highest contamination factors (Table 4) of Cu, Co, Mn and Fe were reported for Kavaratti. Androth comes in the third position, indicating that there can be some contributions from human activities towards the metal concentrations in these islands. With the exception of Kiltan, other islands displayed contamination factor in accordance with their population size.

Regarding the influence of agriculture on pollution, coconut constitutes 99% of the nett sown area, and it is the mainstay in agriculture and economy of Lakshadweep. In addition to this, there is cultivation of vegetables, banana, rice and others. The use of fertilisers makes a contribution, though not significant, to the PLI of metals in the Lakshadweep Archipelago.

Evaluating the role of industries to metal contribution, Lakshadweep is considered as a "no industry zone". There are certain minor industrial units working under public and private sectors. In 1993−1994, there were 29 units under the public sector, the majority of which were related to coir, coir processing and printing. Small establishments like saw mills, general workshops, carpentry units, etc. also function in Lakshadweep.

In addition to the activities of local inhabitants, anthropogenic introduction of pollution can also result from tourist activities. The multi-hued, shallow, placid lagoons with its myriad life forms are a feast to the eye and a life-long experience not easily matched. Being a centre of tourist attraction, activities related to tourism, for e.g. contribution of buildings and mode of transportations (boats/vessels) among these islands, play a significant role in the pollution load of some of the metals.

This study has enlightened the fact that persistent pollutants like heavy metals should be regularly monitored and any variation from the normal distributional pattern can furnish an idea about the proper management of the coral reef ecosystem. Life in Lakshadweep is very much dependent on reefs and its resources and therefore a well-defined understanding of the concerned ecosystem is necessary and can be beneficial. A competent monitoring programme is an essential adjunct to any attempt of managing coral reefs in an ecologically sound and sustainable manner.

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