

Dissolved & Particulate Trace Metals in the Western Bay of Bengal

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Concentrations of Cu, Zn, Mn, Fe, Co, Ni and Pb, both in soluble and particulate forms were studied in the upper 200 m depth. Correlation between the trace metal concentration and the primary productivity was also investigated. Zn, Ni and Co were present in high concentrations in the waters and particulate matter. Zn and Cu concentrations were high in marine phytoplankton. Characteristics of inshore waters with respect to trace metals and total suspended matter could be identified in the offshore waters off Godavari estuary up to 500 km away from the shore. Inshore waters showed higher concentrations of soluble Zn, Ni and Co than that normally found in river water. Zn and Ni were found to be in higher concentration in offshore waters.

Concentrations of toxic and non-toxic heavy metals in Indian waters have been reported¹⁻³. The present paper gives concentrations of Cu, Mn, Fe, Zn, Co, Ni and Pb, both in soluble and particulate forms, their distribution in inshore and offshore waters in the western Bay of Bengal off Godavari and Krishna estuaries, and their interrelationship with biological productivity.

Materials and Methods

Samples were collected from coastal and offshore waters of Western Bay of Bengal (Fig. 1) during the 21st cruise of *R V Gaveshani* (Aug. 1977) using van Dorn samplers in acid treated polyethylene carbuoys and immediately vacuum filtered using a pre-weighed 0.45 μm membrane filters. The filtered sample was acidified and the filter papers were stored under refrigeration till analysis. At the shore based

laboratory, water samples were analysed for dissolved trace elements using the method of Brewer *et al.*⁴ by chelating with APDC and extracting with MIBK. Mn, which is not extracted in APDC-MIBK combination, was separately extracted by chelating with sodium diethyl dithiocarbonate at pH 5-6 and extracting with MIBK. All the extracts were run into atomic absorption spectrophotometer (Hilger Watts Atomspek Model H1550), against the standard concentration of the metals.

Filters containing the suspended matter and blank filters were dried in a desiccator over silica gel and weighed. They were acid digested and analysed by atomic absorption spectrophotometry. Coefficients of variation for the analysis, calculated from replicate samples were 3.5, 13, 4, 7, 12, 5 and 9 for Zn, Mn, Fe, Co, Ni, Cu and Pb respectively.

Primary productivity was measured by ¹⁴C method

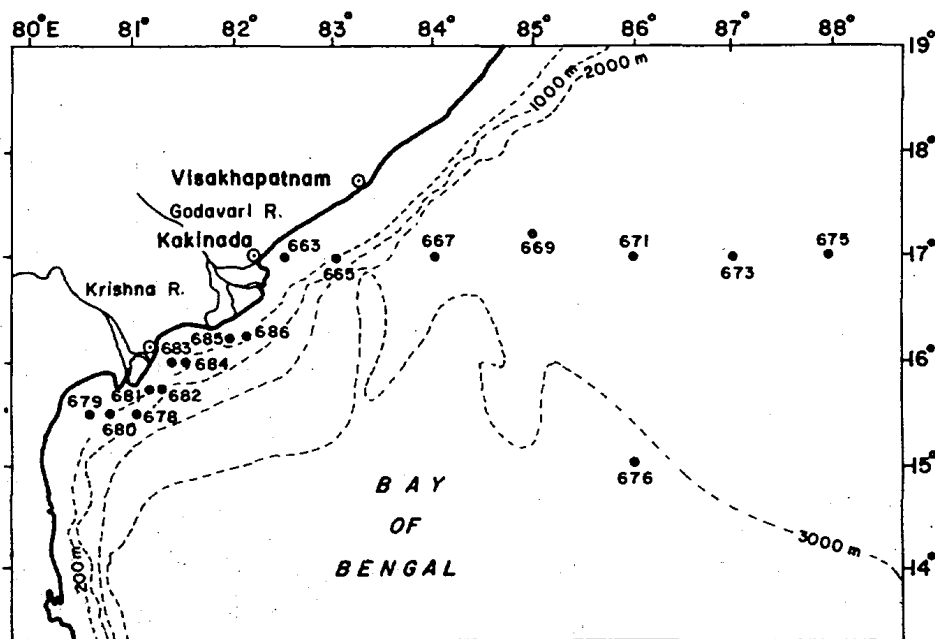


Fig. 1—Sampling stations

by incubating the samples under simulated *in situ* conditions for 24 hr. Chlorophyll *a* was measured on board by fluorometry and these values were corrected for pheophytin. Major nutrients and oxygen were estimated on board using standard methods. Though sampling and measurements were done at all stations shown in Fig. 1, results of only few representative stations are given in other figures to show the trend. However, the data collected from all stations were used for further computations.

