

TRACE METAL LEVELS IN THE SEDIMENTS OF THE COCHIN BACKWATERS*

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ABSTRACT

Levels of Cu, Mn, Co, Ni and Zn at four stations in the northern arm of the Cochin backwaters, which runs through an industrial belt is reported. All metals showed some degree of variation over the area studied. Co showed the lowest variation while Cu and Zn values were found to vary with stations and seasons. The main effluent discharge site showed significant enrichment in Cu during the monsoon season and in Zn during the premonsoon. Barmouth showed an increase in metal content of sediments in the postmonsoon season. Enrichment in Zn was evident downstream of effluent discharge area during post and premonsoon season.

Key words: Pollution, trace metals, backwaters

INTRODUCTION

A steadily growing interest in the research on trace elements has been evinced recently partly due to a concern over the protection of the environment and also due to an increasing awareness of their role in and effects on biological systems. Most of the biological active as well as potentially toxic trace metals are highly reactive and are therefore accumulated in authogenic material and organisms. Some of these like Cu and Zn are also recognized as effective catalysts in biological systems (Mandelli, 1978). The role of rivers in transporting material from continents to oceans is paramount, being 10 times that of glaciers and 100 times that of winds (Goldberg, 1976). They carry metal in solution, absorbed in inorganic solids as metallic coatings on solids in organic solids and in detrital crystalline material (Gibbs, 1973). Super-imposed on effects of weathering and vulcanism human activities constitute an important pathway of metals into the aquatic environment. Due to their easy accessibility and consequent high human influence, rivers, estuaries and coastal areas are found to be more susceptible to pollution effects.

Work on trace elements in India are few and were mostly directed towards levels in biota. Sediments of the west coast have been studied by Murty, Paropakari, Rao and Topgi (1978a & b). Trace metal levels in marine and estuarine waters have

* Paper presented at the International Seminar on Management of the Environment at Bhabha Atomic Research Centre, Bombay.

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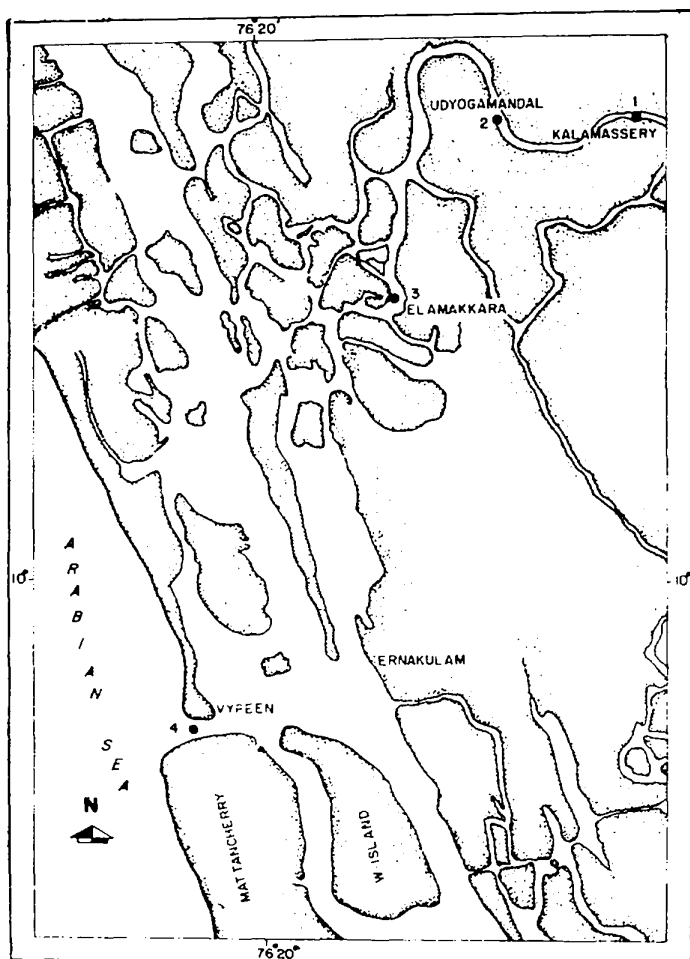


Fig. 1. Station positions and the area of sampling.

also received some attention (Singhal and Sujata, 1977; Sankaranarayanan and Rosamma, 1978), while estuarine sediments have not yet been studied.

