

Particulate trace metals in Cochin backwaters : distribution of seasonal indices

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ABSTRACT

A seasonal analysis of particulate trace metals, viz. iron, manganese, zinc, copper, cobalt and nickel collected from 4 stations in Cochin backwaters are presented. The spatial trend for cobalt, iron and nickel was stationary at surface whereas the metals copper, zinc and manganese showed spatial variations. At subsurface all the trace metals showed relatively an increasing trend at station 4, but for zinc and nickel, station 2 also showed higher values during the period of study. This indicated that surface distribution pattern of the trace metal concentration of cobalt, nickel and iron was almost similar at the four stations thereby stressing the fact that seasonal fluctuations contributed a major part in the surface distribution of these metals while in the case of other metals at surface and all the trace metals at subsurface, concentration varied both spatially and seasonally. Seasonal variations were maximum during August to December which remained almost uniform for all the metals. The rate of increase in the concentration during this period was less than the rate of decrease during the remaining period. Possible causes for this short term fluctuations are discussed. Deseasonalised effects were the least for iron, copper and nickel at subsurface but significant adverse effects were observed for copper and cobalt at surface.

Introduction

Supply of adequate quantity of particulate trace metals into the estuarine region is very significant, since the estuary being the transitional zone between the fresh water and the marine environment through which the river borne materials are transported to the coastal region. For many trace metals the particulate phase is very important as it is the major transporting agency of

metals in the river system. Trace metals supplied to an estuary is mostly in particulate form which in turn is related to the organic and manganese concentration of particles (Turekkian, 1971). It is known that anthropogenic discharge of heavy metals into the environment forms part of the suspended matter in rivers which acts as an effective scavenger for these trace metals. High dispersion for the trace metal concentration could be attributed to several processes

such as precipitation during estuarine mixing and desorption from river borne suspended particulate redox reactions within the mixing zone.

Trace metal concentration varies with respect to time as well as locations. They may be contemporaneously related. One series may lead the others or there may be feed back relationships (Barnard *et al.*, 1962). An attempt has been made to study the spatial variations, seasonal fluctuations and deseasonalised effects in the particulate trace metal concentrations to identify the dynamic relationships, if any among them. This particular analysis has been specifically taken because the consecutive observations are not mutually independent but serially correlated with respect to space and time (Brown, 1962). This type of research is rapidly expanding to many ecosystems. Also knowledge of seasonal effect can be used to include this component into a forecast, if this study is extended for a longer period at a larger number of stations with almost similar environmental conditions. To improve the accuracy of forecast when there is information on one series contained in the historical data of another, better forecast can result when the series are modelled jointly.

Material and methods

Water samples were collected from the surface and bottom at four different stations in the Cochin backwaters during 1988 (Fig. 1). Samples were filtered using a 0.45 μ millipore filter paper and the various metals present in the particulate matter were determined as given in Sankaranarayanan and Rosamma (1978). Eventhough the stations were not very close to each other, no significant difference with respect to surface salinity ($F_{(3,32)} = 2.5881, P > 0.05$)

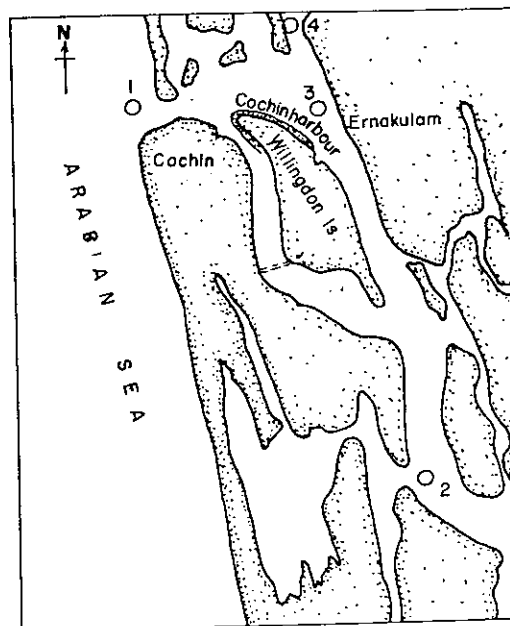


Fig. 1. The station locations and the area of study.

among the stations was observed (Snedecor and Cochran, 1967). Therefore the data from the four stations were pooled to get a four fold replicate sample to enable the study of seasonal variations and deseasonalised effects.

