

DISTRIBUTION OF TOXIC METALS, Hg, Cd AND Pb IN ZOOPLANKTON ALONG THE INDIAN COAST

R. SEN GUPTA & TARIQ W. KUREISHY

National Institute of Oceanography, Dona Paula, Goa - 403 004.

ABSTRACT

Distribution of toxic metals such as Hg, Cd and Pb in zooplankton is assessed with a view to correlate it with the prevalent environmental conditions along the Indian coast. While Hg could not be detected in zooplankton the concentrations of Cd and Pb show interesting ranges which are discussed in the light of the availability and presence of these two toxic metals in the Indian marine environment. The importance of zooplankton in distributing these elements in the marine environment and in the marine food chain is also attempted. The results have shown high concentrations of Cd and Pb in zooplankton collected from the East Coast as compared to the West Coast. Some inferences have been drawn.

INTRODUCTION

Zooplankton is of great importance in the cycling of elements in the oceans. They are second only to phytoplankton in abundance and hence, their role in transporting elements in the marine ecosystems has been suggested. Processes like vertical migration across mixing barriers (Pearcy & Osterberg, 1967); incorporation of elements into fast sinking fecal pellets (Osterberg *et al.*, 1964) and sinking of skeletal structures after death (Arrhenius, 1963) variations in elemental contents of zooplankton samples are certainly to be expected. Any given sample would contain species from several phyla with different morphologies and feeding modes. Species composition will change from place to place, and again with seasons. Armstrong & Atkins (1950) suggested the working mechanisms responsible for the elemental uptake by members of the plankton community which was later described by Brooks & Rumsby (1965) as : particulate ingestion of suspended material from sea water, ingestion of elements via their pre-concentrations in food materials and other mechanisms. Hence it becomes impossible to determine the reasons of one zooplankton sample containing less or more of an element than the other. However, in view of the large surface to volume ratio of the zooplankton, it is reasonable to assume that the differences in the amounts taken up by adsorption - exchange may be mainly responsible for the variations of these elements.

In addition to the amount of available surface area, three main factors govern adsorption rates i.e., concentration of the particular element in the sea water, physical factors such as temperature and finally since adsorption is not instantaneous, the amount taken up will depend on the time factor also. Martin (1970), based on the above assumptions, and considering the copepods to be the most abundant multicellular animals in the world with each member having eleven exoskeletal casts, suggested the possibility of elemental transfer in the World Oceans because a large portion of these moulded insoluble chitin must reach the bottom and since these moults are capable of taking up elements by adsorption exchange even after the moulting process is over, it could be a major source of biological transport of trace metals in the oceans.

Concentrations of metals in zooplankton may vary, nonetheless, they indicate the environmental characteristics of the area of collection. Despite this, very little is known about the concentrations of heavy metals in zooplankton from different areas. Much of the published work deals with trace elements and has been confined to multi-element determinations on bulk collections of zooplankton (Noddack & Noddack, 1939; Vinogradov, 1953; Nicholls *et al.*, 1959; Vinogradova & Kovalisky, 1962; Szabo, 1968; Martin, 1970; Martin & Knauer, 1973; Topping *et al.*, 1973; Knauer & Martin, 1972; & Martin & Broenkow, 1975). While almost all these deal with the analysis of Pb very few give information on Cd and Hg. While Nicholls *et al.* (1959) did spectrographic analyses of several elements in ten species of zooplankton, including Pb, they were unable to detect Cd due to limited scope of the methodology. Some of them reported Cd and Pb and Knauer & Martin (1972) reported Hg. It is evident that there is no consolidated report on these three most toxic elements in zooplankton. Similarly there are a few reports from the Indian coast (Kureishy & George, 1977; George & Kureishy, 1979; and Kureishy *et al.*, 1983) the data from these are also incorporated in this report.

