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# SEASONAL VARIATIONS OF TRACE METAL ACCUMULATION ON CORAL REEF IN GULF OF MANNAR, INDIA

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**ABSTRACT :** Investication of trace metal occumulation on coral and reef environment (sediment and water) of the Gulf of Mannar biosphere reserve was studied during July 2007 to June 2008. The samples were collected for analyzing from Thoothukudi and Vembar group of Islands, Gulf of Mannar. The concentration of trace metal in the water are in the order of Fe > Pb > Zn > As > Mn > Cd > Cu and in sediment in the order of Fe > Mn > Pb > Zn > Cu > Cd and in coral rubbles in the order of Fe > Mn > Pb > Zn > Cu > Cd. In the waters the iron ranks first and copper ranks last; in the sediment iron ranks first in concentration and cadmium ranks the last. In corals the iron ranks first and cadmium ranks the last in concentration and during the entire study periods. SPSS two tailed Correlation coefficients between the months and the temporal variablilities of heavy metals were assessed using the monthly data for each component in all stations and analysis of variances (f values) for the water, sediment and coral rubbles between the stations and month during the study period. Conclude that the values recorded at Thoothukudi group of islands were little higher than the Vembar group of islands, and it might be due to discharges pumped from the industrial belt of Thoothukudi, domestic sewages from Thoothukudi town, harbour activities and thermal power plant operation along the southern side of the Gulf of Mannar. **Key wards:** Trace Metal, Coral reef, Thoothukudi, Vembar, Gulf of Mannar.

# INTRODUCTION

Ocean and coastal waters are the major regions for a variety of human activities like fisheries, agriculture, navigation, oil and mineral exploration and waste disposal (IMCO, 1982). Due to easy accessibility and consequent high human influence, rivers, estuaries and coastal areas are found to be more susceptible to pollution (Ram Mohan *et al.*, 2010). Among the pollutants, heavy metals are a serious threat because most of them have harmful effect on living organisms (Ramesh *et al.*, 1996; Ozlem *et al.*, 2009; Ramanujam *et al.*, 2010). The heavy metal pollution likely results from the pollutants that enter through drains. Untreated urban effluents, mainly industrial and municipal wastes are thus discharged into sea and river (George Thomas, 1995; Kumaresan *et al.*, 1998; Vinithkumar *et al.*, 1999; Palanichamy and Rajendran, 2000).

The coral reef as proxy tools to record environmental changes has increased over the last few years, including parameters such as heavy metals accumulation (Guzman and Jarvis, 1996). The concept of monitoring metal pollution by selecting bioindicators has been fairly developed and accepted. There are considerable reports available in the use of organisms as biological monitor for all pollutants (Butler *et al.*, 1972; Haug *et al.*, 1974; Wilhm, 1975; Phillips, 1977 and 1980). Several authors have recently stressed the need for an indicator organism which can be used to monitor the environmental contamination by trace metals (Preston *et al.*, 1972; Haug *et al.*, 1974; Goldburg, 1975).

Studies on trace metal contamination in the water bodies, sediment and in the biota are very important for quality evaluation and risk assessment. The sources of these metals in water bodies vary from system to system and different organism concentrate metals at different levels in their body (Shiber and Shatila, 1978; Havard, 1991). Some pollutants have no natural function many others are present naturally, of even have an essential role and are toxic only because they are present in the wrong form, place or concentration, so that simple detection of their elemental presence many be irrelevant (Reimann and de caritat, 2000; Glasby *et al.*, 2004; Gonzalez-Macias *et al.*, 2006).

Among the trace metals, iron is considered as essential element and is a common metal found in industrial waste, fertilizers and domestic waste. It is an important metal in sediments in estuaries (Nair *et al.*, 1987). Zinc is an essential element required in small quantities to sustain biological life (Riordan and Vallee, 1976; Kirchgessner *et al.*, 1976; Vallee, 1978), but its large concentration proved to be lethal (Fernandez, 1983; Bryan, 1984). Zinc are discharged into rivers as chemical wastes from some chemical industries like Petroleum refineries, Shipping wastes and Thermal power plant (Dean *et al.*, 1972; Palanichamy and Rajendran, 2000). The Indian standard for the maximum tolerance limit for zinc in the industrial effluents discharged into marine ecosystem area is  $5mg.1^{-1}$ (IS: 1968, 1976).

Manganese is of little direct toxicological significance, but it may control the concentration of other elements, including toxic heavy metals, in surface waters. The primary natural sources of atmospheric Mn are wind borne soil particles and volcanoes and the major anthropogenic sources are coal burning and incineration of municipal wastes. Total manganese in water is extremely variable, ranging from 0.002 to  $> 4 \text{ mg/1}^{-1}$ . Similarly variable concentrations are found in marine estuaries and harbors, but concentrations are uniformly lower in offshore marine areas. A general standard of  $0.05 \text{ mg/1}^{-1}$ , based on aesthetic considerations is used by many nations (Ramesh *et al.*, 1996).

Copper is essential for normal growth of most aquatic organisms, but it is toxic at concentrations as low as  $10.0\mu g$ .<sup>-1</sup> (Steeman and Anderson, 1970). In high productive regions, biological system can significantly alter the distribution of copper in surface water (Boyle and Edmond, 1977). The Indian standard for the maximum tolerance limit for copper in the industrial effluents to marine coastal areas is  $3mg.1^{-1}$  (IS: 1968, 1976). Copper is present in all sewage, being derived from food and due to mixing with industrial waste (IMCO *et al.*, 1982).

Cadmium is found to be one of the most toxic elements in the biological systems (Frenet and Kleeman, 1941; Schroeder, 1965) and has been implicated in some cases of food poisoning. Most of the cadmium entering into the aquatic system was found to be accumulated in the sediment (Dunstan *et al.*, 1975 and Van Hook *et al.*, 1976). Industrial and municipal wastes are usually the main sources of cadmium pollution (Nriagu, 1978). Cadmium concentration in marine and estuarine systems are highly variable due to fresh water runoff, intermittent discharge of domestic sewage and industrial effluents, tides and currents, hydrological parameters and ecological factors (Ramesh *et al.*, 1996).

Arsenic, a rare but ubiquitous element, cycles rapidly through water, land, air and living systems. It occurs in the earth's crust at an average concentration of 2-5mg, principally as sulphate and oxide complexes. Worldwide anthropogenic input of arsenic into water system is approximately  $41x \ 10^3$  metric tons/yr. The most important source is domestic waste water, reflecting the use of arsenic in household preparations and in small industries that discharge effluents into municipal waste systems particularly in developing nations.

Treated or untreated sewage residue and sewage sludge contain enhanced levels of diverse lead compounds. Brackish, estuarine and inshore waters contain high concentration of lead (Rolfe and Edington, 1973; Kavum, 1990). The occurrence of trace metals in water and sediment along the Gulf of Mannar coastal regions has been studied by earlier workers (Kumaresan *et al.*, 1998; Vinithkumar *et al.*, 1999; Palanichamy and Rajendran, 2000; Krishna Kumar *et al.*, 2010).

Thoothukudi is one of the important major port handling several hundreds of ships in a year. It also incorporated with several major chemical industries like SPIC, Copper smelting plant, Dharangadhara chemicals, five units of Thermal power station, several thousands of small scale industrial units in its SIPCOT complex. The Thermal power station directly dumps its ash into the sea. Like wise the other industries also discharge their wastes into the sea. The movement of ships and fishing operation by mechanized boats also release a quantum of effluents and petrochemical products into the sea. The effluents from industries in Thoothukudi coastal region are discharged directly into the sea and hence there is every possibility for accumulation of large concentration of trace metals into the Gulf of Mannar marine ecosystem.

In the present study an attempt has been made to determine the occurrence and distribution of seven important trace metals such as Zinc, Iron, Manganese, Copper, Cadmium, Arsenic and Lead in the waters as well as the sediments and coral rubbles of six selected Islands of Thoothukudi and Vembar group, Gulf of Mannar. The reports on the occurrence and availability of trace elements in the coastal waters of Thoothukudi in particular the Gulf of Mannar islands are lacking and hence this study has been planned. In this study the heavy metals distributed along the different coastal islands of Thoothukudi and Vembar groups, were studied over a period of one year and the findings are discussed in this paper.

# MATERIALS AND METHODS

For the analysis of trace metals in water, sediments and coral rubbles four sites were chosen in each island of Thoothukudi and Vembar group and the samples were collected.

# **Collection of samples**

Monthly samples of water, sediment and coral rubbles were collected from these islands, for a period of twelve months from July 2007 to June 2008. Water samples were collected with the help of Nansen bottle (English *et al.*, 1997) and brought to the laboratory. Sediment samples were collected from sediment trap and coral rubbles collected by SCUBA diving for every month for a period of one year. The sediments traps were taken to lab and new trap was replaced. Samples were processed by adopting standard the methods (EPA, 1983; APHA, 1978).

# Water samples

The dissolved metals were extracted employing Teflon separatory funnels and subsequently their concentrations were estimated by the method of the APDC-DDDC back extraction techniques described by Danielson *et al.*, (1978; 1982).

# Sediment samples

Sediment samples from the sediment trap were transferred to pre washed glasswares and kept in an oven at 80° C  $\pm 1^{\circ}$  C till complete dryness. Dried samples were then ground with mortar and pestle into fine powder. It was then sieved through a 102µ mesh size sieve, weighed out 1.0 gm sieved samples in triplicate and put into 100ml digestion flask , samples were digested with 9 ml concentrated nitric acid (AR) and 1 ml of perchloric acid (AR) over a hot plate, the samples were heated until the solution become clear. The digested samples were then filtered through Whatman No: 1 filter paper diluted with double distilled water and made up to 25 ml in a volumetric flask. The made up samples were stored in pre washed plastic bottles for further analysis on AAS. Blank was also prepared by addition of same quantity of reagents without sediment samples and digested and made up to 25ml (Chester, 1969)

# Coral rubble

The metal concentration in coral rubbles was analyzed by the method of McConchie and Harriott, (1992). The coral rubble was collected in plastic bags by SCUBA diving and dried. Powder was collected from the hard part of coral rubbles with the help of mortar and pestel. Collected powders were acid digested and analyzed for heavy metals in Atomic Absorption Spectrophotometers (AAS).

The mean metal concentration in various samples were calculated by adopting the formula

Concentration of the metal in the sample

Conc. X vol. of sample X dil. factor

Dry weight of the material (gm)

# RESULTS

Among the six islands studied the highest annual record of zinc was observed in Van and Koswari islands. In almost all study sites the maximum zinc value was observed during the monsoon and post monsoon seasons. But in the Van and Koswari islands the zinc level was more during all the four seasons studied (Table 1). The monthwise report also exposed the same trend to a greater extent (Figure 1); followed by Van and Koswari islands the concentration of zinc was declined descendingly in Nallathanni, Pulivinichalli, Upputhanni and Kariyachalli islands (Table 1). Monthly variation in the concentration of zinc in the water, sediment and coral rubbles from the six study stations of Thoothukudi and Vembar group of islands are depicted in Fig 1 and seasonal changes displayed in Table 1.