Multiplicative model for the pooled time series was : $U_t = M_t \times S_t \times C_t \times I_t$, $t = 1, 2, 3, \dots, 48$, where U_t = pooled observed data at time t , M_t = spatial trend effect at time t , S_t = seasonal variation's effect at time t , C_t = cyclical variation's effect at time t and I_t = irregular or random variation's effect at time t .

In this study M_t was taken as the trend of the variations of the metal concentrations due to the varying environmental conditions such as varying hydrographic conditions, water quality, sedimentation rate, turbidity etc. at the four sites. Out of the methods of determining seasonal effects, moving average

method was adopted to eliminate any trend because it is the most suitable for this data (Charles, 1963). Ratio to trend by moving average was adopted to eliminate seasonal variations. C_t was assumed to be absent for this method of determining seasonal indices. It includes all the uncontrollable variations occurring randomly and it gets removed while averaging using moving average method. Raw seasonal variations during a month at a station was defined as $V_{(K,I)} = (U_{(K,I)} * 100) / M_{(K,I)}$, $k=1,2,3,4$; $I=1,2,3, \dots, 12$ for $K=2$ and 3 , $I=7,8, \dots, 12$, ($I=1, 2, \dots, 12$ for $K=1$ and $I=1,2, \dots, 6$ for $K=4$), where $U_{(K,I)}$ = observed data for the I^{th} month at the K^{th} station and $M_{(K,I)}$ = moving average for the I^{th} month at the K^{th} station

$$M_{(K,I)} = M_1 \text{ for } K=1 \text{ and } I=7,8, \dots, 12 \text{ when } t=7,8, \dots, 12.$$

$$M_{(K,I)} = M_1 \text{ for } K=2 \text{ and } I=1,2, \dots, 12 \text{ when } t=13,14,15, \dots, 24.$$

$$M_{(K,I)} = M_1 \text{ for } K=3 \text{ and } I=1,2, \dots, 12 \text{ when } t=25,26, \dots, 36.$$

$$M_{(K,I)} = M_1 \text{ for } K=4 \text{ and } I=1,2, \dots, 6 \text{ when } t=37,38, \dots, 42.$$

$$M_{(t,I)} = (U_{(t-3)} + U_{(t-7)} + 2 \times \sum_{j=2 \text{ to } 12} (U_{(t+j)})) / 24, t=6,7,8,9, \dots, 41.$$

Raw seasonal index for any month is given by:

$$I_1' = \sum_{k=1 \text{ to } 3} (V_{(K,I)} / 3) \text{ for } I = 7,8, \dots, 12.$$

$$I_1' = \sum_{k=2 \text{ to } 4} (V_{(K,I)} / 3) \text{ for } I = 1,2, \dots, 6.$$

Adjusted seasonal index is given by :

$$I_1 = (I_1' \times 100 \times 12) / \sum_{i=1, \text{ to } 12} (I_1')$$

Deseasonalised index which measures the effects other than seasonal effect is given by :

$$C_{(K,I)} = (U_{(K,I)} * 100) / I_1', K, I \text{ are as stated earlier.}$$

Results and discussion

At surface, particulate trace metal concentration of cobalt (Fig. 2a) did not vary much between sampling sites. At subsurface, cobalt (Fig. 2b) concentra-

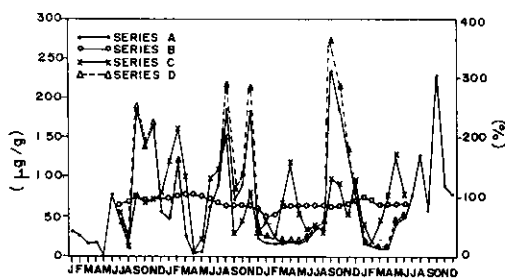


Fig. 2a. The original concentration (a), the trend effect (b), the deseasonalised effect (c) and the seasonal effect (d) for cobalt at surface.

tion showed a marked difference between stations throughout the study period. For zinc the concentration was decreasing both at surface (Fig. 3a) and bottom (Fig. 3b) except at station 2 where it was at a higher level throughout the year. For nickel, trace metal concentration was almost homogeneous except at stations 1 and 2 at surface (Fig. 4a) there being a maximum during the second half of the study period at station 1. A steady decrease was observed during January – June at station 2 and the concentration was at a constant lower level at stations 3 and 4 while bottom concentrations (Fig. 4b) were at a higher level at stations 2 and 4 during January-June. For copper,

