J. Mar. Biol. Ass. India, **52** (1) : 48 - 54, January - June 2010

Heavy metal concentration in sea water, sediment and bivalves off Tuticorin

*P. S. Asha, P. K. Krishnakumar, P. Kaladharan, D. Prema, K. Diwakar, K. K. Valsala and G. S. Bhat

*Tuticorin Research Centre of CMFR Institute, South Beach Road, Karapad, Tuticorin-628 001, Tamil Nadu, India. *E-mail: ashasanil@gmail.com*

Abstract

Concentration of heavy metals Cd, Cu, Fe, Mn, Ni, Pb and Zn in sea water, sediment and bivalve samples from three stations was studied for one year along Tuticorin coast. The concentration was in the order of Fe>Mn>Zn>Cu>Pb>Cd>Ni. Generally the concentration of Fe was very high in the sediment and bivalves when compared to earlier studies from other areas along the Indian coast. High concentration of Fe, Mn, Cu, Pb and Zn was observed during monsoon season. One way ANOVA indicated statistically significant differences ($p<0.01$) among the samples in the concentration of Cu, Fe, Mn, Pb and Zn. Except for Cd and Cu, no significant difference was noticed in the seasonal variation of other metals.

Keywords: Heavy metals, sea water, sediment, bivalve tissue, Tuticorin

Introduction

Tuticorin waters is affected by industrialization in the past few years (Easterson, 1998; Murugan and Edward, 2000). The effluent discharges from various industries, fertilizers, chemical plants and untreated sewage are the main source of heavy metal pollution along Tuticorin coastal waters.

Ganesan and Kannan (1995) showed higher concentration of Fe and Mn in the sea water, sediment and algae in the vicinity of Tuticorin Port. Palanichamy and Rajendran (2000) indicated high concentration of Cd and Pb in the bottom waters than the surface waters off Tuticorin. Satyanarayanan and Murty (1990) showed relatively higher concentration of trace metals and nutrients in low saline inshore waters, but lower with high salinity in the offshore waters of Bay of Bengal. Baskaran *et al*. (2002) observed relatively higher concentration of Fe, Cu, Zn and Al in the fly ash dumping area than in the deeper waters off Tuticorin. Ganesan *et al*. (1991) indicated higher concentration of heavy metals like Mn, Fe, Cu and Zn in the seaweeds off Tuticorin. Senthilnathan *et al*. (1998) showed seasonal variation with an increased metal load during monsoon period in the mussel and oysters from the southeast coast of India. The present paper is on heavy metal concentration in the sediment, water and bivalve samples from three stations off Tuticorin.

Material and Methods

Water, sediment and bivalve samples for heavy metal analysis along with water samples for hydrological parameters were collected every month for one year (2003) from two contaminated areas (stations 1 and 2) and from a relatively clean area, station 3 (Fig. 1). St.1 (08^0 47' N lat.78^0 11' E long.) is located close to the erstwhile Pandian Island, about 300 m away from the shore, inside the fly ash laden dyke II of Tuticorin Thermal Power Station, constructed to retain the fly ash containing slurry. The bivalve selected for analysis from this station was *Marcia opima.* St. 2 (08^0 35' N lat. 78^0 08' E long.) is located nearly 40 km south of Tuticorin, one km away from the exit point of effluent lagoon of Dharangadhara Chemical Works (DCW). Here *Donax cuneatus* was selected for study. St. 3

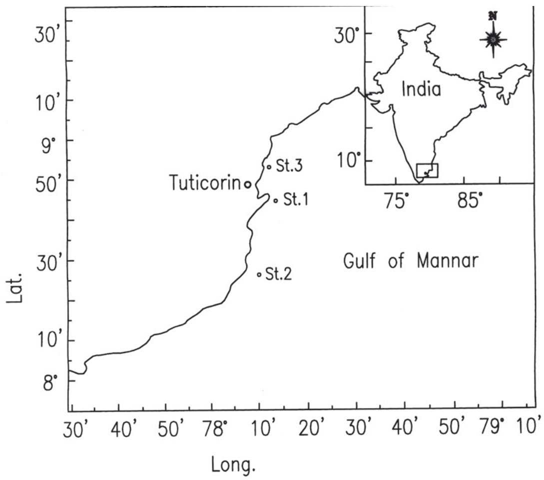

Fig. 1. Map showing sampling stations

(08^{0} 51' N lat. 78^{0} 10' E long.) is located in the sandy beach area nearly 15 km north off Tuticorin and is free from industrial pollution. The bivalve selected was *Donax faba*.

