Indian Journal of Geo-Marine Sciences
Vol. 41(4), August 2012, pp. 359-368

Metal status of water in mangrove ecosystem of Maharashtra coast, India

V. Pahalawattaarachchi[1], C. S. Purushothaman & A. Vennila[*]
Central Institute of Fisheries Education, Fisheries University Road,
Versova, Mumbai 110 061, India
[*E. mail: avennila@gmail.com]

Received 07 April 2010; revised 07 January 2011

Temporal and spatial distribution of dissolved and total elements (Cu, Cd, Fe, Mn, Ni, Zn, Cr, Pb and Hg) and physicochemical parameters of water courses in the vicinity of three mangrove sites along the Maharashtra coast, India was studied. All the metals showed pronounced temporal variations in overall averages except Pb. Average concentrations of all the metals showed significant site-wise variations except Cd and Mn. Inter-relations of physicochemical parameters and metal concentrations were also observed. Contamination of toxic metals was found to be high in the sites having the influence of human habitation as well as industry.

[**Keywords**: Metals, Mangrove, Dissolved metals, Temporal and spatial variations, Distribution]

Introduction

The technological development of large-scale industries along coastal water zones affects the entire zone through anthropogenic pollution inputs. Fluxes of trace elements that have been modified biogeochemically in estuaries and coastal waters are transported to the open ocean and the original composition of seawater is altered[1,2]. With the increased use of a wide variety of metals in industries and in our daily life, there is a greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain. Present study was initiated to investigate the temporal and spatial distributions of Cu, Cd, Ni, Mn, Fe, Zn, Cr, Pb and Hg in waters of three mangrove ecosystems with differing levels of pollution.

Material and Methods

Samples were collected from water courses in three mangrove ecosystems along the Maharashtra coast, *viz.*, Alibag (water canal inside mangrove area), which is located between latitudes 18° 56’ and 18° 29’ N, and longitudes 72° 50’ and 73° 04’ E; Uttan (Manori creek), between 18° 56’ and 18° 29’ N, and 72° 50’ and 73° 04’ E; and Mahul (Mahul creek), between 19° 14’ and 19° 13’ N, and 72° 46’ and 72° 47’ E (Fig. 1).

Sampling was carried out on a quarterly basis during January – December 2007. Water quality parameters (temperature, *p*H, salinity, nitrite-nitrogen, nitrate-nitrogen and phosphate-phosphorus) were estimated on each sampling instance using standard procedures. Two sets of water samples (500 mL each) were collected in triplicates from each of the study area. A 250-mL portion from each sample of a set was preserved by bringing down the *p*H to a level less than 2 using concentrated nitric acid for the total metal analysis. Another 250-ml portion was filtered through Whatman No. 41 (0.45 µm pore size) filter paper for analysis of dissolved metal and preserved in the same way as that of unfiltered samples. Both the portions were pre-concentrated 50 times on a water bath and subjected to nitric acid digestion using the microwave-assisted technique as per instructions given by the manufacturer (Anton Parr, USA). Digested samples were diluted to 50 ml each and subjected to analysis of the eight metals (Cu, Cd, Ni, Mn, Fe, Cr, Zn and Pb) by atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer, USA) using flame atomization. The cold-vapour method (AAnalyst 800, Perkin Elmer with FIAS) was used to measure the concentration of mercury.

---

*Authour for correspondence

[1] present address: National Aquatic Resources Research and Development Agency, Crow Island, Colombo - 15, Sri Lanka

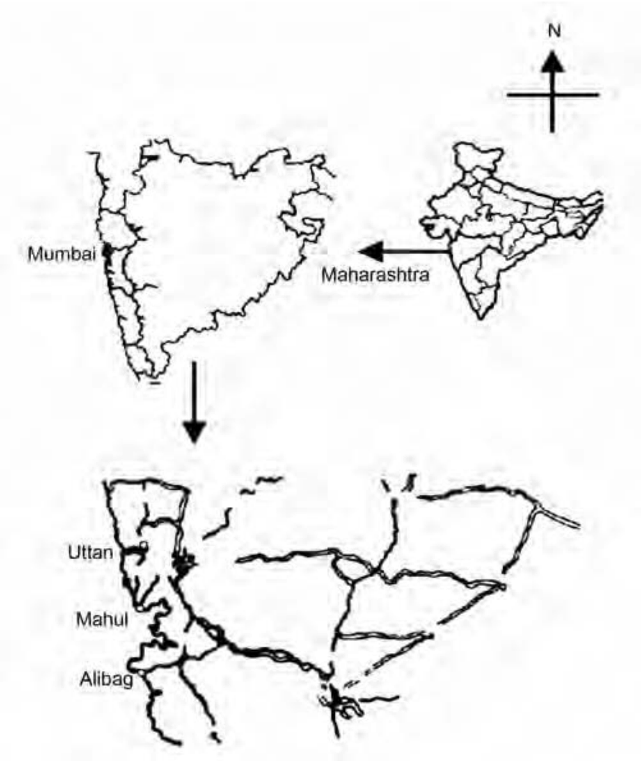


Fig. 1—Map showing the study sites.

The efficiency of the analytical method and instrumentation was verified by the analysis of the reference materials obtained from the National Research Council of Canada for estuarine water (SLEW-3) and lobster hepatopancreas (TORT-2) in five replicates. Heavy metal concentrations and recoveries of the standard reference materials used are presented in Table 1. All the statistical analyses and hierarchical cluster analysis was carried out using the SPSS 16.0 statistical package.

Table 1—Measured and certified values of standard reference material

Standard reference material/ Metal	Analysed SRM value[a]	Certified SRM value	Recovery (%)
SLEW-3[b]			
Cu	1.47 ± 0.04	1.55 ± 0.12	95.4
Cd	0.053 ± 0.001	0.048 ± 0.004	112
Ni	1.26 ± 0.02	1.23 ± 0.07	103
Mn	1.60 ± 0.05	1.61 ± 0.22	99
Fe	0.578 ± 0.009	0.568 ± 0.059	102
Zn	0.184 ± 0.002	0.201 ± 0.037	91
Cr	0.176 ± 0.003	0.183 ± 0.019	96
Pb	0.0096 ± 0.0003	0.0090 ± 0.0014	107
TORT-2[c]			
Hg	0.322 ± 0.013	0.27 ± 0.06	119

[a] Mean and standard deviation of five replicates for each SRM
[b] The data are presented in mg l^{-1}.
[c] The data are presented in μg g^{-1}.

