

## ORGANICALLY ASSOCIATED COPPER IN MANDOVI AND ZUARI ESTUARIES

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### ABSTRACT

Studies were conducted to determine the extent to which copper is associated with organic matter in the estuarine and riverine waters of Mandovi and Zuari. It was observed that in the Mandovi the organically associated copper varies between 0 and 46% of the total copper and in the Zuari it is between 0 and 60%.

Even though copper is one of the most extensively investigated trace metals in sea water, not much is known on its association with organic matter. Most of the workers have concluded that ionic copper is far more toxic to aquatic organisms than organically bound copper and that the more stable the copper complex, the less is its toxicity (Pagenkoft, Russo and Thurston, 1974).

The presence of organically associated copper in sea water has been reported by several workers. Recently, Batley and Florence (1976) quantified the different forms of copper in sea water. The earlier work on copper in the Goa region (Sankaranarayanan and Reddy, 1973; Zingde, Singbal, Moraes and Reddy, 1976) deals only with dissolved inorganic copper. The present work is of a preliminary nature to understand the extent to which copper is associated with organic matter in the estuarine and riverine waters of Mandovi and Zuari.

Samples were collected from three stations in each of the two rivers (Mandovi and Zuari). The first station was located at the mouth of the river and the last station was about 60 km away from the first, where the tidal effect was not felt. The middle station was located about 15 to 20 km from the mouth of the respective rivers. Samples were collected from all the three stations in one river, the same day. Five litres of surface water were collected with acid washed plastic buckets and stored in acid washed polyethylene bottles. The samples were filtered through acid washed Whatman GF/C filter papers. The first one litre of water was discarded. The filtered samples were then acidified to pH 4 with 6N HCl to lessen adsorption losses. Each sample was divided into two portions—one was analysed directly for copper (the soluble extractable form) and the other was digested with persulphate for determining the total copper (Slowey and Hood, 1971). The organically associated form was calculated by difference. For the estimation of copper the method of Strickland and Parsons (1965) was used as described by Williams (1969). All the reagents were prepared in double glass distilled water. The absorbance was measured at 434 nm in a 5 cm cell using ACTA III Beckman Spectrophotometer. The coefficient of variation was 8% for extractable copper and 11% for total copper.

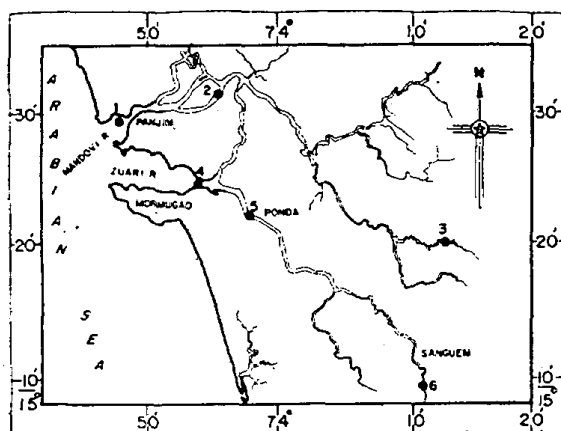


Fig. 1. Station location map.

46% of the total copper in Mandovi and 0 to 60% in Zuari. Bluestein and Smith (1978), Williams (1969) and Foster and Morris (1971) have also reported similar results from elsewhere.

The variations of the extractable and organically associated form of copper along the river are rather complicated. They may be due to the superimposed effects of various factors such as adsorption or desorption by suspended particulate matter (Kharkar, Turekian and Bertine, 1968), inputs by domestic waste, on going construction work along the river floor (Fukai, Murray and Huynh, 1975). In general, both the forms of copper decrease from the mouth to the upper reaches of the rivers. The sharp differences in organically associated copper between the stations at the riverine segments of Mandovi and Zuari estuaries are presumed to be the effect of agricultural activities in the nearby fields. Both the extractable and organically associated forms of copper decrease with the onset of monsoon. The input of copper which is expected to be high in the upper reaches of the river during the monsoon period, might have been affected by the increased load of suspended matter causing adsorption of both the forms of soluble copper in the fresh water zone and gradually released in the gradient zone, reaching maximum near the mouth. Turekian (1971) observed that the adsorbed form of metals in streams and rivers are always released to a greater or lesser extent on contact with sea water due to their displacement by major ions like magnesium

Table I. Organically associated copper in Mandovi and Zuari estuaries during May-September, 1978.

Estuary	St. No.	May		June		July		August		September	
		$\mu\text{g/l}$	%	$\mu\text{g/l}$	%	$\mu\text{g/l}$	%	$\mu\text{g/l}$	%	$\mu\text{g/l}$	%
Mandovi	1	4.0	28.6	2.8	28.2	1.0	26.7	NO	—	1.0	20.0
"	2	2.5	22.2	7.6	45.5	1.0	22.2	NO	—	ND	—
"	3	2.8	28.2	1.3	15.2	1.9	28.9	NO	—	0.38	10.8
Zuari	4	NO	—	2.2	27.6	0.75	18.0	ND	—	1.8	29.2
"	5	NO	—	4.0	33.7	0.5	10.0	1.3	32.0	2.1	54.0
"	6	NO	—	ND	—	ND	—	ND	—	1.5	60.0

N. O.—No observation, ND=Not detectable

The organically associated copper refers to the ionic copper when the dissolved organic matter in sea water is fully oxidised (Foster and Morris, 1971). The monthly variations in the organically associated copper in the two rivers are presented in Table I. Oxidation of the water sample by persulphate caused an increase in the concentration of copper in Mandovi between 0 and 84% and in Zuari between 0 and 150%. The organically associated copper varied between 0 and

and sodium present in sea water. Studies on the nature of suspended matter and its copper content associated with physical and chemical combinations will give a better understanding of the variations of the metal in the system.

## ACKNOWLEDGEMENTS

The authors express their sincere thanks to Dr. S. Z. Qasim, Director, for going through the manuscript and valuable suggestions. Thanks are also due to Mr. C. V. G. Reddy for advice and improving the manuscript and to Mrs. T. Joseph for help in the analysis.

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