In situ observation on temperature was made with a thermometer of 0.5^{o} C accuracy. Standard procedures (Strickland and Parson, 1968) were followed to estimate the hydrological parameters namely salinity, dissolved oxygen, B.O.D, pH, productivity and chlorophyll '*a*'. Ammonia was estimated by following phenol hypochlorite method (Solarzano, 1969).

The sediment samples collected by Van Veen grab were brought to the laboratory in polythene bags. The collected bivalves (*Marcia opima*: 25 - 38 mm; *Donax cuneatus*: 12 – 16 mm; *Donax faba*: 14 – 18 mm) (10 - 35 numbers from each station) were washed and kept in filtered sea water to empty the gut. Whole body tissue of animals were removed and washed in distilled water. The sediment and tissue samples were dried in an oven at 80 ± 2^{o} C. The metals Fe, Mn, Zn, Cu, Cd and Ni were extracted from dried and finely ground tissue and sediment samples in duplicate (5 g each) by following acid digestion procedure (Dalziel and Baker, 1984) and were detected on a Perkin Elmer AAS (Model 2380) in an air acetylene flame.

Surface water samples from 2 m depth were collected from the same locality. The heavy metals Zn, Cu, Pb and Cd in sea water were analysed using Stripping Voltametry in a 757 VA Computrace attached to 765 Dosimat (Metrohm, Switzerland) following the method outlined by Anoop *et al.* (2007). The bioaccumulation factor (BAF) was calculated following Devagi *et al.* (2008). BAF = metal concentration (µg.g dry wt^{-1}) in organism/ metal concentration (µg.l^{-1}) in water x 100. The mean values of each metal were analyzed to test one way analysis of variance (ANOVA) using SPSS 7.5 statistical package.

Results and Discussion

***Hydrography*:** The mean values of hydrographical conditions at sampling stations are given in Table 1. The values were similar to the earlier findings from Gulf of Mannar (Subramanian and Kannan, 1988; Bindu *et al*., 2007). The industrial discharge is not influencing the hydrology of polluted

Table 1. Hydrographical parameters (mean ± S.E., n=36) of sampling stations off Tuticorin

Parameters	Station 1	Station 2	Station 3
SST (^{0}C)	29.5 ± 0.4	31.1 ± 0.8	30.2 ± 0.7
pH	7.9 ± 0.3	7.8 ± 0.05	7.8 ± 0.04
Salinity (ppt)	37.5 ± 0.93	33.5 ± 0.9	35.5 ± 0.6
D.O (ml. l^{-1})	2.5 ± 0.6	2.4 ± 0.2	1.9 ± 0.3
Chlorophyll (µg. ml^{-1})	3.02 ± 0.6	3.3 ± 1.2	4.9 ± 1.5
Productivity (mg C. l^{-1} day ^{1})	0.253 ± 0.1006	1.869 ± .0.069	1.063 ± 0.37
Ammonia (µg .ml^{-1})	68.4 ± 2.4	51.2 ± 7.2	88.9 ± 11.4
B.O.D (mg. ml^{-1})	0.83 ± 0.32	1.58 ± 0.45	2.06 ± 0.6
Total Suspended Solids (TSS) (mg. ml^{-1})	0.274 ± 0.019	0.235 ± 0.015	0.306 ± 0.033

stations as indicated from the insignificant differences in most of parameters between stations.