Table 2—Physicochemical parameters (mean ± SE) of water in the study sites

Parameter	Quarter	Alibag	Uttan	Mahul
Temperature (°C)	Q1	30.1±0.14	29.1± 0.10	28± 0.001
	Q2	29.2 ±0.10	28.6± 0.41	29.6± 0.001
	Q3	25.9± 0.10	24.9± 0.40	26.4±0.05
	Q4	27.7±0.14	26.3±0.30	27.9±0.07
*p*H	Q1	7.5±0.10	7.6±0.02	7.4±0.12
	Q2	7.8±.0.06	7.7±0.02	7.8±0.05
	Q3	7.9±0.03	7.9±0.02	8.0±0.01
	Q4	8.3±0.10	8.1±.0.11	8.0±0.15
Salinity (‰)	Q1	28±0.5	27±0.46	28.0±0.23
	Q2	30±0.10	31±0.98	32.0±0.64
	Q3	5±0.52	6±0.42	5±0.50
	Q4	30±0.10	31±0.89	29±1.10
Nitrate-N (mg l^{-1})	Q1	3.15±0.49	4.12±0.20	2.80±0.42
	Q2	2.23±0.39	3.65±0.21	2.70±0.14
	Q3	4.90±0.14	5.01±0.01	5.08±0.74
	Q4	2.30±0.42	4.99±0.01	5.25±0.21
Nitrite-N (mg l^{-1})	Q1	0.29 ±0.05	0.27±0.02	0.28±0.02
	Q2	0.50±0.01	0.29±0.05	0.24±0.01
	Q3	0.09±0.05	0.18±0.04	0.17±0.02
	Q4	0.06±0.04	0.28±0.03	0.23±0.02
Phosphate-P (mg l^{1})	Q1	1.93 ±0.05	2.78±0.62	2.23 ±0.13
	Q2	1.73 ±0.08	2.05±0.10	2.0 ±0.03
	Q3	3.41±0.24	4.11±0.18	5.16±0.38
	Q4	5.00±0.03	4.72±0.21	5.32±0.16

Results

Physicochemical characteristics of water

Water samples were analyzed for different physicochemical parameters and presented in Table 2. Water *p*H was slightly alkaline and salinity showed consequence of variations in seasons from wet to dry. Nitrite-nitrogen and nitrate-nitrogen showed lower values during monsoon and post-monsoon seasons. In contrast to nitrogen, phosphate-phosphorus in estuarine waters was higher during monsoons and followed the similar trend at all the three sites.

Heavy metals in water

Average concentrations (total and dissolved fractions) of all the metals except lead in water in the study showed significant seasonal variations. Averages of all the fractions except manganese and cadmium show significant spatial variations. The total and dissolved fractions of lead do not differ significantly (Table 3).

The highest quarterly average concentration of dissolved copper was recorded at Uttan in Quarter 4 (0.640 mg l^{-1}) while the lowest (0.013 mg l^{-1}) was at Mahul in Quarter 3. Dissolved copper increased in the post-monsoon period (Quarter 4) at each study site (Fig. 2). The significant highest average concentration of total copper was observed in Quarter 4 (0.709 mg l^{-1}) at Uttan and the lowest (0.012 mg l^{-1}) in Quarter 2 at the same site (Table 4). Variation of cadmium showed a more or less similar pattern throughout the study period in the all three sites except the higher total and dissolved concentrations at Mahul in Quarter 4. Highest concentrations of total cadmium (0.060 mg l^{-1} in Quarter 1) at Uttan and the lowest (0.012 mg l^{-1} in Quarter 2) at Mahul were recorded in water. High temporal variations in cadmium were observed among the four quarters in all the three sites (Fig. 2). The average dissolved cadmium concentration was the highest in Quarter 4 (0.051 mg l^{-1}) at Mahul while it was the lowest (0.012 mg l^{-1}) in Quarter 2 in Mahul. Temporal variation was noteworthy in water of Alibag and Mahul, while high spatial variations were observed in all the quarters except Quarter 4.

Table 3—Summary of results of three way ANOVA showing spatial and temporal differences in dissolved and total metals (fractions) in water

	F value			
	Between quarters	Between sites	Between fractions	Site* fraction
Cu	197.12 (0.000)	96.66 (0.000)	4.50 (0.039)	5.25 (0.009)
Cd	14.41 (0.000)	2.33 (0.108)	6.11 (0.017)	0.03 (0.971)
Ni	77.73 (0.000)	94.42 (0.000)	8.54 (0.005)	1.19 (0.315)
Mn	43.37 (0.000)	0.83 (0.441)	79.63 (0.000)	9.82 (0.000)
Fe	62.23 (0.000)	13.64 (0.000)	144.25 (0.000)	20.88 (0.000)
Zn	23.16 (0.000)	16.03 (0.000)	34.43 (0.000)	7.47 (0.002)
Cr	38.48 (0.000)	17.93 (0.000)	50.20 (0.000)	4.47 (0.017)
Pb	0.97 (0.415)	36.13 (0.000)	1.36 (0.249)	0.184 (0.833)
Hg	50.55 (0.000)	20.40 (0.000)	6.57 (0.014)	2.31 (0.110)

The bracketed values show the level of significance of the calculated *F* values from the ANOVA

