

Distribution of dissolved trace metals in western Bay of Bengal

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Concentrations of Ni, Zn, Cd, Cu, Mn, Pb and Fe have been determined in 93 water samples (17 inshore and 7 offshore stations), collected at different depths, from the western Bay of Bengal (between visakhapatnam and Madras) during March 1988. Surface distributions reveal that relatively high concentrations of trace metals and nutrients are associated with low salinities in inshore and *vice versa* in the offshore waters. The depth profiles of Ni, Zn and Cd with surface depletion and bottom enrichment resemble those of nutrients indicating their involvement in the biogeochemical cycles. While the profiles of Cu are indicative of its involvement in the scavenging process at intermediate depth, those of Mn and Pb with surface enrichment and bottom depletion, appear to be controlled by river inputs and anthropogenic atmospheric flux. However, surface enrichment and bottom depletion observed in the case of Fe profiles, contrary to its normal oceanic distribution, are attributed to the precipitation and/or adsorption on suspended particles leading to its transport to the sediments. The atomic ratios of Ni, Zn and Cd with nutrients are evaluated through their regression equations and compared with those reported earlier for Pacific, Atlantic and Indian Oceans.

Data on trace metal distributions in marine environment are of importance in understanding the role of trace metals in various biogeochemical processes. Significant contributions have been made on the oceanic distribution of various trace metals¹⁻⁵. However, information on the distribution of trace metals along the Indian coast is very limited⁶⁻¹¹. The present study dealing with the detailed distribution patterns of dissolved trace metals (Ni, Zn, Cd, Cu, Mn, Pb and Fe) in inshore and offshore regions of Bay of Bengal is, however, aimed at understanding the dominant processes controlling their distributions.

Materials and Methods

Seawater samples were collected from surface and at different depths with Niskin samplers during the 193 cruise of *R V Gaveshani* (March 1988) along the east coast of India between Visakhapatnam and Madras (Fig. 1). Samples were immediately filtered through a preweighed and acid cleaned membrane filter (0.45 μ m) to separate dissolved and particulate fractions. The dissolved fractions were collected in acid cleaned polyethylene bottles. Aliquots (800 ml) of filtered samples were acidified with HCl to pH of 3-4 and pre-concentrated by APDC-MIBK extraction¹² followed by successive back extraction¹³ with 4N

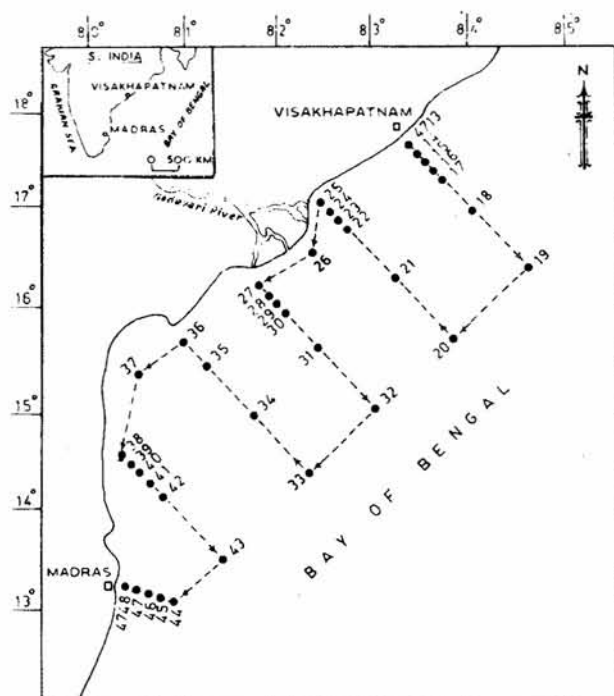


Fig. 1—Location of stations

HNO₃. The acid extracts were then stored under refrigeration till their analysis. Atomic absorption spectrophotometer (Perkin Elmer, model 2380) with air-acetylene fuel mixture was used for the analysis of trace metals. Concentrations of dissolved trace metals in seawater were computed from calibration curves constructed with standards under identical experimental conditions using trace metal free seawater¹². The precision of the method, determined from replicate analyses and reported as percent co-efficient of variation was 5.6, 5.0, 7.5, 3.1, 5.3, 6.3, 2.4 respectively for Ni, Zn, Cd, Cu, Mn, Pb and Fe. Dissolved oxygen and nutrients (nitrate, phosphate and silicate) were determined on board using standard methods¹⁴. Autosal with a precision of ± 0.003 ($\times 10^{-3}$) was used for the determination of salinity of seawater on board the ship.

