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Trace Elements Contamination in Coral Reef Skeleton, Gulf of Mannar, India

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Abstract Coral samples were collected from Kurusadi, Shingle and Appa islands of Gulf of Mannar for analyzing the trace elements. The mean concentrations in the coral reef skeleton ranges from 0.19 to 0.62 μg g^{-1} for Fe, from 6.71 to 15.6 μg g^{-1} for As, from 0.28 to 1.31 μg g^{-1} for Cd, from 0.56 to 5.29 μg g^{-1} for Co, from 7.25 to 22.34 μg g^{-1} for Cr, from 0.63 to 5.08 μg g^{-1} for Cu, from 98.38 to 138 μg g^{-1} for Mn, from 0.18 to 2.53 μg g^{-1} for Ni, from 0.18 to 4.56 μg g^{-1} for Pb and from 44 to 135.25 μg g^{-1} for Zn. The factor analysis revealed the source of trace elements accumulation in the coral skeleton particularly Mn from detrital inputs and Cd from anthropogenic sources. This paper also highlights the nature of trace elements available in coral skeleton.

Keywords Trace elements · Coral reef skeleton · Contamination · Gulf of Mannar

Coral reefs are quite common in the tropical seas and oceans. They have been designated as the marine equivalent of the tropical rain forest. The precipitation of calcium carbonate by calcareous organisms in warm shallow water leads to the formation of coral reefs, which is one of the highly productive ecosystems in the world. Coral reefs play an important role in oceanic CO_2 budget in controlling the green house effect. Corals absorb trace elements into their skeletons from the surrounding water in which they grow. Also, the lattice bound trace metals in coral skeletal structure reflect their concentrations in surface water where the corals grew (Inoue et al. 2004). Therefore, the trace element levels in coral skeletons may function as good proxies for marine pollution. Mostly corals grow in a pristine environment, but are affected by near shore developmental activities such as coastal mining, harbor dredging, discharge of industrial and domestic effluents into the ocean, urbanization and over population (Anu Gopinath et al. 2009). Moreover, the biologically available Pb, Cu and Zn are spread over due to resuspension of sediments during dredging in the harbor channel and riverine inputs (Reichelt and Jones 1994). Therefore, the metal concentration in coral skeletal phase can be used to monitor the environmental metal loads at polluted sites (Esslemont 2000). The incorporation of heavy metals into the coral skeleton by calcium substitution of metals or through the association with particulate organic matter within skeletal pores is widely studied (Howard and Brown 1984).

The Gulf of Mannar coastal region is bestowed with 21 coral islands developed between Rameswaram and Tuticorin (Lat 8° 55′–9° 15′N and Long 78° 0′–79° 16′E). The area has been categorized as Marine Biosphere Reserve by the Government of India. The study area is also endowed with rich marine bioresources such as oysters, coral reefs, fishes etc. In the north eastern monsoonal period (October–December), the coastal region of the Gulf of Mannar receives copious rain and maximum sediment transport to the sea by the rivers such as Thamirabarani, Vaippar,

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Guntar, Karamanayar and Nambiyar. The impact of mining, other land based activities and natural process within the marine environment has been addressed in numerous studies of trace elements in corals (Esslemont 2000; Khaled et al. 2003; Inoue et al. 2004). But in the study area there is very little information available to the researchers on metal content in the coral skeletons. The aim of this study is to report the level of trace element concentration in the coral skeleton of the Gulf of Mannar, India.

Materials and Methods

Representative coral samples were obtained from 18 locations from three coral islands of the Gulf of Mannar, eight samples from Kurusadi Island and five each from Shingle and Appa Islands respectively (Fig. 1). Among them the Kurusadi Island has maximum areal extent followed by Shingle and Appa Islands. The samples were collected with in the reef area in a 1 km^2 area. The water depth in the area ranges from 2 to 5 m.