The highest quarterly average for total nickel in water was recorded (0.182 mg l^{-1}) at Alibag in Quarter 4 and the lowest (0.01 mg l^{-1}) at Mahul in Quarter 4. Nickel concentrations in water at Uttan reveal significant variations in quarterly distribution among three sites (Fig. 2). Highest dissolved concentrations of nickel were recorded at Uttan (0.139 mg l^{-1}) and the lowest (0.004 mg l^{-1}) at Mahul in Quarter 4 (Table 4). Highest quarterly average total manganese concentration (0.980 mg l^{-1}) was recorded in Quarter 3 at Uttan while the lowest (0.12 mg l^{-1}) was in Quarter 2 at Alibag (Fig. 2). Likewise, the highest average quarterly dissolved concentration (0.362 mg l^{-1}) of manganese was recorded in Alibag in Quarter 3 while the lowest was recorded at Uttan in Quarter 2 (Table 4). Highest total concentration (24.40 mg l^{-1}) of iron was recorded in Quarter 3 at Uttan while the lowest (0.239 mg l^{-1}) was recorded in Quarter 4 at the same station (Fig. 2). Concentration of dissolved iron was the highest (3.661 mg l^{-1}) in Quarter 3 at Mahul while it showed the lowest value (0.104 mg l^{-1}) in Quarter 4 at Uttan. The highest (1.465 mg l^{-1}) and the lowest (0.029 mg l^{-1}) total zinc concentrations were recorded at Alibag in Quarter 3 and at Uttan in Quarter 4, respectively (Fig. 2). Concentrations of dissolved zinc ranged from 0.016 mg l^{-1} (lowest) in Uttan in Quarter 4 to 0.352 mg l^{-1} (highest) at Alibag in Quarter 3 (Table 4).

The highest total concentration (0.407 mg l^{-1}) of chromium was recorded in Quarter 4 at Mahul and the lowest (0.019 mg l^{-1}) in Quarter 2 at Alibag. Mahul waters showed higher concentration of chromium in all the quarters. Dissolved concentrations of chromium ranged from 0.014 mg l^{-1} in Quarter 2 at Alibag to 0.195 mg l^{-1} in Quarter 4 at Mahul. Highest quarterly average concentration (0.502 mg l^{-1}) of lead was observed in Quarter 3 at Mahul while the lowest (0.016 mg l^{-1}) in Quarter 1 at Alibag (Fig. 2). Dissolved concentrations ranged from 0.007 mg l^{-1} (Alibag, Quarter 1) to 0.045 mg l^{-1} (Mahul, Quarter 3). Total and dissolved concentrations of mercury were at remarkably lower levels when compared to the other metals. The highest quarterly average of total mercury

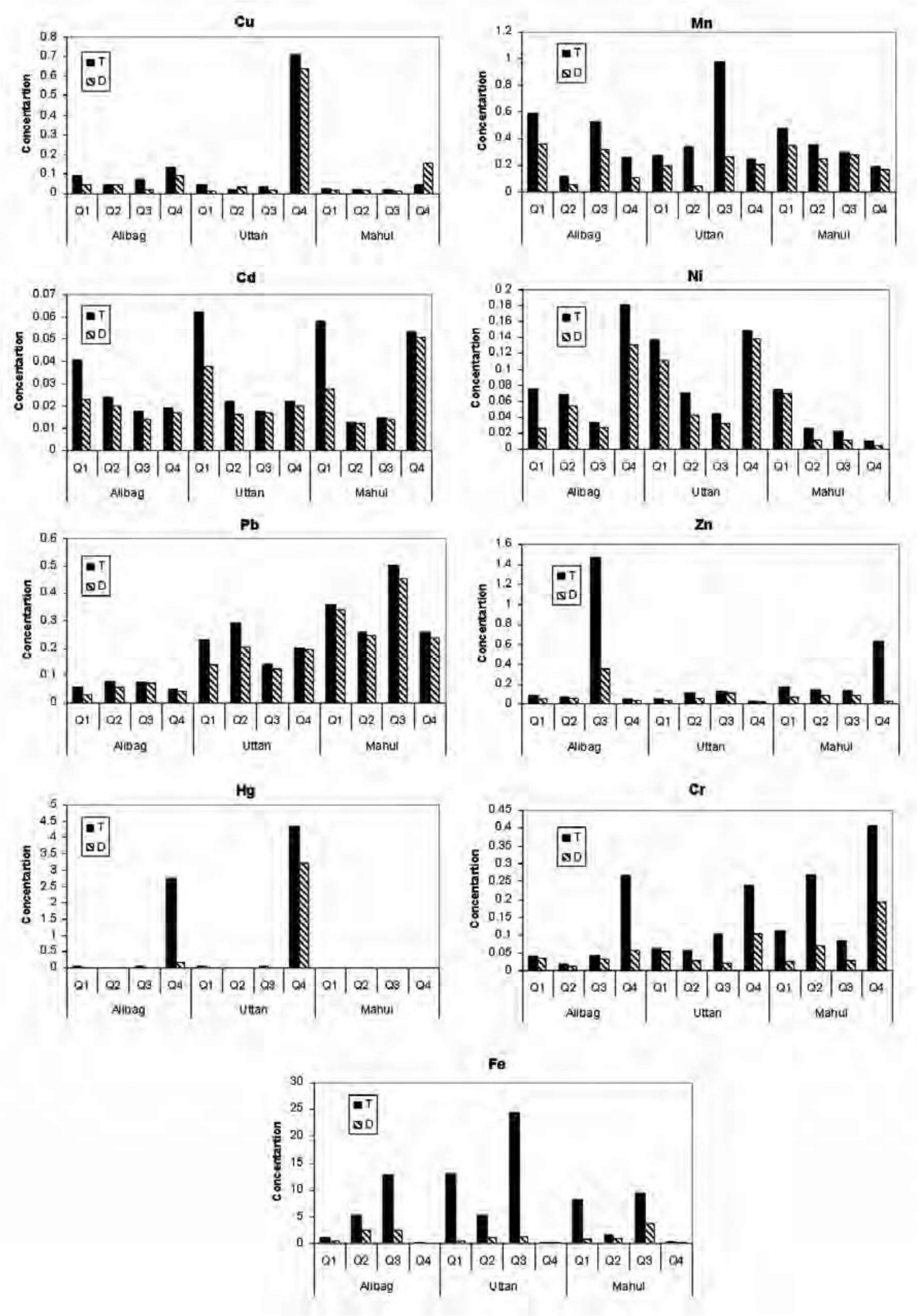


Fig. 2—Temporal variations of total and dissolved metals (All values other than for Hg are given in mg l^{-1} and the values of Hg are in μg l^{-1}).

