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Trace metal variability in nearshore waters along the central west coast of India

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Copper (Cu), zinc (Zn), lead (Pb) and cadmium (Cd) concentrations in water and zooplankton were studied along the central west coast of India to assess spatial and temporal variations. The water and zooplankton samples were collected during different seasons. They were subjected to AAS to know the metal concentrations. Results showed that zinc showed higher concentrations at the study sites while cadmium showed the least content. Anthropogenic sources did not seem to significantly influence the metal concentrations in water and zooplankton.

[**Keywords**: copper, cadmium, lead, zinc, zooplankton, salinity]

Introduction

Nearshore waters along the central west coast of India are highly dynamic in nature. A considerable human population lives along the coast and is dependent on these waters for their livelihood. These waters are used for fishing, recreational activities, discharge of waste waters from residential and commercial establishments and are also subjected to the action of wind and waves [1]. Besides this, they are also home to many organisms including phytoplankton, zooplankton, fishes and other marine invertebrates.

It has been recognized that metals such as Pb, Cd, Zn, Cu in marine waters can be toxic even in trace amounts[2]. Cu and Zn are micronutrients while Pb and Cd are toxic metals. Pb can be toxic at very low concentrations while cadmium acts as a micronutrient at low concentrations and becomes toxic at higher concentrations [3]. Zooplanktons have a short life span and are sensitive organisms, they serve as a link between primary producers and secondary consumers and hence may contribute to the transfer of trace metals to higher trophic levels due to their significant capacity to bioaccumulate metals from their food, as well as from seawater [4]. Marine organisms have the capability of accumulating trace metals in their bodies hundreds of times greater than the level in the sea water [5]. Recent studies show that the waters nearest to the shore have suffered more ecological degradation over the past few decades compared to the open oceans[6]. .

The present study was undertaken in the near shore waters of central west coast of India viz Malvan, Colva and Karwar. Coast is subjected to rapid urbanization and industrialization. Malvan situated in Maharashtra is an open coastal ecosystem. It has an ancient fort, which attracts many tourists. For locals residing here, fishing and boating are important occupations. Colva is located in southern part of the state of Goa. It is an important tourist destination, with several hotels and shacks along the coast. This area is also used for water sports and other water related activities. Hence, throughout the year, the beach is crowded with tourists. In the same area, the sewage generated by several households and hotels of Colva also finds its way into the sea through a drain. Karwar, on the other hand, is a port town, hence, in addition to domestic waste water and sewage, ballast water from ships is also released

here. River Kali meets the ocean in this beach, thus adding nutrients and other matter.

Earlier studies on coastal waters of Malvan and Goa showed high concentrations of Cd, Pb and Hg in marine algae[7]. Extensive studies have been conducted in Mandovi and Zuari estuaries in Goa to study the metal concentration especially iron due to the mining activities and transport of ore [8-9]. The Velsao Bay of Goa and the coastal waters of Goa have been studied for metals [10-11]. Study on coastal waters of Karnataka revealed high concentration of Hg, Cu, Cd, Pb and Zn in the sediments and Bivalve tissue [12]. Karwar waters are more turbid and less saline compared to Colva waters. Also, in Karwar, *Penaeus* species are found to breed very close to the sea [13].

Despite the importance of nearshore waters, information on metals and metals accumulation by zooplankton is fragmentary in these waters. As inshore waters along the central west coast are subjected to high anthropogenic pressure, it would be essential to know the metal content in these waters and zooplankton.

Materials and Methods

Three sites along the central west coast of India (Malvan, Colva and Karwar) were selected for the present study. Sampling was carried out in monsoon (August-September 2012) and winter (December – January 2013) at three points that were 50 m apart,in the nearshore waters of each location Malvan, Colva and Karwar.

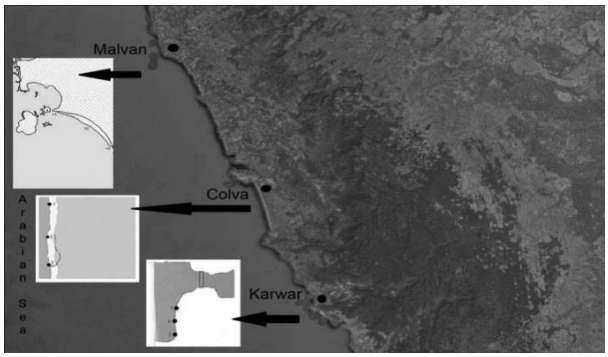


Fig 1: Map of Central west coast of India showing the stations in Malvan, Colva and Karwar

Water and zooplankton were collected from the surface nearshore waters. Total metals in water samples were extracted using the APDC–MIBK procedure [14-15].Zooplankton samples were collected using plankton net (mesh size ~300µ), having small nylon sieve and are thoroughly rinsed with Milli-Q water to remove salts. Subsequently, the samples were dried in an oven at 65°C and stored in a vacuum dessicator. Subsequently, the filters were subjected to acid digestion following the methodology of Rejomon *et al*., 2008. The material was digested with a mixture of 3 ml of HNO_3. Metal concentration was determined using an atomic absorption spectrophotometer with an air/acetylene flame [16].