The samples were collected using stainless steel coated equipments and transferred to polythene bags for avoiding metal contaminations. The coral samples were initially washed with sodium hypochloride for 24 h, and then with distilled water. They were oven-dried at 60°C and powdered in an agate mortar. Loring and Rantala (1992) method was followed for analyzing trace elements in the coral samples. 0.5 g of powdered coral sample was digested in 25 mL of HCl and 15 mL HNO_3—HClO4 (5:1) acid mixture at 80°. The digested sample was centrifuged at 200 rpm and the centrifuged liquid was used for the

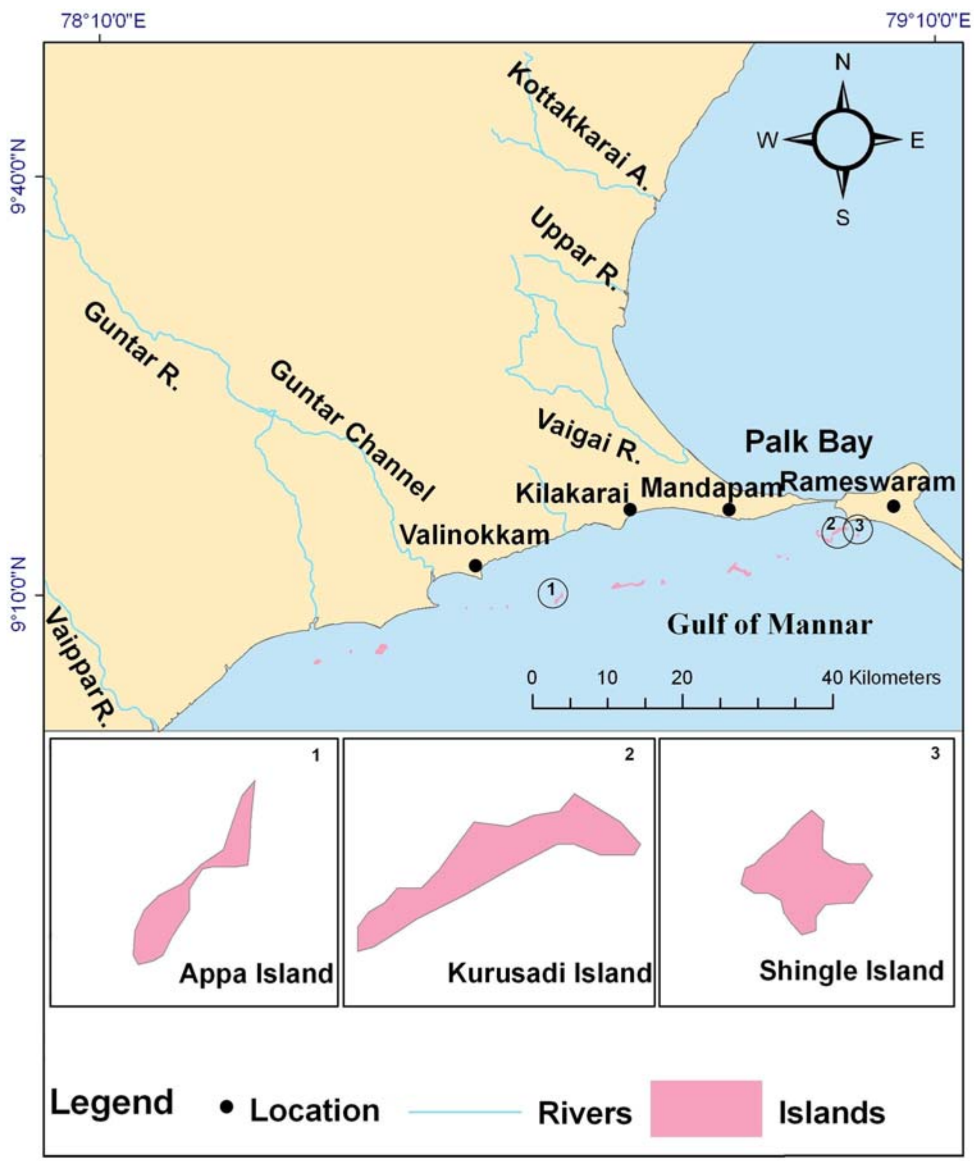

Fig. 1 Selected sampling islands of the Gulf of Mannar, India

determination of trace elements in coral samples using an Inductively Coupled Plasma Atomic Emission Spectrophotometer (Model No. IRIS INTREPID II XSP-Thermo Electron Corporation). Mercury concentration in the sample was determined by $SnCl_2$ reduction method (Goncalves 1993). The laboratory results showed that the recovery efficiency ranges 95%–99.9% and coefficient of variation (CV) 6%–9% for the trace elements studied. The limits of detection (LODs) of trace elements were 0.01 ppm for Fe, Cd, Ni, Cu, Co, Cr, Zn, Hg and Mn, 0.02 ppm for As and 0.05 ppm for Pb. In order to validate the method for accuracy and precision, carbonate reference valuations were analysed for the corresponding elements. A control sample was digested and analysed to check the effectiveness of the digestion procedures.

Results and Discussion

The concentration of trace elements in corals helps to monitor terrestrial inputs and anthropogenic pollution. The result of minimum, maximum, mean and standard deviation of trace elements concentration in coral samples were shown in Table 1. The concentration of metal transfer efficiencies vary from tissue to skeleton (Esslemont 2000). The concentration of Fe ranges from 0.19 to 0.62 μg g^{-1} with an average value of 0.38 μg g^{-1}. The low level of Fe in the coral samples suggests low influence of riverine process in the study area. The concentration of As ranges from 6.71 to 15.6 μg g^{-1} with an average of 10.64 μg g^{-1}. As is a naturally occurring toxic element and it is widely distributed in natural ecosystems. The concentration of Cd ranges from 0.28 to 1.31 μg g^{-1}. Pb and Cd in corals are well known indicators of anthropogenic activity (Shen and Boyle 1987). Severe contamination of Cd gives raise to itai-itai disease (Yosumura et al. 1980). The concentration of Co ranges from 0.56 to 5.29 μg g^{-1} the average being 2.55 μg g^{-1}. The concentration of Cr ranges widely from 7.25 to 22.34 μg g^{-1} with an average value of 13.27 μg g^{-1}. However, the concentration of Hg in the coral skeleton is below detection limit.