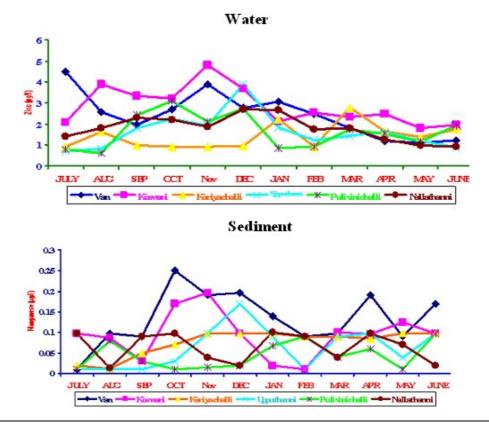
The relationship of zinc level in the water, sediment and coral rubbles showed in the figure 1. The concentration of zinc in the water collected from Van Island had the range of  $2.08\mu g.l^{-1}$  to  $3.89\mu g.l^{-1}$  and the annual mean was  $2.85\mu g.l^{-1}$ . In Koswari Island, zinc concentration ranged from  $1.18\mu g.l^{-1}$  to  $3.12\mu g.l^{-1}$  and the mean annual concentration was  $2.44\mu g.l^{-1}$ , Kaiyachalli it ranges from  $1.05\mu g.l^{-1}$  to  $2.25\mu g.l^{-1}$  and average annual zinc concentration was  $1.8\mu g.l^{-1}$ . In Upputhanni concentration of zinc in water differed between  $1.28\mu g.l^{-1}$  to  $2.64\mu g.l^{-1}$  and mean annual concentration was  $1.66\mu g.l^{-1}$ , Pulivinichalli range between  $1.1\mu g.l^{-1}$  to  $2.69\mu g.l^{-1}$  and annual mean zinc content was  $1.64\mu g.l^{-1}$ . The concentration of zinc in water from Nallathanni island from  $0.936\mu g.l^{-1}$  to  $1.98\mu g.l^{-1}$ , however the annual mean zinc content was  $1.42\mu g.l^{-1}$ . In all the study stations highest concentration of zinc was noticed during month of November and December, the monsoon season, while the lowest concentration during June and July the pre-monsoon season in all the stations.

International Journal of Applied Biology and Pharmaceutical Technology Page: 63 Available online at <u>www.ijabpt.com</u>

	observations and $\pm$ SD.								
		Pre		Post					
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual			
	Water (µg/l)	$3.1 \pm 0.94$	$3.89\pm0.82$	$2.32 \pm 0.22$	$2.08\pm0.36$	$2.85\pm0.82$			
	Sediment (µg/g)	$91.7 \pm 5.42$	$93.8 \pm 4.41$	$86.9 \pm 9.03$	$83.4 \pm 5.01$	$88.9 \pm 4.69$			
1	Coral (µg/g)	$2.05 \pm 0.51$	$2.556 \pm 0.25$	$2.72 \pm 0.35$	$0.97 \pm 0.2$	$2.07 \pm 0.79$			
	Water (µg/l)	$3.02 \pm 1.32$	$3.121 \pm 0.68$	$2.45 \pm 0.62$	$1.18 \pm 0.07$	$2.44\pm0.89$			
	Sediment (µg/g)	$86.1 \pm 9.47$	$89.06 \pm 7.48$	83.8±13.6	$87 \pm 5.77$	$86.5 \pm 2.17$			
2	Coral (µg/g)	$1.54 \pm 0.38$	$1.911 \pm 0.49$	$2.89 \pm 0.3$	$1.1 \pm 0.38$	$1.86 \pm 0.76$			
	Water (µg/l)	$1.83 \pm 0.45$	$2.25 \pm 0.42$	$2.07 \pm 0.52$	$1.05 \pm 0.17$	$1.8 \pm 0.53$			
	Sediment (µg/g)	$94.1 \pm 3.42$	$84.92\pm9.82$	$83.9 \pm 2.95$	$80 \pm 9.56$	$85.7 \pm 5.98$			
3	Coral (µg/g)	$1.18 \pm 0.22$	$1.844 \pm 0.38$	$2.77 \pm 0.55$	$1.19 \pm 0.2$	$1.74 \pm 0.75$			
	Water (µg/l)	$1.28 \pm 1.01$	$2.64 \pm 0.51$	1.17 ±0.49	$1.55 \pm 0.38$	$1.66 \pm 0.67$			
	Sediment (µg/g)	$76.8 \pm 2.14$	89.11 ± 7.55	$83.5 \pm 14.1$	$88 \pm 7.51$	$84.4 \pm 5.58$			
4	Coral (µg/g)	$0.96 \pm 0.5$	$1.478 \pm 0.5$	$2.07 \pm 0.3$	$1.23 \pm 0.1$	$1.43 \pm 0.47$			
	Water (µg/l)	$1.18 \pm 0.39$	$0.936 \pm 0$	$1.98 \pm 0.96$	$1.59 \pm 0.19$	$1.42 \pm 0.46$			
	Sediment (µg/g)	$66.8 \pm 2.75$	$73.32 \pm 5.64$	$91.46 \pm 6.11$	$81.8\pm10.7$	$78.3 \pm 10.7$			
5	Coral (µg/g)	$1.03 \pm 0.9$	$1.711 \pm 0.28$	$1.822 \pm 0.26$	$0.58 \pm 0.11$	$1.29\pm0.59$			
	Water (µg.l <sup>-1</sup> )	$1.11 \pm 0.6$	$2.689 \pm 1.06$	$1.502 \pm 0.31$	$1.24 \pm 0.37$	$1.64 \pm 0.72$			
	Sediment (µg/g)	$50.2\pm7.09$	$63.66 \pm 6.51$	$80.19 \pm 1.15$	$63.3\pm5.22$	$64.3 \pm 12.3$			
6	Coral (µg/g)	$1.34 \pm 0.16$	$1.7 \pm 0.59$	$1.167 \pm 0.59$	$0.47\pm0.41$	$1.17 \pm 0.52$			

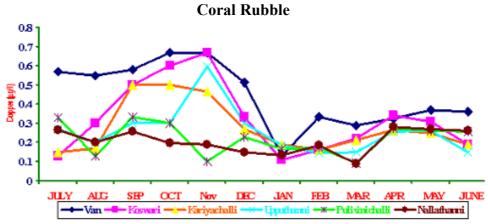
Table 1 Seasonal variation in the concentration of Zinc in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of three observations and  $\pm$  SD.

Stns- Stations, 1- Van Island, 2- Koswari Island, 3- Kariyachalli Island, 4- Upputhanni Island, 5- Pulivinichalli Island and 6- Nallathanni Island.



International Journal of Applied Biology and Pharmaceutical Technology Available online at <u>www.ijabpt.com</u>

Page: 64

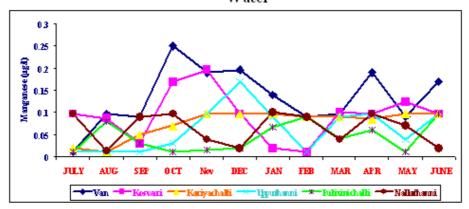


# Figure 1 Monthwise variation observed in the concentration of Zinc in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008)

For sediment, the result revealed that at Van Island an average annual value of  $88.9\mu g.g^{-1}$  of zinc was determined with the lowest and highest values  $83.4\mu g.g^{-1}$  and  $93.8\mu g.g^{-1}$  respectively. A similar range of zinc content was noticed in Koswari sediments also that is  $83.83\mu g.g^{-1}$  and  $89.06\mu g.g^{-1}$  value being the lowest and highest respectively, with an average annual of  $86.5\mu g.g^{-1}$ . Kariyachalli average annual value of  $85.7\mu g.g^{-1}$  of zinc was determined with the lowest and highest values  $80\mu g.g^{-1}$  and  $94.1\mu g.g^{-1}$  respectively, Upputhanni island the value ranged as  $76.8\mu g.g^{-1}$  to  $89.1\mu g.g^{-1}$  and the average annual value as  $84.4\mu g.g^{-1}$ , Pulivinichalli island an average annual value of  $78.3\mu g.g^{-1}$  with lowest and highest values of  $66.8\mu g.g^{-1}$  to  $91.46\mu g.g^{-1}$  respectively and in Nallathanni island the annual mean values was  $64.3\mu g.g^{-1}$  and minimum and maximum values was  $50.2\mu g.g^{-1}$  to  $80.19\mu g.g^{-1}$  respectively. During the end of the monsoon and post monsoon the highest concentration of zinc was determined in the sediment and the least was during pre-monsoon season for all the stations.

In coral rubbles, the concentration of zinc in Van Island varied from  $0.97\mu g.g^{-1}$  to  $2.7\mu g.g^{-1}$  with an annual mean value of  $2.07\mu g.g^{-1}$ . In Koswari, the zinc content ranged from  $1.1\mu g.g^{-1}$  to  $2.89\mu g.g^{-1}$  and the annual average concentration was  $1.86\mu g.g^{-1}$ . In Kariyachalli Island, values of zinc in coral differed from  $1.18\mu g.g^{-1}$  to  $2.77\mu g.g^{-1}$  with an average annual mean value of  $1.74\mu g.g^{-1}$ . In Upputhanni Island, the zinc concentration varied and the minimum value was  $0.96\mu g.g^{-1}$  to maximum  $2.07\mu g.g^{-1}$ . However the annual mean value was  $1.43\mu g.g^{-1}$ . Pulivinichalli Island, the values of zinc differed from  $0.58\mu g.g^{-1}$  to  $1.82\mu g.g^{-1}$  with an annual mean value was  $1.29\mu g.g^{-1}$ . The mean annual concentration of zinc was  $1.17\mu g.g^{-1}$  for Nallathanni island with lowest value was  $0.47\mu g.g^{-1}$ .

Van Island showed the highest concentration of zinc for water, sediment and coral rubbles samples, when compared with all the other stations, whereas Nallathanni Island recorded the lowest value throughout the year. Monthly variation of zinc in water, sediment and coral rubbles have not shown much different in all the stations. Data on the concentration of iron in water, sediment and coral rubbles samples from all study areas along the Thoothukudi coast are presented in table 2 and graphically displayed in Figure 2.



International Journal of Applied Biology and Pharmaceutical Technology Page: 65 Available online at <u>www.ijabpt.com</u>

Water

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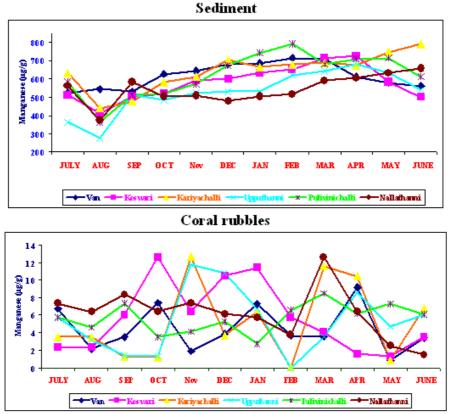
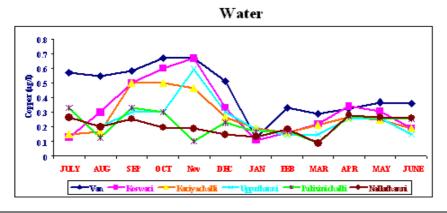


Figure 2 Monthwise variations observed in the concentration of Iron in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008)

In Van Island, the iron content in water ranged from  $7.89\mu g.l^{-1}$  to  $18.05\mu g.l^{-1}$ . An annual average of  $11.7\mu g.l^{-1}$  was noticed at station one during the period of study. In Koswari Island, the concentration of iron ranged from  $6.56\mu g.l^{-1}$  to  $12.23\mu g.l^{-1}$ . An annual average concentration of  $10.6\mu g.l^{-1}$  was recorded in this station. Kariyachalli island iron concentration in water varied from  $5.51\mu g.l^{-1}$  to  $16.04\mu g.l^{-1}$ . An annual average of  $9.96\mu g.l^{-1}$  was noticed at this station. In Upputhanni island concentration of Iron varied between  $5.38\mu g.l^{-1}$  to  $11.48\mu g.l^{-1}$ . Average annual concentration of iron was recorded as  $8.54\mu g.l^{-1}$ . Pulivinichalli Island, the iron content ranged from  $5.17\mu g.l^{-1}$  to  $10.99\mu g.l^{-1}$  and average annual concentration  $8.38\mu g.l^{-1}$  was recorded and in Nallathanni Island  $5.37\mu g.l^{-1}$  to  $10.18\mu g.l^{-1}$  of iron content was noticed, average annual iron content noted  $7.89\mu g.l^{-1}$ .

