Heavy metal distribution in the biotic and abiotic matrices along Karnataka coast, west coast of India

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Sediment and soft tissue of bivalve samples collected from various sites of Karnataka coast were analysed for the estimation of the natural and anthropogenic heavy metal fluxes. Seasonal variations of heavy metals in sediment and bivalves collected from selected *hot spots* from Binage, Karwar and Thannirbavi, Mangalore were monitored. High concentrations of Hg was observed in the environment near the vicinity of a caustic soda plant at Binage, Karwar, indicating Hg pollution. Total Hg concentration in the tissue of oysters sampled from a contaminated stream from the above site, exceeded the safe limit of 0.5 $\mu g\ g^{-1}$ wet weight. The base-line heavy metal concentrations in sediment and bivalves from selected sites of coastal Karnataka are presented.

Karnataka coast is well known for its abundant fishery resources particularly mackerel, oil sardine, prawns, perches, carangids etc. The inshore waters off Karwar and Mangalore, west coast of India receives effluents from industries like the caustic soda factory, fertilizer plant, iron ore processing plant, dyes and pigment manufacturing plant and a petroleum refinery. Although there were reports on spot observations of heavy metal levels from Karwar Bay[1,2], a comprehensive account on the heavy metal levels in the coastal environment of Karnataka is lacking. In the present study an attempt is made to quantify the natural and anthropogenic contaminants of toxic heavy metals in the sediment and bivalves of Karnataka coast. Seasonal variations of heavy metals in sediment and bivalves of selected *hot spots* along the coast are monitored.

Materials and Methods

Superficial sediment, and bivalve molluscs such as mussel (*Perna viridis*) oyster (*Crassostrea cucullata*) and clam (*Meretrix casta*) were collected from 5 sites around Karwar, (Oct. 93-Sep. 94) and from 6 sites around Mangalore (Aug. 94-July 95) (Fig. 1). Bivalves were sampled as determined by their availability at each site and time-bulking method was followed for the collection[1]. Monthly samples of seawater, sediment and oysters were collected from two stations in a stream which originates from the vicinity of a caustic soda factory and enters into the sea at Binage, Karwar for the estimation of total Hg (Fig. 1). Sediment samples were collected from Thannirbavi and Hejmadi for heavy metal analysis (Fig. 1).

Air dried sediment samples and wet soft tissue of bivalves were acid digested for the determination of Cu, Zn, Pb and Cd using a Perkin Elmer 2380 AAS and Hg by cold vapour technique using a Hg analyser (MA 5800 E, ECIL)[1,3]. Seawater samples were analysed for Hg, after a pre-concentration step[4]. Seawater samples were digested with H_2SO_4, con. HNO_3, $KMnO_4$ and $K_2S_2O_8$ over a water bath. Repeated digestion and analysis of same samples were carried out and the precision of analysis was found to be within 10% (seawater 4%, sediment 10% and biological samples 6%). The percentage recovery of mercury from the

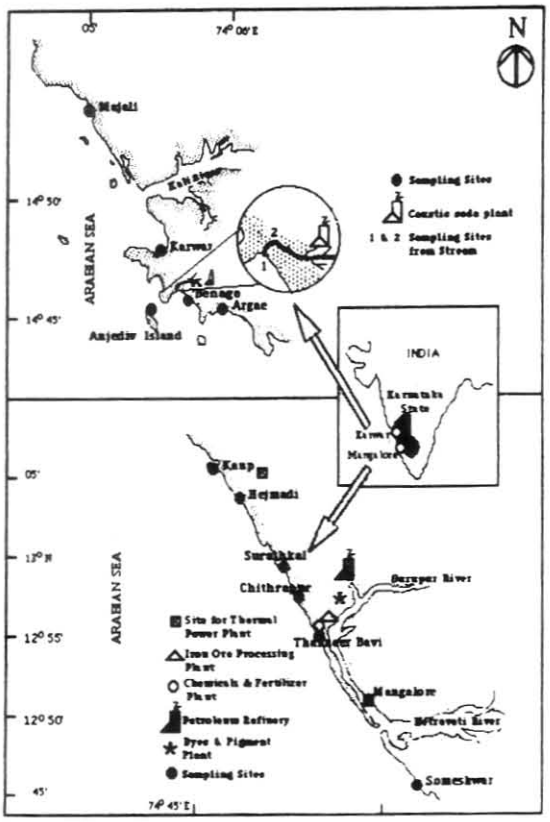

Fig. 1—Location of study.

samples was found to be >90% (seawater 98%, sediment 90% and biological samples 95%). The accuracy of the analytical procedure was checked using the standard reference materials, sediment (BCSS-1) and biological samples (NIES Ref. Mat. no.9 "*Sargasso*") supplied by NRC, Canada and NIES, Japan respectively[5] (Table 1).

