

In addition to the distribution of Sr and Mg the Sr/Ca \times 1000 ratios have been utilized to infer the history of the reef. In recent coral sand from Bikini¹¹ Sr/Ca ratio is 10.89 and in living corals it is 12.65, Siegel¹¹ distinguished pleistocene and living reefs in Florida Keys and shoals based on Sr/Ca ratios. He stated that the reef is in a process of alteration from aragonite to calcite¹⁴; lower Sr/Ca ratios and high Mg values are observed¹¹. Sr/Ca \times 1000 ratios on the reef and lagoon at Minicoy range from 4.9 to 8.7; the ratios are generally higher in the lagoon and lower on the reef. The ratios seem to indicate that the reef at Minicoy is not very active and may in part be in a state of alteration. The Indian Naval Hydrographic Chart of Minicoy shows that the lagoon is deeper in the centre with a number of coral knolls. Visual observations also indicate a luxuriant coral growth in the knolls and patchy reefs in the lagoon. Pillai³ has recorded 70 species of hermatypic corals from Minicoy atolls and indicated a luxuriant growth of certain corals in the lagoon. Some of the species were non-existent or not reported by Gardiner³ but are flourishing now and according to Pillai³ these colonies have grown during the last 70 yr. However, it is difficult at this stage to conclude on the basis of Sr/Ca \times 1000 ratios alone the activeness or relative ages of the reef or coral knolls in the lagoon.

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Concentrations of Few Trace Metals in Coastal & Offshore Regions of the Bay of Bengal

ANALIA BRAGANCA & SUJATA SANZGIRY

National Institute of Oceanography, Dona Paula, Goa 403004

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Cu, Fe, Mn, Zn, Co and Ni in dissolved and particulate fractions of sea water at different depths were estimated from 9 stations in the Bay of Bengal. Concentrations of dissolved and particulate Fe were fairly high at coastal stations, specially at the river mouths. Cu at the nearshore stations was high but there was no marked difference between the nearshore and offshore concentrations, so as to reflect the possibility of river input. Dissolved Zn and Ni were low at the surface than in deeper layers contrary to Mn. Particulate fractions of Fe and Zn were significant, while Co and Ni were not significant; Cu and Mn showed intermediate values.

As a part of the ongoing project on 'Protection of marine environment and monitoring of pollutants in the seas around India', studies were carried out on some of the heavy metals in dissolved and particulate form. The main interest has been in the transition group metals which are necessary for the life cycle of marine organisms but which can be cumulative poisons as well. Concentrations of heavy metals were estimated along 2 transects in the Arabian Sea¹ and later in the sea around the Laccadive islands². In the present paper results of estimations carried out during the 35th and 36th cruises of *RV Gaveshani* in the Bay of Bengal are presented. During the 36th cruise, sampling was mainly done at some river mouths, to study the influence of river input, if any.

Samples were collected at 9 stations (Fig. 1), using van Dorn PVC water samplers. Collection of samples was done at 10 m depth instead of surface in order to avoid contamination due to the 3.5 m deep metallic hull of the ship. Samples were transferred to acid-washed jerry cans and filtered through 0.45 μ m membrane filters (Millipore HA). The water samples were then stored in acid-washed polyethylene carboys and acidified to pH 3-4 with 1 N HCl. Filter papers with the particulate matter were stored under refrigeration, in prewashed plastic containers. Samples, both dissolved and particulate fractions, were returned to the shore laboratory for analyses. The samples were analysed for Cu, Fe, Mn, Zn, Co and Ni using atomic absorption spectrophotometry. The procedure used for the analysis of dissolved metals was same as given by Brewer *et al.*³.