Cu was detected in all the coral samples, the concentration ranges from 0.63 to 5.08 μg g^{-1} with an average 2.40 μg g^{-1}. Zn and Cu are essential elements for living organisms and play an important role in growth, cell metabolism and survival of most animals including corals. Moreover, some micro organisms often tolerate greater concentration of certain metal compounds than can higher forms of life. The average concentration of Mn ranges from 98.38 to 138 μg g^{-1} with an average 188 μg g^{-1}. Mn

Table 1 Trace element concentrations (μg g^{-1}) in coral reef skeleton, Gulf of Mannar, India

S.no	Fe	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Hg	PLI
1	0.39	11.02	0.55	2.12	11	2.07	118.26	0.21	2.18	86.02	ND	3.74
2	0.42	8.5	0.32	2.06	22.34	1.12	112.06	1.76	3.04	53.16	ND	4.24
3	0.36	9.3	0.74	3.27	9.06	1.17	127	2.53	1.23	44	ND	4.14
4	0.62	13.04	0.46	1.78	13.54	4.86	120.31	1.47	0.18	51.26	ND	3.85
5	0.28	12.9	0.28	4.19	15	2.42	113.76	0.37	0.34	112.08	ND	3.46
6	0.34	6.71	1.06	3.22	18.07	0.89	123.05	0.9	3.11	61.13	ND	4.39
7	0.28	7.08	1.27	2.34	14.43	2.27	131.9	0.74	4.56	59.76	ND	4.69
8	0.19	7.13	0.57	1.09	12.38	3.08	129.82	0.53	2.08	98.05	ND	3.68
9	0.32	14.18	0.93	5.29	7.25	4.15	98.38	0.61	0.76	77.45	ND	4.34
10	0.36	15.6	0.68	4.07	13	0.99	100.09	0.74	1.43	112.21	ND	4.34
11	0.59	11.36	1.31	3.68	11.04	2.53	107.44	1.08	0.88	123	ND	5.08
12	0.47	9.9	0.48	2.4	9.18	2.42	126.35	1.23	3.23	118	ND	4.84
13	0.39	13.43	0.33	0.89	12.14	1.17	111	0.18	0.79	135.25	ND	2.93
14	0.41	11.47	0.53	1.43	11.05	5.08	106.14	0.33	2.12	108.03	ND	4.17
15	0.4	8.19	0.78	3.18	10.12	4.57	113.18	0.51	1.78	117.23	ND	4.63
16	0.24	9.56	0.66	0.56	19.26	0.63	118.07	0.56	0.69	124.13	ND	3.00
17	0.38	12.03	1.13	2.23	13.54	1.41	138	1	1.23	97.78	ND	4.53
18	0.32	10.15	0.73	2.18	16.5	2.39	129.12	0.78	1.84	99.27	ND	4.54
Minimum	0.19	6.71	0.28	0.56	7.25	0.63	98.38	0.18	0.18	44	ND	2.93
Maximum	0.62	15.6	1.31	5.29	22.34	5.08	138	2.53	4.56	135.25	ND	5.08
Mean	0.38	10.64	0.71	2.55	13.27	2.40	118.00	0.86	1.75	93.21	ND	4.14
SD	0.11	2.59	0.32	1.25	3.86	1.43	11.17	0.59	1.16	28.75	ND	0.60