In all the six stations maximum concentration of iron in water samples was recorded during the monsoon and minimum concentration of iron was observed during the pre - monsoon season. In the month of October - December maximum value of iron recorded in all the study areas and minimum values were recorded in the month of June to August in all the six stations (Figure 3).



International Journal of Applied Biology and Pharmaceutical Technology Available online at <u>www.ijabpt.com</u>

Page: 66

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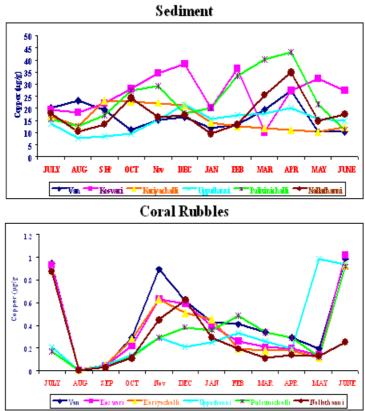


Figure 3 Monthwise variations observed in the concentration of Manganese in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008)

Monthly variation in the concentration of iron in sediment samples are shown in Table 2 and Figure 3. In Van island the concentration of iron in sediments ranged from  $4706\mu g.g^{-1}$  to  $5934\mu g.g^{-1}$ . Average annual concentration of iron in sediments was  $5484\mu g.g^{-1}$ . In Kaiyachalli Island the concentration of iron varied between  $3791\mu g.g^{-1}$  and  $5567\mu g.g^{-1}$ . Koswari Island the concentration of iron in sediments was  $4337\mu g.g^{-1}$  to  $6365\mu g.g^{-1}$  and annual concentration of iron  $5455\mu g.g^{-1}$ , Upputhanni Island the annual concentration of iron in sediment was  $5181\mu g.g^{-1}$  and minimum and maximum of iron concentration was  $3903\mu g.g^{-1}$  to  $5937\mu g.g^{-1}$ , Pulivinichalli  $2825\mu g.g^{-1}$  to  $4005\mu g.g^{-1}$  and annual ranged  $3190\mu g.g^{-1}$ . The mean annual concentration of iron was  $3189\mu g.g^{-1}$  and the highest value was  $3843\mu g.g^{-1}$  at Nallathanni Island.

In Van Island the concentration of iron in coral rubble ranged from  $29.5\mu$ g.g<sup>-1</sup> to  $53.81\mu$ g.g<sup>-1</sup>. Average annual concentration of iron in sediments was  $40.4\mu$ g.g<sup>-1</sup>. In Koswari Island the concentration of iron varied between  $27.06\mu$ g.g<sup>-1</sup> and  $55.67\mu$ g.g<sup>-1</sup> and average annual concentration was calculated and the value was  $35.5\mu$ g.g<sup>-1</sup>. Kariyachalli Island the concentration of iron in Coral rubble was  $28.2\mu$ g.g<sup>-1</sup> to  $41.39\mu$ g.g<sup>-1</sup> and annual concentration of iron  $34.7\mu$ g.g<sup>-1</sup>, Upputhanni Island, the annual concentration of iron in coral rubbles was  $34.4\mu$ g.g<sup>-1</sup> and minimum and maximum of iron concentration was  $29.68\mu$ g.g<sup>-1</sup> to  $37.8\mu$ g.g<sup>-1</sup>, Pulivinichalli  $28.5\mu$ g.g<sup>-1</sup> to  $38.05\mu$ g.g<sup>-1</sup> and annual ranged  $31.8\mu$ g.g<sup>-1</sup>. The mean annual concentration of iron was  $27.7\mu$ g.g<sup>-1</sup> and the range was  $24.54\mu$ g.g<sup>-1</sup> to  $30.3\mu$ g.g<sup>-1</sup> at Nallathanni Island.

The concentration of Manganese in water collected from Van Island had the lowest value of  $0.07 \mu g.l^{-1}$  and the highest value of  $0.12 \mu g.l^{-1}$ ; annual mean content was 0.13. In Koswari Island, Manganese concentration ranged from  $0.043 \mu g.l^{-1}$  to  $0.154 \mu g.l^{-1}$  and the mean annual concentration was  $0.09 \mu g.l^{-1}$ . Kaiyachalli 0.03 to  $0.092 \mu g.l^{-1}$  and average annual concentration of Manganese concentration was  $0.07 \mu g.l^{-1}$ . In Upputhanni concentration of Manganese in water differed between  $0.01 \mu g.l^{-1}$  to  $0.099 \mu g.l^{-1}$  and mean annual concentration was  $0.06 \mu g.l^{-1}$ . The concentration of Manganese in water from Nallathanni Island was from  $0.04 \mu g.l^{-1}$  to  $0.066 \mu g.l^{-1}$ , however the annual mean content was  $0.04 \mu g.l^{-1}$ .

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#### Yogesh Kumar and Geetha

Table 2 Seasonal variations in the concentration of Iron in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of three observations and + SD.

	observations and $\pm$ SD.									
		Pre		Post						
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual				
	Water (µg/l)	$8.88\pm0.47$	$18.05 \pm 2.32$	$11.8 \pm 2.06$	$7.89\pm0.22$	$11.7 \pm 4.58$				
	Sediment (µg/g)	$4706\pm734$	$5512 \pm 341$	$5783 \pm 209$	$5934 \pm 381$	$5484\pm547$				
1	Coral (µg/g)	$29.5 \pm 9.72$	$39.27 \pm 14.9$	53.81 ±3.4	$38.9\pm2.35$	$40.4 \pm 10$				
	Water (µg/l)	$6.56 \pm 0.19$	$16.13 \pm 2.77$	12.23±2.09	$7.55 \pm 1.17$	$10.6 \pm 4.43$				
	Sediment (µg/g)	$4337 \pm 1056$	$5376 \pm 101$	$5743 \pm 138$	$6365 \pm 426$	$5455\pm850$				
2	Coral (µg/g)	$28.6 \pm 10.4$	$27.06 \pm 0.92$	$55.62 \pm 3.2$	$30.8 \pm 2.34$	$35.5 \pm 13.5$				
	Water (µg/l)	$5.51 \pm 0.3$	$16.04 \pm 0.83$	11.94±1.64	$6.36\pm0.66$	$9.96 \pm 4.96$				
	Sediment (µg/g)	$3791 \pm 1632$	$4947 \pm 1502$	7200±1100	$5562 \pm 146$	$5375 \pm 1421$				
3	Coral (µg/g)	$39.3 \pm 17.1$	$41.39\pm20$	29.94±9.55	$28.2\pm6.87$	$34.7\pm6.6$				
	Water (µg/l)	$6.52 \pm 0.74$	$11.48 \pm 3.27$	10.79±0.78	$5.38\pm0.27$	$8.54 \pm 3.04$				
	Sediment (µg/g)	$3903 \pm 723$	$5398 \pm 411$	$5487 \pm 218$	$5937\pm383$	$5181 \pm 884$				
4	Coral (µg/g)	$37.8 \pm 13.2$	$29.68 \pm 12.3$	36.35±21.6	$33.7 \pm 3.89$	$34.4\pm3.55$				
	Water (µg/l)	$5.17 \pm 0.77$	$10.99 \pm 2.54$	$10.85 \pm 1.55$	$6.52\pm0.36$	$8.38\pm2.98$				
	Sediment (µg/g)	$2825 \pm 347$	$2927 \pm 185$	$4005 \pm 444$	$3004 \pm 334$	$3190\pm548$				
5	Coral (µg/g)	$31.4 \pm 9.1$	$29.34 \pm 1.08$	38.05±23.1	$28.5 \pm 6.23$	$31.8\pm4.32$				
	Water (µg.l <sup>-1</sup> )	$5.37\pm0.47$	$10.18 \pm 5.33$	9.684±1.03	$6.31 \pm 0.54$	$7.89 \pm 2.4$				
	Sediment (µg/g)	$2723\pm773$	$3843\pm497$	3501±1193	2688±1074	$3189\pm575$				
6	Coral (µg/g)	$30.3 \pm 8.86$	$24.54 \pm 16$	25.76±0.98	$30.3 \pm 10.2$	$27.7 \pm 3.03$				

Stns- Stations, 1- Van Island, 2- Koswari Island, 3- Kariyachalli Island, 4- Upputhanni Island, 5- Pulivinichalli Island and 6- Nallathanni Island.

In all the study stations concentration of Manganese was not show much difference during the seasons. The month of October-December recorded the highest value of Manganese in all the study stations. Month of June and July the Manganese observation was minimum at all the six stations (Table 3 and Figure 3).

Table 3 Seasonal variations in the concentration of Manganese in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of three observations and  $\pm$  SD.

three observations and $\pm$ SD.									
		Pre		Post					
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual			
	Water (µg/l)	$0.07 \pm 0.05$	$0.212 \pm 0.03$	$0.1 \pm 0.03$	$0.15 \pm 0.05$	$0.13 \pm 0.06$			
	Sediment (µg/g)	$518 \pm 102$	$633.9 \pm 63.5$	$678 \pm 13.5$	$739 \pm 60.4$	$642 \pm 93.1$			
1	Coral (µg/g)	$7.34\pm0.97$	$6.67\pm0.65$	$7.36 \pm 4.62$	$3.46 \pm 2.57$	$6.21 \pm 1.86$			
	Water (µg/l)	$0.07\pm0.04$	$0.154 \pm 0.05$	$0.04 \pm 0.05$	$0.11 \pm 0.02$	$0.09 \pm 0.05$			
	Sediment (µg/g)	$487 \pm 111$	$589.9\pm80.3$	$741 \pm 55.1$	$679 \pm 57.9$	$624 \pm 111$			
2	Coral (µg/g)	$5.9 \pm 1.37$	$4.287\pm0.89$	$5.92 \pm 2.92$	$6.52 \pm 0.68$	$5.66 \pm 0.96$			
	Water (µg/l)	$0.03\pm0.02$	$0.087\pm0.02$	$0.092 \pm 0$	$0.09 \pm 0.01$	$0.07\pm0.03$			
	Sediment (µg/g)	$533\pm9.28$	$650.7\pm29.1$	$704.9\pm15$	$585 \pm 25.5$	$619 \pm 75$			
3	Coral (µg/g)	$3.57 \pm 2.12$	$9.829 \pm 3.12$	$7.06 \pm 3.84$	$2.14 \pm 1.16$	$5.65 \pm 3.47$			
	Water (µg/l)	$0.01 \pm 0$	$0.099\pm0.07$	$0.06 \pm 0.05$	$0.08 \pm 0.03$	$0.06\pm0.04$			
	Sediment (µg/g)	$477 \pm 55.3$	$570.1 \pm 45$	667.4±42.5	$603 \pm 112$	$580\pm79.3$			
4	Coral (µg/g)	$3.46 \pm 2.21$	$7.961 \pm 5.79$	$3.39 \pm 3.35$	$6.43 \pm 1.96$	$5.31 \pm 2.27$			
	Water (µg/l)	$0.07\pm0.05$	$0.05\pm0.04$	$0.08 \pm 0.03$	$0.06 \pm 0.04$	$0.06 \pm 0.01$			
	Sediment (µg/g)	$507 \pm 116$	$499.1 \pm 15.4$	536.9±46.4	$632 \pm 28.2$	$544\pm61.3$			
5	Coral (µg/g)	$2.73 \pm 1.3$	$5.848 \pm 6.04$	$5.95 \pm 5.78$	$6.01 \pm 4.85$	$5.13 \pm 1.6$			
	Water (µg.l <sup>-1</sup> )	$0.04 \pm 0.04$	$0.015 \pm 0$	0.066±0.03	$0.06 \pm 0.04$	$0.04 \pm 0.02$			
	Sediment (µg/g)	$383 \pm 121$	$512.8 \pm 25.6$	598.8±59.1	620±71.1	$529\pm108$			
6	Coral (µg/g)	$4.13 \pm 2.32$	$4.394 \pm 2.81$	$4.811 \pm 2.12$	$4.47 \pm 4.26$	$4.45 \pm 0.28$			
Stns- Sta	tions, 1- Van Island, 2-	Koswari Island, 3	- Kariyachalli Isla	nd, 4- Upputhanni	Island, 5- Pulivi	inichalli Island and			

6- Nallathanni Island.