METHODS

In all, 49 zooplankton samples could be obtained for analyses. All these samples were collected by Indian Ocean Standard Net (10SN), H-T net and the Neuston net with stainless steel frame. All these nets were of 500 μ mesh size. On completion of the haul the net was not washed with the ship's sea water but the cake from the bucket (PVC) was removed by stainless steel spatula (precleaned) and transferred to a beaker. This plankton cake was rinsed with double glass-distilled water. After decanting, the cake was stored at -5 to -10°C in polythene bags or acid washed glass tubes till analysis. No effort was made to divide the zooplankton samples on the basis of various groups and were preserved as a whole, Cd and Pb were analysed using the method described by Topping *et al.* (1973). Briefly 2.5 - 3.0 wet weight of zooplankton cake was digested in a 100 ml conical flask using conc. HNO_3 (20-25ml) followed by conc. HClO_4 (1-2 ml) until a clear solution was obtained. The digestion was done at $200^{\circ}\text{C} \pm 10^{\circ}\text{C}$ for about 10-12 hrs. Blanks were run simultaneously with each set of samples using maximum amount of acid used for digestion. After the digestion, the acid volume, reduced to 1-2 ml, was transferred to a 10 ml measuring flask and made up to the mark with glass distilled water. Hg was analysed using the methods discussed earlier (Kureishy *et al.*, 1979). The samples were aspirated in Hilger and Watts AAS. Accuracy and reproducibility of the result were controlled periodically through participation in national and international intercalibration exercises.

RESULTS AND DISCUSSION

A preliminary analysis on species composition of all the zooplankton samples, based on sub-samples or other samples taken from the same station, revealed that copepods were the most dominant group in all the samples. Chaetognaths and euphausiids were next in abundance. It was, however, felt that minor changes in the composition would not really be a factor causing the wide variation as discussed here.

The station positions of sample collections are given in Fig. 1 and the results of all the analysis are given in Table I. As is evident (Fig. 1) the areas covered for sampling are mostly spread along the coastal regions of India including the Andaman group of islands with a few samples from areas away from the coast, specially in the Bay of Bengal. The results in Table I are divided into three areas i.e., Arabian Sea, Bay of Bengal and the Andaman Sea. We discuss the distribution of each metal separately:

Hg:

This element could not be detected in any of the zooplankton sample barring one where the value was 0.001 ppm. This is quite understandable when we observe the values of total Hg (dissolved and particulate) from the areas of zooplankton sampling, which range from 0.01 to 0.13 $\mu\text{g/l}$ with an average value of 0.07 $\mu\text{g/l}$, through localised high values were observed at certain places, Sanzgiri *et al.* (in press). This trend is also passed on to the smaller variety of fishes which feed on zooplankton where too, lower concentrations of Hg observed throughout the Indian coast (Kureishy, 1985). Comparing our values with those of other workers it becomes rather difficult to assign reasons for the differences since the data from other areas are restricted to off California (Monterey Bay) and Hawaii. Martin & Knauer (1973) reported 0.05–0.29 ppm (dry weight) in different groups and 0.14 ppm (dry weight) in mixed zooplankton from areas between California and Hawaii. Knauer & Martin, (1972) reported 0.012 from Monterey Bay, California. However, it is obvious that low concentrations of Hg in zooplankton is associated with low concentrations of this element in particulate and dissolved form prevalent almost all along the coast.