Dissolved Mn could not be extracted with ammonium pyrolydine dithiocarbamate and methyl isobutyl ketone at the pH at which other metals were analysed. It was therefore chelated with sodium-diethyl dithiocarbamate and extracted in methyl

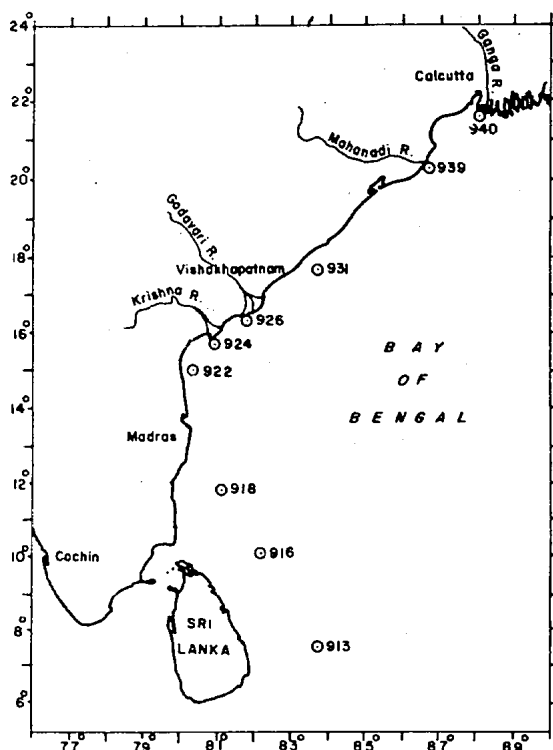


Fig. 1 Station locations

isobutyl ketone at pH 5-6 followed by aspiration in atomic absorption spectrophotometer (Hilger and Watts model H 1550).

The precision of the analyses, determined from 2 to 3 repeats of 15 samples and reported as coefficients of variation, was 5, 6, 13, 15, 8 and 9% for Cu, Mn, Fe, Zn, Ni and Co respectively.

Filter papers with the particulate matter were digested with HClO_4 followed by 2 aliquots (2 ml each) of HNO_3 and a drop of HCl . The dried residue was dissolved in 0.1 N HCl making the volume to 10 ml. Blanks and standards were similarly treated. Reagents and standards were prepared, using analytical grade chemicals dissolved in metal-free distilled water.

Six of the stations were coastal, four of which were located at the mouth of rivers Krishna, Godavari, Mahanadi and Ganga (Fig. 1). The main objective was to study the influence of the coast and river runoff, if any, on the concentrations of different metals.

Higher concentrations of Fe and Zn, both in dissolved and particulate forms in surface waters were found at stations near the river mouths showing that the inflowing water is richer in Fe and Zn, than in other metals (Table 1). Removal of metals by natural agencies and their incorporation in the sediments are quite likely. This may be the reason why the coastal stations do not show very distinct richness in the concentrations of most of the metals compared to stations away from the coast.

Dissolved Fe in sea water was reported to range from 0 to $> 10 \mu\text{g/litre}$ depending on the proximity to shore⁴. The dissolved Fe values in the present study range from 6.3-131.5 $\mu\text{g/litre}$ which is almost an order higher than that reported by Topping⁵ in the Indian Ocean region (0.1-61.8 $\mu\text{g/litre}$). These observations show that Fe concentrations in nearshore waters are influenced by the coastal input.

Comparison of average surface concentrations of Fe at sts 913, 916 and 918 with those at sts 924, 926, 939, 940 indicates that dissolved and particulate Fe at the river mouths is almost 3 times more than at the other stations. At sts 913 and 916, the surface dissolved Fe concentrations are almost same as the average between 100 and 1000 m layers, while at sts 918, the surface Fe concentration is appreciably lower than that between 100 and 1000 m.

Particulate Fe to dissolved Fe at coastal stations (10 m depth samples) show that high values of the former are associated with low values of the latter. High concentration of particulate Fe at the river mouth stations is thus, due to the removal of the metal in solution when the inflowing river water meets the saline water⁶.

Concentrations of dissolved Mn range from 1.6-40.8 $\mu\text{g/litre}$. The average concentration of dissolved Mn at the river mouth stations is 10.8 $\mu\text{g/litre}$ whereas at offshore stations it is 6.3 $\mu\text{g/litre}$, indicating that the metal concentration is not appreciable at the river mouths to show a possible input by the rivers. Considerably low particulate Mn at the river mouth stations indicates a very low removal of the metal when river water meets saline water.

Chemistry of Mn in sea water is dominated by redox changes. The pH of present samples varied between 7.33-8.29. Oxidation of Mn^{2+} to Mn^{4+} takes place above pH 8.5⁷. This shows that soluble Mn measured was in the ionic Mn^{2+} form. Soluble Mn is found to be higher at the surface than in the intermediate or deep waters.