The present paper reports the trace element levels over an year at four stations (Fig. 1) on the northern limb of the Cochin backwaters. The river Periyar, recipient of a variety of industrial effluents at Eloor (Udyogamandal) joins the estuary on its northern side. The stations sampled were upstream of industrial complex (stn. 1), the effluent discharge site (stn. 2), Flamakkara (stn. 3) about midway from stn. 2 and stn. 4 (barmouth), but located upstream of the retting grounds. Hydrographic features, water quality and characteristics of sediments of the area of investigation have previously been reported (Sarala Devi, Venugopal, Remani, Lalitha and Unni-

than, 1979; Remani, Venugopal, Sarala Devi and Unnithan, 1980). At Station 2, the effluent discharge area the principal pollutants are the industrial effluents, while conditions at barmouth (stn. 4) are also influenced by the discharge of domestic wastes and harbour activity (Vijayan, Remani and Unnithan, 1976; Sarala Devi, Venugopal, Remani, Lalitha and Unnithan, 1979; Remani, Venugopal, Sarala Devi and Unnithan, 1980).

MATERIAL AND METHODS

Sediment samples were collected with a van Veen grab. The samples were dried at 100 – 105°C to a constant weight, homogenised and digested in a mixture of perchloric acid and nitric acids as recommended by Lithnor (1975), followed by 0.5 ml of conc. HCl. The solution was made up to 25 ml with glass double distilled water. The above method, is reported (Ellis and Kanamori, 1977) to give values, only slightly lower than the total digestion method of Bear (1964). A blank correction was applied by subjecting the acid digestion mixture to the same sequence of treatments. Metal concentrations were estimated by Atomic Absorption Spectrophotometer (Hilger Watts Atomspek H1550). The values reported are averages of duplicate and in some cases triplicate estimates and pertain to the bulk sample. Fig. 1 shows the area of sampling and stations.

RESULTS AND DISCUSSION

Table 1 gives the coefficient of variation of the sediment analyses at the four stations. Except at stn. 2 in February for Zn and Cu the coefficients of variations are not large, indicating the suitability of subsampling procedures. Figs. 2-5 show the seasonal variations in the trace metal levels studied. There was some degree of seasonal variations in concentrations for all metals at all stations, probably governed by the prevailing physico-chemical conditions and backland influence. Allersma and de Groot (1974) observed the trace metal levels in Chao Phya river (Thailand) and Tji Tarun river in Indonesia, to remain almost constant at low levels. They have attributed the lack of mobility to the low organic content of the sediments and the river. A high organic matter content (3.55%) was observed in the area of investigation. Remani, Venugopal, Sarala Devi and Unnithan, 1980). This relatively high organic content also perhaps encourages mobilisation processes and contribute to the variations noticed. The metal levels, in general, showed good relationship with the amount of finer fractions present, which agrees with studies made elsewhere (Murty, Paropakari, Rao and Topgi, 1978 a & b; Loring and Nota, 1968).

Table I. Precision of Sediment Analysis. Coefficient of variation (\pm) ranges are given where more than one series was done.

Station	Cu	Mn	Co	Ni	Zn
1	1.6—10.4	0.6—3.6	4.1—8.7	2.3—9.7	2.3—10.8
2	5.6—11.7	3.0—9.8	0.8—15.4	5.3—8.3	2.1—4.7
3	4.6	4.3	2.6	12.9	12.7
4	3.2	1.7	12.4	6.6	2.0

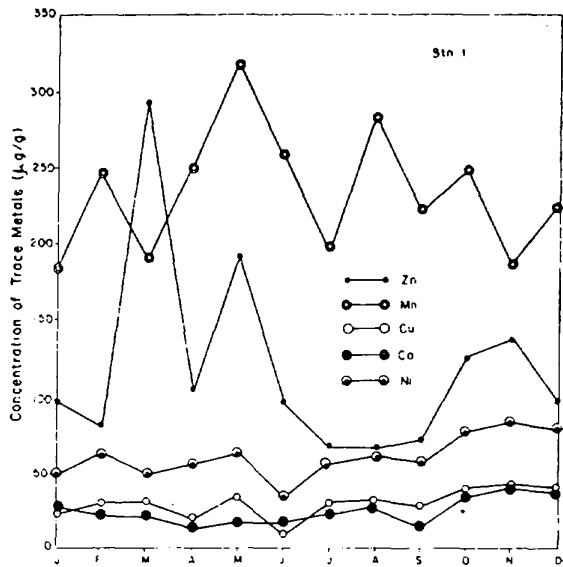


Fig. 2 Seasonal variations in metal levels at Station 1.