Results and Discussion

Surface waters—Concentration levels of trace metals in inshore waters are relatively higher when compared with those of offshore waters (Table 1). While higher concentrations of inshore waters are accompanied by relatively lower salinities and higher nutrients, the lower concentrations of offshore waters are accompanied by relatively higher salinities and lower nutrient concentrations. Increase of trace metal and nutrient concentrations followed by a decrease of salinity in the inshore surface waters can be attributed to the land run-off and fresh water inputs into the coastal region. In order to ascertain the effect of fresh water inputs on the trace metal concentration levels in inshore waters, the data on trace metals are plotted against

salinity (Fig. 2) along Godavari river transect (sts. 4722-25 and 4727-30). The data fall along salinity mixing line (with values ranging from -0.71 to -0.90 , significant at 90.0-99.9% confidence level) indicating conservative behaviour. However, wide scattering of data particularly observed in case of Fe, Ni and Pb can be attributed to several processes such as precipitation during estuarine mixing, desorption from river borne suspended particulate matter, redox reactions, and anthropogenic inputs within the mixing zone¹⁵. Another potential source is their remobilization into the overlying water column by sediments. Kremling and Hydes¹⁶ have proposed that such processes along

Table 1—Concentrations of dissolved trace metals, nutrients and salinity of surface waters of Bay of Bengal

Parameter	Inshore		Offshore	
	Range	Average	Range	Average
Mn ($\mu\text{g.l}^{-1}$)	1.83-6.42	4.04	1.83-5.04	3.97
Fe "	0.89-14.8	5.48	2.41-6.23	4.84
Ni "	0.82-2.25	1.56	0.41-1.23	0.81
Cu "	0.82-5.58	3.02	1.92-3.71	3.08
Zn "	0.69-5.62	3.41	ND-2.19	1.19
Cd "	0.21-2.11	0.90	0.11-0.63	0.35
Pb "	1.56-3.74	2.64	2.34-3.89	3.05
NO ₃ -N ($\mu\text{g.at.l}^{-1}$)	ND-30.6	7.28	0.83-3.31	1.83
PO ₄ -P "	ND-2.07	0.57	ND-1.08	0.27
SiO ₄ -Si "	1.31-26.1	10.6	ND-13.1	7.83
Sal. ($\times 10^{-3}$)	33.00-34.30	33.72	33.60-35.20	34.10