Average surface concentration of dissolved Cu was 4.9 $\mu\text{g/litre}$. Deeper stations (100 and 1000 m) were richer in dissolved Cu coinciding with the dissolved oxygen minima observed between these depths in the Bay of Bengal. As compared to deeper layers, the 100 m depth layer at all stations is fairly rich in dissolved as well as in particulate Cu (Table 1).

Topping⁵, Riley and Taylor⁸ have reported distribution of copper in oceanic waters with no significant trends of variation. Determining ionic, particulate and total soluble Cu in the waters off Florida, Alexander and Corcoran⁹ reported that inshore waters had twice the total Cu concentrations of the offshore waters. Although sufficient data are not available in the present study the fact that the

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Table 1—Concentrations of Metals in Dissolved Form ($\mu\text{g}/\text{litre}$) and Particulate Form ($\mu\text{g}/\text{g}$)

Sampling depth m	Cu		Fe		Mn		Zn		Ni		Co	
	D	P	D	P	D	P	D	P	D	P	D	P
	St 913											
10	6.5	211	27.5	5646	9.4	219	2.6	1878	3.7	40	1.5	93
100	37.2	252	47.2	9000	4.6	422	2.7	2486	7.5	83	1.0	ND
500	11.2	398	14.2	5676	2.2	175	12.8	1869	6.5	54	ND	ND
1000	7.0	65	16.5	7683	7.2	265	4.8	511	6.0	18	ND	37
	St 916											
10	2.7	10	15.5	5308	5.5	208	5.1	994	3.5	ND	ND	41
100	3.3	169	17.5	8360	1.6	190	4.4	621	3.0	14	5.2	134
500	10.8	170	8.0	6735	3.7	204	13.6	2816	4.7	53	1.5	107
1000	3.0	71	20.5	2586	2.5	113	8.5	742	4.4	ND	1.5	53
3000	6.7	54	10.5	3271	3.0	243	14.0	1073	4.7	ND	ND	23
	St 918											
10	4.2	36	6.5	5479	4.0	129	3.4	1004	3.5	36	ND	36
100	10.0	45	6.2	7022	40.8	572	14.3	1616	5.5	ND	1.2	63
500	2.2	18	41.5	4539	15.5	344	2.4	—	1.7	74	1.5	251
1000	9.5	53	71.5	3168	37.0	323	20.0	1311	6.8	44	1.5	66
2000	8.8	ND	30.5	5063	4.0	131	13.5	—	3.7	ND	7.9	160
3000	6.0	34	10.5	3673	32.0	266	11.3	869	11.2	ND	1.2	ND
	St 922											
10	—	161	—	11802	22.5	401	—	2065	—	ND	—	113
100	—	84	—	11859	8.2	99	—	1564	—	ND	—	217
175	—	183	—	23204	1.8	—	—	2471	—	146	—	ND
	St 924											
10	6.2	108	69.0	9353	3.8	56	15.1	1595	2.2	28	ND	151
	St 926											
10	2.8	143	61.0	15942	25.0	137	7.6	2338	ND	115	4.0	28
	St 931											
10	6.8	197	131.5	4506	3.8	101	15.3	2853	12.2	74	7.0	144
100	7.2	176	70.5	42408	4.0	115	7.9	2095	2.5	ND	ND	163
	St 939											
10	5.5	80	47.0	27965	8.0	10	8.0	796	4.2	83	ND	41
	St 940											
10	4.8	77	19.0	—	2.0	28	6.7	644	4.0	81	2.0	ND

ND = Non-detectable; — = Not analysed
D = Dissolved; P = Particulate

nearshore surface water have higher dissolved and particulate Cu than the waters at the stations further away from the shore compares well with their observation. Distribution of particulate Cu at 10 m depth at the coastal stations shows a similar pattern as that of particulate Zn.

Study of Zn concentrations is of considerable interest in view of its interaction with marine biosphere. For elements such as Zn, which can form complexes with hydroxides, a considerable fraction can be expected to be colloidal or adsorbed on to particulate matter⁷. Values for dissolved Zn (Table 1) clearly show that deeper layers have higher content than the surface. The particulate fractions are in

considerable amounts at the surface and at intermediate depths but are lower in deeper waters. These observations show that there is considerable uptake of Zn by organisms. This agrees well with the work of Hagerhall¹⁰. It is also clear that Zn bearing particles formed at the surface, where the pH is relatively high, sink down to waters of low pH and add to soluble Zn due to release. Present data compare well with observations of Zirino and Healy¹¹ in the Northeastern Pacific waters.