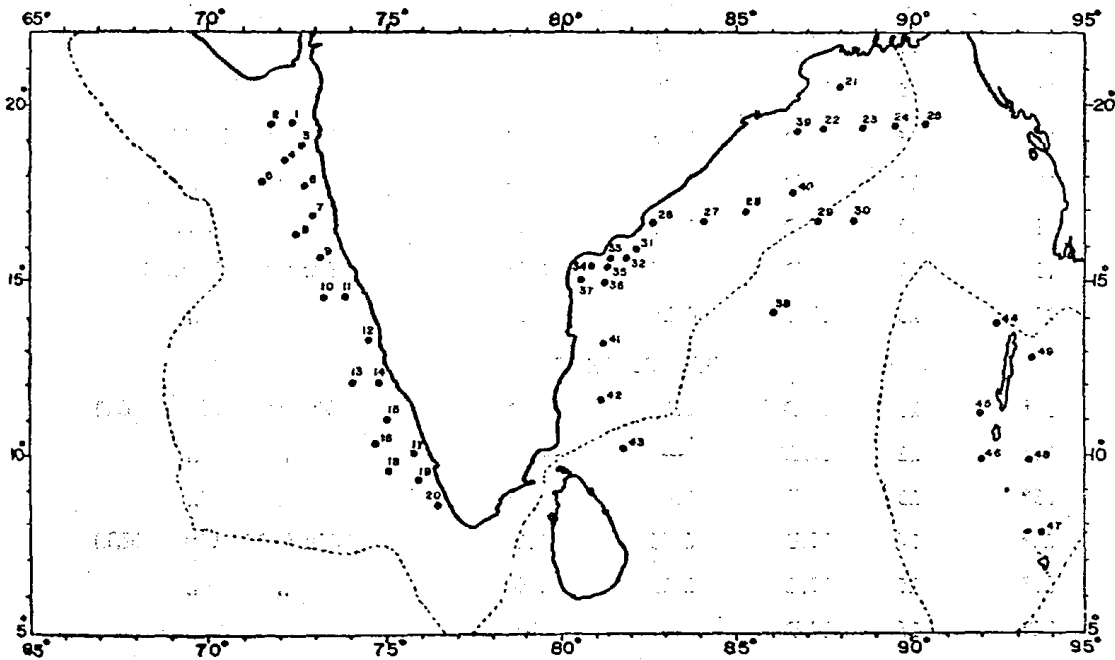


Fig. 1. Station positions from where Zooplankton samples were collected

TOXIC METALS IN ZOOPLANKTON

TABLE I

Hg, Cd and Pb in Zooplankton (whole) samples (ppm wet weight)

<i>Sample No.</i>	<i>Stn. No.</i>	<i>Hg</i>	<i>Cd</i>	<i>Pb</i>	<i>Type of Haul (net used)</i>	
1	2	3	4	5	6	
ARABIAN SEA						
1	1	N.D	0.83	6.73	Surface	(Neuston)
2	2	N.D	1.22	13.02	"	"
3	3	N.D	0.09	2.35	"	"
4	4	N.D	3.33	34.25*	Vertical	(IOSN)
5	5	N.D	0.13	9.22	Surface	(Neuston)
6	6	N.D	1.12	3.14	Vertical	(IOSN)
7	7	N.D	0.89	1.28	"	"
8	8	N.D	0.93	8.15	"	(H.T)
9	9	N.D	0.76	2.08	"	(H.T)
10	10	N.D	0.02	11.23	"	"
11	11	N.D	0.13	6.05	Surface	(Neuston)
12	12	N.D	1.25	4.13	"	"
13	13	0.001	2.01	1.12	"	"
14	14	N.D	0.53	1.89	"	"
15	15	N.D	0.88	7.31	"	"
16	16	N.D	1.06	3.67	Vertical	(IOSN)
17	17	N.D	1.63	3.28	"	"
18	18	N.D	1.00	3.11	"	(H.T)
19	19	N.D	0.46	2.86	Surface	(Neuston)
20	20	N.D	0.25	1.16	"	"
BAY OF BENGAL						
21*	21	N.D	1.73	34.6*	Vertical	Haul (H.T)
22*	22	N.D	—	—	"	"
23*	23	N.D	1.68	41.6*	"	"
24*	24	N.D	0.88	2.2	Vertical	Haul (H.T)
25*	25	N.D	2.12	1.0	"	"
26*	26	N.D	—	—	"	"
27*	27	N.D	0.97	23.8*	Vertical	Haul (H.T)

TABLE I (contd.)