Results and Discussion

Copper—Dissolved copper in surface samples of the inshore and offshore waters varied from 4 to 6 $\mu\text{g/l}$. The variation in the soluble Cu in the upper layers of 200 m (Fig. 2) was from 2.75 to 6.62 $\mu\text{g/l}$. Though the particulate Cu did not show much variation between surface and 200 m at st 665 (0.23 to 0.28 $\mu\text{g/l}$), the variation was very wide at 686 (0.22 to 0.95 $\mu\text{g/l}$) where it decreased gradually from surface to 200 m (Fig. 2). At most of the other stations, particulate Cu was not detectable.

Manganese—Dissolved Mn in the inshore surface waters showed higher values than that of the offshore area. While inshore surface samples showed variation of 2.5 to 4 $\mu\text{g/l}$, except st 679 where it was 7 $\mu\text{g/l}$, the surface samples from offshore stations showed variation of 1.25 to 2.7 $\mu\text{g/l}$. The inshore samples showed an increase in the concentration with depth showing a marked decrease at 100 m. But the trend was reverse in the offshore waters (Fig. 3).

Particulate Mn from inshore waters showed a very wide variation (0.06 to 2.52 $\mu\text{g/l}$). Particulate samples collected near the mouth of Krishna river showed low Mn values (0.5 $\mu\text{g/l}$), whereas the samples collected in the nearshore waters off Godavari estuary showed

higher (av. 3.5 $\mu\text{g/l}$) values. At st 685, the value was as high as 7.15 $\mu\text{g/l}$. The offshore stations always showed lower concentration of particulate Mn in the surface waters with a range of 0.05 to 0.35 $\mu\text{g/l}$ (mean 0.2 $\mu\text{g/l}$). At other depths also, particulate Mn continued to be lower in the offshore samples than that of inshore waters (Fig. 3).

Zinc—Soluble Zn in the inshore waters was very high (17.1 to 46.26 $\mu\text{g/l}$). The samples collected in the inshore waters off Krishna river estuary always showed very high values of dissolved Zn, 47.26 and 36 $\mu\text{g/l}$ at sts 678 and 680 respectively. Though the surface samples showed high concentrations of Zn, it decreased at deeper layers to 3.75 $\mu\text{g/l}$ at 200 m at st 665 (Fig. 4A). Dissolved Zn in the offshore surface samples showed relatively wider variation from 7.5 to 35.5 $\mu\text{g/l}$ (mean 19.12 $\mu\text{g/l}$).

Particulate Zn of inshore waters showed a variation from 0.66 to 5.44 $\mu\text{g/l}$. The samples collected from the