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Monthly variation in the concentration of manganese in the sediments from the study stations of Thoothukudi and Vembar group of islands revealed that at Van Island an average annual value of  $642\mu$ g.g<sup>-1</sup> of manganese was determined with the range of  $518\mu$ g.g<sup>-1</sup> and  $739\mu$ g.g<sup>-1</sup> respectively. A similar range of manganese content was noticed in Koswari sediments also that is  $487\mu$ g.g<sup>-1</sup> and  $679\mu$ g.g<sup>-1</sup> as the lowest and highest with an average annual value of  $624 \mu$ g.g<sup>-1</sup>. In Kariyachalli the average annual value was  $619\mu$ g.g<sup>-1</sup> with the lowest and highest values as  $533\mu$ g.g<sup>-1</sup> and  $704.9\mu$ g.g<sup>-1</sup> respectively. In Upputhanni Island, the range of manganese values was  $477\mu$ g.g<sup>-1</sup> and  $667.4\mu$ g.g<sup>-1</sup> with the average annual value as  $580\mu$ g.g<sup>-1</sup>. In Pulivinichalli Island an average annual value of  $544\mu$ g.g<sup>-1</sup> was noted with the values ranged as  $499.1\mu$ g.g<sup>-1</sup> to  $632\mu$ g.g<sup>-1</sup> and in Nallathanni Island the annual mean value observed was  $529\mu$ g.g<sup>-1</sup> with the lowest and highest values of  $383\mu$ g.g<sup>-1</sup> to  $620\mu$ g.g<sup>-1</sup> respectively. It was very clear from the statistical analysis (Table 8) that during the end of the summer the highest concentration of manganese was determined in the sediment and the least was during pre-monsoon and monsoon season for all the six station.

Monthly variation in the concentration of manganese (Table 4) in the coral rubble from the six study stations of Thoothukudi and Vembar group of islands result revealed that at Van Island an average annual value of  $6.21\mu g.g^{-1}$  of manganese was determined with the lowest and highest values of  $3.46\mu g.g^{-1}$  and  $7.36\mu g.g^{-1}$  respectively. A similar range of manganese content was noticed in Koswari coral rubble also  $(4.29\mu g.g^{-1}$  and  $6.52\mu g.g^{-1}$ ) with an average annual value of  $5.66\mu g.g^{-1}$ . In Kariyachalli the annual average value obtained was  $5.65\mu g.g^{-1}$  of with the differential values of  $2.14\mu g.g^{-1}$  to  $9.83\mu g.g^{-1}$  respectively. In Upputhanni Island manganese value ranged between  $3.39\mu g. g^{-1}$  to  $7.96\mu g.g^{-1}$  with the annual average value of  $5.31\mu g.g^{-1}$ . In Pulivinichalli Island the average annual value was  $5.13\mu g.g^{-1}$  with lowest and highest values of  $2.73\mu g.g^{-1}$  to  $6.01\mu g.g^{-1}$  respectively. In Nallathanni Island the annual mean value of manganese observed was  $4.45\mu g.g^{-1}$  with the range of  $4.13\mu g.g^{-1}$  to  $4.8\mu g.g^{-1}$  respectively. It was very clear from the statistical analysis (Table 8) that during the end of the Monsoon the highest concentration of manganese was determined in the coral reef sediment and the least was during pre- monsoon season for all the six station. As far as the sampling stations were concerned, In Van island maximum manganese content was observed where as in Nallathanni island the minimum level was noted during the one year sampling period.

three observations and $\pm$ 5D.									
		Pre		Post					
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual			
	Water (µg/l)	$0.57 \pm 0.02$	0.616±0.09	0.251±0.11	0.35±0.02	$0.45 \pm 0.17$			
	Sediment (µg/g)	$19.9 \pm 1.98$	33.75±5.22	22.34±13.3	29.1±2.69	$26.3 \pm 6.31$			
1	Coral (µg/g)	$0.33 \pm 0.53$	0.597±0.3	0.392±0.05	0.49±0.43	$0.45 \pm 0.12$			
	Water (µg/l)	$0.31 \pm 0.19$	0.533±0.18	0.163±0.06	0.28±0.08	$0.32 \pm 0.15$			
	Sediment (µg/g)	$15.3 \pm 2.26$	24.86±6.2	31.19±10.2	25.4±16.3	$24.2 \pm 6.59$			
2	Coral (µg/g)	$0.33 \pm 0.53$	0.481±0.23	0.286±0.1	0.45±0.49	$0.39 \pm 0.09$			
	Water (µg/l)	$0.27 \pm 0.2$	0.411±0.12	0.187±0.03	0.23±0.04	$0.28\pm0.1$			
	Sediment (µg/g)	$14 \pm 3.82$	19.31±4.37	16.12±8.35	22.4±10.8	$18 \pm 3.66$			
3	Coral (µg/g)	$0.31 \pm 0.49$	0.472±0.18	0.273±0.16	0.41±0.45	$0.37 \pm 0.09$			
	Water (µg/l)	$0.26 \pm 0.05$	0.399±0.17	0.16±0.02	$0.22 \pm 0.06$	$0.26\pm0.1$			
	Sediment (µg/g)	$20.9 \pm 2.06$	14.29±2.69	15.01±3.95	16±10	$16.5 \pm 2.96$			
4	Coral (µg/g)	$0.09 \pm 0.11$	0.213±0.08	0.282±0.04	0.71±0.45	$0.32\pm0.27$			
	Water (µg/l)	$0.27 \pm 0.12$	0.209±0.1	0.143±0.04	0.26±0.01	$0.22\pm0.06$			
	Sediment (µg/g)	$17.5 \pm 5.25$	22.03±0.75	12.79±1.09	11.3±0.95	$15.9\pm4.87$			
5	Coral (µg/g)	$0.07 \pm 0.09$	0.265±0.13	0.393±0.08	0.44±0.42	$0.29\pm0.17$			
	Water (µg.l <sup>-1</sup> )	$0.24 \pm 0.04$	0.179±0.03	0.135±0.05	0.27±0.01	$0.21\pm0.06$			
	Sediment (µg/g)	10± 3.23	15.45±5.99	16.84±1.21	16.9±2.83	$14.8\pm3.24$			
6	Coral (µg/g)	$0.3 \pm 0.49$	0.392±0.26	$0.199 \pm 0.09$	0.17±0.07	0.27±0.1			
ns- Stati	ions, 1- Van Island, 2-	Koswari Island, 3	- Kariyachalli Isla	nd, 4- Upputhann	i Island, 5- Puliv	vinichalli Island			

Table 4 Seasonal variations in the concentration of Copper in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of

International Journal of Applied Biology and Pharmaceutical Technology	<b>Page: 69</b>
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6- Nallathanni Island.

three observations and  $\pm$  SD.

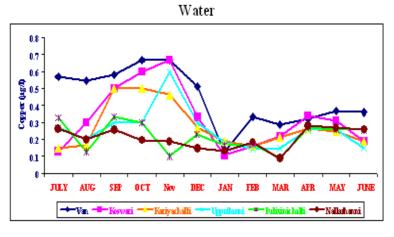
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		Pre		Post		
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual
	Water (µg/l)	$0.003 \pm 0.002$	$0.004 \pm 0.002$	$0.005 \pm 0.003$	$0.003 \pm 0.0009$	0.004±0.001
	Sediment (µg/g)	0.46±0.36	0.573±0.24	0.186±0.03	$0.11 \pm 0.07$	0.33±0.22
1	Coral (µg/g)	0.14±0.12	0.27±0.12	0.122±0.05	0.15±0.05	0.17±0.07
	Water (µg/l)	$0.0018 \pm 0.001$	$0.006 \pm 0.001$	$0.003 \pm 0.0006$	$0.0019 \pm 0.00$	0.003±0.002
	Sediment (µg/g)	0.14±0.16	0.23±0.06	0.18±0.04	0.19±0.11	0.19±0.04
2	Coral (µg/g)	0.09±0.03	0.326±0.12	0.159±0.06	$0.05 \pm 0.01$	0.16±0.12
	Water (µg/l)	$0.0026 \pm 0.001$	$0.003 \pm 0.001$	0.0032±0.001	$0.0022 \pm 0.0$	$0.003 \pm 0.0004$
	Sediment (µg/g)	0.13±0.17	0.123±0.06	0.029±0.03	$0.03 \pm 0.03$	$0.08 \pm 0.06$
3	Coral (µg/g)	0.1±0.05	0.34±0.24	0.154±0.06	$0.06 \pm 0.01$	0.16±0.12
	Water (µg/l)	$0.0013 \pm 0.001$	$0.002 \pm 0.001$	$0.0031 \pm 0.001$	$0.002 \pm 0.0002$	$0.002 \pm 0.001$
	Sediment (µg/g)	0.23±0.32	$0.02 \pm 0.03$	0.026±0.02	$0.03 \pm 0.03$	0.08±0.1
4	Coral (µg/g)	0.11±0.06	$0.259 \pm 0.08$	0.114±0.05	$0.07 \pm 0.02$	$0.14{\pm}0.08$
	Water (µg/l)	$0.0014 \pm 0.001$	$0.002 \pm 0.001$	$0.0028 \pm 0.001$	$0.0019 \pm 0.00$	$0.002 \pm 0.001$
	Sediment (µg/g)	0.09±0.14	$0.028 \pm 0.02$	0.018±0.03	$0.04 \pm 0.02$	0.05±0.03
5	Coral (µg/g)	$0.07 \pm 0.02$	0.123±0.06	0.13±0.03	0.19±0.05	0.13±0.05
	Water (µg.l <sup>-1</sup> )	$0.0015 \pm 0.002$	$0.004 \pm 0.003$	$0.0029 \pm 0.001$	$0.002 \pm 0.001$	$0.002 \pm 0.001$
	Sediment (µg/g)	0±0	$0.007 \pm 0.01$	0.113±0.2	$0.02 \pm 0.04$	0.04±0.05
6	Coral (µg/g)	0.12±0.05	0.13±0.04	0.089±0	$0.06 \pm 0.01$	0.1±0.03

Table 5 Seasonal variations in the concentration of Cadmium in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of three observations and  $\pm$  SD.

Stns- Stations, 1- Van Island, 2- Koswari Island, 3- Kariyachalli Island, 4- Upputhanni Island, 5- Pulivinichalli Island and 6- Nallathanni Island.

In Van Island, the Copper content in water sample ranged from  $0.25\mu g.l^{-1}$  to  $0.62\mu g.l^{-1}$  with an annual average of  $0.45\mu g.l^{-1}$ . In Koswari Island, the concentration of Copper ranged from  $0.16\mu g.l^{-1}$  to  $0.53\mu g.l^{-1}$  with an annual average concentration of  $0.32\mu g.l^{-1}$ . In Kariyachalli island the Copper concentration in water varied from  $0.19\mu g.l^{-1}$  to  $0.41\mu g.l^{-1}$  with an annual average value of  $0.28\mu g.l^{-1}$ . In Upputhanni Island the concentration of Copper varied between  $0.16\mu g.l^{-1}$  to  $0.399\mu g.l^{-1}$  with an average annual concentration of  $0.26\mu g.l^{-1}$ . In Pulivinichalli Island, the Copper content ranged between  $0.14\mu g.l^{-1}$  to  $0.27\mu g.l^{-1}$  with an average annual concentration of  $0.22\mu g.l^{-1}$  and in Nallathanni Island the range was  $0.14\mu g.l^{-1}$  to  $0.27\mu g.l^{-1}$  with an average annual content of  $0.21\mu g.l^{-1}$ . In general during the month of October and November the maximum concentration of Copper was recorded in all the study stations and minimum values were recorded during the month of January (Table 4 and Figure 4).