Results

Trace metals in seawater and zooplankton

Table 1 and 2 gives the average concentration of metals recorded from inshore waters and zooplankton from Colva, Karwar and Malvan in monsoon and winter. The marine waters along the central west coast of India showed higher content of zinc followed by lead, copper and cadmium. Whiles in zooplankton, higher concentration of zinc followed by copper, lead and cadmium was observed.

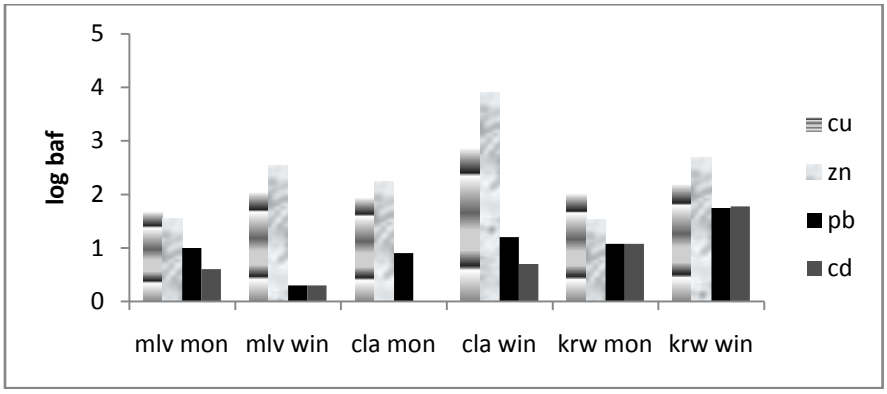
The concentration of copper in Colva waters was higher in monsoon than in Karwar and Malvan. Malvan waters showed very little variations in copper concentrations. Karwar waters recorded high copper content in winter. Copper content in zooplankton at Colva was higher than, in Malvan and Karwar. The zinc level in the coastal waters showed similar trend as copper. In Colva, zinc concentration was higher in monsoon, than in Malvan and Karwar. In winter, zinc concentration was high in Karwar. Zooplankton from coastal waters of Colva showed higher zinc content in monsoon than Karwar and Malvan. Concentration of lead in the coastal waters of Colva was high in monsoon, and almost similar in Karwar and Malvan. In winter, it was maximum in Malvan, followed by similar concentrations of Colva and Karwar. Cadmium occurred in least concentration among all the metals studied.

Table 1- Average concentration of dissolved trace metals from Malvan, Colva and Karwar

Seasons/stations		Copper (Cu) ug/l	Zinc (Zn) ug/l	Lead (Pb) ug/l	Cadmium (Cd) ug/l
Malvan	Monsoon	1.25±1.05	6.13±3.93	5.14±2.20	0.66±0.13
	Winter	0.42±0.51	1.00±0.71	12.05±0.11	2.22±0.18
Colva	Monsoon	4.82±1.71	15.52±4.08	4.63±1.15	1.22±0.08
	Winter	1.97±1.10	0.09±0.07	9.56±0.84	1.25±0.09
Karwar	Monsoon	1.30±0.20	1.91±2.12	6.17±1.17	1.47±0.03
	Winter	3.16±0.03	34.19±2.0	10.81±1.49	1.44±0.05

Table 2- Average concentration of trace metals in zooplankton from Malvan, Colva and Karwar

Seasons/stations		Copper (Cu) mg/l	Zinc (Zn) mg/l	Lead (Pb) mg/l	Cadmium (Cd) mg/l
Malvan	Monsoon	0.04±0.01	0.04±0.01	0.03±0.01	0.0014±0.00002
	Winter	0.04±0.02	0.32±0.05	0.02±0.03	0.0018±0.00003
Colva	Monsoon	0.54±0.10	3.18±0.51	0.05±0.01	0.0008±0.00001
	Winter	1.11±0.13	0.69±0.17	0.09±0.04	0.00136±0.0002
Karwar	Monsoon	0.12±0.44	0.89±0.34	0.02±0.04	0.01±0.002
	Winter	0.45±0.16	0.16±0.06	0.31±0.01	0.08±0.020