ND = Non-detectable

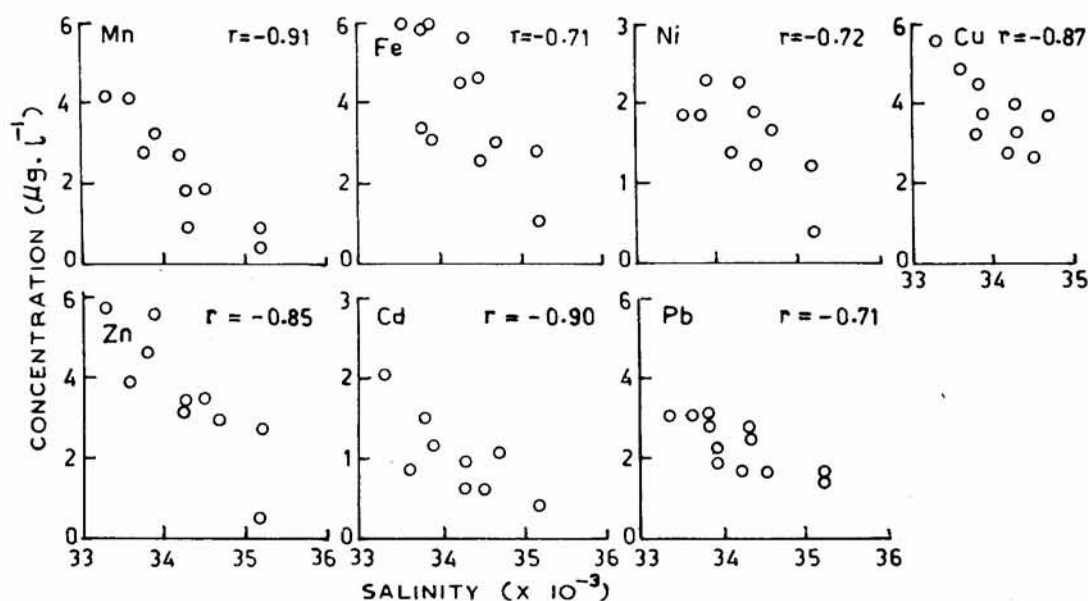


Fig. 2—Trace metal concentrations vs salinity off Godavari river transect (sts. 4722-25 and 4727-30)

with resuspension of Mn rich bottom sediments are responsible for the pronounced enrichment of Cd, Cu, Ni and Mn in continental shelf waters of British Isles. The theoretical river-water trace metal concentrations estimated in the present study from the intercept at zero salinity off Godavari river are shown in Table 2. In the absence of dissolved trace metal data for Godavari river, the extrapolated zero salinity values obtained in the present study are within the limits of average global river water concentrations^{17,18} taking into account the different processes that affect the trace metals or their pathways through the river and the estuarine systems.

Depth profiles—Typical vertical profiles of Ni, Zn, Cd, Fe, Mn, Cu and Pb along with nitrate, phosphate and silicate in the offshore stations (4719, 4720, 4721 and 4734) are shown in Fig. 3. The profiles of Ni, Zn and Cd in general, represent an increase from surface to a depth of 500-800 m followed by near constancy in their concentrations from 800 m to the bottom. Further, the shapes of these trace metal profiles resemble those of nutrients exhibiting surface depletion and bottom enrichment indicating their involvement in biogeochemical cycles.

Nickel: Ni profiles show evidence of surface depletion and deep water maximum (Fig. 3) with surface values ranging from 0.41-1.23 $\mu\text{g.l}^{-1}$ and increasing in the range of 1.80-2.41 $\mu\text{g.l}^{-1}$ at 1000-2000 m depth. The vertical profiles of Ni, in the top 500 m appear similar to phosphate, nitrate and silicate and are in agreement with those earlier reported for Pacific Ocean¹⁹. Ni has exhibited a significant positive correlation with nutrients ($r=0.83, 0.55, 0.77$ for NO_3 , PO_4 , SiO_4 respectively at $P > 99\%$). While the Ni:P atomic ratio (8.40×10^{-3}) derived from the regression equation in the present study is in broad agreement with the reported values for Pacific¹⁹ (0.95×10^{-3}) and Atlantic^{20,21} oceans (1.44×10^{-3} and 1.20×10^{-3}), the Ni:Si ratio (6.5×10^{-4}) is higher than the reported value for Pacific¹⁹ (3.3×10^{-5}), Atlantic²⁰ (1.9×10^{-5}) and Indian⁵ (4.8×10^{-5}) oceans.

Zinc: Vertical profiles of Zn (Fig. 3) show, as in case of Ni, surface depletion and bottom enrichment. Comparing the profiles of Zn with those of nutrients, it is apparent that their distributions are similar except in silicate, which exhibits steady increase in its concentration up to 2000 m depth. A plot of dissolved Zn versus nutrients indicate significant positive correlation ($r=0.72, 0.90, 0.86$ for NO_3 , PO_4 , SiO_4 respectively at $P > 99.9\%$) suggesting its removal from surface waters and transportation to the bottom as a trace constituent of some biological carrier phase. Since phytoplankton is known to concentrate large amounts of Zn, it is probable that diatoms may play an important role in its biogeochemical cycling. The atomic ratio of

Table 2—Extrapolated zero salinity trace metal concentrations and river water (average) concentrations ($\mu\text{g.l}^{-1}$)

Element	Correlation coefficient ($P=99.9\%$)	Extrapolated zero salinity end member	Average global river waters	
			(Ref. 18)	(Ref. 17)
Mn	-0.91 (10)	67.7	8.2	7.0
Fe	-0.71* (12)	80.0	40.0	670.0
Ni	-0.72* (10)	26.4	2.2	—
Cu	-0.87 (10)	77.0	10.0	7.0
Zn	-0.85 (10)	70.3	30.0	20.0
Cd	-0.90 (9)	26.7	—	—
Pb	-0.71* (12)	30.7	1.0	3.0

* $P=99.0\%$

Zn:Si (1.40×10^{-3}) derived from the regression equation is higher than the reported value of 5.4×10^{-5} for Pacific Ocean¹⁹.