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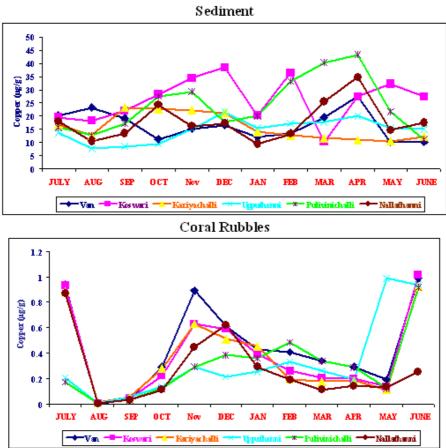


Figure 4 Monthwise variations observed in the concentration of Copper in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008)

As for as, the copper concentration in sediments were concerened, the highest annual value was observed in Van island  $(26.3\mu g.g^{-1})$  and Koswari island  $(24.2\mu g.g^{-1})$  where as in other islands it was gradually reduced as the distance of location of the island from Thoothukudi shore. The annual values observed in other islands were  $18\mu g.g^{-1}$ ,  $16.5\mu g.g^{-1}$ ,  $15.9\mu g.g^{-1}$  and  $14.8\mu g.g^{-1}$  in Kariyachalli, Upputhanni, Pulivinichalli and Nallathanni islands respectively (Table 4 and Figure 4). The copper concentration in coral rubbles also showed almost the same trend (Table 4 and Figure 4).

Data on the monthly concentration of cadmium in water, sediment and coral rubbles of six stations studied are presented in Table 5 and graphically shown in Fig 5. In general the Cadmium concentration in water showed very low values in all the study stations. In Van island, the concentration of cadmium ranged from 0.0028 to 0.005  $\mu$ g.l<sup>-1</sup>, with the annual concentration of 0.004 $\mu$ g.l<sup>-1</sup>, In Koswary it was from 0.0018 to 0.006 $\mu$ g.l<sup>-1</sup> with the annual value of 0.003 $\mu$ g.g<sup>-1</sup>, In Kariyachalli Island it was ranged from 0.0022 $\mu$ g.l<sup>-1</sup> to 0.0032 $\mu$ g.l<sup>-1</sup> with the annual value of 0.003 $\mu$ g.g<sup>-1</sup>, In Upputhanni Island it was 0.00127 to 0.0031 $\mu$ g.l<sup>-1</sup>, with the annual value of 0.002 $\mu$ g.g<sup>-1</sup>, In Pulivinichalli Island it was 0.00143 to 0.0028 $\mu$ g.l<sup>-1</sup> with the annual value of 0.002 $\mu$ g.g<sup>-1</sup> and In Nallathanni it was from 0.00154 to 0.004 $\mu$ g.l<sup>-1</sup> with the annual value of 0.002 $\mu$ g.g<sup>-1</sup>.

As for as the cadmium concentration in the sediments and coral rubbles were concerned the annual highest concentration were noted in the samples of Van and Koswari Islands  $(0.33\mu g.g^{-1} \text{ and } 0.19\mu g.g^{-1} \text{ in sediment and } 0.17\mu g.g^{-1} \text{ and } 0.19\mu g.g^{-1} \text{ in coral rubbles respectively}) which were followed by the Kariyachalli, Upputhanni, Pulivinichalli and Nallathanni Islands. Seasonwise data also showed a lot of differences. The concentration of cadmium was generally high during monsoon and postmonsoon period where as it was very low during the summer season (Table 5 and Figure 5). Data on the monthwise concentration and season wise observation of lead in water, sediment and coral is shown in Table 6 and graphically represented in Figure 6.$ 

International Journal of Applied Biology and Pharmaceutical Technology Page: 71 Available online at <u>www.ijabpt.com</u>

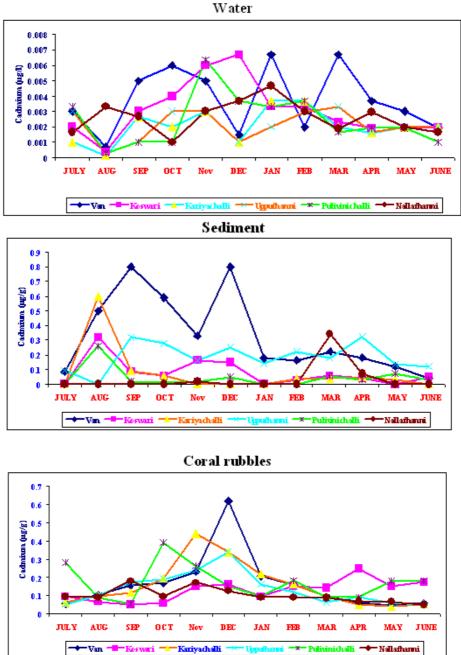


Figure 5 Monthwise variations observed in the concentration of Cadmium in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008).

The concentration of lead in water collected from Van Island showed the least value of  $0.74\mu g.l^{-1}$  during premonsoon and the highest value during monsoon period  $2.134\mu g.l^{-1}$  with an annual value of  $1.28\mu g.l^{-1}$ . In Koswari Island, concentration of lead ranged between  $0.48\mu g.l^{-1}$  to  $1.596\mu g.l^{-1}$  with an annual concentration of  $1.09\mu g.l^{-1}$ , In Kaiyachalli as  $0.53\mu g.l^{-1}$  to  $1.726\mu g.l^{-1}$  with the annual concentration of  $1.08\mu g.l^{-1}$ , in Upputhanni the range of lead between  $0.53\mu g.l^{-1}$  to  $1.48\mu g.l^{-1}$  with the annual value of  $1.02\mu g.l^{-1}$ , In Pulivinichalli the range between  $0.45\mu g.l^{-1}$  to  $1.391\mu g.l^{-1}$  with the annual value of  $0.95\mu g.l^{-1}$  and In Nallathanni Island it was from  $0.36\mu g.l^{-1}$  to  $1.294\mu g.l^{-1}$  with the annual concentration of  $0.93\mu g.l^{-1}$ .

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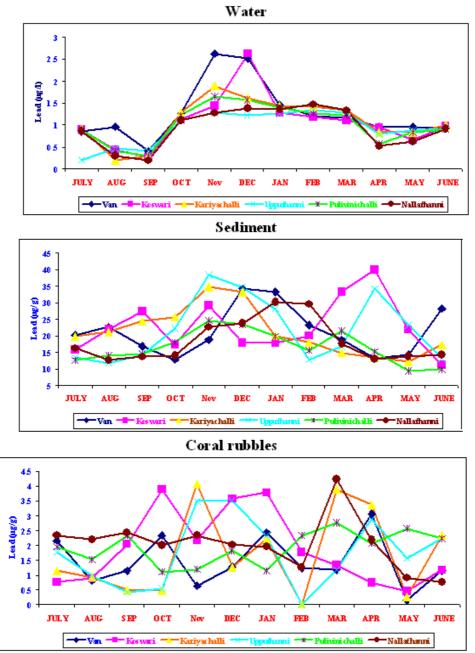


Figure 6 Monthwise variations observed in the concentration of Lead in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008)

In all the study stations the highest concentration of lead was noticed during monsoon season and lowest concentration during pre-monsoon season. The range of value was not much differing in all the seasons. During the month of October and November (monsoon) the highest value of lead was recorded in all the study stations and the lowest values were recorded during August and September (pre-monsoon) in all the six stations (Figure 6). As for as the lead accumulation in the sediments and coral rubbles were concerened in almost all study stations more or less the same trend was observed. When compared the samples of all islands, the samples of Van and Koswari Island showed maximum annual concentration of lead in both the sediment and coral rubble samples. The concentration of lead in sediment was  $22.8\mu g.l^{-1}$  and  $21.9\mu g.l^{-1}$  and in coral rubbles was  $2.05\mu g.l^{-1}$  and  $1.09\mu g.l^{-1}$  in Van and Koswari Islands respectively.

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#### Yogesh Kumar and Geetha

Minimum concentration of lead was observed in Nallathanni Island (Table 6). The month wise observation showed that the concentration of lead was high during monsoon in water and during monsoon and summer in sediments and during summar in coral rubbles (Figure 6) of all the study sites. Analysis of variance also revealed that maximum lead content in Van Island and minimum lead concentration in Nallathanni Island. Monthwise accumulation of lead in sediments and corals showed no correlation.

Arsenic traces were represented as very minimum in the samples of sediments and corals in all the study stations and hence it was not detected during the analysis. But the water samples contain the detectable amount of arsenic in all the study sites. In all the stations the arsenic level was very low during the pre-monsoon and gradually increased during monsoon and post monsoon period and the peak was observed during the month of January and February in almost all stations (Table 7 and Figure 7). The maximum annual concentration was observed in the Van Island and Koswari Islands ( $0.08\mu$ g.l<sup>-1</sup> and  $0.07\mu$ g.l<sup>-1</sup> respectively) and more or less the similar observations were made in all other islands.

	$\frac{1}{1}$									
		Pre		Post						
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual				
	Water (µg/l)	0.74±0.3	2.134±0.76	1.274±0.16	$0.95 \pm 0.02$	1.28±0.61				
	Sediment (µg/g)	21.8±5.87	21.44±6.79	23.71±8.35	24.4±14.6	22.8±1.43				
1	Coral (µg/g)	2.32±0.12	2.117±0.19	2.479±1.56	1.28±0.78	2.05±0.53				
	Water (µg/l)	$0.48 \pm 0.4$	1.596±0.3	1.396±0.05	0.88±0.09	1.09±0.51				
	Sediment (µg/g)	13.2±1.3	31.76±8.51	19.23±8	23.6±10.5	21.9±7.82				
2	Coral (µg/g)	1.94±0.4	1.373±0.39	$2.082 \pm 0.84$	2.28±0.26	1.92±0.39				
	Water (µg/l)	0.53±0.33	1.726±0.79	$1.192 \pm 0.08$	0.86±0.17	$1.08 \pm 0.51$				
	Sediment (µg/g)	19.9±2.98	21.93±11.1	25.09±7.42	18.6±8.32	21.4±2.84				
3	Coral (µg/g)	1.23±0.71	3.224±0.91	2.297±1.31	0.78±0.37	1.88±1.1				
	Water (µg/l)	0.53±0.32	1.48±0.23	1.288±0.09	0.77±0.18	$1.02 \pm 0.44$				
	Sediment (µg/g)	21.8±2.42	31.18±4.94	17.62±2.67	14.3±2.61	21.2±7.31				
4	Coral (µg/g)	$1.06 \pm 0.67$	2.506±1.71	1.167±1.17	2.23±0.66	1.74±0.74				
	Water (µg/l)	0.45±0.36	1.257±0.13	1.391±0.07	0.69±0.2	0.95±0.45				
	Sediment (µg/g)	14.1±1.87	20.16±5.32	25.77±7.14	13.7±0.61	18.5±5.7				
5	Coral (µg/g)	0.86±0.33	1.931±1.9	2.033±1.96	1.99±1.58	1.7±0.56				
	Water (µg.l <sup>-1</sup> )	0.36±0.13	$1.202 \pm 0.08$	$1.294 \pm 0.04$	$0.87 \pm 0.06$	0.93±0.42				
	Sediment (µg/g)	13.7±1.02	22.05±3.51	18.89±2.99	11.5±3.28	16.5±4.82				
6	Coral (µg/g)	1.37±0.7	1.417±0.86	1.618±0.71	1.45±1.47	1.46±0.11				

Table 6 Seasonal variations in the concentration of Lead in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of three observations and + SD

Stns- Stations, 1- Van Island, 2- Koswari Island, 3- Kariyachalli Island, 4- Upputhanni Island, 5- Pulivinichalli Island and 6- Nallathanni Island.