Table 1—Accuracy of the analytical procedure estimated using Standard Reference materials, sediment (BCSS-1) and biological samples (NIES Reference Material no.9 "*Sargasso*")

Metal	Certified values ($\mu g\ g^{-1}$)	Observed values ($\mu g\ g^{-1}$)	Accuracy (%)
Sediment (BCSS-1)			
Copper	18.5	20.4	+ 9.2
Zinc	119.0	123	+ 3.3
Lead	22.7	20.8	- 9.1
Cadmium	0.25	0.27	+ 7.4
Mercury	0.129	0.12	- 7.5
NIES Ref. Mat. 9 (*Sargasso*)			
Copper	4.9	5.2	+ 5.8
Zinc	15.6	17.3	+ 9.8
Lead	1.3	1.46	+ 9.6
Cadmium	0.15	0.16	+ 8.0
Mercury	0.04	0.037	- 8.1

Table 2—Heavy metal concentration ($\mu g\ g^{-1}$ dry wt) in sediment samples collected from coastal waters of Karnataka

Site	Cu	Zn	Pb	Cd	Hg
North Canara					
Majali	28.4	12.2	7.6	N.D.	0.01
Karwar	24.4	1.9	4.0	0.01	0.003
Binage	157	72.0	112.5	2.13	0.203
Anjedev Is.	44.9	2.8	8.29	N.D.	0.01
Argae	67.1	31.3	7.5	N.D.	0.01
South Canara					
Hejmadi	26.1	51.9	6.72	0.704	0.002
Chithrapur	3.1	7.0	5.48	1.38	N.D.
Thannirbavi	37.0	68.8	5.92	0.629	0.016

ND= not detectable

Results and Discussion

Results of heavy metal distribution in the sediment and bivalve tissue samples collected from the coastal waters of Karnataka are shown in Tables 2 and 3 respectively. Mean Hg and other toxic heavy metals in the sediment and oysters sampled from Binage, Karwar from a stream which originates from the vicinity of a caustic soda factory were relatively high. The Hg concentration in seawater collected from the above stream varied from 0.05 $\mu g\ l^{-1}$ to 1.8 $\mu g\ l^{-1}$, in sediment varied from 0.07 $\mu g\ g^{-1}$ to 0.47 $\mu g\ g^{-1}$ and in oyster tissue varied from 0.18 $\mu g\ g^{-1}$ to 0.54 $\mu g\ g^{-1}$. Similar trend was reported by earlier workers from the above area[1,2]. Relatively high concentrations of Cu and Zn were observed in the sediment (Cu, 37 $\mu g\ g^{-1}$; Zn 68.8 $\mu g\ g^{-1}$) and tissue of bivalves (Cu, 128 - 201 $\mu g\ g^{-1}$; Zn 70.5-127.3 $\mu g\ g^{-1}$) collected from Thannirbavi, Mangalore from the vicinity of effluent discharge points of a Chemicals & Fertilizer Factory and a Iron Ore processing plant (Tables 2, 3). Predominance and persistence of certain species of phytoplankton and a slight decline of zooplankton biomass and density were reported from Thannirbavi[6]. Metal concentration in sediment and bivalves from all other sites of coastal waters of Karnataka such as Majali, Argae, Hejmadi, Chithrapur and Someshwar were found

to be more or less within the normal range. The sampling site at Chithrapur near Mangalore is close to the effluent discharge point of a newly established oil refinery and dyes and pigment plant. However, sampling from this site was done prior to the commencement of effluent discharge.

Monthly monitoring of total Hg levels in seawater, sediment and oyster tissue from two stations in a contaminated stream at Binage are shown in Fig. 2. Hg levels in the water sampled from both the above stations were relatively high (0.05 to 1.8 $\mu g\ l^{-1}$) during Jan-May. However, water Hg contents were low (0.05 to 0.14 $\mu g\ l^{-1}$) during southwest monsoon starting from June (Fig. 2). Similarly, Hg concentration in the sediment and oyster tissues sampled from the stream were relatively high throughout the year. High concentrations Cu, Zn, Cd and Pb were also observed in the sediment (Cu-157 $\mu g\ g^{-1}$; Zn-72 $\mu g\ g^{-1}$; Cd-2.13 $\mu g\ g^{-1}$ [1]; Pb-112.5 $\mu g\ g^{-1}$) and oyster tissue (Cu-159 $\mu g\ g^{-1}$; Zn-703 $\mu g\ g^{-1}$; Cd-

Table 3—Heavy metal concentration ($\mu g\ g^{-1}$ wet wt) in bivalves samples collected from coastal waters of Karnataka.