1	2	3	4	5	6	
28*	28	N.D	0.93	12.6	"	"
29*	29	N.D	—	—	"	"
30*	30	N.D	2.24	11.89	"	(IOSN)
31*	37	N.D	1.94	10.8	"	"
32*	36	N.D	1.88	11.6	"	"
33*	38	N.D	2.04	34.0 ^a	"	(H.T)
34*	34	N.D	2.00	1.6	"	"
35*	35	N.D	0.93	1.4	"	"
36*	33	N.D	0.79	1.0	"	"
37*	32	N.D	—	—	"	"
38*	31	N.D	5.43	37.1 ^a	"	"
39	39	N.D	3.87	21.8 ^a	"	"
40	40	N.D	1.87	13.7	Surface	(Neuston)
41	41	N.D	1.22	10.7	"	"
42	42	N.D	1.21	2.48	"	"
43	43	N.D	0.45	2.13	"	"
ANDAMAN SEA						
44*	44	N.D	1.96	11.22	Surface	(Neuston)
45*	45	N.D	2.37	5.24	Vertical	(H.T)
46*	46	N.D	0.69	4.36	"	"
47*	47	N.D	1.36	31.87 ^a	"	"
48*	48	N.D	1.53	4.27	"	"
49*	49	N.D	5.99	7.19	Surface	(Neuston)
Averages						
Arabian Sea						
		0.001	0.92	4.83		
Bay of Bengal						
		N.D	1.74	6.39		
Andaman Sea						
		N.D	2.31	6.45		

a = not included for averages

* = converted from ppm dry weight to ppm wet weight

N.D — Not detected

Cd:

Cd, in general, showed quite high values in zooplankton. In the Arabian Sea the values range from 0.02–3.33 ppm with an average of 0.92 ppm, while in the Bay of Bengal they are from 0.45–5.43 ppm, av. 1.74 ppm. In the Andaman Sea, based on six samples, the range was 0.69–5.99 ppm with an average of 2.31 ppm. Thus the difference from the West to the East Coast is apparent, being higher in the Bay of Bengal than in the Arabian Sea. This agrees well with the higher concentrations of Cd observed in dissolved as well as that associated with the particulate matter all along the coastline (Kureishy, 1985). This reveals the availability and presence of this element in higher concentrations in the Bay of Bengal as compared to the Arabian Sea which is reflected in the concentrations of Cd observed in zooplankton. It may, however, be pointed out that the number of observations on Cd concentrations in surface sea water are not enough to reach a definite conclusion.

No significant difference between coastal and offshore stations were observed. Average values for coastal stations was 1.3 ppm (range 0.09 – 5.43) and for offshore stations it was 1.56 (range 0.02 – 5.99). Comparing our values with those reported by other workers, for Cd in Zooplankton, from different areas, it becomes evident that Cd is generally observed in higher concentrations in zooplankton. A comparative analysis is presented here:

Cd Concentrations in zooplankton from different areas

<i>Area of sampling</i>	<i>Type of sample</i>	<i>Concentration in ppm wet weight</i>	<i>Source</i>
Off California	Mixed	0.28–1.44*	Martin, 1970
Off Baja California, Coastal	Mixed	3.58–4.18 ^a	Martin & Broenkow, 1975
Offshore	Mixed	3.24–3.44 ^a	
Monterey Bay, California	different groups	0.16–1.92 ^a	Martin & Knaüer, 1973
	Mixed	1.2 –1.28 ^a	
Firth of Clyde	Mixed	0.14–1.03 ^a	
Scottish waters Firth of Clyde	70– 250 μ	0.2 ^a	
	250– 100 μ	0.16 ^a	
Moray Firth	70– 250 μ	0.57 ^a	Topping <i>et al.</i> , 1973
	250–1000 μ	0.84 ^a	
North	70– 250 μ	0.06 ^a	
Channel	250–1000 μ	0.15 ^a	
Atlantic Ocean	Mixed	0.2–6.5 ^a	
Arabian Sea	Mixed	0.02–3.33	
Bay of Bengal	Mixed	0.45–5.43	This study
Andaman Sea	Mixed	0.69–5.99	

* = Converted from ppm ash weight

a = Converted from ppm dry weight

Pb:

Results show quite high values of Pb in most of the samples. The three areas of sampling show very interesting results. In the Arabian Sea the range was 1.12 – 13.02 (Average 4.83 ppm) with a single value of 34.25 which was not included to calculate the average. In the Bay of Bengal the range was 1.0 – 13.7 ppm with an average of 6.39 ppm. In the Bay of Bengal, too, a few very high values were omitted in calculating the average. Similarly in the Andaman sea the range was 4.27 – 11.22 ppm with an average of 6.45 ppm.

