

# COPPER CONTENT IN THE INSHORE AND ESTUARINE WATERS ALONG THE CENTRAL WEST COAST OF INDIA

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THE importance of copper as a biologically active element in the natural waters needs no special emphasis. The occurrence of copper in the chloroplasts, haemocyanin and in several enzymes<sup>1</sup> renders it all the more important perhaps in controlling the productivity of the waters. Paradoxically, copper concentrations of more than 1 ppm through land drainage from natural and artificial sources are also known to be toxic<sup>1</sup> to aquatic life. In view of the extensive ore-bearing land mass along the Goa coast and the growing industrialisation of the region, preliminary studies are undertaken to know the distribution of this important element in the inshore, estuarine and the river waters of this area.

Surface samples have been collected using a clean plastic bucket and the bottom samples using a Vandorn sampler taking care not to contaminate the samples during sampling. Samples were analysed for copper by the method described by Strickland and Parsons<sup>2</sup> using sodium diethyldithiocarbamate and extracting the copper with carbon tetrachloride. The extinction was measured at 434 m $\mu$  using Unicam SP 500 Spectrophotometer. The copper estimated is non-complexed or weakly complexed ions.

Four perpendicular sections have been selected along the coast for the collection of samples in the month of January. Nine stations have been sampled in the Zuari river from the mouth of the river upstream to a distance of about 25 miles. In Mandovi river samples have been collected from 12 stations upto a distance of about 25 miles upstream. The station positions are as shown in Fig. 1. In order to understand the influence of freshwater discharge a few stations have also been worked during the month of July when land drainage is at its maximum.

The concentration of copper in the bottom waters is invariably higher than those of the surface in the inshore, estuarine and river waters. In the inshore region the surface values range between 3–46  $\mu\text{g/l}$  (Table I) and the bottom values between 10 and 76  $\mu\text{g/l}$ . High concentrations (> 20  $\mu\text{g/l}$ ) at the surface and at the bottom are encountered at all sections except off Cape Ramas. A general increase in the levels towards north is also noticeable. The copper concentrations in the two river systems, viz., Mandovi and Zuari show diverse trends in their general concentration levels.

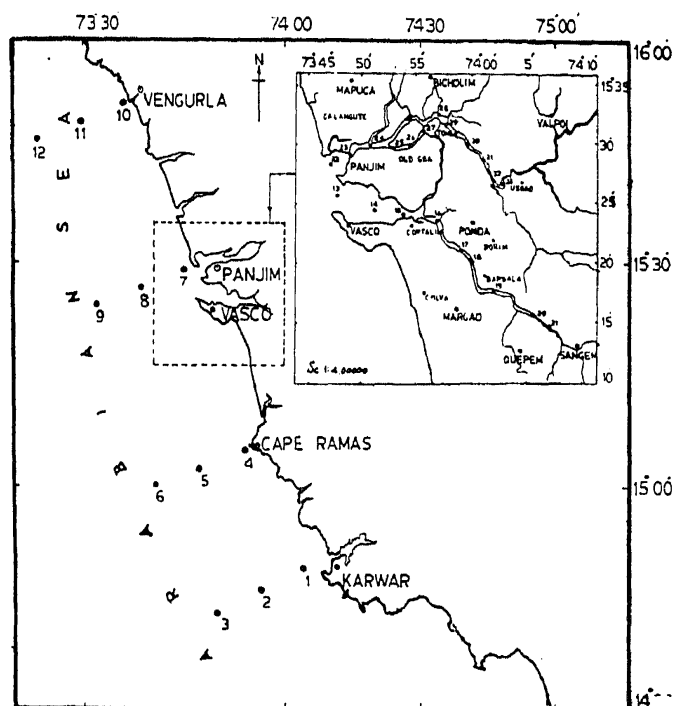


FIG. 1. Map showing the station locations along the Central West Coast of India.

*Inset: Station Locations in the Mandovi and Zuari rivers.*

TABLE I

*Copper concentrations in the inshore waters*

Station numbers	Salinity ‰		Copper $\mu\text{g/l}$	
	Surface	Bottom	Surface	Bottom
Pre-monsoon				
1	33.58	33.49	4.77	23.87
2	33.30	33.49	25.03	31.41
3	33.78	33.73	30.88	50.91
4	32.99	32.97	3.41	17.66
5	33.28	33.60	18.00	10.12
6	34.07	34.83	17.20	19.06
7	33.66	33.55	34.34	42.06
8	33.66	33.89	21.41	31.15
9	33.98	34.58	19.28	35.41
10	33.89	33.82	38.87	69.77
11	34.02	33.80	46.33	67.10
12	34.22	34.33	13.58	76.12

The range of values were between 2–67  $\mu\text{g/l}$  (Table II). The levels in Mandovi river are extremely low (2–14  $\mu\text{g/l}$ ) as compared with those of Zuari. Another significant feature is that while concentrations in the Zuari river tend to increase from the mouth towards upstream, consistent with the normal feature in other river systems, in the Mandovi the concentrations remained the same over the entire stretch. However, during the monsoon period when the freshwater discharge is at maximum the copper levels increased to 74  $\mu\text{g/l}$ . It