Table 4—Concentration of total (T) and dissolved (D) metals (mean ± SE) in the water of the study sites (Q1-quarter 1; Q2-quarter 2; Q3-quarter 3; Q4-quarter 4)

Site		Q1		Q2		Q3		Q4	
		T	D	T	D	T	D	T	D
Alibag	Cu	0.095±0.04	0.046±0.00	0.114±0.06	0.047±0.02	0.070±0.01	0.015±0.00	0.133±0.02	0.093±0.00
	Cd	0.041±0.00	0.023±0.00	0.025±0.00	0.021±0.00	0.018±0.00	0.015±0.00	0.019±0.00	0.017±0.00
	Ni	0.076±0.03	0.020±0.02	0.069±0.01	0.054±0.01	0.033±0.00	0.020±0.00	0.182±0.02	0.131±0.00
	Mn	0.596±0.15	0.36±0.13	0.120±0.00	0.057±0.02	0.529±0.01	0.31±0.00	0.256±0.03	0.106±0.01
	Fe	1.054±0.11	0.520±0.05	5.297±0.07	2.557±0.73	12.84±0.79	2.63±0.62	0.266±0.03	0.058±0.01
	Zn	0.091±0.01	0.052±0.00	0.070±0.01	0.058±0.01	1.465±0.09	0.352±0.07	0.049±0.01	0.040±0.01
	Cr	0.042±0.00	0.036±0.00	0.019±0.00	0.014±0.00	0.045±0.01	0.034±0.01	0.266±0.03	0.058±0.01
	Pb	0.057±0.01	0.030±0.01	0.079±0.00	0.058±0.01	0.077±0.00	0.073±0.00	0.049±0.00	0.045±0.00
	Hg	0.016±0.00	0.007±0.00	0.008±0.00	0.006±0.00	0.015±0.00	0.003±0.00	2.752±1.47	0.187±0.01
Uttan	Cu	0.044±0.00	0.012±0.01	0.034±0.01	0.022±0.02	0.036±0.01	0.015±0.00	0.709±0.03	0.640±.01
	Cd	0.060±0.01	0.038±0.00	0.022±0.00	0.016±0.00	0.018±0.00	0.017±0.00	0.022±0.00	0.021±0.00
	Ni	0.136±0.00	0.110±0.01	0.071±0.01	0.042±0.00	0.045±0.00	0.032±0.00	0.148±0.01	0.139±0.01
	Mn	0.278±0.00	0.202±0.02	0.338±0.08	0.045±0.01	0.980±0.02	0.268±0.00	0.254±0.03	0.207±0.01
	Fe	12.99±0.44	0.607±0.00	5.287±2.75	1.146±0.58	24.40±0.31	1.298±0.05	0.239±0.09	0.104±0.01
	Zn	0.052±0.00	0.042±0.00	0.106±0.00	0.057±0.00	0.122±0.01	0.109±0.00	0.025±0.00	0.016±0.00
	Cr	0.064±0.00	0.054±0.00	0.057±0.01	0.030±0.01	0.105±0.00	0.022±0.00	0.239±0.09	0.104±0.01
	Pb	0.232±0.02	0.1387±0.02	0.293±0.01	0.205±0.01	0.140±0.00	0.123±0.00	0.205±0.01	0.195±0.01
	Hg	0.015±0.00	0.005±0.00	0.011±0.00	0.008±0.00	0.027±0.01	0.009±0.00	4.343±0.01	3.420±0.00
Mahul	Cu	0.023±0.00	0.013±0.00	0.018±0.00	0.013±0.00	0.019±0.00	0.009±0.00	0.153±0.01	0.046±0.01
	Cd	0.059±0.00	0.028±0.00	0.013±0.00	0.012±0.00	0.015±0.00	0.014±0.00	0.054±0.03	0.051±0.00
	Ni	0.074±0.00	0.069±0.01	0.026±0.01	0.012±0.00	0.022±0.00	0.017±0.00	0.010±0.00	0.004±0.00
	Mn	0.483±0.03	0.348±0.03	0.357±0.01	0.249±0.06	0.300±0.00	0.280±0.02	0.195±0.00	0.170±0.02
	Fe	8.270±4.07	0.77±0.23	1.685±0.34	0.877±0.03	9.410±14.57	3.661±0.71	0.407±0.08	0.154±0.01
	Zn	0.169±0.02	0.07±0.00	0.148±0.02	0.088±0.01	0.141±0.00	0.087±0.01	0.634±0.33	0.029±0.00
	Cr	0.110±0.04	0.027±0.00	0.270±0.01	0.071±0.03	0.084±0.04	0.030±0.01	0.407±0.08	0.195±0.00
	Pb	0.357±0.00	0.341±0.01	0.263±0.01	0.245±0.00	0.502±0.22	0.456±0.21	0.262±0.01	0.237±0.02
	Hg	0.006±0.00	Nd	0.009±0.00	0.004±0.00	0.011±0.00	0.006±0.00	Nd	Nd

Value in bold face is significantly different among quarters at $p < 0.05$ level. All values other than for Hg are given in mg l^{-1} and the values of Hg are in μg l^{-1}.
Nd: Not detected

level (4.34 mg l^{-1}) was observed at Uttan in Quarter 4, while it was below the detectable limit at Mahul in the same period (Fig. 2). Dissolved mercury also followed the same pattern of distribution ranging from below detectable level at Mahul in Quarter 4 to 3.312 mg l^{-1} at Uttan in the same quarter (Table 4).

With respect to the annual average metal concentrations in water, total iron is significantly higher than the dissolved fraction in all the sites. At Alibag, no significant difference between dissolved and total concentrations of nickel, manganese, zinc, chromium, lead and mercury is observed. Dissolved copper and cadmium are significantly lower than their respective total contents at Alibag. At Uttan, no other metals show any significant difference among the total and dissolved concentrations except manganese, iron and lead. At Mahul, dissolved iron, zinc, chromium and mercury are significantly lower than the respective total contents. Annual average concentrations of total and dissolved copper are the highest at Uttan followed by Alibag and Mahul in that order. Annual averages of total and dissolved nickel are the highest at Alibag. The highest average annual concentration of total manganese was 0.462 mg l^{-1} at Uttan and that of the dissolved fraction was 0.262 mg l^{-1} at Mahul. The highest annual average total iron concentration was observed at Uttan while the lowest was observed at Alibag. The annual average dissolved iron was the highest at Alibag and the lowest at Uttan. The variations in annual average of total and dissolved chromium and lead followed the same pattern of distribution at all the three sites and the order was Mahul > Uttan > Alibag (Table 5).