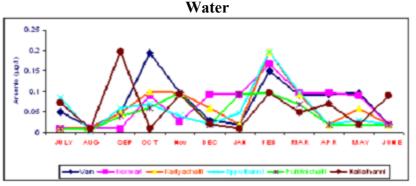


Figure 7 Monthwise variations observed in the concentration of Arsenic in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008)

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		Pre		Post		
Stns	Sample	Monsoon	Monsoon	Monsoon	Summer	Annual
	Water (µg/l)	$0.04 \pm 0.02$	$0.107 \pm 0.08$	$0.087\pm0.07$	$0.07 \pm 0.04$	$0.08 \pm 0.03$
	Sediment (µg/g)	BDL	BDL	BDL	BDL	BDL
1	Coral (µg/g)	BDL	BDL	BDL	BDL	BDL
	Water (µg/l)	0.01±0	$0.07 \pm 0.04$	$0.119 \pm 0.04$	$0.07 \pm 0.04$	$0.07 \pm 0.04$
	Sediment (µg/g)	BDL	BDL	BDL	BDL	BDL
2	Coral (µg/g)	BDL	BDL	BDL	BDL	BDL
	Water (µg/l)	$0.02 \pm 0.02$	$0.085 \pm 0.02$	$0.103 \pm 0.09$	$0.03 \pm 0.02$	$0.06 \pm 0.04$
	Sediment (µg/g)	BDL	BDL	BDL	BDL	BDL
3	Coral (µg/g)	BDL	BDL	BDL	BDL	BDL
	Water (µg/l)	$0.05 \pm 0.04$	$0.043 \pm 0.03$	$0.114 \pm 0.08$	$0.02 \pm 0.01$	$0.06 \pm 0.04$
	Sediment (µg/g)	BDL	BDL	BDL	BDL	BDL
4	Coral (µg/g)	BDL	BDL	BDL	BDL	BDL
	Water (µg/l)	$0.02 \pm 0.02$	$0.059 \pm 0.04$	$0.086 \pm 0.02$	$0.02 \pm 0$	$0.05 \pm 0.03$
	Sediment (µg/g)	BDL	BDL	BDL	BDL	BDL
5	Coral (µg/g)	BDL	BDL	BDL	BDL	BDL
	Water (µg.l <sup>-1</sup> )	$0.09 \pm 0.09$	0.041±0.05	$0.073 \pm 0.03$	$0.06 \pm 0.04$	$0.07 \pm 0.02$
	Sediment (µg/g)	BDL	BDL	BDL	BDL	BDL
6	Coral (µg/g)	BDL	BDL	BDL	BDL	BDL

Table 7 Seasonal variations in the concentration of Arsenic in Water, Sediment and Coral rubbles of different stations during the study period (July 2007 to June 2008). The values indicated are the mean of three observations and  $\pm$  SD.

Stns- Stations, 1- Van Island, 2- Koswari Island, 3- Kariyachalli Island, 4- Upputhanni Island, 5- Pulivinichalli Island and 6- Nallathanni Island.

BDL – Below Deductable level.

# Statistical analysis

In Van Island water was positively correlated with iron, copper, cadmium and lead and negatively correlated with manganese and arsenic. Iron showed high significant correlation with lead (0.05%) and manganese (0.01%) and positively correlated with other metals. Zinc in sediment was positively correlated with copper and cadmium and negatively correlated with iron and manganese. Iron was significantly showed a positive correlation with manganese and negative correlation with copper, cadmium and lead. Manganese showed positive correlation with copper and cadmium. Copper was positively correlated with cadmium and negatively correlated lead. Lead was positively correlated with cadmium. Zinc in coral rubbles was positively correlated with cadmium, lead, manganese and negatively correlated with iron, copper. Cadmium was negatively correlated with lead, manganese, iron and positively correlated with copper. Lead significantly showed a positive correlation with manganese (0.01%), iron (0.01%) and copper. Manganese also positively correlated with iron (0.01%), copper. Iron was negatively correlated with copper Table 9, 15 and 21.

In Koswari Island zinc concentration in water positively correlated and highly significant with copper. Iron was positively correlated and highly significant with cadmium and lead. Manganese was significantly showed positive correlation with copper and negatively correlated with arsenic. Copper also negatively correlated with arsenic. Cadmium significantly showed the positive correlation with lead. Arsenic positively correlated with lead. In sediment the zinc concentration was significantly showed positive correlation with copper and cadmium (0.05%) and negatively correlated with iron, manganese and lead. Iron was significantly showed positive correlation with manganese (0.05%), copper and negative correlation with cadmium and lead. Manganese was positively correlated with copper and lead (0.05%) and negative with cadmium. Copper also negatively correlated with cadmium and lead. But the cadmium was positively correlated with lead.

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# Yogesh Kumar and Geetha

In coral rubbles zinc was significantly showed a positive correlation with lead (0.05%), manganese (0.05%), iron and negative correlation with cadmium and copper. Cadmium was negatively correlated with other metals except copper. Lead significantly showed positive correlation with other metals. Manganese also showed positive correlation with other metals. Iron was negatively correlated with copper.

Parameters	Variable	SS	df	MS	F	Sig.
	Month	13.9	11	1.27	1.526	0.15
Water . Zinc	Stations	18.4	5	3.68	5.364	0.0003
	Month	801.5	11	72.86	15.19	1.5
W.Iron	Stations	130.4	5	26.08	1.795	0.13
	Month	0.04	11	0.003	1.188	0.3
W.Manganese	Stations	0.06	5	0.012	5.359	0.0003
	Month	0.6	11	0.057	3.435	0.001
W.Copper	Stations	0.5	5	0.09	5.223	0.0004
	Month	0.00006	11	5.25	2.706	0.007
W.Cadmium	Stations	0.00003	5	5.05	2.24	0.06
	Month	0.09	11	0.008	5.003	0.00002
W.Arsenic	Stations	0.01	5	0.001	0.44	0.8
	Month	14.06	11	1.28	17.8	5.05
W.Lead	Stations	0.94	5	0.19	0.715	0.6
	Month	1165.99	11	105.99	0.654	0.8
Sediment. Zinc	Stations	4940.4	5	988.09	10.97	1.04
	Month	29753738.7	11	2704885	1.429	0.18
S. Iron	Stations	77005690.9	5	15401138	15.34	5.5
	Month	424580.9	11	38598.26	6.66	3.85
S.Manganese	Stations	128841.9	5	25768.39	2.643	0.03
	Month	933.4	11	84.85	1.334	0.23
S.Copper	Stations	1367.2	5	273.44	5.337	0.0004
	Month	0.4	11	0.039	1.252	0.28
S.Cadmium	Stations	0.79	5	0.16	7.035	0.00003
	Month	1280.7	11	116.4	2.546	0.01
S. Lead	Stations	344	5	68.8	1.234	0.3
Coral	Month	21.16	11	1.9	6.412	6.7
rubbles.Zinc	Stations	7.5	5	1.5	3.128	0.01
	Month	0.29	11	0.03	3.512	0.0008
C.Cadmium	Stations	0.04	5	0.008	0.778	0.57
	Month	18.59	11	1.69	1.709	0.09
C.Lead	Stations	2.51	5	0.5	0.439	0.82
	Month	170.44	11	15.49	1.603	0.12
C.Manganese	Stations	21.07	5	4.21	0.381	0.86
	Month	3308.75	11	300.79	2.373	0.02
C.Iron	Stations	1051.35	5	210.27	1.407	0.23
	Month	4.02	11	0.37	9.447	1.4
C. Copper	Stations	0.28	5	0.06	0.6	0.69

Table 8 Analysis of variances (f values) for the water, trap sediment and coral rubbles between the stations and month during the study period (July 2007 – June 2008)

Page: 76

# Table 9 Correlations coefficient (r) values obtained between heavy metals in sea water during the study period (July 2007 to June 2008) at Van Island

	W.ZINC	W.IRON	W.MANG	W.COPP ER	W.CAD MIU	W.ARSE NI	W.LEAD
W.ZINC	1						
W.IRON	.530	1					
W.MANG	180	.633(*)	1				
W.COPPER	.436	.405	.160	1			
W.CADMIU	.100	.415	.187	150	1		
W.ARSENI	041	.418	.302	.217	.315	1	
W.LEAD	.427	.744(**)	.506	.195	.019	.034	1

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

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

Table 10 Correlations coefficient (r) values obtained between heavy metals in sea water during the study period (July 2007 to June 2008) at Koswari Island

			W.MAN	W.COPPE	W.CADM	W.ARSE	
	W.ZINC	W.IRON	G	R	IU	NI	W.LEAD
W.ZINC	1						
W.IRON	.503	1					
W.MANG	.410	.368	1				
W.COPPER	.743(**)	.418	.653(*)	1			
W.CADMIU	.528	.832(**)	.289	.469	1		
W.ARSENI	291	.282	260	232	.217	1	
W.LEAD	.232	.661(*)	.176	.009	.806(**)	.389	1

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

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

 Table 11 Correlations coefficient (r) values obtained between heavy metals in sea water during the study period (July 2007 to June 2008) at Kariyachalli Island.

	W.ZINC	W.IRON	W.MAN G	W.COPPE R	W.CADM IU	W.ARSE NI	W.LEAD
W.ZINC	1						
W.IRON	186	1					
W.MANG	.223	.476	1				
W.COPPER	434	.387	.069	1			
W.CADMIU	.030	.407	.582(*)	.219	1		
W.ARSENI	263	.538	.374	.181	.541	1	
W.LEAD	031	.852(**)	.679(*)	.090	.468	.497	1

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

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

Table 12 Correlations coefficient (r) values obtained between heavy metals in sea water during the studyperiod (July 2007 to June 2008) at Upputhanni Island.

	<b>^</b>		NY NA ANI		WCADM	WADEE	
			W.MAN	W.COPPE	W.CADM	W.ARSE	
	W.ZINC	W.IRON	G	R	IU	NI	W.LEAD
W.ZINC	1						
W.IRON	.643(*)	1					
W.MANG	.662(*)	.513	1				
W.COPPER	.343	.369	.176	1			
W.CADMIU	188	.234	074	.117	1		
W.ARSENI	181	.253	414	258	.626(*)	1	
W.LEAD	.456	.700(*)	.547	.052	.417	.283	1
		* Correlation	n is significa	nt at the 0.05 le	vel (2-tailed)		

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

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# Table 13 Correlations coefficient (r) values obtained between heavy metals in sea water during the study period (July 2007 to June 2008) at Pulivinichalli Island.

	W.ZINC	W.IRON	W.MAN G	W.COPPE R	W.CADM IU	W.ARSE NI	W.LEAD
W.ZINC	1						
W.IRON	.064	1					
W.MANG	443	104	1				
W.COPPER	.270	634(*)	308	1			
W.CADMIU	029	.854(**)	280	351	1		
W.ARSENI	.055	.805(**)	.067	539	.540	1	
W.LEAD	.253	.723(**)	227	455	.735(**)	.620(*)	1

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

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

Table 14 Correlations coefficient (r) values obtained between heavy metals in sea water during the study period (July 2007 to June 2008) at Nallathanni Island

	•		W.MAN	W.COPPE	W.CADM	W.ARSE	
	W.ZINC	W.IRON	G	R	IU	NI	W.LEAD
W.ZINC	1						
W.IRON	.452	1					
W.MANG	.085	.059	1				
W.COPPER	646(*)	645(*)	.252	1			
W.CADMIU	.541	.305	051	361	1		
W.ARSENI	093	172	.193	.375	110	1	
W.LEAD	.339	.841(**)	035	699(*)	.150	310	1

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

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

Table 15 Correlations coefficient (r) values obtained between heavy metals in sediment during the study period (July 2007 to June 2008) at Van Island.