Site	Species	Cu	Zn	Pb	Cd	Hg
North Canara						
Majali	*Perna viridis*	1.8	11.1	0.31	0.16	0.01
Karwar	*Perna viridis*	1.5	14.4	0.33	0.31	0.01
	Crassostrea cucullata	37.3	155	0.38	2.01	
Binage	*Crassostrea cucullata*	159	703	7.5	10.9	0.57
Anjedev Is.	*Crassostrea cucullata*	37.5	155	1.43	3.2	0.18
Argae	*Perna viridis*	1.57	14	0.8	0.22	0.02
	Crassostrea cucullata	32	31	0.3	1.47	
South Canara						
Kaup	*Perna viridis*	17.1	23.3	1.48	0.54	ND
Hejmadi	*Meretrix casta*	18.4	34.9	1.1	0.52	0.01
Surathkal	*Perna viridis*	23.6	49.7	1.8	0.71	0.02
	Crassostrea cucullata	21.2	78.1	4.44	1.93	0.04
Chithrapur	*Meretrix casta*	3.94	11.1	2.8	0.89	ND
Thannirbavi	*Perna viridis*	128	70.5	2.52	0.81	0.02
	Crassostrea cucullata	201	127.3	3.98	2	0.05
Someshwar	*Crassostrea cucullata*	22.6	125.2	1.95	2.76	ND

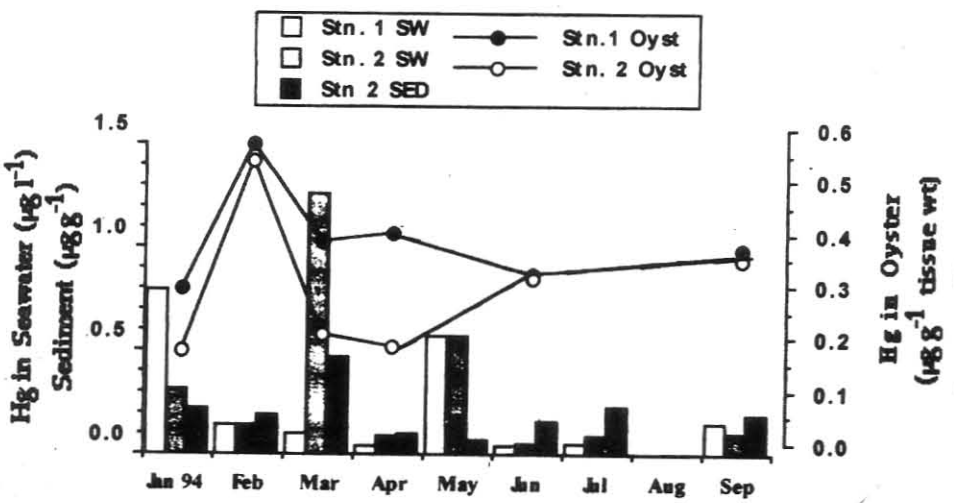

Fig. 2—Variation of mercury concentration in seawater, sediment and soft tissue of oyster (*Crassostrea cucullata*) of Binage, Karwar.

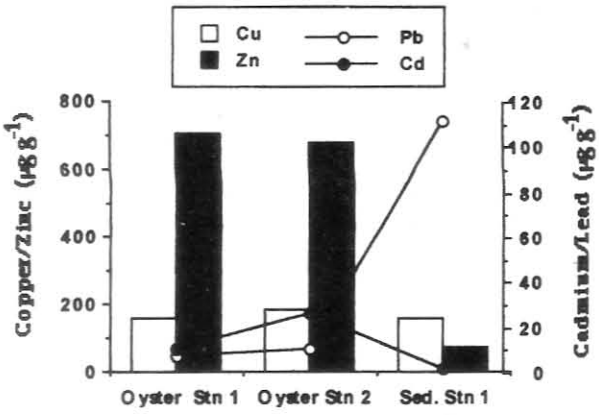

Fig. 3—Variation of copper, zinc, lead and cadmium concentration in sediment and soft tissue of oyster (*Crassostrea cucullata*) of Binage, Karwar.