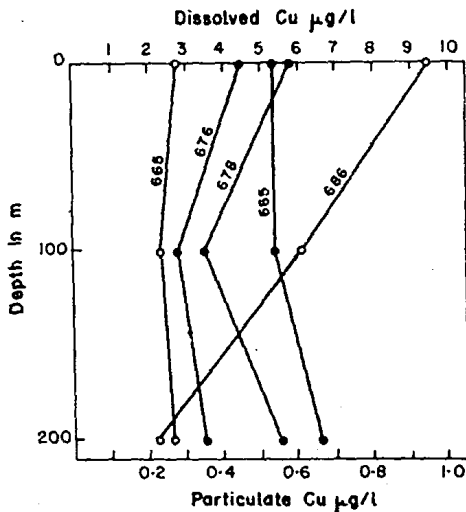
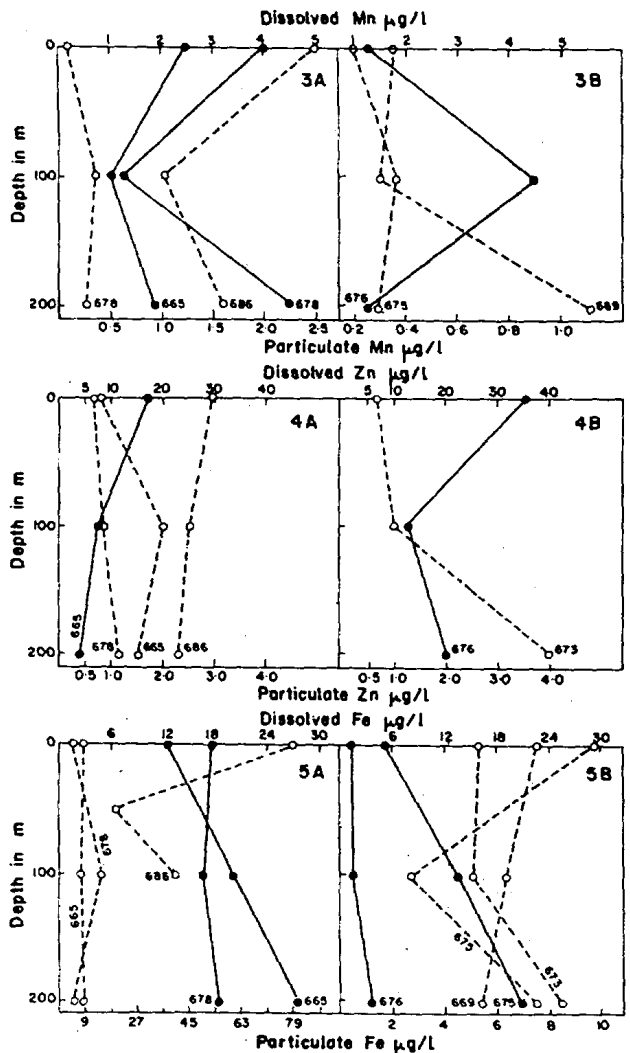


Fig. 2—Distribution of dissolved (●—●) and particulate (○—○) Cu



Figs. 3 to 5—Distribution of dissolved (●—●) and particulate (○—○) Mn (3), Zn (4) and Fe (5) in samples from coastal (A) and offshore (B) stations

stations off Krishna river estuary showed very high values ranging 4.18 to 6 $\mu\text{g/l}$ (mean 3.97 $\mu\text{g/l}$), whereas the stations off Godavari estuary showed lower values ranging 1.54 to 2.98 $\mu\text{g/l}$ (mean 2.26 $\mu\text{g/l}$). Particulate Zn of the offshore waters showed a range of 0.06-0.74 $\mu\text{g/l}$ (mean 0.35 $\mu\text{g/l}$). Particulate Zn in offshore waters increased with increasing depth, (Fig. 4B) whereas inshore waters did not show this trend (Fig. 4A) at most of the stations.

Iron—Dissolved Fe in the inshore surface samples varied from 12.1 to 17.75 $\mu\text{g/l}$. Subsurface samples showed higher concentrations up to 28.25 $\mu\text{g/l}$ (Fig. 5A). The offshore surface samples always showed relatively lower values for the dissolved Fe. Among the offshore stations, those situated off Kakinada (Godavari estuary) showed more or less the characteristics of inshore waters with respect to dissolved Fe. For example, st 675 showed higher concentration of Fe (4.92 $\mu\text{g/l}$) than st 676 (1 $\mu\text{g/l}$). Subsurface waters of st 675 also showed higher values; for example they were 13.6 and 21 $\mu\text{g/l}$ at 100 and 200 m respectively (Fig. 5B). The characteristics of inshore waters, particularly with respect to some physical and chemical parameters are found in the offshore waters off Godavari even up to 500 km.

Particulate Fe varied generally between 4 and 7 $\mu\text{g/l}$ in the inshore surface samples with the exception of samples collected off Godavari estuary (st 686) which showed a concentration as high as 27 $\mu\text{g/l}$ (Fig. 5A).

Generally, in offshore waters, the dissolved Fe showed an increase with depth, uniformly. Particulate Fe showed a decrease at 100 m depth which again increased in deeper layer (200 m), excepting at st 669 where it showed uniform decrease.

Cobalt, nickel and lead—Soluble Co in nearshore stations varied from traces or non-detectable amounts to 1.18 $\mu\text{g/l}$. The surface water always showed lower values than the subsurface waters (Table 1). Offshore stations showed low values of Co at all depths than the inshore stations and it varied from traces to 1 $\mu\text{g/l}$. However, the surface samples showed higher values than the samples collected from 100 or 200 m. Particulate Co varied from nil to 1.34 $\mu\text{g/l}$ and most of the surface values are non-detectable. Higher concentrations were observed at 100 and 200 m depths. Only one nearshore station (st 679) showed a value of 2.14 $\mu\text{g/l}$ (Table 1).