	•	· · ·		S.COPPE	S.CADM	
	S.ZINC	<b>S.IRON</b>	S.MANG	R	IU	S.LEAD
S.ZINC	1					
S.IRON	542	1				
S.MANG	448	.322	1			
S.COPPER	.085	496	224	1		
S.CADMIU	.142	550	052	.145	1	
S.LEAD	049	055	.319	259	.047	1

# Table 16 Correlations coefficient (r) values obtained between heavy metals in sediment during the studyperiod (July 2007 to June 2008) at Kaswori Island.

				S.COPPE	S.CADM	
	S.ZINC	S.IRON	S.MANG	R	IU	S.LEAD
S.ZINC	1					
S.IRON	396	1				
S.MANG	508	.690(*)	1			
S.COPPER	.061	.273	.079	1		
S.CADMIU	.578(*)	524	484	025	1	
S.LEAD	284	094	.578(*)	194	.091	1

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

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Table 17 Correlations coefficient (r) values obtained between heavy metals in sediment during the study period (July 2007 to June 2008) at Kariyachalli Island

	S.ZIN	S.IRON	S.MANG	S.COPPER	S.CADM IU	S.LEAD
S.ZINC	1					
S.IRON	.533	1				
S.MANG	.477	.884(**)	1			
S.COPPER	.124	253	435	1		
S.CADMIU	436	759(**)	691(*)	167	1	
S.LEAD	.330	211	330	.863(**)	036	1

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

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

#### Table 18 Correlations coefficient (r) values obtained between heavy metals in sediment during the study period (July 2007 to June 2008) at Upputhanni Island

	S.ZIN	S.IRON	S.MANG	S.COPPE R	S.CADMI U	S.LEAD
S.ZINC	1					
S.IRON	221	1				
S.MANG	148	.858(**)	1			
S.COPPER	.362	.535	.674(*)	1		
S.CADMIU	059	.435	.587(*)	.260	1	
S.LEAD	.550	.366	.362	.541	.353	1

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

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

#### Table 19 Correlations coefficient (r) values obtained between heavy metals in sediment during the study period (July 2007 to June 2008) at Pulivinichalli Island

	S.ZIN	<b>S.IRON</b>	S.MANG	S.COPPER	S.CADMIU	S.LEAD
S.ZINC	1					
S.IRON	.838(**)	1				
S.MANG	.799(**)	.662(*)	1			
S.COPPER	.751(**)	.700(*)	.481	1		
S.CADMIU	215	385	607(*)	284	1	
S.LEAD	.232	.355	.104	.368	172	1

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

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

#### Table 20 Correlations coefficient (r) values obtained between heavy metals in sediment during the study period (July 2007 to June 2008) at Nallathanni Island.

	S.ZIN	S.IRON	S.MANG	S.COPPER	S.CADMIU	S.LEAD
S.ZINC	1					
S.IRON	.331	1				
S.MANG	.215	160	1			
S.COPPER	.202	.471	.395	1		
S.CADMIU	.436	.639(*)	.229	.482	1	
S.LEAD	.701(*)	.077	286	406	087	1

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

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		C.CAD				
	C.ZIN	MIU	C.LEAD	C.MANG	<b>C.IRON</b>	C.COPPER
C.ZINC	1					
C.CADMIU	.417	1				
C.LEAD	.061	056	1			
C.MANG	.040	068	.997(**)	1		
C.IRON	223	059	.749(**)	.768(**)	1	
C.COPPER	353	.129	.084	.089	042	1

Table 21 Correlations coefficient (r) values obtained between heavy metals in coral rubbles during the study period (July 2007 to June 2008) at Van Island

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

In Kariyachalli Island zinc was positively correlated with manganese and cadmium, and negatively correlated with iron, copper and arsenic. Iron was positively correlated with other metals at 0.01% level of significance with lead. Manganese also positively correlated with other metals and showed significant correlation with cadmium and lead. In sediment the zinc was significantly showed positive correlation with other metals except cadmium. Iron was significantly showed negative correlation with other metals except manganese. Manganese also negatively correlated with other metals. Copper significantly showed positive correlation with lead and negative correlation with cadmium. Cadmium was negatively correlated with lead. In coral rubbles zinc was positively correlated with cadmium, lead, manganese and negatively correlated with iron and copper. Cadmium was positively correlated with other metals. Lead, manganese, iron also positively correlated with other metals. Lead showed positive correlated with other metals.

In Upputhanni Island the zinc in water was positively correlated with iron and manganese. Iron was positively correlated with other metals at 0.05% significant level. Cadmium also positively correlated with other metals at 0.05% significant level. In upputhanni Island zinc was significantly showed positive correlation with copper and lead and negatively correlated with iron, manganese and cadmium. Iron was significantly showed positive correlation with all metals. Manganese also positively correlated with copper (0.05%), cadmium (0.05%) and lead. Copper was positively correlated with cadmium and lead. Cadmium also showed positive correlation with lead. In coral rubbles zinc was negatively correlated with iron and copper (0.05%) and positively correlated with lead, manganese and negatively correlated with iron and copper. Lead was positively correlated with manganese (0.01%), copper and negatively correlated with iron. Manganese was positively correlated copper and negatively correlated with iron.

In pulivinichalli Island iron in water was positively correlated significant with cadmium, arsenic and lead and negatively correlated with copper. Lead was (0.05%) significantly showed positive correlation with cadmium and arsenic. In sediment negative correlation was noted with cadmium, zinc, iron, manganese and copper. In coral rubbles zinc was negatively correlated with other metals except lead. Cadmium also negatively correlated with other metals except lead. Cadmium also negatively correlated with other metals except copper. Lead was positively correlated with other metals except copper. Manganese positively correlated with iron and negatively correlated with copper. Iron was positively correlated with copper. In Nallathanni Island zinc in water was negatively correlated with copper and arsenic. Copper was positively correlated with copper and arsenic. Lead was (0.01%) significantly correlated with iron. Copper also showed (0.05%) significant correlation with iron. In Nallathanni Island zinc was significantly showed positive correlated with iron and negatively correlated with zinc. Cadmium correlated with iron and negatively correlated with zinc. Cadmium correlated with iron and negatively correlated with argenese, manganese with lead, copper with lead and cadmium with lead. In rubbles zinc was positively correlated with other metals except copper. Cadmium positively correlated with other metals except iron. Lead showed highly positive significant correlation with manganese (0.01%). Manganese positively correlated with iron and copper. Iron also positively correlated with copper.

International Journal of Applied Biology and Pharmaceutical Technology Page: 80 Available online at <u>www.ijabpt.com</u> Table 22 Correlations coefficient (r) values obtained between heavy metals in coral rubbles during the<br/>study period (July 2007 to June 2008) at Kaswori Island

	C.ZIN	C.CAD MIU	C.LEAD	C.MANG	C.IRON	C.COPPER
C.ZINC	1					
C.CADMIU	336	1				
C.LEAD	.630(*)	338	1			
C.MANG	.635(*)	369	.996(**)	1		
C.IRON	.008	178	.320	.302	1	
C.COPPER	058	.528	.021	.020	157	1

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

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

Table 23 Correlations coefficient (r) values obtained between heavy metals in coral rubbles during the<br/>study period (July 2007 to June 2008) at Kariyachalli Island

		C.CAD	,	· · ·		C.COPP
	C.ZIN	MIU	C.LEAD	C.MANG	<b>C.IRON</b>	ER
C.ZINC	1					
C.CADMIU	.407	1				
C.LEAD	.114	.252	1			
C.MANG	.112	.256	.998(**)	1		
C.IRON	116	.448	.361	.375	1	
C.COPPER	295	.210	.277	.258	.442	1

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

Table 24 Correlations coefficient (r) values obtained between heavy metals in coral rubbles during the study period (July 2007 to June 2008) at Upputhanni Island

		Č.CAD		at opputnar		C.COPP
	C.ZIN	MIU	C.LEAD	C.MANG	<b>C.IRON</b>	ER
C.ZINC	1					
C.CADMIU	.544	1				
C.LEAD	.266	.398	1			
C.MANG	.327	.429	.992(**)	1		
C.IRON	030	299	173	194	1	
C.COPPER	604(*)	389	.146	.093	.016	1

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

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

Table 25 correlations coefficient (r) values obtained between heavy metals in coral rubbles during the study period (July 2007 to June 2008) at Pulivinichalli Island

		C.CAD	ĺ ĺ			C.COPP
	C.ZIN	MIU	C.LEAD	C.MANG	<b>C.IRON</b>	ER
C.ZINC	1					
C.CADMIU	401	1				
C.LEAD	.057	424	1			
C.MANG	009	384	.977(**)	1		
C.IRON	173	005	.555	.640(*)	1	
C.COPPER	131	.457	145	175	.270	1

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

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

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		C.CAD				C.COPP
	C.ZIN	MIU	C.LEAD	C.MANG	C.IRON	ER
C.ZINC	1					
C.CADMIU	.121	1				
C.LEAD	.247	.322	1			
C.MANG	.239	.432	.989(**)	1		
C.IRON	.685(*)	131	.151	.094	1	
C.COPPER	023	.117	012	.008	.391	1

Table 26 Correlations coefficient (r) values obtained between heavy metals in coral rubbles during the study period (July 2007 to June 2008) at Nallathanni Island coral

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

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

# DISCUSSION

Metals in particulate forms are important in determining their concentration in filter feeding forms (Boyden and Romeril, 1974). The forms in which metals are found in water may have an important bearing on its availability to aquatic animals (Wright, 1978). Several metals are capable of forming complexes of low solubility which effectively reduce their concentration (Wright, 1978). Coral reefs are useful indicator organisms for environmental monitoring (Harland and Nganro, 1990; Guzman and Jarvis, 1996). Cross *et al.*, (1970) reported that it is difficult to correlate metal concentration in organism with that of water and sediments. The concentration of metals in the corals is an indication of detrital input into the sea (Linn *et al.*, 1990). Sediments represent the largest reservoir of trace metals and have designated the bottom sediments as a sink for most of the pollutants causing injuries to the biota (Refro, 1973; Mathis and Cuming, 1973).

Scleractinian corals absorb trace elements into their skeletons from 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 coral are affected by near shore developmental activities such as coastal mining, harbour dredging, dumping of industrial and domestic effluents into the ocean, urbanization and over population (Anu Gopinath et al., 2009). 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 (Howard and Brown, 1984). In general the level of iron recorded during the study period in the waters of the present study was with in the normal limit  $(6.6\mu g.l^{-1} to 18.08\mu g.l^{-1})$  as reported by Palanichamy et al., (2002). The study report showed that the iron concentration observed in water, sediments and coral rubbles of Van and Koswari Island was very high when compared to other study sites. Mahajan et al., (1987) stated that the iron concentration in the water column of Bombay coast as  $41.81\mu$ g.l<sup>-1</sup>. On the other hand the concentration of iron in sediments and coral rubbles seemed to be very high. It ranged from  $3189 \mu g.g^{-1}$  to 5484 $\mu$ g.g<sup>-1</sup> in sediments and 27.7 $\mu$ g.g<sup>-1</sup> to 40.4 $\mu$ g.g<sup>-1</sup> in the coral rubbles respectively during the study period in most of the study sites. Palanichamy et al., (2002) had reported similar values of iron concentration in the sediment of the Gulf of Mannar region. Dumping of fly ash by the Thoothukudi Thermal power station in the Karapadu Bay of Thoothukudi might contribute to about 4 to 6% of iron in this region as it was spread to the near by islands by the prevailing current and shifting of sediment to the northern side of Gulf of Mannar by the current. The concentration of iron in the study sites may also be due to the iron enrichment resulted from reduction of iron in the sediments during the oxidation of organic matter (Francois, 1988).