TABLE II  
Copper concentrations in Zuari and Mandovi rivers

Station numbers	Salinity ‰		Copper µg/l	
	Surface	Bottom	Surface	Bottom
Pre-monsoon				
13	36.59	36.11	4.80	8.75
14	36.63	37.63	8.85	10.12
15	36.81	36.54	14.42	20.13
16	36.04	36.33	15.07	15.78
17	35.16	34.56	29.23	32.62
18	31.33	30.65	62.71	35.40
19	25.52	24.25	61.71	67.27
20	13.44	12.90	28.33	55.64
21	5.93	6.13	27.92	51.59
22	35.35	35.44	2.02	3.04
23	34.65	33.95	5.15	4.25
24	33.04	33.58	14.32	43.50
25	31.44	31.64	6.39	4.80
26	28.51	27.79	5.57	5.87
27	27.07	27.07	8.04	8.75
28	24.38	25.19	6.64	5.57
29	23.84	23.84	4.10	6.19
30	20.95	20.68	4.75	5.16
31	14.33	14.15	4.75	7.38
32	9.74	10.14	3.38	3.59
33	7.81	4.31	1.97	2.33
Monsoon				
23	0.77	3.55	28.33	73.83
25	0.77	0.77	32.47	59.18
26	0.41	0.41	34.39	36.94

may be mentioned here that there is no significant relation between salinity and the copper concentration, in the inshore as well as in the river systems.

The ionic copper concentration in the coastal waters is predominantly controlled by land run off<sup>3,4</sup>. It occurs mainly in the cupric form, and depending on the pH conditions it transforms gradually into sparingly soluble basic carbonate, the solubility of which limits the copper concentration in the waters<sup>1</sup>. The high magnitude of variations of copper in the inshore waters is perhaps due to its chemically labile nature under the prevailing complex physico-chemical conditions of the inshore waters and also due to its biological involvement. Part of the concentrations especially in the shallow depths may be contributed by the microbial action on the bottom sediments. The present investigations on the ionic copper in the inshore and estuarine waters are undertaken as a first step, viewing its important role in promoting or inhibiting effects on the growth of marine life at different concentration levels. A contrasting feature of the present observations in the inshore waters as well as in the rivers is that the concentrations are very high than those from elsewhere reported by several workers<sup>3-7</sup>.

There are four important rivers opening into the sea in the region of observation. These rivers flowing through the ore bearing (iron and manganese)

terrain might be picking up the element and thus perhaps responsible for the very high values observed. It may be mentioned here that the manganese ore in the gondites formation of the Central Provinces of India contains significant amounts of copper<sup>8</sup>. Some observations made in the Mandovi estuary during the monsoon period, when the run off is at its maximum, showed very high concentration of copper indicating the influence of land run off on the copper concentrations in the inshore region.

During the pre-monsoon period the copper concentrations in the inshore waters and Zuari river remained relatively high, which is unexpected since the river discharge is minimum during this period. Only in the Mandovi river the values were low. These features suggest that some factors other than the contribution from land run off might be governing the distribution. The diverse feature in the two rivers might be due to the difference in the physico-chemical conditions of the waters and sediments and their regenerative activities. The maintenance of high levels of copper in the inshore region is suggestive of active re-cycling of the element. Much of the copper appears to be bound organically and the ionic copper is released when the organic matter is oxidised<sup>4</sup>. The bottom values are consistently high showing perhaps the profound influence of the active mud-water interface. The sinking and decaying organisms may be the main source in releasing the organic compounds into the water<sup>9</sup> and subsequent oxidation to ionic copper.

Detailed investigations are in progress which may elucidate more about the complex behaviour of the copper in these waters.

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1. Harvey, H. W., *The Chemistry and Fertility of Sea Waters*, Cambridge University Press, 1955.
2. Strickland, J. D. H. and Parsons, T. R., *A Practical Handbook of Sea Water Analysis*, Fish. Res. Bd., Canada, 1968, Bull. No. 167.
3. Spencer, D. W. and Brewen, P. G., *Geochim. Cosmochim. Acta*, 1969, 33, 325.
4. Foster, P. and Morris, A. W., *Deep. Sea Res.*, 1971, 18 (2), 231.
5. Alexander, F. F. and Corcoran, J. E., *Limnol. Oceanogr.*, 1967, 12, 236.
6. Graham. Topping, *J. Mar. Res.*, 27 (3), 318.
7. Sundaraj, V. and Krishnamurthy, K., *Curr. Sci.*, 1972, 41, 315.
8. Varentsov, I. M., *Sedimentary Manganese Ores*, Elsevier Publishing Company, 1964.
9. Slowey, J. F., Jeffrey, L. M. and Hood, D. W., *Nature*, 1967, 214, 377.