Dissolved Ni in the coastal waters varied from 2.7 to 9.5 $\mu\text{g/l}$, except one sample from 100 m at st 678 which showed a value of 15 $\mu\text{g/l}$ (Table 1). Variation in

Table 1—Distribution of Some Heavy Metals in Western Bay of Bengal

Station	Sampling depth m	Cobalt		Nickel		Lead (Particulate) $\mu\text{g/l}$	Total suspended matter mg/l
		Dissolved $\mu\text{g/l}$	Particulate $\mu\text{g/l}$	Dissolved $\mu\text{g/l}$	Particulate $\mu\text{g/l}$		
Nearshore Stations							
665	0	ND	ND	9.5	0.41	0.52	0.896
	100	1.37	0.68	2.7	0.50	ND	0.526
	200	0.87	1.21	6.5	ND	0.76	0.736
678	0	1.75	ND	2.75	ND	ND	0.977
	100	1.75	ND	15.00	0.72	2.19	1.783
	200	1.50	0.98	3.25	ND	ND	0.786
679	0	0.5	2.14	4.5	ND	0.36	0.750
680	0	0.25	ND	8.0	ND	0.76	2.350
	75	0.75	ND	3.5	ND	0.28	0.916
Offshore Stations							
669	0	0.75	ND	5.5	ND	0.88	1.200
	100	0.62	1.26	3.5	ND	1.51	1.373
	200	1.00	0.16	ND	ND	0.28	1.019
673	0	0.75	ND	2.5	ND	ND	1.189
	100	0.75	ND	2.0	0.78	0.88	1.188
	200	NA	1.34	NA	0.79	1.36	2.991
675	0	0.62	1.12	5.0	ND	1.88	1.547
	100	0.50	ND	5.0	ND	0.15	0.852
	200	ND	ND	9.5	0.79	2.75	0.401
676	0	0.75	NA	6.25	NA	NA	NA
	100	0.25	NA	4.00	NA	NA	NA
	200	0.25	NA	ND	NA	NA	NA

ND = Not detectable

NA = Not analysed

dissolved Ni in offshore stations was between 2 and 9.5 $\mu\text{g/l}$. There is not much variation between the nearshore and offshore stations. Particulate Ni showed a variation from non-detectable to 0.79 $\mu\text{g/l}$. The surface samples collected at nearshore stations showed low values (0.4-0.5 $\mu\text{g/l}$) and the offshore surface samples showed values which are not detectable. Higher concentrations were observed at the offshore deeper waters.

Pb in particulate matter varied from 0 to 0.76 $\mu\text{g/l}$ in the nearshore stations, except the sample collected from 100 m at st 678 which is situated at the mouth of the Krishna river estuary near Machilipatnam. In the offshore stations particulate Pb showed variation

between 0 and 2.75 $\mu\text{g/l}$. Dissolved Pb values were so low that it could not be analysed within the sensitivity of the instrument.

Chlorophyll a and productivity—Fig. 6 shows the distribution of chl *a* in both inshore and offshore waters. It showed a maximum in the depth range of 10 to 50 m in inshore waters. The value of chl *a* normally varied from 0.03 to 0.095 mg/m^3 . In offshore waters (Fig. 6B), most of the stations showed an increase in chl *a* from surface to 30 m depth.

Primary productivity in inshore waters increased with depth and the maximum was observed at 20 m depth (Fig. 7A). Surface waters showed a variation in the primary productivity from 2 to 9.4 $\text{mg C/m}^3/\text{day}$.