Cadmium: Cd concentration rapidly increases in the top 200-500 m and remain fairly constant up to the near bottom (Fig. 3). The mean concentration levels of surface and deep waters show an enrichment in the deeper waters by a factor of about 9 which is higher than that observed for Ni(3) and Zn(5). Similar enrichment factors of about 10 for Pacific Ocean²² and 5 for Sargasso Sea²³ have been reported. The enrichment of Cd at deeper waters suggests its covariation with nutrients. This is evident from the significant positive correlations observed between Cd and phosphate ($r=0.90$), Cd and nitrate ($r=0.75$) and Cd and silicate ($r=0.77$). These correlations can be explained by the removal of Cd in the surface water from the dissolved phase to the particulate organic tissue which is regenerated *via* oxidative processes. Since Cd has no physiological role, it is probably adsorbed on the surface of planktonic debris or faecal pellets during its transportation to bottom waters²⁴. Such correlations between Cd and labile nutrients have been observed^{19,20,22}. The atomic ratio of Cd:N (2.8×10^{-4}) derived from the regression equation is in general agreement with the value (0.91×10^{-4}) reported for Atlantic Ocean surface waters²⁵. However, the atomic ratio of Cd:P (6.20×10^{-3}) is higher than the reported value for Pacific¹⁹ (3.47×10^{-4}), Atlantic²¹ (1.9×10^{-4}) and Indian⁵ ($1.4-2.3 \times 10^{-4}$) oceans.

Higher atomic ratios observed in case of Ni and Zn with Si and Cd with P can be attributed to relatively higher intercepts (concentrations) obtained in the present study than those observed by the earlier workers for open oceans. This supports the assumption that the elemental correlations must be treated as