ND not detectable, *PLI* pollution load index concentration in the corals is an indicator of detrital inputs (Linn et al. 1990). Ni was also detected in all coral samples, the concentration ranges from 0.18 to 2.53 μg g^{-1} with an average 0.86. μg g^{-1}.

The concentration of Pb ranges from 0.18 to 4.56 μg g^{-1} with an average 1.74 μg g^{-1} while Zn ranges from 44 to 135.25 μg g^{-1} with an average 93.21 μg g^{-1}. The concentration of Pb is lower than the Zn in coral skeleton. Pb is a toxic element to corals (Beyersmann 1994), whereas Zn is an essential micro nutrient of coral reefs and also commonly used for protein synthesis and repair of cells (Brown and Howard 1985). The main sources of Pb in the marine environment are from storm water runoff from hinterland and sewage input (Peters et al. 1997). Table 1 indicates the quantitative profile of different trace elements in coral skeletons collected form the 18 locations. The sources of trace elements in the skeleton are from untreated sewage and industrial waste probably from thermal power plant fly ash pond. Some trace metals can impart stress and affect the growth of corals in their early life stages including fertilization success, larval motility and larval settlement success (Negri and Heyward 2001; Reichelt-Brushett and Harrison 2004). This was clearly noticed in the living corals of the study area. But the detailed study on effect of metal pollution on coral reef are still unknown (Brown 1987). Comparisons of trace element concentrations in the coral reef area of Mannar with other regions of the world indicate that the metal values are low except few locations. Fe, As, Co, Mn and Ni were not reported from other coral regions (Table 2). The presence of these elements in our samples is due to the distribution of ilmenite ($FeTiO_2$) in the sediments and coal fly ash. The average metal accumulation levels in coral samples of the study area is in the following order Fe > Cd > Ni > Pb > Cu > Co > As > Cr > Zn > Mn.

Pollution load index (PLI) is used to find out the mutual pollution effect from different locations by various elements. PLI is calculated based on Salomons and Forstner (1984) equation.

$$\mathrm{PLI} = \sqrt[n]{(Cf_1 \times Cf_2 \times Cf_3 \times \ldots \times Cf_n)}$$

in which Cf is the concentration of examined elements in the sample. PLI varies between 2.93 and 5.08 with an average and standard deviation of 4.14 and 0.60 respectively. Based on this results it is found that most of the samples are contaminated with metal pollutants from fly ash of thermal power plant located in the coastal area.

Statistical analysis was performed using SPSS software package on the metal concentration values to detect the difference between the coral samples. The metal accumulation in coral is characterized by metals such as Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. The correlation matrix on metal ions was presented in Table 3. The factor loading showed good positive factor loading between Mn, Pb, Cr, Ni, Cd in factor loading 1, while Ni, Co, Fe, Cd, Cu have good factor loading in factor 2 and Cd, Pb, Co and Zn have positive factor loading in factor 3 (Fig. 2). It is evident that industrial effluents and riverine inputs have contributed for trace elements accumulation in coral skeleton.