***Heavy metal concentrations*:** The mean values of heavy metal concentration in the tissue, sediment and seawater samples in the three stations and bioaccumulation factor (BAF) are given in Table 2. The mean concentration of Cd in the water (1.01 $\mu g.l^{-1}$) and sediment (1.65 $\mu g.g^{-1}$); Cu in the water (7.45 $\mu g.l^{-1}$) and clam tissue (17.97 $\mu g.gl^{-1}$) and Zn in the water (27.83 $\mu g.l^{-1}$) samples were the highest at station 2, indicating heavy metal pollution caused by DCW.

to 2072 $\mu g.g^{-1}$) and Mn in the clam (27.9 to 165.7 $\mu g.g^{-1}$) and sediment (63.6 to 91.6 $\mu g.g^{-1}$) samples were higher than those observed in the earlier studies of Ganesan and Kannan (1995) off Tuticorin, indicating enhanced industrial pollution off Tuticorin. In this study the mean concentration of Pb in water varied from 7.23 to 11.2 $\mu g.gl^{-1}$, much higher than the previous studies of Palanichamy and Rajendran (2000) who observed high concentration of Pb in the sediment than in water off Tuticorin. Phillips (1976) indicated the importance of fuels as a source of lead in the marine environment.

Table 2. Heavy metal concentration (mean ± SE., n = 36) in sea water ($\mu g.\ l^{-1}$), sediment ($\mu g.g^{-1}$) and bivalves ($\mu g.\ g^{-1}$) off Tuticorin coast; bioaccumulation factors are given in parenthesis

	Station 1			Station 2			Station 3		
Metal	Water	Sediment	Clam	Water	Sediment	Clam	Water	Sediment	Clam
Fe	-	2071.8± 331.7	353.07± 65.5	-	1721.4± 387.2	667.6± 122.4	-	696.25± 146.9	496.03± 143.7
Mn	-	91.56± 19.9	42.32± 14.2	-	77.85± 9.3	27.88± 3.7	-	63.62± 10.1	165.71 ±36.4
Zn	7.59± 1.4	17.94± 4.2	85.68± 33.4 (1128.9)	27.83± 4.5	10.31± 3.2	180.36± 35.7 (648.08)	25.54± 5.6	10.55± 3.9	227.67± 39.6 (891.4)
Cu	6.84± 1.4	9.78± 2.6	5.69± 2.3 (83.2)	7.45± 1.7	1.08± 0.8	17.97± 5.7 (241.2)	6.77± 1.3	0.86± 0.7	7.91± 4.9 (116.8)
Pb	7.23± 1.5	-	-	10.0± 3.2	-	-	11.2± 6.8	-	-
Cd	0.55± 0.1	0.60± 0.3	1.21± 0.5 (220)	1.01± 0.7	1.65± 0.5	0.44± 0.3 (43.6)	0.28± 0.0	1.16± 0.4	1.24± 0.4 (442.9)
Ni	-	0.77± 0.4	0.63± 0.4	-	-	0.28± 0.2	-	-	0.007± 0

The fly ash laden sediment of St.1 recorded the highest Cu (9.78 $\mu g.g^{-1}$), Zn (17.94 $\mu g.g^{-1}$), Fe (2071.8 $\mu g.g^{-1}$) and Mn (91.56 $\mu g.g^{-1}$) concentrations. Meetu *et al.* (2000) observed high values of Cu, Zn, Fe and Mn in the tissue samples of plants growing in the fly ash areas of northern India. The relatively clean St. 3 recorded the highest Zn (227.7 $\mu g.g^{-1}$), Mn (165.7 $\mu g.g^{-1}$) and Cd (1.24 $\mu g.g^{-1}$) among the tissue samples, which might be due to the mixing up of water between the contaminated St.1 and 3 due to currents as the distance between them is only 15 km.

The range of mean concentration of Fe in the clam (353 to 667.6 $\mu g.g^{-1}$) and sediment (696.3

One way ANOVA indicated statistically significant difference (p<0.01) in the variation of Fe, Mn and Ni among stations (Table 3) as well as in the variations of Cu, Fe, Mn, Pb and Zn among samples (Table 4). Except for Cd and Cu, no significant difference was noticed in the seasonal variation of other metals (Table 5).