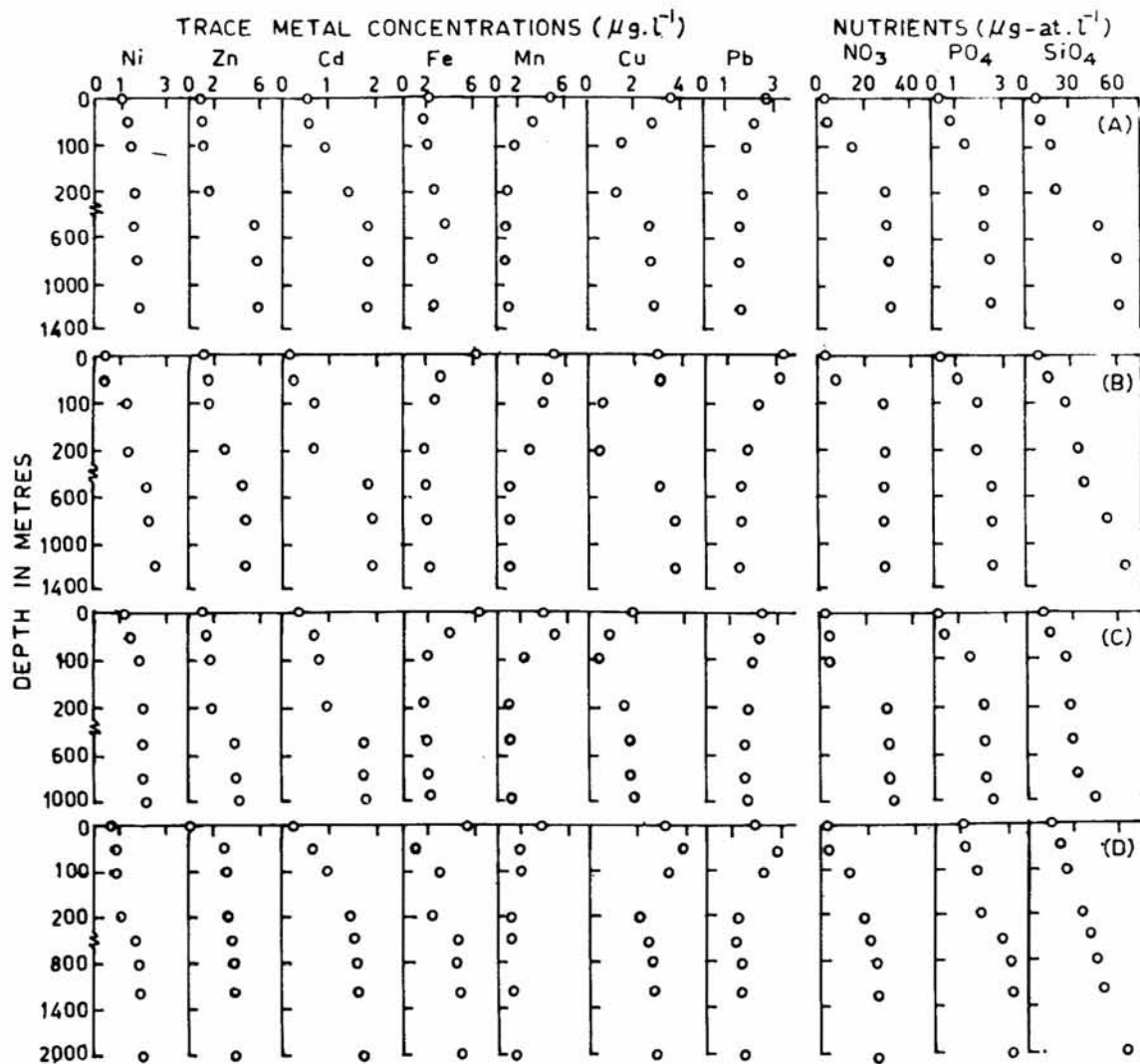


Fig. 3—Vertical profiles of trace metals (Ni, Zn, Cd, Fe, Mn, Cu and Pb) and nutrients (NO_3 , PO_4 and SiO_4) at offshore stations of Bay of Bengal (A = st. 4719, B = st. 4720, C = st. 4721 and D = st. 4734)

statistical properties and that the co-efficients are not globally valid particularly in regions where specific details on the biological uptake of metals and the relative importance of atmospheric flux are not available²⁵.

Copper: Vertical distribution of Cu (Fig. 3) shows least evidence for surface depletion or covariance with nutrients. It exhibits a decrease in its concentration with depth up to 100-200 m followed by an increase up to the bottom, indicating a mid-depth minimum in all offshore stations (Fig. 3). This can be explained in terms of surface inputs of Cu, its scavenging in the water column and excessive regeneration at the sediment-water interface¹⁹. Danielsson⁵ has reported similar sub-surface minimum at about 200 m with a steady increase with depth in the northern Indian Ocean. The mid-depth minima obtained in the

distribution of copper is similar to that of Mn and Pb in the present study.

Manganese: Vertical profiles of Mn in offshore stations (Fig. 3) show surface enrichment and depletion at a depth of about 100-200 m followed by a slight increase at bottom near the sediment-water interface. Enrichment of Mn in the surface water relative to the rest of the water column can be attributed to the river input and deposition of atmospheric particulates²⁶. Resuspension of sediment near the sediment-water interface can markedly increase the dissolved Mn concentration^{27,28}. Braganca and Sanzgiri⁸ have also reported enrichment of manganese at surface relative to intermediate or deep waters in coastal and offshore waters of Bay of Bengal.

Lead: Depth profiles of Pb indicate relatively higher concentrations in surface with a slight decrease at

100-200 m depth followed by a slight increase or near constancy in the bottom waters (Fig. 3). Relatively high concentrations of Pb in surface waters can be attributed to its anthropogenic (atmospheric) input²⁹ and depletion at intermediate depths (100-200 m) may be due to its scavenging from the water column by suspended solids.