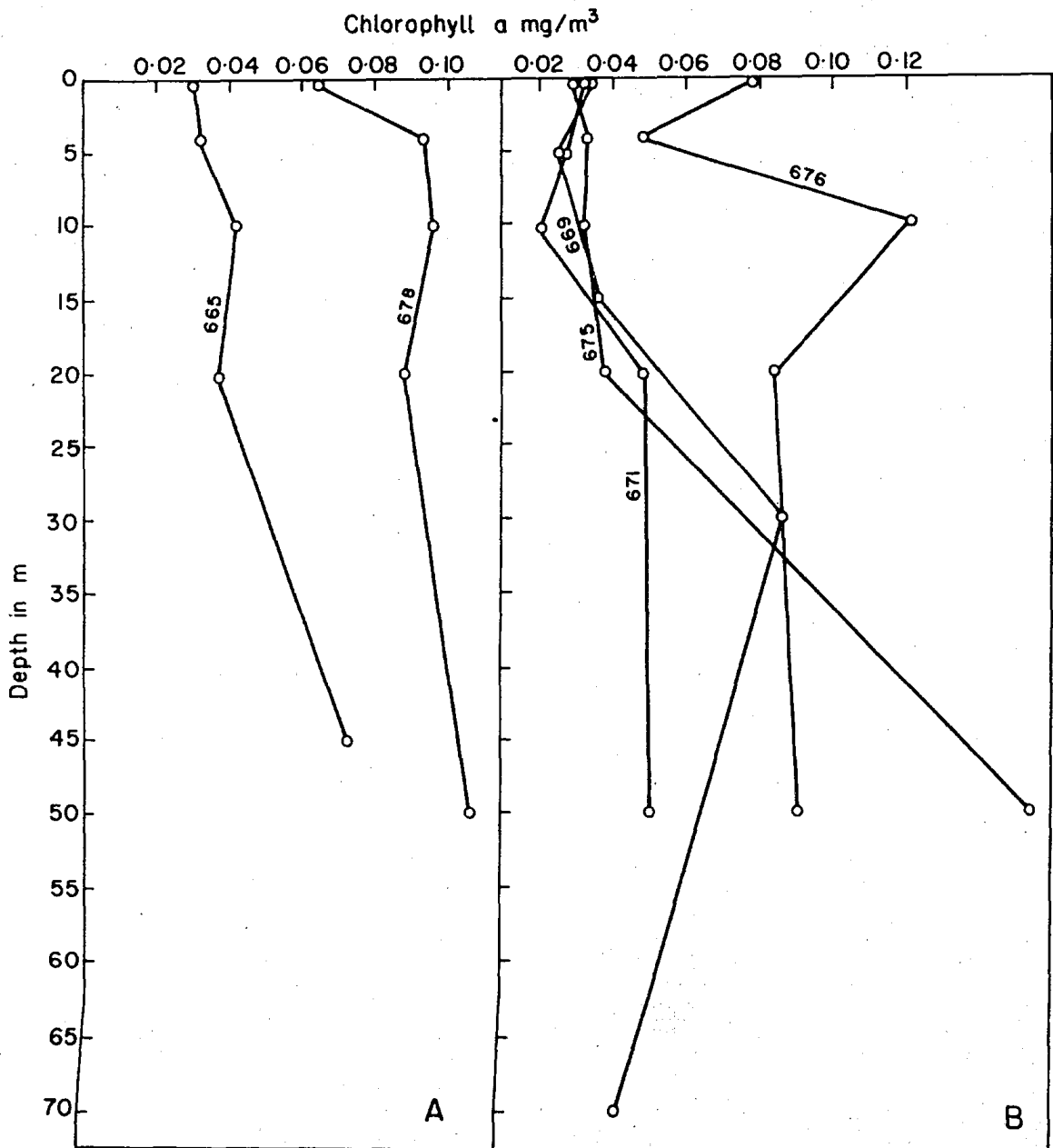


Fig. 6—Distribution of chlorophyll *a* in samples from coastal (A) and offshore (B) stations

But the station at the mouth of Godavari estuary showed a very high value (31.36 mg C/m³/day). In offshore water, the productivity showed a gradual decreasing trend from the surface (Fig. 7B) and surface productivity values varied between 11.99 and 14.57 mg C/m³/day.

Total suspended matter (TSM)—In the inshore surface waters TSM varied widely from 0.896 to 3.35 mg/l. In offshore waters, the variation was not much (1.19 to 1.55 mg/l). Samples collected at the river mouths showed high TSM and the high values extended off Godavari estuary as far as 500 km. TSM of surface samples off Godavari estuary at the continental edge varied from 0.89 and 7.97 mg/l and those off Krishna river varied between 0.75 to 2.89 mg/l. Relatively high values of TSM as far as 500 km, for example at sts 669, 673 and 675 were also

recorded during the present study and they were always in the range 1.19 to 1.55 mg/l.