The two different phases of annual average metals in water at the three sites indicate two different clusters: elemental association with salinity (Cluster 1), and association with water *p*H (Cluster 2). This exhibits a negative correlation between the two above mentioned clusters, especially salinity and *p*H (Fig. 3A). Distribution patterns of both the fractions (phases) show the same clustering pattern but for the small deviations in Cluster 2 of the dissolved metals (Fig. 3B). Likewise, the metals between clusters 1 and 2 in each phase have negative effects while within a cluster, the metal shows same behaviour and positive effects.

Discussion

Physicochemical characteristics of water

The water *p*H in all the three sites showed more or less similar trends and exceptional high values were observed during the rainy period (Quarter 3) at Mahul. Results showed that there is an increasing trend in *p*H during the monsoons though it did not exhibit any significant temporal or spatial variation. *p*H values recorded in the present study are slightly alkaline and comparable with the observations of Tripathy *et al.*[3] The variations in salinity at all the three stations seem to be high with lower values during the monsoon period and higher ones in the dry periods. Fluctuations in salinity seem to be the consequence of varied influxes of fresh water into the system and the variations in tidal cycles. During high tide, the creek water showed high values and on the contrary, during low tide, a reverse trend could be observed as has been reported earlier[4,5]. Salinity levels recorded are comparable with those observed by Krishnamurthy & Sundararaj[6]. The quarterly variations in nitrite-nitrogen and nitrate-nitrogen showed a comparable trend at Uttan and Mahul, while Alibag had a few exceptions. Lower values recorded during monsoon and post-monsoon seasons in both the parameters again prove the phenomenon of mixing and dilution of water[4]. Although nitrite-nitrogen was lower than that recorded earlier, nitrate-nitrogen was in the range of previously recorded data in mangrove waters in India[3,6]. In contrast to nitrogen, phosphate-phosphorus in estuarine waters was higher during monsoons and followed the similar trend at all the three sites. The phosphate-phosphorus levels in the study are also comparable with the earlier findings[3]. The higher level during monsoons may be due to the influx of runoff water with nutrients.

Heavy metals in water

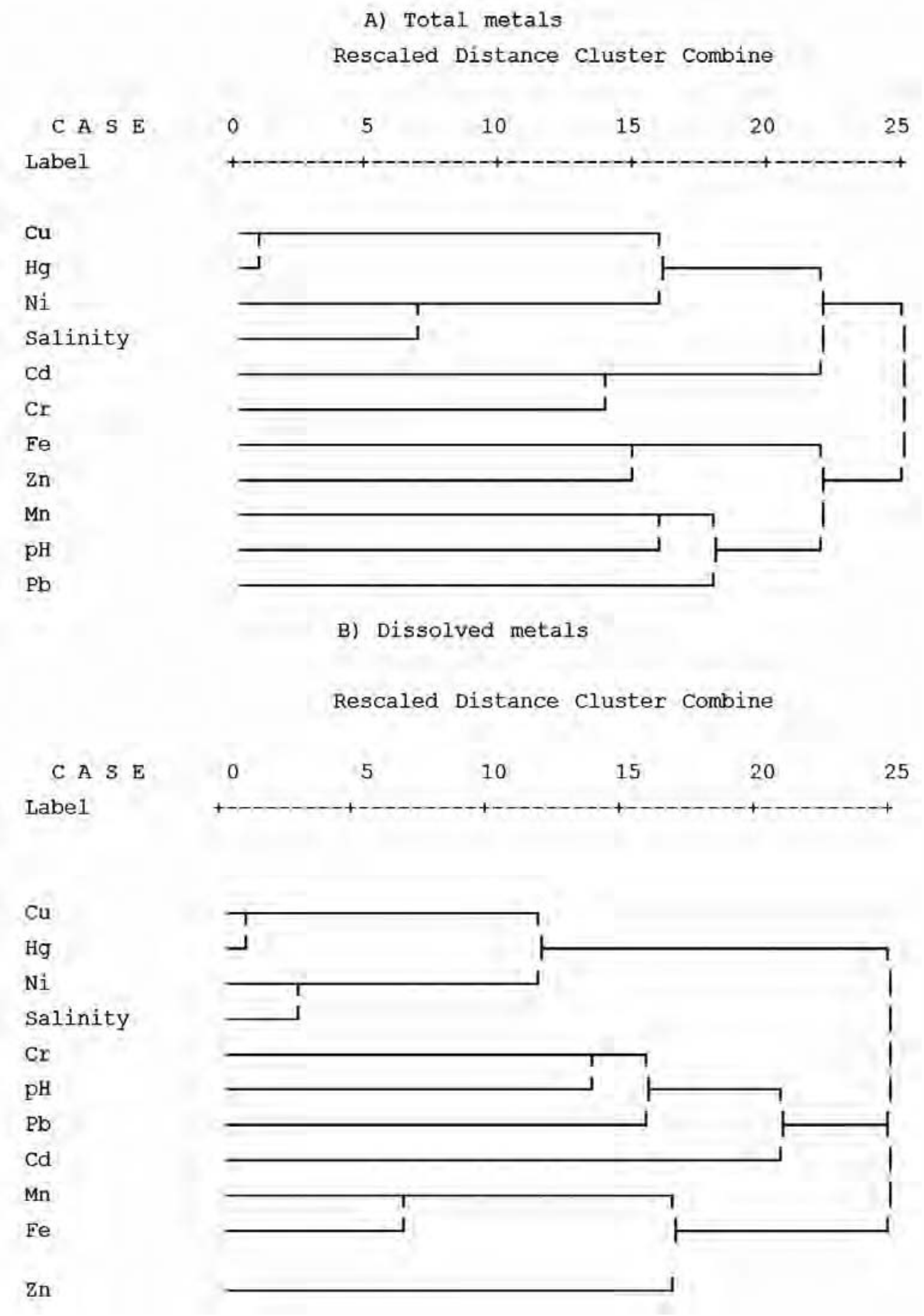
Metals in water contain a substantial natural contribution from the earth's upper continental crust. Apart from this, considerable quantities of metals contributed by human activity to the environment form an essential part of metal contamination.