Pb, too, shows similar trends in different areas as Cd, being lower in the Arabian Sea as compared to the Bay of Bengal. While Cd values did not show much variations between these two sampling areas. While the range of Pb in zooplankton from coastal status was 1.0 – 13.02 ppm with an average of 4.5 ppm, the offshore stations showed a range of 1.0–23.8 with an average of 8.14 ppm. It may be mentioned here, too, that some very high values were omitted for averaging. It is quite apparent that zooplankton from coastal areas show lower concentrations than the offshore counterparts. It agrees well with the earlier observations (Kureishy, 1985) of higher dissolved and particulate Pb along the coastline as well as offshore areas attributed to precipitation or river run off or both.

High concentrations of Pb is also observed by various workers from different areas of the marine environment. Though there are wide variations in this data arising out of different analytical methodologies employed as well as areas of sampling, the values do show high levels. A comparative chart of Pb values in zooplankton from different areas is given here.

Pb concentrations in zooplankton from different areas

Area of sampling	Type of sample	Concentration in ppm wet weight	Source
Unknown	Two species only	0.12–52.0*	Nicholls <i>et al.</i> , 1959
Unknown	Mixed	5.4 ^a	Noddack & Noddack, 1939
Off California	Mixed	N.D–128*	Martin, 1970
Monterey Bay, California	Different groups	N.D–2.52 ^a	Martin & Knauer, 1973
	Mixed	1.0–1.76 ^a	
Firth of Clyde Scottish waters	Mixed	9.8–20.6 ^a	
Firth of Clyde	70–250 μ	4.06 ^a	
	250–1006 μ	0.42 ^a	Topping <i>et al.</i> , 1973
Moray Firth	70–250 μ	1.3 ^a	
	250–1000 μ	1.22 ^a	
North Channel	70–250 μ	10.34 ^a	
	250–1000 μ	44.2 ^a	
Atlantic Ocean	Mixed	0.04–1.78 ^a	
Arabian Sea	Mixed	1.12–13.02	
Bay of Bengal	Mixed	1.0 –13.7	This study
Andaman Sea	Mixed	4.27–11.22	

* = Converted from ppm ash weight

a = Converted from ppm dry weight

From the results presented above a few very interesting observations come to light. While Hg, one of the most toxic metals, was not detected in any of the sample analysed (barring one), the concentrations of Cd and Pb show increased levels in this vital link of the marine food chain, which is of considerable importance in the transfer mechanisms of metals in the food chain. Apart from this, the role of zooplankton in transporting elements through the water column by various processes, as mentioned earlier, is also very significant.

The differences in concentrations of Cd and Pb in zooplankton from Arabian Sea and the Bay of Bengal including the Andaman Sea is probably due to the weathering and anthropogenic releases of these elements through river runoff and then subsequent availability in dissolved and particulate form. The differences in concentrations of these elements (Pb in particular) in coastal and offshore zooplankton probably results from several factors. One of which could be the peculiar gyral circulation pattern in the Bay of Bengal. Another reason for this interesting observation could be that since the coastal areas have a large amount of solid particles emanating through river run off, the metals are adsorbed on these particles and are probably removed more quickly by sinking to the bottom than in the open ocean area which has very little particulate matter, thus making less metal available in the coastal areas than in the open oceans. This observation is, however, not supported conclusively by the concentrations of Pb and Cd in the dissolved form from the surface waters because of very few observations.

The above assumptions have, however, been shown to be true in the case of chlorinated hydrocarbons in coastal sediments of the Bay of Bengal (Sarkar & Sen Gupta, unpublished). On the other hand, these high concentrations of Cd and Pb in zooplankton do give an indication on the availability and presence of these two elements in the marine environment around India. The possible impact it may have on animals higher up on the food chain is, too, complex a subject to be discussed under the purview of this report here. However, no definite food chain magnification pattern is yet established based on the work carried out in this laboratory.