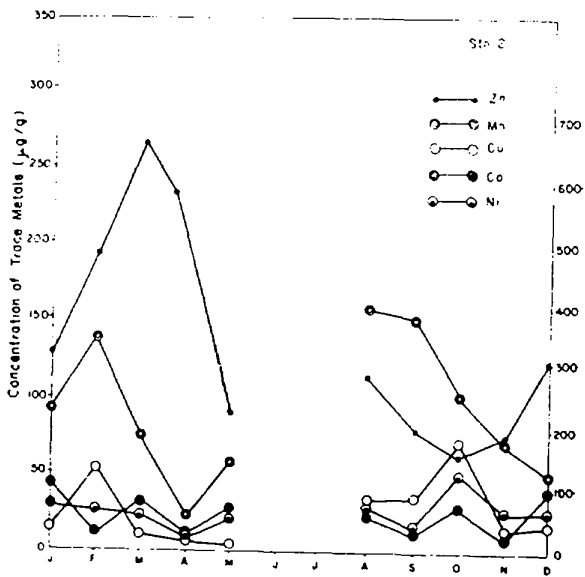


Fig. 3 Seasonal variations in metal levels at Station 2

The highest values for Cu (70.8 ppm), Zn (663.5 ppm) and Co (43.1 ppm) were recorded at stn. 2 during October/March and January respectively (Fig. 3). Manganese showed the highest concentration at stn. 1 in May (317.5 ppm) and Ni (85.9 ppm) at the same station in November.

Peak values for Cu, Co and Ni at stn. 1 were in postmonsoon season (Nov.) and those of Mn and Zn in premonsoon (May, Fig. 2). At stn. 2, Cu and Ni showed the highest values in October, Manganese in August, Cobalt in January and Zinc in March (Fig. 3). At stn. 3 (Fig. 4), Cu and Co showed peak values in January, Mn in February and Ni and Zn in July. At stn. 4 all peak values were observed in the monsoon and postmonsoon seasons with Cu, Co and Ni showing highest values in November, Mn in June and Zn in July (Fig. 5). The contribution from up-stream sources seems to be considerable at this station. The enrichment in Ni and Zn during the monsoon (at stns. 3 & 4) indicates some degree of downstream transport with the monsoon floods. Settling of trace metals at the area of confluence between river and sea water could lead to such effects. Dyer (1972) has indicated that settling of trace metals occur in estuaries by flocculation and sedimentation.

Table II gives the seasonal and annual averages of metals for the 4 stations. Postmonsoon season showed higher average values for metals at stn. 1 with the exception of Mn which was higher in the monsoon season. Cu, Mn and Ni values were higher in the monsoon season at stn. 2, Cobalt in the postmonsoon season and

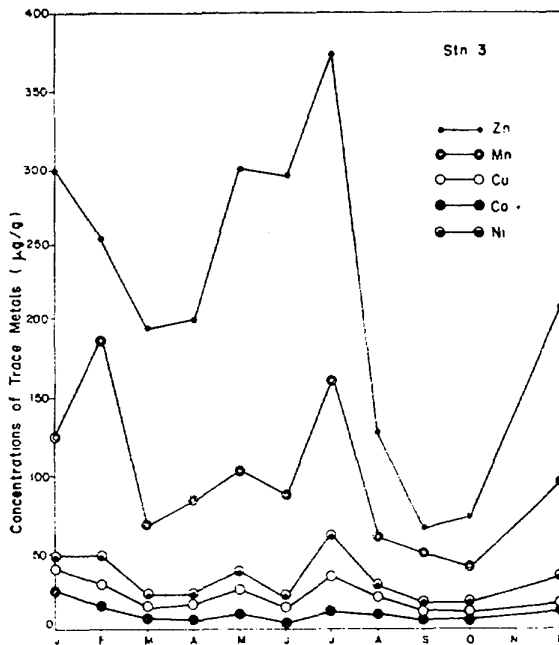


Fig. 4 Seasonal variations in metal levels at Station 3.