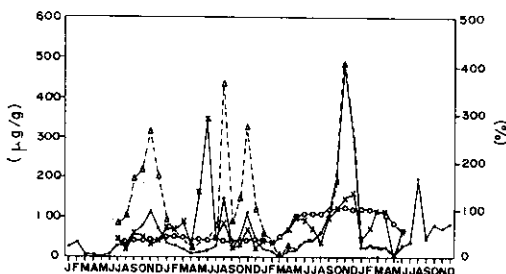


Fig. 2b. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for cobalt at subsurface (see Fig. 2a for explanation to graphs).

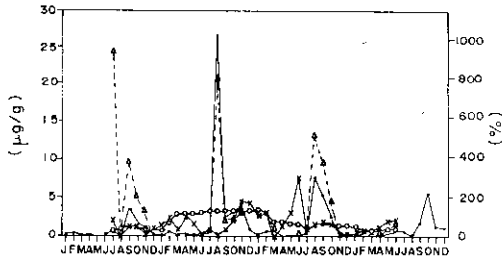


Fig. 3a. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for zinc at surface (see Fig. 2a for explanation to graphs).

there was a gradual increase in concentration both at surface (Fig. 5 a) and subsurface (Fig. 5b) at all the stations except at station 4 where it was almost homogeneous at a higher value. The particulate trace metal concentration of manganese showed a slight increase towards the surface (Fig. 6a) while that of iron indicated decrease (Fig. 7a). However, both manganese and iron exhibited a gradual rise in concentration at subsurface levels from station 1 to 4 (Figs. 6b & 7b) which strengthens the fact that station 4 has a more favourable condition for manganese and iron deposition particularly at the bottom. This steady increase in the trace metal concentration of manganese and iron could be attributed to their relative

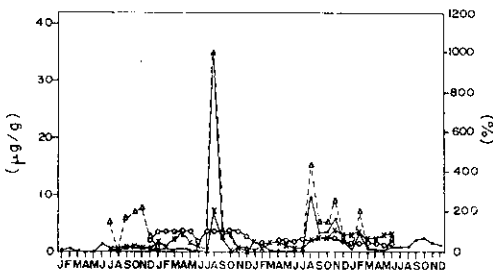


Fig. 3b. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for zinc at subsurface (see Fig. 2a for explanation to graphs).

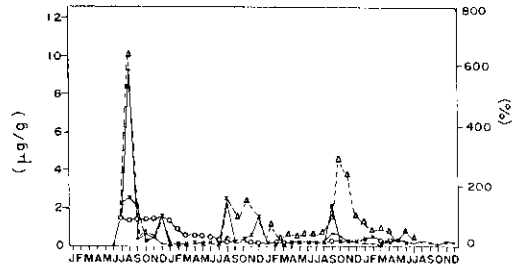


Fig. 4a. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for nickel at surface (see Fig. 2a for explanation to graphs).

abundance in river borne suspended matter which remains fixed during its transport to the estuary (Eric and Ingemar, 1980). The variation in the maximum concentration of some of the metals like iron and manganese indicates the occurrence of physico-chemical processes during estuarine mixing. Flocculation of colloidal species and sedimentation of fine material in suspension and the processes of sorption and co-precipitation also contribute a significant part as factors responsible for spatial variation in the distribution of copper, manganese and iron concentration (Duinker and Nolting, 1977).

Bottom values of metals such as copper, manganese and iron clearly

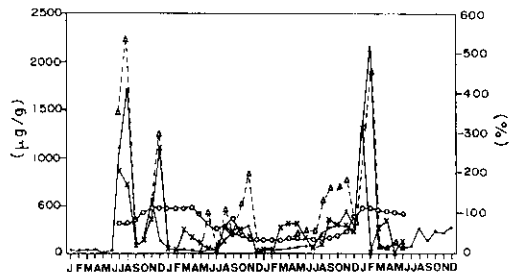


Fig. 4b. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for nickel at subsurface (see Fig. 2a for explanation to graphs).