The bioaccumulation factor (BAF) varied between bivalve species and elements. BAF of Zn was the highest followed by Cd and Cu. The clam *Marcia opima* accumulates Zn in higher concentration, whereas *Donax cuneatus* is a good accumulator of Cu. *D. faba* accumulates higher

Table 3. ANOVA on the concentration of heavy metals between stations

Metals	Treatments	Sum of Squares	df	Mean Square	F value	Sig
Cd	Between stations	1.110	2	555	.279	.757
	Within station	208.88	105	1.989		
	Total	209.99	107			
Cu	Between stations	244.824	2	122.41	1.056	.351
	With in station	12167.7	105	155.89		
	Total	12412.7	107			
Fe	Between stations	5905231	2	2952616	3.038	.054*
	Within station	67000000	69	971961.6		
	Total		71			
Pb	Between stations	33.286	2	16.643	.176	.838
	Within station	9901.64	105	94.301		
	Total					
Mn	Between stations	50361.29	2	25180.7	4.668	.013*
	Within station	372174.4	69	5393.83		
	Total	422535.6	71			
Ni	Between stations	6.143	2	3.072	3.835	.026*
	Within station	55.272	69	.801		
	Total	61.415	71			
Zn	Between stations	49047.32	2	24523.7	2.257	0.110
	With in station	1141082	105	10867.5		
	Total		107			

* $p < 0.05$

Table 4. ANOVA on the concentration of heavy metals between samples

Metals	Treatments	Sum of Squares	df	Mean Square	F value	Sig
Cd	Between sample	19.99	8	2.498	1.302	.252
	Within sample	190.01	99	1.919		
	Total	209.99	107			
Cu	Between sample	2441.6	8	305.20	3.030	.004*
	Within sample	9971.1	99	100.72		
	Total	12412.7	107			
Fe	Between sample	31000000	8	3816863	5.667	.000*
	Within sample	42000000	63	673582.2		
	Total	73000000	71			
Mn	Between sample	142418.4	8	17802.3	4.004	.001*
	Within sample	280117.2	63	4446.3		
	Total	422535.6	71			
Ni	Between sample	6.76	8	.845	.974	.465
	Within sample	54.66	63	.868		
	Total	61.42	71			
Pb	Between sample	2255.55	8	281.94	3.635	.001*
	Within sample	7679.38	99	77.57		
	Total	9934.93	107			
Zn	Between sample	654689.8	8	81836.2	15.131	.000*
	Within sample	535439.8	99	5408.5		
	Total	1190130	107			

* $p < 0.05$

Table 5. ANOVA on the seasonal variation of heavy metals

Metals	Treatments	Sum of Squares	df	Mean Square	F value	Sig
Cd	Between months	55.68	11	5.062	3.149	.001*
	Within month	154.32	96	1.607		
	Total	209.99	107			
Cu	Between months	2220.9	11	201.90	1.902	.048*
	Within month	10191.8	96	106.17		
	Total	12412.7	107			
Fe	Between months	10000000	11	917930.4	.876	.568
	Within month	63000000	60	1047889		
	Total	73000000	71			
Mn	Between months	48703.4	11	4427.58	.711	.724
	Within month	373832.3	60	6230.64		
	Total	422535.6	71			
Ni	Between months	15.76	11	1.433	1.883	.060
	Within month	45.66	60	.761		
	Total	61.42	71			
Pb	Between months	927.29	11	84.30	.898	.545
	Within month	7679.38	96	77.57		
	Total	9934.93	107			
Zn	Between months	66813.9	11	6073.99	.519	.886
	Within month	1123316	96	11701.20		
	Total	1190130	107			

* $p < 0.05$

concentration of Cd. Kaladharan *et al.* (2005) reported that clam *M. opima* is a good accumulator of Cu and Fe in Kochi waters. Krishnakumar *et al.* (1990) opined that the oyster *Crassostrea cuculata* is an effective accumulator of Zn, Cd and Cu and green mussel *Perna viridis* of Pb and Mn. Relatively higher concentrations of Cd, Cr and Pb were observed in green mussels collected from coastal waters near the industrial areas of Mangalore (Geetha *et al.*, 2006). Senthilnathan *et al.* (1998) suggested that the bioconcentration of metals in bivalve tissues would be mainly from dissolved fractions.