In the present study the concentration of zinc in the study materials of Van Island showed higher values than all other five stations (Table 3). This high occurrence might be due to the continuous discharge of domestic sewage into this region by the Thoothukudi Municipal corporation particularly near the Thirespuram coastal village. The increased trend noticed in the water samples during the monsoon and post monsoon season in all the stations, might be due to the run off rainwater from mainland.

Ramalingom *et al.*, (1994) noticed the same trend in the waters along the south west coast of India. Venugopal *et al.*, (1982) observed and reported the seasonal variation of Zinc in Cochin Backwaters. In relation to water, the concentration of zinc in sediments ( $83.4\mu g.g^{-1}$  to  $93.8\mu g.g^{-1}$ ) and corals ( $0.97\mu g.g^{-1}$  to  $2.7\mu g.g^{-1}$ ) also high in Van island than in other islands. Venugopal *et al.*, (1982) estimated high concentration of zinc in the sediments of Cochin backwaters and Nguyen *et al.*, (2009) in the sediments of Jeju Island of Korea. The present study value falls between these two study reports. Rajendran, *et al.*, (1993) observed the presence of zinc ( $48\mu g.g^{-1}-95\mu g.g^{-1}$ ) in reef associated seaweeds collected from the north east coast of Tamil nadu.

Manganese is an element of low toxicity having considerable biological significance. It is one of the most biogeochemical and active transition metals in aquatic environment (Evans *et al.*, 1977; JanakiRaman *et al.*, 2007). Manganese is an essential trace element required by both plant and animals. The primary natural sources of atmospheric Mn are wind- borne soil particles, volcanoes coal burning and incineration of municipal wastes (Ramesh and Anbu, 1996). During the present study it was noted that the concentration of manganese was low during the pre-monsoon and high during the summer in the materials of all the stations (Table 3 and Figure 3). Ram Mohan *et al.*, (2010) reported correlate with the findings of the present study. The manganese concentration of the sediment in the study stations ranged from  $383\mu g.g^{-1}$  to  $739\mu g.g^{-1}$  and coral rubbles from  $2.14\mu g.g^{-1}$  to  $7.35\mu g.g^{-1}$ . Valentina Caccia *et al.*, (2003) reported high values of Manganese in Florida Bay sediments and these values are quite similar to our findings. The observed concentration of Mn in the sediment of the study stations might be due to the discharge of large quantum of industrial and domestic sewages into the sea.

The concentration of copper in the water collected from the study sites in Gulf of Mannar Coast ranged from  $0.14\mu$ g.l<sup>-1</sup> to  $0.62\mu$ g.l<sup>-1</sup> and in sediment ranged from  $12.8\mu$ g. g<sup>-1</sup> to  $31.2\mu$ g.g<sup>-1</sup> and in coral rubbles from  $0.27\mu$ g.g<sup>-1</sup>  $0.59\mu$ g.g<sup>-1</sup> which were very close to the reports of previous workers (Kumaresan *et al.*, 1998; Mathews *et al.*, 2006; Cao *et al.*, 2007; Krishna kumar *et al.*, 2010). The rainfall and river may be the prominent source of copper metal into the marine system. Copper content in sea water, sediment and coral rubble samples collected from Van and Koswari Islands showed the highest value than the other stations studied. The various industries established in the main land which is very close to these island, may be the main contributing factor for the high concentration of copper in these sites. Industrial development and their waste discharge into coastal water affect the coral reefs (Esslemnont, 1999). Mahajan *et al.*, (1987) reported very low concentration of copper in the sea water of Thana creek. Copper is a widely distributed trace metals in the sediment that has biological importance, Its widespread use in industries leads to elevated levels in the marine environment and therefore it is considered as potentially one of the most hazardous elements in the environment. In the present study the observed copper level in the sediments and coral rubbles might be due to the effluents discharged from the industries of Thoothukudi, urban runoff, harbour wastes and the antifouling paints painted on the boats and ships that are parked in the harbour (Fernandez, 1983; Kennish, 1996; Cao *et al.*, 2007).

The level of cadmium ranged from 0.001µg.l<sup>-1</sup> to 0.006µg.l<sup>-1</sup> in the waters of Thoothukudi and Vembar group of islands (Palanichamy and Rajendran, 2000). Palanichamy et al., (2004) recorded high concentration of cadmium in Arumuganeri waters which are very close to the study sites. The main source of cadmium to the marine environment is anthropogenic input and atmospheric loading (Kennish, 1996). Cadmium concentration in sediment was lower than all other trace metals analyzed in Thoothukudi and Vembar group of island, Gulf of Mannar. In some months the cadmium level was completely below detectable limit (BDL) and in some months (monsoon) the concentration of cadmium shoot upto  $0.57\mu g.g^{-1}$ . In the cleaner inshore areas a range of  $0.04\mu g.g^{-1}$ to  $0.33\mu$ g.g-1 was common. The concentration of cadmium in sediment collected from near by the present study sites such as Kanyakumari (0.4µg.g<sup>-1</sup> to 1.0µg. g<sup>-1</sup>), Arumuganeri (BDL to 4.33µg.g<sup>-1</sup>), Thoothukudi (BDL to  $3.95\mu$ g.g<sup>-1</sup>), Mandapam ( $1.15\mu$ g.g<sup>-1</sup> to  $3.6\mu$ g.g<sup>-1</sup>) and Thondi ( $1.55\mu$ g.g<sup>-1</sup> to  $2.9\mu$ g.g<sup>-1</sup>) also showed a very close range (Palanichamy and Rajendran, 2000). Unlike the other metals in cadmium, the chance of adsorption into particulate material is limited, they usually settled to bottom sediment (Jickells and Knap, 1984) and hence an increased concentration in the sediments. In all the coral rubbles samples studied, cadmium was found to be in a considerable low concentration when compared to the other metals. Mathews et al., (2006) and Krishna kumar (2010) also reported low values  $(0.01\mu g.g^{-1} to 0.02\mu g.g^{-1})$  of cadmium for different species of corals from Gulf of Mannar coast.

International Journal of Applied Biology and Pharmaceutical Technology Page: 83 Available online at <u>www.ijabpt.com</u>

The annual concentration of lead in the waters collected from the study sites of Gulf of Mannar Coast ranged from  $0.93\mu$ g.l<sup>-1</sup> to  $1.28\mu$ g.l<sup>-1</sup>. The lead content of water sample collected from Van and Koswari islands showed the highest range when compared to other stations (Table 6). The various industries located in the main land which are closer to these island, may contribute to the high concentration of lead into these sites. According to Esslemnont, (1999), Industrial development and their waste discharge into coastal water affect the coral reefs and he reported more or less the same limit as in the present study in the harbours of Australian coast. During the present study the lead concentration in the sediments of Vembar and Thoothukudi group of islands was found to be ranged between 16.5  $\mu$ g.g<sup>-1</sup> to 22.8  $\mu$ g.g<sup>-1</sup> (Cao *et al.*, 2007) and the lead content of the coral rubble samples during the present study ranged from 1.46 to 2.05 $\mu$ g.g<sup>-1</sup> in Thoothukudi and Vembar group of islands (Rajendran *et al.*, 1993; Mathews *et al.*, 2006; Krishnakumar *et al.*, 2010). The values recorded in the present study is slightly higher than previous reports of Gulf of Mannar (Palanichamy and Rajendran, 2000). The higher concentration of lead observed in the sediments of the present study may be due to the several sources such as boat exhaust systems, spillage of oil, and other petroleum products exhausted from mechanized boats employed in fishing and cargo handling ships of Thoothukudi harbour and the discharge of sewage effluents from the industries of Thoothukudi into the water (Abu-Hilal, 1987 and Laxen, 1983).

Arsenic is ubiquitous in nature and is found in detectable concentrations in all environmental matrices. The occurrence of arsenic in the continental crust of the earth is generally given as 1.5mg/l. to 2mg/l. Very limited data indicate that sand and clay exhibit high arsenic concentration. Coal and it's by product the fly ash also contain sufficient quantities. Thus combustion of coal for generating power as well as the disposal of fly ash, may contribute as input into the environment (Ramesh and Anbu, 1996). In the present study the various observed concentrations of arsenic in the waters of the Gulf of Mannar recorded (ranged from 0.05mg/l to 0.08mg/l), may be due to the ash dumping activity of Thoothukudi thermal power station, dumping of sewage and by the degradation of beachrocks of the Gulf of Mannar region, which contain appreciable amount of arsenic (Dajkumar *et al.*, 2010).

Overall the metal analysis in the study area showed that the concentration of trace elements in the water are in the order of Fe > Pb > Zn > As > Mn > Cd > Cu and in sediment in the order of Fe > Mn > Pb > Zn > Cu > Cdand in coral rubbles in the order of Fe > Mn > Pb > Zn > Cu > Cd. In the waters the iron ranks first and copper ranks last, in corals the iron ranks first and cadmium ranks the last in concentration. In the sediment, iron ranks first in concentration and cadmium ranks the last in concentration and during the entire study periods. It was noted, that the values recorded at Thoothukdi group of islands were little higher than the Vembar group of islands, and it might be due to discharges pumped from the industrial belt of Thoothukudi, domestic sewages from Thoothukudi town, harbour activities and thermal power plant operation along the southern side of the Gulf of Mannar. Of all the metals observed the iron ranks first because almost all effluents mentioned contains iron and also the iron could be converted to complex hydroxyl compounds that may eventually precipitate (Riley and Chester, 1973) and this would lead to the co-precipitation of metals in the sediments. Fe and Mn, when entering into marine environment rapidly precipitate and other metals like Zn, Cu, Pb, and Cd could precipitate in a linear manner with time (Lowman et al., 1971). At the same time, many metal minerals present in the marine sediments are capable of absorbing large quantities of certain trace elements from the water column (Krauskopf, 1956; Turenkian, 1971). In the same way, continual resuspension of bottom sediments occurring in the southern part of Gulf of Mannar may serve to scavenge and concentrate metals that are naturally present in the water column as well as those introduce by anthropogenic activities. This mechanism could increase the metal concentration in southern part of the Gulf of Mannar. Moreover, the northeward movement of sediments and currents are the pathways for increase in the concentration of these metals in the Vembar group of islands also. In the present study sediment iron shows significant positive correlation with Pb and Zn. It indicated that the acid

In the present study sediment iron shows significant positive correlation with Pb and Zn. It indicated that the acid leachable iron mainly available in the form of oxic phase/oxide coatings on sediment particles (Rao and Murty, 1990). The role of Fe oxides and anthropogenic contribution of metals become a major factor in affecting the distribution of metals in the Gulf of Mannar (Subramanian and Mohanachandran, 1990).

Zn and Cu are essential elements for living coral organisms and play an important role in growth, cell metabolism and survival. Pb and Cd in corals are well known indicators of anthropogenic activity (Shen and Boyle, 1988). Several contamination of Cd leads to disease in corals (Yosumura *et al.*, 1980).

The concentration of Pb was higher than the Zn in coral skeleton. Pb was a toxic element to corals (Beyersmann 1944), whereas Zn is an essential micro nutrient of coral reefs and also commonly used for protein systhesis and repair of cells (Brown and Howard 1985). The values of Zn observed in the present study an indicator for promoting the coral growth (Hanna and Muir, 1990).

In conclusion the trace element concentrations observed in the coral rubbles of Gulf of Mannar when compared with other regions of world indicated that the metal values of the study sites does not interfere with the growth and the survival of corals at present to a greater extent. But in future, the Gulf of Mannar Bay may experience an accelerated growth in the input of heavy metals due to the proposed expansion project of Thoothukudi port and establishment of few more thermal power stations and expansions of the existing Thermal Power Station by the addition of 1000 MW unit and expected other ancillary and allied industrial unites, there will be definitly an increase in the anthropogenic activites and dumping of several thousand tons of wastes and sewages into the sea of the study area. These will definitely resulted in the increase of toxic load and a thorough change in the present marine environment.

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