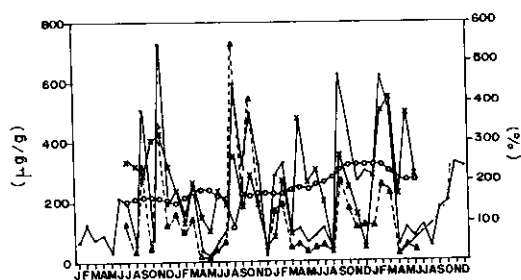


Fig. 5a. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for copper at surface (see Fig. 2a for explanation to graphs).

show a high concentration during post monsoon and beginning of premonsoon when the salinity was higher. Lower concentrations and less seasonal variations observed during certain months for copper, manganese and iron may be due to the possible mechanisms such as mobilisation into the dissolved state or sedimentation to the sea bed which are all spatial variations. Another possible explanation may be the presence of low metal-level bottom derived material which can contribute to higher suspended load as a function of sampling position.

Generally a stationary spatial trend was more frequently observed for most

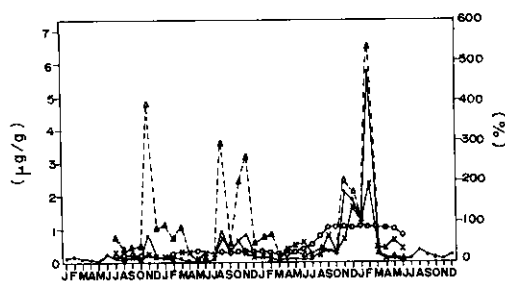


Fig. 5b. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for copper at subsurface (see Fig. 2a for explanation to graphs).

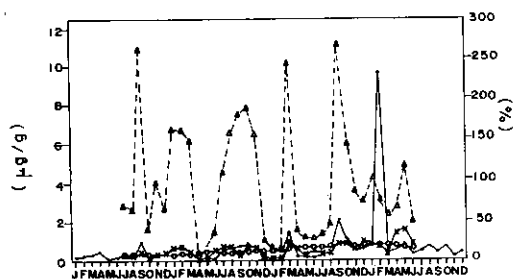


Fig. 6a. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for manganese at surface (see Fig. 2a for explanation to graphs).

of the metals. It can be suggested that variation in the trace metal concentration was mostly due to seasonal or short term fluctuations. At surface (Table 1a), peak values of seasonal indices (>100) were around August-November for cobalt, zinc and nickel and during August-November and January-February for copper while during August-November and March for manganese and September-December and February for iron (Table 1a and Figs. 2a-7a). Subsurface maximum values (>100) of seasonal variations were observed during August-December for cobalt, zinc and nickel (Table 1b) and October-February for

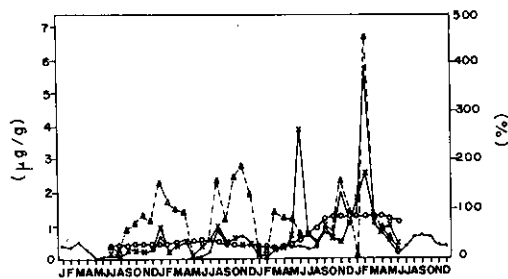


Fig. 6b. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for manganese at subsurface (see Fig. 2a for explanation to graphs).

TABLE 1. The adjusted seasonal indices expressed as % at (a) surface and at (b) subsurface for various trace metal concentrations

Months	Trace metals					
	Cobalt	Zinc	Nickel	Copper	Manganese	Iron
(a) Surface						
January	41.01	20.91	43.30	101.21	98.51	56.40
February	69.94	25.04	38.14	125.04	87.15	163.73
March	26.42	27.91	41.66	95.47	156.92	49.11
April	15.56	13.59	23.73	23.84	39.72	73.65
May	32.91	19.20	43.03	23.18	56.76	74.56
June	63.09	32.01	33.71	29.24	38.71	65.55
July	83.93	45.25	80.88	56.71	73.91	56.22
August	123.61	455.88	369.92	169.74	93.54	48.24
September	242.41	285.60	171.77	177.13	249.58	260.21
October	201.96	160.23	178.96	173.08	130.26	128.13
November	227.47	89.07	97.11	172.09	117.61	118.36
December	71.67	25.37	77.77	59.15	57.35	105.82
(b) Subsurface						
January	50.01	23.33	94.78	103.57	69.17	89.75
February	40.73	88.78	154.14	248.09	228.54	386.25
March	21.41	15.57	17.55	48.37	115.40	63.91
April	22.45	12.84	19.13	24.13	93.46	130.07
May	17.45	8.49	24.96	17.01	50.58	26.81
June	41.01	29.49	53.30	13.56	32.57	44.86
July	60.84	59.26	131.20	39.70	43.80	78.33
August	174.22	481.48	243.07	131.77	83.31	49.75
September	113.08	138.45	79.37	41.59	79.70	139.77
October	158.94	144.01	99.82	99.98	113.98	73.31
November	321.96	165.47	157.30	318.99	170.64	67.77
December	176.32	63.57	125.40	113.18	118.99	76.19

copper and manganese. September, February and April were the highly favourable short term periods for iron (Figs. 2b-7b).