Iron: Unlike its normal behaviour, depth profiles of Fe in the study region (Fig. 3) indicate surface enrichment and mid-depth minimum (100-200 m). The surface enrichment of Fe may be probably due to the contamination or the influx of Godavari and Krishna river waters in the study region. Absence of bottom enrichment indicates that some processes other than biological removal, for example, precipitation and/or adsorption, governs its concentration in the offshore region. Fe released from the breakdown of planktonic

matter may be quickly converted into colloidal hydroxide at the pH (7.5-8.4) prevailing in the water column and may be readily adsorbed onto the descending particles, which in turn, get transported to the sediments⁵.

Comparison of the present results with those reported earlier^{5,8-11} (Table 3) shows that while the concentrations of Mn, Ni, Cu, Cd and Pb are in agreement with those reported for inshore and offshore waters of Bay of Bengal⁹ and coastal and offshore waters of northern Bay of Bengal¹⁰, concentrations of Fe and Zn are lower. However, the concentration of Zn obtained in the present study is in agreement with that reported for the coastal and offshore waters of Bay of Bengal⁸. Though the concentration levels for Fe, Ni and Zn are in the same range, levels of Cu, Cd and Pb obtained in the present study are higher than those reported for Indian Ocean⁵.

Table 3—Comparison of range and average column concentrations of dissolved trace metals ($\mu\text{g.l}^{-1}$) in Bay of Bengal

	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Bay of Bengal (present study)							
Inshore	0.92-6.42 (2.80)	0.98-14.8 (3.9)	0.21-2.25 (1.33)	0.37-6.18 (2.87)	ND-6.85 (3.16)	0.11-2.11 (0.75)	1.40-3.74 (2.24)
Offshore	0.46-6.42 (1.98)	0.89-6.23 (2.88)	0.41-2.61 (1.64)	0.37-5.20 (2.25)	ND-5.80 (3.18)	0.11-1.91 (1.05)	1.09-3.98 (1.98)
Overall	0.46-6.42 (2.36)	0.89-14.8 (3.35)	0.21-2.61 (1.50)	0.37-6.18 (2.54)	ND-6.85 (3.17)	0.11-2.11 (0.91)	1.09-3.89 (2.10)
Bay of Bengal (ref. 8)							
Coastal	1.8-22.5 (8.8)	19-132 (66.3)	ND-12.2 (4.18)	2.8-7.2 (5.6)	6.7-15.3 (10.1)	—	—
Offshore	1.6-40.8 (11.5)	6.2-41.5 (22.9)	1.7-11.2 (5.09)	2.2-37.2 (8.6)	2.4-20.0 (8.9)	—	—
Andaman Sea (ref. 11)							
	1.5-24.7 (10.4)	2.0-21.7 (6.24)	ND-1.0 —	1.0-5.0 (2.61)	2.1-12.7 (5.60)	0.2-2.0 (0.64)	ND-6.2 (2.02)
Western Bay of Bengal (ref. 9)							
Inshore	1.0-7.0 (3.57)	12.1-28.3 (19.0)	2.70-15.0 (6.19)	3.5-6.62 (5.37)	3.75-46.3 (25.4)	—	—
Offshore	1.25-6.75 (3.33)	1.0-4.92 (3.06)	2.0-9.5 (4.81)	2.0-6.0 (4.94)	3.75-38.5 (18.3)	—	—
Northern Bay of Bengal (ref. 10)							
Coastal	1.6-9.4 (3.50)	8.0-44.1 (16.9)	ND-6.1 (2.0)	0.5-6.2 (2.3)	2.9-39.5 (25.3)	0.8-1.9 (1.0)	0.9-22.8 (6.7)
Offshore	1.9-6.0 (3.4)	11-25.8 (15.5)	ND-2.7 (0.8)	1.0-2.5 (1.8)	17.6-35.7 (25.7)	0.7-1.2 (0.9)	5.3-13.2 (9.4)
Indian Ocean (ref. 5)							
--	—	0.15-10.0 (0.83)	0.18-0.95 (0.52)	0.08-0.48 (0.23)	0.6-13.8 (3.06)	0.01-0.16 (0.06)	0.02-0.18 (0.07)

ND = Non-detectable

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