Distribution pattern of TSM was studied in this area by Rao⁵, who found that the measured concentrations of TSM varied from 0.05 to 1.22 mg/l in surface waters. Higher concentrations of TSM were reported off the river mouths and in the nearshore regions while in the case of the samples off Godavari estuary, higher values persisted to a distance of about 300 km away from coastline during Aug.-Sept. 1976⁵. As mentioned earlier, concentration of some trace metals, particularly Fe in soluble and particulate form, did not show any marked variation in offshore waters from that of coastal samples off Godavari estuary. Varadachari *et al.*⁶ found low saline waters extending seaward as far as 300 km off Godavari river and this feature was conspicuously absent in the vicinity of

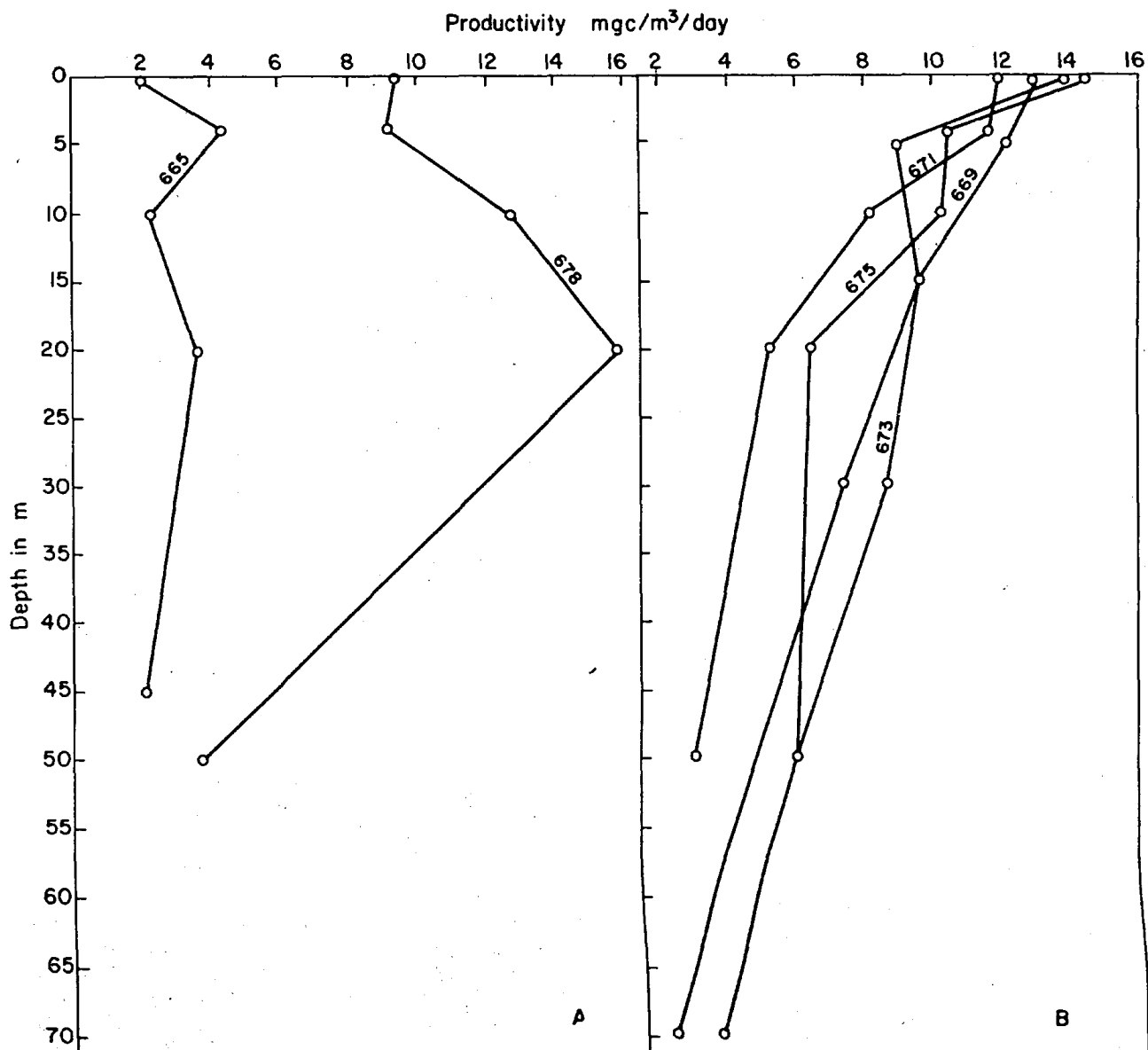


Fig. 7—Primary production in samples from coastal (A) and offshore (B) stations

Krishna river indicating the low intensity of discharge and circulation influenced by the prevailing coastal currents running parallel to the coast in southerly direction.