ACKNOWLEDGEMENTS

We thank the Director, NIO for encouragement. Thanks are also due to Ms. Analia Mesquita and Sujata Sanzgiri for their help in analysis.

REFERENCES

- Armstrong, F. A. T. & Atkins, W.R.G. 1950. The suspended matter of sea water *J. Mar. Biol. Ass. U.K.*, 29: 139-143.
- Arrhenius, G.O.S. 1963. Pelagic sediments. In: *The sea*, pp. 655-727 Ed. by M.N. Hill, Interscience.
- Brooks, R. R. & Rumsby, M.G. 1965. The biogeochemistry of trace element uptake by some New Zealand bivalves. *Limn. Oceanogr.*, 10: 521-527.
- George, M.D. & Kureishy, T.W. 1979. Trace metals in zooplankton from the Bay of Bengal. *Ind. J. Mar. Sci.*, 8: 190-192.
- Knauer, G.A. & Martin, J.H. 1972. Mercury in a marine pelagic food chain. *Limn. Oceanogr.*, 17: 868-876.

- Kureishy, T.W. & George, M.D. 1977. Trace metals in Zooplankton from the Arabian Sea. NIO. Tech. Rep. 'Health of the Arabian Sea'.
- Kureishy, T.W., George, M.D. & Sen Gupta, R. 1979. Total mercury content in some marine fish from the Indian ocean. *Mar. Poll. Bull.*, 10: 357-360.
- Kureishy, T.W., Sujata Sanzgiri, George, M.D. & Analia Braganca. 1983. Mercury, Cadmium and Lead in different tissues of fishes and in zooplankton from the Andaman Sea. *Ind. J. Mar. Si.*, 12: 60-63.
- Kureishy, T.W. 1985. Studies on Mercury, Cadmium and Lead in marine organisms in relation to marine pollution from the sea around India. Ph.D. Thesis. Aligarh Muslim University, 183 pp.
- Martin, J.H. 1970. The possible transport of trace metals via moulted copepod exoskeletons. *Limnol. Oceanogr.*, 15: 756-780.
- Martin, J. H. & Knauer, G.A. 1973. The elemental composition of plankton. *Geochem. Cosmochem. Acta.*, 37: 1639-1643.
- Martin, J.H. & Broenkow, W.W. 1975. Cadmium in plankton. Elevated concentrations off Baja, California, *Science*: 190: 884-885.
- Nicholls, G.D. Cure, H. jr & Bowen, V.T. 1959. Spectogra-analyses of marine plankton. *Limnol. Oceanogr.*, 4: 472-475.
- Noddack, I. & Noddack, W. 1939. Der Hanjig Keiten der Schwermetalle in Meerestrien. *Arkiv. F. Zool.*, 32 A: 1-35.
- Osterberg, C.L. Cavey, W.Q. & Curl, H. jr. 1964. Radioactivity and its relationship to the oceanic food chain. *J. Mar. Res.*, 22: 2-12.
- Pearcy, W.G. & Osterberg, C.L. 1967. Depth, diel, seasonal and geographic variations in Zinc-65 of underwater animals off Oregon. *Int. J. Oceanolog. Limnol.*, 1: 103-116.
- Szabo, B.J. 1968. Trace element content of plankton population from the Bahamas. *Carib. J. Sci.*, 8: 185-186.
- Topping, G., Pirie, J. M. & Graham, W.C. 1973. Trace metals in zooplankton from scottish waters. ICES, CM 1973/E:31, Fishery improvement committee.
- Vinogrador, A.P. 1953. The elementary chemical composition of marine organisms. *Sears Found. Mar. Res. Memoir.* 2, XIV: 647 pp.
- Vinogradora, Z.A. & Kovalisky, V.V. 1962. Elemental composition of thd Black Sea plankton (In Russian). *DOKL Acad. Nauk. USSR*, 147: 1458-1460.