Thus time series analysis indicates that for all the metals the concentra-

tions of the particulate fraction are at a higher level during the period August-November, the end of monsoon period favouring the surface concentration more than the subsurface concentration. This can be explained in terms of surface

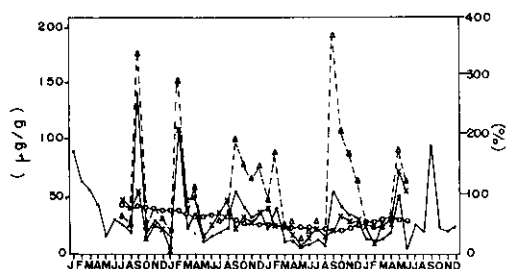


Fig. 7a. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for iron at surface (see Fig. 2a for explanation to graphs).

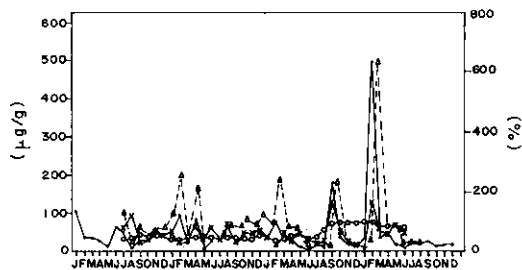


Fig. 7b. The original concentration, the trend effect, the deseasonalised effect and the seasonal effect for iron at subsurface (see Fig. 2a for explanation to graphs).

inputs of copper, its scavenging in the water column and excessive regeneration at the sediment-water interface. Enrichment of manganese in the surface water can be attributed to the riverine inputs during August-November and also due to the deposition of atmospheric particulates (Bender *et al.*, 1977).

Resuspension of sediment near the sediment-water interface can markedly increase the dissolved manganese concentration (Yeats and Bewers, 1985; Jickells and Burton, 1988). Relatively higher concentration of iron at the subsurface during February and September can be attributed to the fact that iron released from the breakdown of planktonic matter may be quickly converted into colloidal hydroxide at the high pH prevailing in the water column and may be readily adsorbed on to the descending particles which in turn gets transported to the sediments. It has been observed that the rate of increase in the trace metal concentration during August-December is much less than the rate of decrease in concentration during the rest of the study period. March, April and May were the periods with least seasonal effect for all the metals at both surface and subsurface and this can be explained as follows.

The high value of seasonal effect during August-November can be attributed to the large amount of fresh water discharge which brings in large quantities of suspended matter. The coarse particles sediment out when the flow velocity slackens and the finely grained particles and colloidal materials which have very low settling velocities may remain in suspension for a longer period.

Rama Raju *et al.* (1979) also ob-

served a general increase in the suspended matter during the seasons of high seasonal variations. Subramanyam and Ananthalakshmy (1990) observed that iron, manganese, zinc and copper in water showed relatively higher values during monsoon while the values exhibited were high in the pre/post monsoon in Visakhapatnam area along the east coast of India. Deseasonalised effects as measured by deseasonalised index, followed almost the same pattern of distribution as the observed concentrations for iron, copper and nickel at subsurface and also for manganese except at station 3 where deseasonalised effects are inversely related to the observed data. Distribution of deseasonalised effects was almost homogeneous for manganese. It was inversely related with the observed concentrations in the case of iron, nickel and zinc at surface with significant inverse relation for copper at surface and for cobalt at both positions. High similarity in the pattern of distribution of seasonal indices and the original data highlight the fact that short term fluctuations are more pronounced than spatial variations and irregular fluctuations. Trace metal concentrations as well as seasonal effects were not significantly different between surface and subsurface samples for any metal ($P > 0.05$, Table 2). But the deseasonalised effects showed marked differences between surface and subsurface samples for the metals such as nickel at station 1 and for zinc at station 4 ($P < 0.05$, Table 2). Therefore the seasonal variations almost completely controlled the variations in the concentration of the metallic species. Thus the study of short term fluctuations in the concentrations of particulate trace metals are very useful for assessing the reliability of the trace metal measure-