Data obtained for trace metals (both dissolved and particulate) productivity, chl *a* and major nutrients were computed for their interrelationships and the correlation matrices for selected ones are given in Table 2. A very significant negative correlation was observed between productivity and phosphate at 100m depth of inshore waters, while at the surface both phosphate and nitrate showed highly positive correlation with productivity. Among the trace elements, Cu and Zn showed significant correlations with productivity in inshore waters but Cu showed a negative (-0.77) correlation and Zn showed a positive one. In offshore waters, Mn showed a very high positive correlation with productivity both at surface and 100m depth. However, Fe did not show any positive correlation with productivity. These results indicate that Zn and Cu appear to be concentrated by marine phytoplankton. The correlation matrices between chl *a* and these metals in particulate matter also showed similar trend.

Sen Gupta⁷ while correlating the concentration of metals with productivity in Baltic waters stated that Zn and Cu appeared to be concentrated by organisms and that the soluble Fe did not show any appreciable variation that corresponded to production. Subrahmanyam and Sen Gupta⁸ also showed that measurements of total iron concentration did not show any limiting factor on plant production in the sea.

Dissolved species of metals and oxygen were also correlated (Table 2). Among the metals studied, no metal showed any correlation with oxygen in inshore surface waters whereas highly negative correlation was found with Mn at 100m depth. Interestingly, there was a positive correlation between Mn and oxygen in the subsurface offshore waters and these results may indicate that both pH and redox potential play an essential role with respect to Mn dissolution. In offshore surface waters, high positive correlation between Fe and oxygen was observed. Sen Gupta⁷ indicated that the solubility of Fe in seawater was more dependent on pH than on the redox potential. Cu, in the present study, however did not show any appreciable negative correlation with oxygen which is a very usual phenomenon in anoxic waters where Cu forms copper sulphide and due to its low solubility, will be removed by precipitation.

An attempt has also been made to study the correlation between the dissolved and particulate forms of Cu, Mn, Zn and Fe to understand the possible exchange of elements between both the forms. There

was absolutely no correlation in inshore waters for all 4 metals. Appreciably high concentration of these metals in inshore waters may mask any probable correlation. However, in offshore stations, the surface water showed high positive correlation between the particulate and dissolved forms of both Mn and Zn. Knauer and Martin⁹ felt that even heavy utilisation of Mn by phytoplankton could not produce such large changes in Mn concentration in seawater. An inverse relationship was found between the particulate Fe and dissolved Fe concentrations in some estuaries^{10,11}, and Aston and Chester¹² noted that the quantity of particulate matter was the dominant factor in regulating the concentration of dissolved Fe in seawater. In the present study also, a high negative correlation was observed between soluble and particulate Fe in offshore surface and at 200m depth (Table 2).

Table 2 - Correlation Matrices for Different Selected Interrelationships between Trace Elements and Other Parameters

Inter-relationship	Correlation coeff. at 0.1% level of significance				
	Inshore surface	Inshore 100 m	Offshore surface	Offshore 100 m	Offshore 200 m
Pr-Fe	0.36	-0.13	-0.63	-0.35	-
Pr-Mn	0.52	0.10	0.87	0.85	-
Pr-Cu	-0.77	0.31	0.14	-0.63	-
Pr-Zn	0.85	-0.62	0.66	0.16	-
Pr-PO ₄	0.83	-0.99	-0.70	0.12	-
Pr-NO ₃	0.85	-0.72	0.53	-0.86	-
Fe(P)-Fe	-0.12	-0.56	-0.93	0.91	-0.99
Mn(P)-Mn	0.34	0.57	0.93	-0.74	0.10
Zn(P)-Zn	0.10	0.47	0.93	0.00	-0.20
Cu(P)-Cu	-0.57	-0.47	0.00	0.75	0.86
Fe-O ₂	-0.64	-0.56	0.99	-0.59	-0.83
Mn-O ₂	-0.18	-0.98	-0.80	0.97	-0.75
Cu-O ₂	0.18	-0.51	-0.63	-0.19	-0.31
Zn-O ₂	0.36	0.78	-0.34	0.81	-0.60
Chl <i>a</i> -Zn(P)	0.93	0.65	0.83	0.96	-
Chl <i>a</i> -Cu(P)	0.37	0.65	-0.13	0.98	-
Chl <i>a</i> -Mn(P)	0.99	0.51	0.21	-0.12	-
Chl <i>a</i> -Fe(P)	0.41	-0.64	-0.62	0.24	-