Zn during the dry premonsoon season. Average values for seasons did not fluctuate much at stn. 3 with the exception of Zn which showed a marked increase in the pre and postmonsoon seasons. Peak average values for all metals at stn. 4 were during the postmonsoon season.

To study the interdependency between metals, correlation matrices were constructed for the 4 stations (Table III), using the formula,

$$r = \frac{\sum (x - \bar{x})(y - \bar{y})}{n\sigma_x \sigma_y}$$

where \bar{x} , \bar{y} denote average values and σ_x , σ_y standard deviation and n stands for the number of observations. Levels of significance were read from the Fisher and Yates tables. Significant positive correlations were observed at stn. 1 between Cu and Co, Cu and Ni, and Co and Ni, indicating a common source (Ellis and Kanamori, 1977). The correlation between Cu and Zn though positive was not significant. All other correlations at stn. 1 were negative. At stn. 2, significant correlations were observed between Cu and Ni. The correlations between Cu and Mn, Ni and Co and Ni and Mn were positive though not significant. The correlation between Mn and Zn was significantly negative indicating little chance of their occurrence together at this station. At stn. 3 all correlations were positive. Significant correlation were seen between Cu and Mn, Cu and Co, Cu and Ni, Ni and Mn and Co and Ni. At stn. 4 all correlations were positive except between Co and Zn which showed very feeble negative correlation. Significant correlation was observed between Cu and Ni. In all cases the levels of significance varied from 5 to 0.1%.

Coefficients of correlation of metal with some environmental parameters were calculated. Significant positive correlation was observed between Cu and suspended solids and Zn and suspended solids only at stn. 4 ($P < 0.001$).

The fate of metals in the estuarine waters have been the subject of considerable discussion (Gibbs, 1973; de Groot, 1973; Duincker and Nolting, 1976). Flocculation and sedimentation of colloidal and fine material in suspension may cause a net settling of trace elements (Dyer, 1972). It has also been suggested that they may be taken up from solution (Coonley, Baker and Holland, 1971). Trace elements may undergo net sedimentation in estuaries even if they have undergone initial desorption (Turekian, 1971). The positive metal to metal correlations and correlation of some metals to suspended solids (at stns. 3 & 4) suggest that a net sedimentation of metals occur in the estuary.

Sankaranarayanan and Rosamma (1978) have observed an increase in particulate metals downstream of the effluent discharge area. The highly variable physico-chemical conditions especially of pH and temperature at stn. 2 (Sarala Devi, Venugopal, Remani, Lalitha and Unnithan, 1979; Jayapalan, Sasidharan and Nair, 1976) do not seem conducive to sedimentation of metals at stn. 2, the effluent discharge site. The lack of clear correlation between metals at stn. 2, is perhaps not surprising considering the variety of sources of input at this area.

Levels of metals in sediments can be deemed to be a close approximation to the end product of the processes to which these are subjected to in an estuary. A study of these levels have also the added advantage of being less amenable to local

Table II. Averages and standard deviation of values (in ppm) of trace metals at stations 1-4 (1976-77). Standard deviation \pm values are given in parenthesis.