Dissolved copper and cadmium are significantly lower than their respective total contents at Alibag. The annual average concentrations of total and dissolved copper were the highest at Uttan followed by Alibag and Mahul. Dissolved copper increased in the post-monsoon period (Quarter 4) in each study site. The significant highest average concentration of total copper was observed in Quarter 4 at Uttan. Copper is an anthropogenic contaminant and its concentrations in the coastal and estuarine waters vary widely. A review of available data suggests that the dissolved median copper concentrations of 100 ng l^{-1} should be regarded as background concentration[7]. Significant difference among the two fractions in the present study may be due to the higher level of

Table 5—Annual average total (T) and dissolved (D) metals (mean ±SE) in water of the study sites

	Alibag		Uttan		Mahul	
	Dissolved	Total	Dissolved	Total	Dissolved	Total
Cu	0.051±0.010	0.103*±0.016	0.175±0.081	0.203±0.088	0.047±0.024	0.026±0.004
Cd	0.019±0.001	0.026*±0.003	0.023±0.003	0.031±0.006	0.026±0.007	0.035±0.008
Ni	0.072±0.012	0.091±0.017	0.081±0.014	0.100±0.014	0.024±0.008	0.033±0.008
Mn	0.210±0.049	0.375±0.067	0.180±0.026	0.462*±0.092	0.262±0.024	0.334±0.032
Fe	1.443±0.407	4.864*±1.513	0.789±0.189	10.729**±2.810	1.367±0.438	4.943*±1.547
Zn	0.125±0.042	0.419±0.183	0.056±0.010	0.076±0.012	0.068±0.008	0.273*±0.095
Cr	0.035±0.006	0.093±0.031	0.052±0.011	0.116±0.030	0.081±0.022	0.218*±0.044
Pb	0.051±0.006	0.065±0.005	0.165±0.017	0.217*±0.017	0.320±0.052	0.346±0.056
Hg	0.051±0.028	0.698±0.475	0.809±0.419	1.099±0.565	0.002±0.001	0.006*±0.001

All values other than for Hg are given in mg l^{-1} and the values of Hg are in µg l^{-1}.
Significance between total and dissolved metals * at $p < 0.05$ level; ** at $p < 0.01$ level


A) Total metals

B) Dissolved metals

Fig. 3—Dendrogram for annual average metal concentration in water of the study sites A) Total and B) Dissolved.

particulate copper which is not separated from the total metal in the present study. Values obtained in the present study are far higher than the recorded values for coastal areas of India[8]. The increase in copper at all the stations may be from land-based sources, chemical, metallurgical and industrial complexes, and also from the high organic copper complexing ligands originating from sewage and industrial effluents[9]. Total and dissolved copper concentrations in the water of Uttan are the highest and are justifiable as the sampling location is in the vicinity of one of the biggest garbage dumps in Greater Mumbai.

The fractions of organically-bound dissolved copper in seawater widely vary from 3 to 99% of the total dissolved copper[10,11]. Present range of dissolved copper also showed a wide variation and the highest was recorded during the monsoon period.

Annual average cadmium concentrations reveal site-wise and quarter-wise significant variations. High annual average (0.026 mg l^{-1}) of total cadmium corresponds to the highly industrialized zone (Mahul), although the variation was also high at the site showing the lowest total cadmium concentration. Uttan water revealed relatively higher cadmium concentrations throughout the study period except in Quarter 4. Higher concentration of dissolved cadmium at Uttan may be due to leaching from the domestic garbage dump since cadmium has a greater affinity for biological particulate organic matter than for abiogenic particles, which can be supported by the agricultural activities surrounding the site. This finding is comparable to the findings of Turner *et al.*[12] Moreover, the dissolved average values present here were much higher than those reported earlier[13,14] but less than the strongly polluted estuaries, such as the Rio Tinto-Ria Huelva on Southwest Spain where values close to 45 µg l^{-1} have been reported[15].

Total quarterly values as well as annual average values of nickel were recorded high in Uttan waters. Though the total and dissolved fractions were significant, dissolved fractions contributed considerable quantities to total nickel. Dissolved nickel varied from 0.024 mg l^{-1} at Mahul to 0.081 mg l^{-1} at Uttan. Dissolved nickel was higher than that recorded in earlier studies. The observations on dissolved nickel in Uttan and Mahul waters indicate that these are anthropogenic inputs from the industrial effluents. Total annual average manganese and total annual dissolved manganese differ significantly at Uttan, while the dissolved annual manganese was the highest at Mahul. Highest dissolved manganese concentration at Mahul is probably due to the release of manganese from particles in the saline water as Mahul showed significantly high total salinity values compared to the other two sites. The above observation indicates that manganese adsorption could be on the suspended particulate matter and in higher saline regions, it is derived from desorption from suspended particulate matter, which is also remobilized from estuarine sediments[16]. Total average manganese, like most of the other metals, does not show any site-wise difference, but there exist significant seasonal variations as well as spatial differences within the quarters. However, the recorded values for total as well as dissolved manganese in the present study showed strikingly higher values than those recorded in earlier studies[8,13], although in anoxic hypolimnia of some lakes, more than 1000 µg l^{-1} soluble manganese was observed[17]. Manganese mobilizations in lakes have, however, been reported by several groups and such events are often seasonal, depending on temperature, availability of suitable organic substrates, etc[18]. Anthropogenic activities may also affect manganese mobilization. Hydrological changes caused by constructions of hydroelectric dams in the Rhone Valley resulted in greatly increased manganese (II) concentrations exceeding 1000 µg l^{-1} in aquifers occasionally[19].

The annual average concentration of total iron in water is significantly higher than that of the dissolved fraction at all the sites. Highest and the lowest annual average iron (total and dissolved) concentrations were observed in Uttan and Alibag, respectively, while dissolved iron was at its highest at Uttan and at the lowest at Mahul. Some of the values recorded for annual average dissolved iron in the present study are comparable with the values recorded earlier[20], and the highest recorded values in the present study are less than the value recorded in Kalpakkam coastal waters in the Bay of Bengal. Also, the dissolved iron concentration (3750 µg l^{-1}) in the bottom waters of Uppanar River in the southeast coast of India revealed more or less comparable values[20].