The concentration of various trace metals estimated in the present study revealed its proximity with previous studies conducted along Tuticorin coast (Palanichamy and Rajendran, 2000; Chandrasekhar, 2001; Baskaran *et al.,* 2002). In this study, the metals were accumulated in the order Fe>Mn>Zn>Cu>Pb>Cd>Ni, in the samples at three stations, which is in conformity with the observations of Ganesan *et al.* (1991) in Bay of Bengal, Kaladharan *et al.* (2005) in Kochi waters, Senthilnathan *et al.* (1998) along selected areas of southeast coast of India and Chandrasekar (2001) in Tuticorin waters.

The concentration of trace metals especially Fe, Mn, Cu, Pb and Zn was higher during October - December, *i.e.*, during the northeast monsoon in all the samples. This higher concentration might be due to the increased inputs of land derived metals due to rainfall as indicated by Ganesan and Kannan (1995). The mean salinity at St. 2 observed was 33.5 ppt. Comparatively the concentrations of heavy metals were higher in the sediment and tissue at St. 2. The lower salinity might have increased the accumulation rate as suggested by Senthilnathan *et al.* (1998).

The concentrations of Cd and Cu were higher in the sediments at St. 2 and the concentration of Cu, Fe, Mn, Ni and Zn were higher in the sediments at St. 1. This indicated the extent of pollution in the sediment off Tuticorin. Baskaran *et al.* (2002) also observed high concentration of Fe,

Table 6. Comparison of metal concentration in seawater (µg. l^{-1}) and tissue (µg.g^{-1}) samples with permissible limit

Metals	EEC (water)	WHO (1987) (tissue)		Present study Sea water	Tissue
Cu	5	130	St.1	6.84	_
			St.2	7.45	_
			St.3	6.77	_
Zn	40	217	St.3	_	227.7
Fe	_	100	St.1	_	353.1
			St.2	_	667.6
			St.3	_	496
Mn	_	1	St.1	_	42.32
			St.2	_	27.9
			St.3	_	165.7

Cu and Zn in the sediment at fly ash dumping dyke at Tuticorin Thermal Power Plant. Satyanarayanan and Murty (1990) indicated that accumulation of metals and its stability are more in fine grain sediment. Chandrasekar (2001) also observed higher levels of heavy metals in the sediments of Tuticorin waters.

The present study shows that the extent of heavy metal pollution along Tuticorin coast has exceeded the recommended safe level in many samples, such as Cu level in the seawater samples at all stations, Zn level in the tissue samples at St. 3, Fe and Mn level in the tissue samples at all stations (Table 6). The results of this study warrant the need for an effective treatment and management measures for industrial effluents and other anthropogenic discharges into the Tuticorin coastal waters so as to reduce the impact of heavy metal pollution.

Acknowledgements

The authors are thankful to the Director and Head of Fishery Environment and Management Division, CMFRI, Kochi for providing necessary facilities and encouragements.

References

Anoop, A. K., P. K. Krishnakumar and M. Rajagopalan. 2007. *Trichodesmium erythraeum* (Ehrenberg) bloom along the southwest coast of India (Arabian Sea) and its impact on trace metal concentrations in seawater. *Estuar. Coast. Shelf Sci.,* 71: 641 - 646.

Baskaran, M., V. Ramadhas and R. Santhanam. 2002. Metal pollution in Tuticorin coastal waters due to fly ash of thermal power plant. *Proc. National Seminar on Marine and Coastal Ecosystems: Coral and Mangrove- Problems and Management Strategies. SDMRI Res. Publ.,* 2: p.190 - 193.

Bindu, S., P. K. Krishnakumar, D. Prema, P. Kaladharan, K. K. Valsala, G. S. Bhat and K. Muniandi. 2007. Trace metal contamination of the marine environment in Palk Bay and Gulf of Mannar. *J. Mar. Biol. Ass. India,* 49(1): 12 - 18.

Chandrasekar, N. 2001. Trace elements in the suspended sediments of salt marsh area of Karapad creek, Tuticorin. *Indian J. Environ. Ecoplan.*, 5(1): 81 - 86.

Dalziel, J. and C. Baker. 1984. Analytical methods for measuring metals by atomic absorption spectrophotometry. *FAO Fish. Tech. Paper*, 212: 14 - 20.