Average surface Zn concentration at stations very near to the coast are much higher than those at the stations further away (Table 1). These values cannot be

solely attributed to river input, since the concentration in sea water ranges from 1-50 $\mu\text{g}/\text{litre}^4$.

Concentrations of dissolved Co were very low. Dissolved Ni concentrations vary between non-detectable levels to 12.2 $\mu\text{g}/\text{litre}$, the trend of variation does not show any definite order. However, deeper waters were slightly richer in dissolved Ni than surface (Table 1). Probably Ni taken up by the organisms in the photic zone is released in the lower layers¹².

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Distribution of Petroleum Hydrocarbons in Goa Coastal Waters

S P FONDEKAR, R S TOPGI & R J NORONHA

National Institute of Oceanography, Dona Paula, Goa 403 004

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Average hydrocarbon concentrations in water, plankton and sediment samples collected from the central west coast of India between 14°40'N and 15°50'N were 30.9 $\mu\text{g}/\text{litre}$, 46.9 $\mu\text{g}/\text{g}$ dry wt and 7.1 $\mu\text{g}/\text{g}$ dry wt respectively. The data suggest that marine plankton are useful indicators of oil pollution in this region.

Coastal zone receives a considerable amount of oil from shipping which includes dumping of bilge, accidental discharge of oil from tankers, exhaust discharge from small craft, runoff of oil via sewage, land waste and industrial effluents¹. Chemical and biological studies have shown that petroleum hydrocarbons from an oil spill can persist in marine sediments for at least 2 yr (ref. 2) and that the spilled oil has an adverse effect on marine organisms³⁻⁵.

As a part of an ongoing project on the origin, role and fate of hydrocarbons in the sea, a survey has been

carried out to estimate the amount of petroleum hydrocarbons present in the coastal waters of Goa. Such a study would provide a base to determine any changes that might occur in the future.

Water (24), plankton (6) and sediment (9) samples were collected during the 46th cruise of *RV Gaveshani* in Dec. 1978 (Fig. 1), for the analysis of petroleum derived hydrocarbons.

Sampling and preservation—Collection and preservation of water samples was done as described previously⁶. Plankton samples were collected with the help of a Neuston net (mesh size—500 μm) while the ship was running dead slow. Samples were then wrapped in clean aluminium foil, placed in glass jars and frozen till analysed. Sediment samples were obtained by La Fond Dietz Snapper which sampled the upper 5 cm of the sediment. The samples were kept frozen in glass jars till analysed.

Extraction and analysis—On reaching the shore laboratory, water samples were thawed and shaken again before they were transferred to a separating funnel. After separation, the sample was extracted with hexane for a 2nd time. The combined hexane extract was freed from the residual water by treatment with anhydrous sodium sulphate. It was then concentrated to about 20 ml by evaporation at 50°C on a controlled water bath. The hexane extract was then passed through a column of silica gel (60-120 mesh) which had been treated and deactivated before use. The column was then washed with 30-40 ml hexane. The combined hexane extract was evaporated and final volume made up to 10 ml. Hexane was used as a blank and a Saudi Arabian crude oil was taken as a standard. Both these were treated by the same way as the samples. Petroleum hydrocarbon concentrations were measured with a Beckman ACTA-C-III double beam recording spectrophotometer⁶.

Plankton and sediment samples were thawed and the former were checked for tar particles and paint chips, and whenever they were found contaminated the samples were discarded.

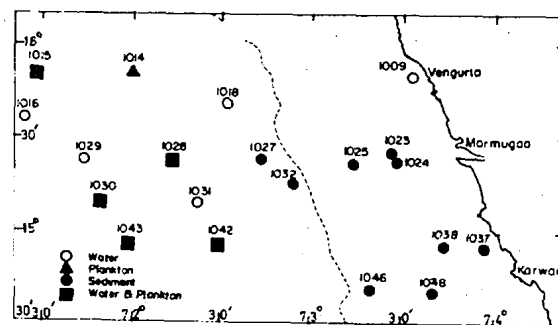


Fig. 1—Station locations