The anthropogenic activities taking place in the area over the last five decades have a damaging effect on the marine ecosystem due to the large quantities of industrial waste water discharge and the domestic sewage through rivers joining the study area. Hence the study area is getting contaminated by trace elements and if the levels of trace elements continue to increase the toxic effect on marine ecosystem will also be increased. Therefore, the trace element accumulation in coral skeleton is a direct indicator of industrial effluents discharge. However, the elemental concentration in seawater, suspended particles and bottom marine sediments should also be studied in future which is very much essential to correlate with the trace elements available in coral skeleton. The pretreatment

Table 2 Average trace element concentration (μg g^{-1}) in coral reef skeletons of various other coral regions around the world

S.no	Fe	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Hg	References
1	0.38	10.64	0.71	2.55	13.27	2.4	118	0.86	1.75	93.21	ND	This study
2	NA	NA	0.09	NA	29	3.8	NA	NA	0.33	28	NA	Esslemont (2000)
3	NA	NA	0.19	NA	67	7.2	NA	NA	0.24	37	NA	
4	NA	NA	0.18	NA	31	14	NA	NA	8.2	447	NA	
5	NA	NA	NA	NA	0.8	16.33	NA	NA	1.4	10.67	2.5	Bastidas and Garcia (1999)
6	NA	NA	NA	NA	2	12.52	NA	NA	1.1	9.12	5.2	
7	NA	NA	7.5	NA	7.3	2	NA	NA	31	10.2	NA	Guzman and Jimenez (1992)
8	NA	NA	7.6	NA	9.9	3.8	NA	NA	32.3	8.9	NA	

ND not detected, *NA* not available

1 This study; 2 Pioneer Bay; 3 Nelly Bay; 4 Townsville Harbor; 5 Punta Brava; 6 Bajo Caiman; 7 Costa Rica; 8 Panama

Table 3 Correlation coefficient matrix (*R*2) of trace elements concentration in coral reef skeleton of the study area

Correlation	Fe	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Fe	1									
As	0.302	1								
Cd	0.022	−0.232	1							
Co	0.077	0.327	0.326	1						
Cr	−0.207	−0.33	−0.139	−0.356	1					
Cu	0.311	0.12	−0.064	0.102	−0.488	1				
Mn	−0.215	−0.573	0.212	−0.418	0.183	−0.233	1			
Ni	0.348	−0.197	0.079	0.135	0.073	−0.205	0.267	1		
Pb	−0.191	−0.67	0.237	−0.139	0.202	−0.141	0.36	0.058	1	
Zn	−0.061	0.317	−0.138	−0.15	−0.182	−0.003	−0.278	−0.633	−0.307	1

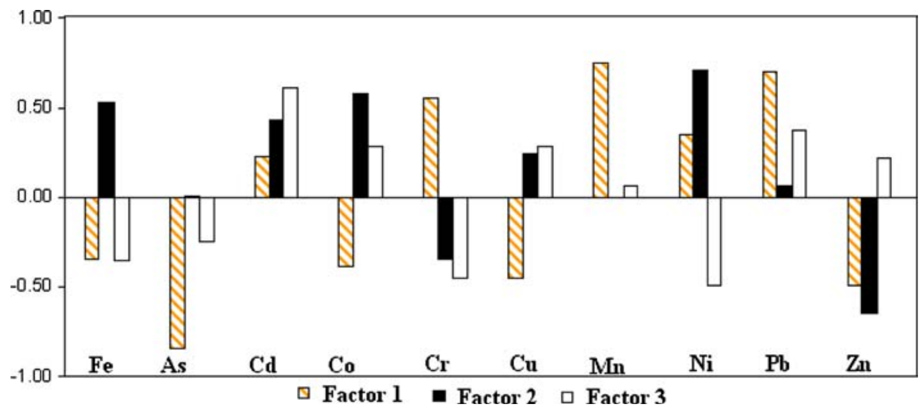

Fig. 2 Factor analysis results (R-mode) for primary associated variables of trace elements concentration in coral reef skeleton

of industrial and domestic effluents before discharged into coastal area of Gulf of Mannar is warranted to protect the marine ecosystem.

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