10.9 $\mu g\ g^{-1}$; Pb-7.5 $\mu g\ g^{-1}$) sampled from the above stream (Fig. 3).

Total Hg concentration in oysters sampled from the above contaminated stream during February exceeded the safe limit of 0.5 $\mu g\ g^{-1}$ wet weight as laid out by FAO. Before the construction of the present submarine effluent pipeline, effluents from the factory were directly discharged into this stream which enters into the Binage Bay.[7] Evidence of discharge containing Hg into this stream was reported[1,2] during 1987 and 1990. The results of the present study also clearly show that effluents containing Hg and other toxic metals are continuing to reach the stream.

Monthly variations in heavy metal concentration in sediment collected from Hejmadi and

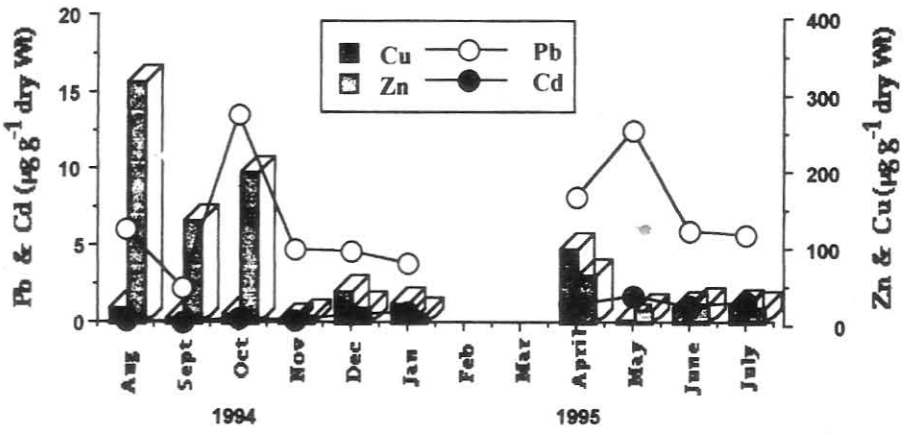

Fig. 4—Variation of copper, zinc, lead and cadmium concentration in sediment of Hejmadi.

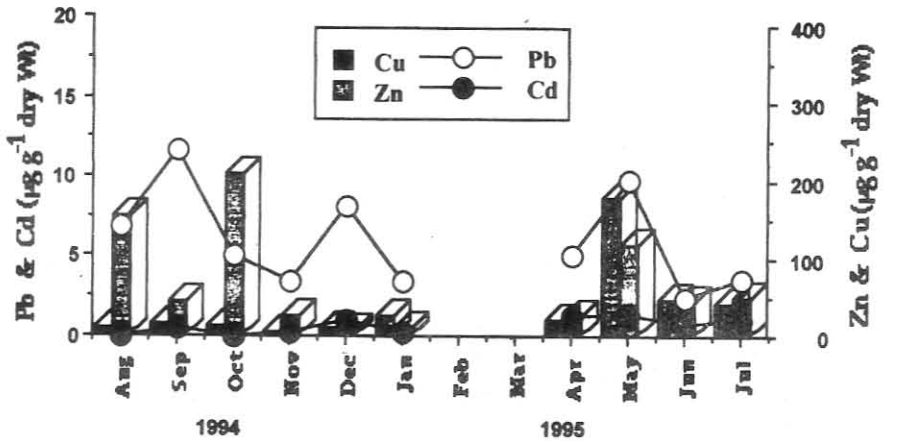

Fig. 5—Variation of copper, zinc, lead and cadmium concentration in sediment of Thannirbavi.

Thannirbavi near Mangalore are shown in Figs 4 and 5 respectively. Difference in monthly metal concentration in sediment collected from the two sites was not significant (ANOVA). During May-July relatively high concentrations of Cu and Zn were observed in the sediment samples collected from Thannirbavi.

It is reported that heavy metal concentration in the biota is a function of the element, its source, time of sampling, total metal load and the organism tested.[8] Therefore, varying heavy metal concentration and different distribution pattern at different environments are expected. However, increased buildup of Hg observed in a site in the vicinity of a caustic soda plant at Binage near Karwar clearly demonstrated Hg pollution in and around the above site. Heavy metal concentrations in sediment and bivalves from all other sites of Karnataka were more or less within the normal range.

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