Devagi, K., F. Ibrahim and M. N. Berseli. 2008. Comparative study of heavy metal concentrations in razor clam (*Solen regularis*) in Moyan and Serpan, Sarawak *Global J. Environ. Res.,* 2(2): 87 - 91.

Easterson, D. C. V. 1998. Impact of marine pollution on the ecological resources of Gulf of Mannar. *Proc. Biodiversity of Gulf of Mannar Marine Biosphere Resource*, MSSRF *Spl. Publ.,* p. 56 - 57.

Ganesan, M. and L. Kannan. 1995. Iron and manganese concentrations in sea water, sediment and marine algae of Tuticorin coast, southeast coast of India. *Indian J. Mar. Sci.,* 24: 236 - 237.

Ganesan, M., R. Kannan, K. Rajendran, C. Govindasamy, P. Sampathkumar and L. Kannan. 1991. Trace metals distribution in seaweeds of the Gulf of Mannar, Bay of Bengal. *Mar. Poll. Bull.*, 22: p. 205.

Geetha, S., P. K. Krishnakumar and G. S. Bhat. 2006. Monitoring the tracemetal contaminants in green mussel *Perna viridis* from the coastal waters of Karnataka, southwest coast of India. *Arch. Environ. Contam. Toxicol.*, 51: 206 - 214.

Kaladharan, P., D. Prema, K. K. Valsala, K. S. Leelabai and M. Rajagopalan. 2005. Trends in heavy metal concentrations in sediment, fin fishes and shellfishes in inshore waters of Cochin, southwest coast of India. *J. Mar. Biol. Ass. India,* 47(1): 1 - 7.

Krishnakumar, P. K., V. K. Pillai and K. K. Valsala. 1990. Bioaccumulation of trace metals by marine flora and fauna near caustic soda plant (Karwar, India). *Indian J. Fish.,* 37(2): 14 - 20.

Meetu, G., A. Kumar and M. Yunus. 2000. Effect of fly-ash on metal composition and physiological responses in *Leucaena leucocephala* (Lamk) De. Wit. *Environ. Monit. Assess.,* 61: 399 - 406.

Murugan, A. and J. K. P. Edward. 2000. Factors threatening biodiversity of marine mollusks in Tuticorin, Gulf of Mannar. *PMBC Spl. Publ.,* 21(1): 159 - 162.

Palanichamy, S. and A. Rajendran. 2000. Heavy metal concentrations in sea water and sediments of Gulf of Mannar and Palk Bay, southeast coast of India. *Indian J. Mar. Sci.,* 29: 116 - 119.

Phillips, D. J. H. 1976. The common mussel *Mytilus edulis* as an indicator of pollution by zinc, cadmium, lead and copper. II. Relationship of metals in the mussel to those discharged by industry. *Mar. Biol.,* 38(1): 71 - 80.

Satyanarayana, D. and P. V. S. P. Murty. 1990. Distribution of dissolved trace metals in western Bay of Bengal. *Indian J. Mar. Sci.,* 19: 206 - 211.

Senthilnathan, S., T. Balasubramanian and V. K. Venugopalan. 1998. Metal concentration in mussel *Perna viridis* (Bivalvia/ Anisomyaria) and oyster *Crassostrea madrasensis* (Bivalvia/ Anisomyaria) from some parts in southeast coast of India. *Indian J. Mar. Sci.,* 27: 206 - 210.

Solarzano, L. 1969. Determination of ammonia in natural waters by the phenol hypochlorite method. *Limnol. Oceanogr.*, 14: 799 - 801.

Strickland, J. D. H. and T. R. Parson. 1968. A practical hand book of sea water analysis. *Bull. Fish. Res. Bd. Canada*, 167: 311 pp.

Subramanian, S. K. and L. Kannan. 1998. Environmental parameters of Indian marine biosphere reserve of Tuticorin in Gulf of Mannar. *Seaweed Res. Utilin.*, 20(1&2): 85 - 90.

WHO. 1987. Evaluation of certain food additives and contaminants. Thirty – third report of joint FAO/WHO expert committee on food additives, Geneva. *WHO Technical Report Series*, 776: 80 pp.

Received : 05.12.08
Accepted : 12.03.10