TABLE 2. The significance of the difference between surface and subsurface values, tested using Student's 't' statistic for (a) trace metal concentration, (b) deseasonalised effects and (c) seasonal effects at the 4 stations

Stations	Values of 't' statistic						df
	Trace metals						
	Cobalt	Zinc	Nickel	Copper	Manganese	Iron	
(a) Trace metal concentrations							
1	1.174	1.232	0.977	0.379	0.741	0.780	22
2	1.403	0.113	0.582	0.548	0.084	0.497	22
3	0.813	0.484	0.335	1.129	0.182	1.041	22
4	0.547	0.337	1.638	1.013	0.278	0.925	
(b) Deseasonalised effects							
1	1.667	1.548	2.418*	1.879	1.469	1.367	10
2	0.301	0.059	1.688	1.548	0.365	0.700	22
3	1.146	0.486	1.425	2.015	0.437	1.809	22
4	0.220	4.345*	0.487	1.664	0.993	1.298	10
(c) Seasonal effects							
1	0.337	0.966	0.531	0.388	1.232	0.491	10
2	0.184	0.036	0.330	0.720	0.674	0.027	22
3	0.963	0.061	0.264	0.975	0.677	0.781	22
4	1.050	1.011	1.133	0.293	0.500	0.649	10

df = degrees of freedom,* Calculated 't' is significant at 5% level ($P < 0.05$).

ments and to correlate their effect on the ecosystem since they may have effects greater than those of more common pollutants in the sense that trace elements in higher concentrations may be toxic to certain living organisms, at less than toxic levels, may be essential to physiological functions of certain other organisms or to the ecosystem as a whole. Lower concentrations of essential trace elements may suppress the physiological action, leading to abnormal growth of biological organisms.

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References

- Barnard, G.A., G.M. Jenkins and C.B. Winsten 1962. Likelihood inferences and time series. *J. Royal Stat. Soc., Series A*. **125** : 321.
- Bender, M.L., G.P. Klinkhammer and D.W. Spencer 1977. Manganese in sea water and the marine manganese balance. *Deep Sea Research*, **24**(9) : 799-812.
- Brown, R.G. 1962. *Smoothing, Forecasting and Prediction of Discrete Time Series*. Prentice Hall, Engle Wood, New Jersey, 468pp.
- Charles, T.H. 1963. *Statistical Methods in Hydrology*. Iowa State University Press, Amsterdam.

- Duinker, J.C. and R.F. Nolting 1977. Dissolved and particulate trace metals in the Rhine Estuary and the Southern Bight. *Marine Pollution Bulletin*, **8**(3) : 65-71.
- Eric Olausson and Ingemar Cato 1980. *Chemistry and Biochemistry of Estuaries*. John Wiley and Sons, New York, 451 pp.
- Jickells, T.D. and J.D. Burton 1988. Cobalt, copper, manganese and nickel in the Sargasso Sea. *Marine Chemistry*, **23**: 131-144.
- Rama Raju, V.S., P. Udaya Varma and Abraham Pylee 1979. Hydrographic characteristics and tidal prism at the Cochin Harbour mouth. *Indian J. Mar. Sci.*, **8**(2) : 78-84.
- Sankaranarayanan, V.N. and Rosamma Stephen 1978. Particulate iron, Manganese, copper and zinc in waters of the Cochin backwaters. *Indian J. Mar. Sci.*, **7** : 201-203.
- Snedecor, G.W. and W.G. Cochran 1967. *Statistical Methods*. 6th edition, I.B.H. Publishing Company, 563 pp.
- Subramanyam, M.N.V. and K.V.V. Ananthalakshmy Kumari 1990. Trace metals in water and phytoplankton of Visakhapatnam Harbour sea, east coast of India. *Indian J. Mar. Sci.*, **19**: 177-180.
- Turekkian, K.K. 1971 *Rivers, Tributaries and Estuaries. Impingement of Man on the Oceans*. D.W. Hood (Ed.), Wiley Interscience, New York.
- Yeats, P.A. and J.M. Bewers 1985. Manganese in the western north Atlantic Ocean. *Marine Chemistry*, **17**: 255-263.