Values for total iron show negative a relationship with salinity and it could be due to the strong association of dissolved iron with finer particles and colloids. Similar observations were recorded during the mixing of river water and seawater [21]. But the seasonal variation pattern of dissolved iron in the present study does not show any remarkable trend with salinity changes.

Distribution of zinc among the three sites is significantly different. The highest annual average zinc concentration was at Alibag and the lowest at Uttan. Total zinc is significantly higher than dissolved zinc in water at Mahul but no such significant difference is observed at Alibag and Uttan. Zinc is a non-soluble element even at low salinities and shows adsorption effects[20]; but the present study does not agree with the statement as the highest concentration of dissolved zinc was observed in the low saline period (monsoon) at Alibag.

In the present study, the highest total concentration (0.407 mg l^{-1}) of chromium was recorded at Mahul in the post-monsoon period while the lowest (0.019 mg l^{-1}) was recorded at Alibag in the pre-monsoon period. Concentrations of dissolved chromium also followed the same pattern as of total chromium. Mahul waters showed higher concentration of chromium in all the quarters. No significant difference between dissolved and total concentrations of chromium is observed at Alibag and Uttan but at Mahul, total chromium is significantly higher than dissolved chromium. The variation of annual average in total and dissolved chromium and lead followed the same pattern of distribution among the three sites and the order was Mahul > Uttan > Alibag. Dissolved chromium levels were far higher than the levels recorded by the earlier workers in different estuaries[8,22]. Further, the values (14–226 µg l^{-1}) recorded at Richards Bay and Mhlathuze Estuary (South Africa) [23] were in the range of the present study. However, the highest total chromium value recorded in the present study (407 µg l^{-1}) is still far higher than the levels recorded in earlier studies. The concentrations in the two stations, which showed higher values, could be attributed to the anthropogenic input from estuarine discharges. In addition, the high values at Mahul in the post-monsoon season may be due to the low salinity regime and the input through sedimentary fluxes. Similar observations on dissolved chromium have been reported by Cutter[24].

The total and dissolved fractions of lead do not differ significantly. No significant quarter-wise difference is observed. The variations in average total lead among the three sites are significant at $p < 0.001$. Likewise, dissolved concentration of the dissolved form followed the same pattern of distribution showing the highest values at Mahul during monsoon and the lowest in Quarter 1 at Alibag. Dissolved lead decreases with increasing salinity, but in lower salinities, a complex behaviour exists with high concentration[20]. This fact can be applied for the present study as it is proved that the low saline periods (monsoons) record the highest level of lead in both the fractions. Other than this, the significant site-wise differences may be attributed to the dissimilarity of anthropogenic contributions at the different sites. Mahul is the site which is highly industrialized and the major source of lead is supposed to be from oil and petroleum refinery wastes[25], while Uttan receives principally domestic wastes.

The total and dissolved concentrations of mercury were detected in remarkably lower levels (µg l^{-1}) when compared to other metals. Total mercury is significantly higher than dissolved mercury in water at Mahul, but no such significant difference is observed at Alibag and Uttan. Mercury is a source of metal pollution both in inorganic and organic forms. It has attracted more attention after the infamous Minamata disease when mercury was recognized as a highly toxic element to aquatic organisms[26]. Many studies have pointed out that sublethal concentrations of mercury have minimal effects on organisms under optimum conditions. However, it becomes toxic under stressful conditions such as extreme temperature and salinity[27]. The partitioning of mercury between sediment and water is *p*H dependent[28]. The highest quarterly average (4.34 µg l^{-1}) total mercury level observed at Uttan, which receives domestic sewage, was recorded during the post-monsoon season and was below the detectable level at Mahul, which receives industrial wastes. Dissolved mercury also followed the same pattern and ranged from below detectable level to 3.31 µg l^{-1}. The highest values recorded at Uttan in Quarter 4 could be due to a sudden increase of metal input to water due to anthropogenic inputs. Nevertheless, the distribution of mercury in natural waters of Mahul prevails during the first three quarters of the year. The industrial activity of Chembur (Mahul is an industrial area in Chembur) is responsible for high concentrations of mercury in the air (up to 41.5 ng m^{-3})[25]. Estuarine water contained 0.0015-0.0045 µg l^{-1} mercury while the backwater had 0.0020-0.0025 µg l^{-}1and the mangrove water 0.0030-0.0035 µg l^{-1}. The mercury content of the particulate matter was 0.15-0.40 µg l^{-1}, while it was 0.28 µg l^{-1} in estuarine water, 0.13-0.30 µg l^{-1} in backwater and 0.18-0.35 µg l^{-1} in mangrove water[25]. The mercury values of the present study fall within the range reported above; nevertheless, it was found that the maximum concentration of mercury (0.0763 µg l^{-1}) in Ennore Estuary water[29].

Conclusion

All the three sites are contaminated with cadmium (IS = 10 µgl^{-1}). Lead (IS = 100 µgl^{-1}) contamination could be observed at both Uttan and Mahul, and that of chromium was confined to Mahul water (IS = 50 µg l^{-1}). Copper levels were far higher in

Uttan, and zinc remained at levels that could be termed uncontaminated (IS for Cu = 50 µg l^{-1}; Zn = 5000 µg l^{-1}) according to the Indian Standards for drinking water[30]. However, the metal levels allowed by Indian Standards are higher than the drinking-water quality guidelines of World Health Organization[31]. Hence, the metals in these waters may contaminate the drinking water sources and also enter the food chain.

References

1 Ackroyd D R, Bale A J, Howland R J M, Knox S, Millward G E & Morris A W, Distributions and behavior of dissolved Cu, Zn and Mn in the Tamar estuary. *Estuarine Coastal Shelf Sci.,* 23 (1986) 621-640.

2 Saager P M, De Baar H J W, De Jong J T M, Nolting R F & Schijf J, Hydrography and local sources of dissolved trace metals Mn, Ni, Cu, Cd in the northeast Atlantic Ocean. *Mar. Chem.*, 57 (1997) 195-216.