Graph 1- Average bioaccumulation factor (log) for trace metals in zooplankton (mlv=Malvan, cla= Colva, krw=Karwar, mon=monsoon, win=winter)

Bioaccumulation of Copper, cadmium, lead and zinc in zooplankton

Graph 1 gives the average bioaccumulation factor (log) of Copper, cadmium, lead and zinc in zooplankton from coastal waters of Malvan, Colva and Karwar. Bioaccumulation factor considers the metal accumulated by an organism from its surrounding waters. It was calculated using the formula BAF=metal concentration in organism/metal concentration in water.

Maximum enrichment of zinc and least enrichment of cadmium were observed.

Discussion

The occurrence of metals showed high variability. Metal concentrations in the study sites were well below the maximum limit specified by CPCB (1996)[17]. Copper is an essential nutrient, required in trace amounts, for all living beings, as it is a key component of many enzymes. It may enter marine environment through natural sources like weathering, atmospheric deposition or anthropogenic sources like sewage. The overall concentration of copper was below 5ug/l, and the waters were relatively free from copper pollution. Dissolved copper in the coastal waters of Malvan was lower than the previous studies in inshore waters of Malvan[18]. In Colva and Karwar, dissolved copper was in agreement with the earlier studies[10, 19]. Zinc in aquatic environments occurs in dissolved form and also in association with other suspended matter. It enters marine environment through natural or anthropogenic sources like sewage, industrial discharge, dry batteries, roofing etc. Dissolved zinc in coastal waters of Malvan was lower than the previous studies in inshore waters of Malvan[18]. The present study recorded higher zinc concentrations in coastal waters of Colva and Karwar than the earlier studies[10,19]. Zinc is an important nutrient required by phytoplankton. Higher zinc levels in Karwar waters and zooplankton may be due to upwelling, anthropogenic inputs like port activities, ballast water, discharge of sewage and other domestic waste etc. Among all the metals studied, zinc exhibited higher enrichment in zooplankton, which agrees with the earlier studies[16]. Zinc is a micronutrient, which is an essential component of zooplankton diet and is required in minute quantities for its growth. There was no significant copper and zinc pollution was observed in the present study, suggesting that, there is minimum impact of anthropogenic activity, on copper and zinc levels in nearshore waters.

Dissolved lead concentrations were slightly higher than the previous studies [20]. Lead enrichment in the coastal surface waters may be mainly due to atmospheric deposition [20-21].According to Rejomon *et al*., (2010) [20] , higher industrial emission along the west coast of India along with the winds are responsible for higher lead in surface waters of eastern Arabian Sea. Combined effects of atmospheric deposition and boat trafficking, harbor activities and organic matter deposition could also be the reason for lead in coastal waters (Udayakumar *et al*., 2011)[22]. Cadmium enters the ocean, mainly through natural sources, such as weathering, erosion, volcanic activity etc., Cadmium showed the least concentrations and the least variability among the metals studied, suggesting that, cadmium concentrations along the central west coast may not be influenced significantly by external inputs. Compared to the three study sites, Karwar waters and zooplankton showed higher cadmium.

Bioaccumlation

Zooplankton can accumulate metal into its body either from the surrounding water or the food it consumes [20, 23]. In Colva and Malvan, cadmium showed least enrichment while in Karwar, cadmium enrichment was slightly higher in zooplankton. Diaz *et al*., [24] and Green *et al*., [25] showed in their experiments on clams and bacteria respectively that bioaccumulation associated with cadmium was higher at low salinity and increased pH and temperature. In addition, zinc metal is also known to enhance the toxicity of cadmium to aquatic invertebrates[26]. As observed, Karwar waters have less salinity and have higher zinc concentrations. Zooplankton in Karwar, especially in monsoon, is composed of juvenile *Penaeus* sps. Nunez-Noqueira[27], reported that, juvenile *Penaeus vannamei* can not only regulate zinc and lead, but also accumulate cadmium without excretion. These might be the reasons for slightly higher cadmium enrichment in Karwar.

Conclusion

From the present study, it can be concluded that, the coastal waters of Malvan, Colva and Karwar are relatively free of metal pollution. Copper and zinc show higher variability, than lead and cadmium. As on date, the anthropogenic sources do not seem to significantly influence the metal concentrations in water. Based on the observations, it was clear that, lower the salinity, as in Karwar, bioaccumulation of cadmium was higher in certain organisms like *Penaeus* sp.

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