(P) = Particulate metal
Pr = Productivity

Table 3 -- Ratio Between Metal Concentration in Particulate Matter (P) and Total Suspended Matter (TSM)

Depth	Inshore water			Offshore water		
	0 m	100 m	200 m	0 m	100 m	200 m
Fe(P)/TSM	0.0143	0.0137	0.0133	0.0054	0.0040	0.0090
Cu(P)/TSM	0.0005	0.0003	0.0002	0.0010	0.0005	0.0002
Zn(P)/TSM	0.0017	0.0015	0.0016	0.0018	0.0005	0.0020
Mn(P)/TSM	0.0006	0.0007	0.0007	0.0001	0.0002	0.0006
Pb(P)/TSM	0.0005	0.0008	0.0014	0.0012	0.0007	0.0026

Table 4—Concentration of Some Metals in Oceanic and River Waters Compared with Those Observed in the Western Bay of Bengal

Element	Ocean water* µg/l (S = 35‰)	River water* µg/l	Present study in the Bay of Bengal µg/l			
			Inshore waters		Offshore waters	
			Range	Mean	Range	Mean
Cu	3	5	3.5 - 6.62	5.37	2.0 - 6.0	3.94
Zn	5	10	3.75-46.26	25.41	3.75-38.5	18.31
Mn	2	5	1.00- 7.00	3.57	1.25-6.75	3.33
Fe	3	670	12.10-28.25	18.96	1.00- 4.92	3.06
Co	0.08	0.2	0.25- 1.75	1.09	0.25- 1.00	0.67
Ni	2	0.3	2.70-15.0	6.19	2.00- 9.5	4.81

*from Riley and Chester¹⁷

The correlation matrices (Table 2) show how far the concentration of the metals affect or stimulate the productivity and also the probable metal ions preferably concentrated by phytoplankton. The concentration of heavy metals in seawater may not seem to be high enough to be toxic at times but their toxic effect as pollutants will be magnified when they are concentrated in various trophic levels. Riley and Roth¹³ showed that the uptake of an element by phytoplankton was related to its concentration in the medium and generally phytoplankton concentrate Mn, Fe, Cu and Zn from sea water to high levels⁹.

Table 3 shows the ratio between the metal concentration in the suspended matter and the concentration of TSM. With regard to inshore waters, almost all the ratios are decreasing with respect to depth except the particulate Pb which increased in deeper waters. This trend was not observed in the offshore waters where this ratio decreased at 100 m depth and again increased at 200 m depth. It should be pointed out that the adsorption of metal onto the suspended matter is governed by pH of the water sample and also by the nature of the suspended particles. Runoff from land is a major source of addition of trace elements to the sea. River waters bring the trace metals both as dissolved species and also as adsorbed onto the finely divided suspended detrital matter, the concentration of which is controlled by the nature of the rocks in catchment area. When the river water enters the seawater, the trace metals in suspended matter may be displaced by major cations of seawater¹⁴.

Comparison of the concentrations of dissolved metals in the Western Bay of Bengal with those given for the average oceanic water and river water (Table 4) indicated that except Fe in offshore stations, other metals studied showed higher concentrations. In offshore waters, Zn, Ni, Cu and Co showed higher

values than the average values found in oceanic waters. Except Mn, all other elements in coastal waters were in higher concentration than the offshore waters. Mean values for soluble Zn, Co and Ni in inshore waters were higher than that normally found in river water. The prevailing condition may be due to the effluents in the coastal waters off Visakhapatnam where 4 major industries, viz. (1) Coramandel fertilizers, (2) Hindustan Zinc Ltd, (3) Indian Oil Refineries and (4) Iron Ore Handling jetty were located. Moreover, Visakhapatnam port has several activities such as ship building, loading of ferromanganese ore and loading and unloading of other cargo. In addition to these, a part of the city sewage effluent is dumped in the port waters, through a narrow channel, thus increasing the pollution load¹⁵. Comparatively, the metal concentration observed in this area are however lower than those found in the Arabian Sea^{1,2,16} except the concentrations of Zn and Ni.

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