	Station 1		Station 2		Station 3		Station 4		
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	
Premonsoon	28.2 (6.0)	218.6 (28.2)	24.0 (8.2)	59.1 (10.9)	26.3 (9.0)	113.0 (41.6)	14.3 (6.8)	36.0 (11.0)	241.6 (35.0)
Monsoon	26.3 (8.4)	256.0 (42.9)	17.5 (6.3)	53.6 (10.1)	20.5 (8.6)	80.0 (44.8)	9.7 (4.0)	28.8 (16.9)	165.4 (110.7)
Postmonsoon	39.8 (1.3)	217.4 (30.8)	38.1 (1.8)	82.3 (3.5)	27.2 (4.6)	94.2 (4.6)	16.4	34.6	233.2
Annual	31.4 (8.5)	230.7 (40.2)	26.5 (10.2)	65.0 (14.6)	24.6 (8.9)	95.7 (44.1)	13.4 (6.0)	33.1 (13.5)	213.3 (87.0)
Premonsoon	17.1 (18.7)	77.1 (24.9)	24.7 (13.0)	22.2 (6.7)	20.9 (3.3)	347.9 (174.2)	22.7 (8.1)	56.8 (6.1)	150.3 (34.2)
Monsoon	47.2 (16.6)	131.5 (24.7)	20.4 (8.3)	32.3 (14.1)	28.2 (3.9)	230.8 (74.7)	20.0 (2.7)	62.8 (6.8)	191.0 (116.2)
Postmonsoon	17.4 (1.9)	72.5 (2.3)	25.2 (15.6)	26.4 (1.5)	36.3 (6.4)	241.3 (6.4)	35.3	82.9	289.6
Annual	27.2 (21.2)	94.3 (41.6)	23.4 (12.6)	27.0 (10.1)	28.6 (6.6)	190.0 (141.9)	26.0 (10.6)	67.4 (11.1)	210.3 (84.4)

Table III. Metal to metal correlation coefficients.

	Station 1		Station 2		Station 3		Station 4	
	Copper	Manganese	Cobalt	Nickel	Copper	Manganese	Cobalt	Nickel
Copper	—	—	—	—	—	—	—	—
Manganese	-0.102	—	0.802*	—	0.954 [†]	—	—	—
Cobalt	0.732**	-0.268	0.534	—	0.902 [†]	0.662*	—	—
Nickel	0.888 [†]	-0.101	0.818**	—	0.221	0.305	0.410	—
Zinc	0.340	-0.102	-0.013	-0.056	0.379	0.403	-0.004	0.377

* P < 0.05, ** P < 0.01, + P < 0.001

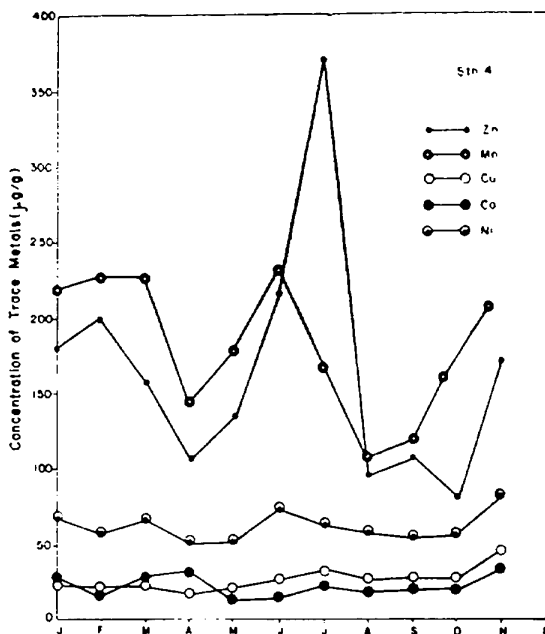


Fig. 5 Seasonal variations in metal levels at Station 4.

variations seen in dissolved and particulate fractions. Information on the total content of any metal, without any knowledge of its physical and chemical state, is of limited value in assessing its ecological significance. However, some broad generalisations can be drawn from the present data. Previous work (Sarala Devi, Venugopal, Remani, Lalitha and Unnithan, 1979) has shown the absence of benthic life at the effluent discharge area (stn. 2). The higher levels of Zn with fairly high and occasionally very high values of Cu (Fig. 3) here is of interest. These two metals classified as having very high pollution potential Pringle, Hissong, Katz and Mulluwaka, 1968), are also known to act synergistically (Perkins, 1974). This combination of elements where one gains in toxic potential in presence of the other may also be one of the causative factors for the absence of benthic life in the vicinity of the effluent discharge area.

ACKNOWLEDGEMENT

The authors are grateful to the Director, NIO, for facilities and encouragement. We are also grateful to Mr. C.V.G. Reddy for guidance in the analyses and fruitful discussions and to Dr. R. Sen Gupta for improving the manuscript. Our thanks are also due to Mrs. Thresiamma Joseph and Messrs. M.D. George and R.S. Topgi for generous help in metal analyses and Mr. H. Krishna Iyer, CIFT, Cochin, for help in statistical interpretations. One of the authors (KNR) is thankful to the CSIR for an award of a fellowship.

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