3 Tripathy S C, Ray A K, Patra S & Sarma V V, Water quality assessment of Gautami - Godavari mangrove estuarine ecosystem of Andhra Pradesh, India during September 2001. *J. Earth Syst. Sci.,* 114 (2005) 185-190.

4 Bava K A & Seralathan P, Interstitial water and hydrochemistry of a mangrove forest and adjoining water system, south west of India, *Environ. Geol.* 38 (1999) 47-52.

5 Harbison P, Diurnal variations in the chemical environment of a shallow tidal inlet, Gulf of St. Vincent, South Australia: implications for water quality and trace metal migration. *Mar. Environ. Res.,* 20 (1986) 162-194.

6 Krishnamurthy K & Sundararaj V, Nutrients and plankton: backwater and mangrove environment. *Mar. Biol.*, 23 (1973) 229-237.

7 Sadiq M, *Toxic metal chemistry in marine environments*, (Marcel Deker Inc., New York) 1992, pp. 392.

8 Jonathan M P, Ram-Mohan V & Srinivasalu S, Geochemical variations of major and trace elements in recent sediments, off the Gulf of Mannar, the southeast coast of India. *Environ. Geol.,* 45 (2004) 466-480.

9 Dauby P, Frankignoulle M, Gobert S & Bouquegneau J M, Distribution of POC, PON, and particulate Al, Cd, Cr, Cu, Pb, Ti, Zn and 13C in the English Channel and adjacent areas. *Oceanol. Acta,* 17 (1994) 643-657.

10 Burland K W & Frank R P, Mn, Ni, Cu, Zn, and Cd in the Western North Atlantic. In: *Trace metals in seawater*, edited by Wong C S, Boyle E, Bruland K W, Burton J D & Goldberg E D (Plenum Press, New York) 1983, pp. 395-414.

11 van den Berg C M G, Buckley P J M, Huang Z Q & Nimmo M, An electrochemical study of the speciation of copper, zinc and iron in two estuaries in of England. *Estuarine Coastal Shelf Sci*., 22 (1986) 479-486.

12 Turner A, Millward G E, Bale A J & Morris A W, The solid solution partitioning of metals in the southern North Sea: *in-situ* radiochemical experiments. *Cont. Shelf Res*., 12 (1992) 311-1329.

13 Joseph P V and Chacko J, Distribution of dissolved and particulate heavy metals in Chitrapuzha - A tropical tidal river, Kerala, India. *Pollut. Res*., 24 (2005) 513-521.

14 Rajendran A, De Sousa S N & Reddy C V G, Dissolved and particulate trace metals in the western Bay of Bengal. *Indian J. Mar. Sci.,* 11 (1982) 43-50.

15 Achterberg E P, Herzl V M C, Braungardt C B & Millward G E, Metal behaviour in an estuary polluted by acid mine drainage: the role of particulate matter. *Environ. Pollut*., 121 (2003) 283-292.

16 Callaway R J, Specht D T, Ditsworth G R, Manganese and suspended matter in the Yaquina estuary, Oregon. *Estuaries,* 11 (1988) 217-225.

17 Ehrlich H L, *Geomicobiology*, (Marcel Dekker, New York) 1996.

18 Johnson D B, Microorganisms and the biogeochemical cycling of metals in aquatic environments. In: *Metal metabolism in aquatic environments*, edited by Langston W J & Bebianno M J (Chapman & Hall, London) 1998, pp. pp. 31-58.

19 Gounot A M, Microbial oxidation and reduction of manganese: consequences in ground water and applications. *FEMS Microbiol. Rev.,* 14 (1994) 339-350.

20 Jonathan M P, Srinivasalu S, Thangadurai N, Ayyamperumal E T, Armstrong S, Altrin E J S & Ram-Mohan E V, Contamination of Uppanar River and coastal waters off Cuddalore, Southeast coast of India. *Environ. Geol*., 53 (2008) 1391-1404.

21 Sholkovitz E R, Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta*, 40 (1976) 831-845.

22 Cuong D T & Obbard J P, Metal speciation in coastal marine sediment from Singapore using a modified BCR-sequential extraction procedure. *Appl. Geochem*., 21 (2006) 1335-1346.

23 Mzimela H M, Wepener V & Cyrus D P, Seasonal variation of selected metals in sediments, water and tissues of the groovy mullet, *Liza dumerelii* (Mugilidae) from the Mhlathuze Estuary, South Africa. *Mar. Pollut. Bull.*, 46 (2003) 659-676.

24 Cutter G A, Trace elements in estuarine and coastal waters of US - studies from 1986–1990. *Rev. Geophys. AGU (Suppl.)*, (1991) 639-644.

25 Krishnamurti C R, The cycling of arsenic, cadmium, lead and mercury in India. In: *Lead, mercury, cadmium and arsenic in the environment SCOPE 31*, edited by Hutchinson T C & Meema K M, (John Wiley & Sons Ltd, Chichester) 1987, pp. 315-333.

26 Chin T S & Chen H C, Toxic effect of mercury on the hard clam, *Meretrix lusoria* in various salinities. *Comp. Biochem. Physiol*.,105C (1993) 501-507.

27 Denton G R W & Burdon-Jones C, Influence of temperature and salinity on the uptake distribution and depuration of mercury, cadmium and lead by the black lip oyster *Saccostrea echinata*. *Mar. Biol*., 64 (1981) 317-326.

28 Miller D & Akagi H, pH affects mercury distribution not methylation. *Ecotoxicol. Environ. Saf.*, 3 (1979) 36-38.

29 Rajendran N, Baskara S, Sanjeevi S, Khan A & Balasubramanian T, Ecology and biodiversity of Eastern Ghats - Eastuaries of India. *EPTRI - ENVIS Newsletter,* 10 (2004) 3.

30 Awasthi S K, *Prevention of Food Adulteration Act No.37 of 1954, Central and State Rules as amended for 1999*, Ashoka Law House, New Delhi, 2000.

31 WHO, Guidelines for drinking-water quality - incorporating first and second addenda, third edition - Volume 1. World Health Organization, Geneva, 2008.