

DISTRIBUTION OF THE TRACE ELEMENTS, IRON, COPPER, MANGANESE AND COBALT IN THE BAY OF BENGAL*

V. CHALAPATI RAO AND T. S. SATYANARAYANA RAO

*Central Public Health Engineering Research Institute, Nagpur ;
and Indian Ocean Biological Centre, National Institute of Oceanography, Cochin*

ABSTRACT

Data on the distribution of trace elements viz., iron, copper, manganese and cobalt incorporated in this paper deals with values obtained in the inshore waters of the Bay of Bengal off the coast of Waltair for a period of two years (1961 to 1962) and also from different regions of the Bay of Bengal obtained during March-April 1963 on board R. V. ANTON BRUUN during the International Indian Ocean Expedition.

Surface average values of iron, copper and manganese exhibit a seasonal variation from high values ranging from 72-104 $\mu\text{g/l}$ in August for iron, 19.5-21 $\mu\text{g/l}$ in October-November for copper and 13-17 $\mu\text{g/l}$ in August for manganese to low values ranging from 15.2-26.5 $\mu\text{g/l}$ in March-April for iron, 15.8-6.8 $\mu\text{g/l}$ for copper in April, and 1.5-2.2 $\mu\text{g/l}$ in April for manganese. Cobalt shows a small variation from 0.44 $\mu\text{g/l}$ in August to 0.28 $\mu\text{g/l}$ in March-April in 1961 and 0.38 $\mu\text{g/l}$ in July to 0.24 $\mu\text{g/l}$ in April in 1962. High values of iron, copper, manganese and cobalt are attributed to contribution from rivers and storm water channels draining the areas of mineral deposits located north of Waltair during the south-west monsoon period. Low values of these four elements during March-April period suggest utilisation by the phytoplankton crop.

Average values of iron, copper, and manganese in the surface water of the different regions of the Bay of Bengal reveal only a slight variation during March-April 1963 and show a tendency to increase in a south to north direction from the Nicobar Sea towards the head of the Bay. The concentrations are higher near the coasts and lower in the oceanic areas. The vertical distribution reveals that iron and copper content is generally high in surface water and decreases with depth upto 500 metres after which the content shows a rise at 1000 metres.

INTRODUCTION

A study of the trace elements in the sea is significant in that they act as limiting factors in the growth of phytoplankton. Some invertebrates, oysters in particular, concentrate copper in their bodies. Copper is present in the blood of some invertebrates in hemocyanin and serves as an oxygen carrier in a role somewhat analogous to that of iron in hemoglobin in the blood of mammals. Many marine plants are known to concentrate large quantities of copper from sea water. Addition of manganese to deficient *Chlorella* cells was shown by Pirson (1937) to cause an immediate increase in photosynthesis. Manganese is important in nitrogen metabolism and Kylin (1945) showed that it stimulated growth of sporelings of *Ulva lactuca*.

Considerable amount of literature is available on the distribution of trace elements in different water masses of the world. Distribution of iron was summarised by Lewis and Goldberg (1954), copper by Goldberg (1961), manganese by Thompson and Wilson (1935), Harvey (1947), and Goldberg and Arrhenius (1958) and cobalt by

* Presented at the 'Symposium on Indian Ocean and Adjacent Seas—Their Origin, Science and Resources' held by the Marine Biological Association of India at Cochin from January 12 to 18, 1971.

Goldberg (1954), Noddack and Noddack (1939), Malyuga (1945), Ishibashi *et al.*, (1951), Black and Mitchell (1952), and Thompson and Laevastu (1960). The only data on the distribution of iron, copper and manganese in Indian waters comes from Kappanna *et al.* (1962) at Bhavanagar, north of Bombay in the Arabian sea. A single value for each element was presented and the concentrations were iron—160 $\mu\text{g/l}$, copper—30 $\mu\text{g/l}$, and manganese 2.5 $\mu\text{g/l}$. No details are available regarding the time of the year when this value was recorded.

We are grateful to Dr. N.K. Panikkar, Director, National Institute of Oceanography, India for his useful suggestions in the preparation of this paper. Thanks are due to Dr. P.N. Ganapati for research facilities at Andhra University, Waltair and to Dr. John H. Rhyther of the Woods Hole Oceanographic Institute, U.S.A. for facilities on R. V. *ANTON BRUUN* during the International Indian Ocean Expedition.

MATERIAL AND METHODS

Sea water samples for routine work were collected from the surface once in ten days from January 1961 to December 1962 from a station (Fig. 1) located about 3 km off the coast of Visakhapatnam opposite the entrance channel. The depth at this station was about 46 metres.

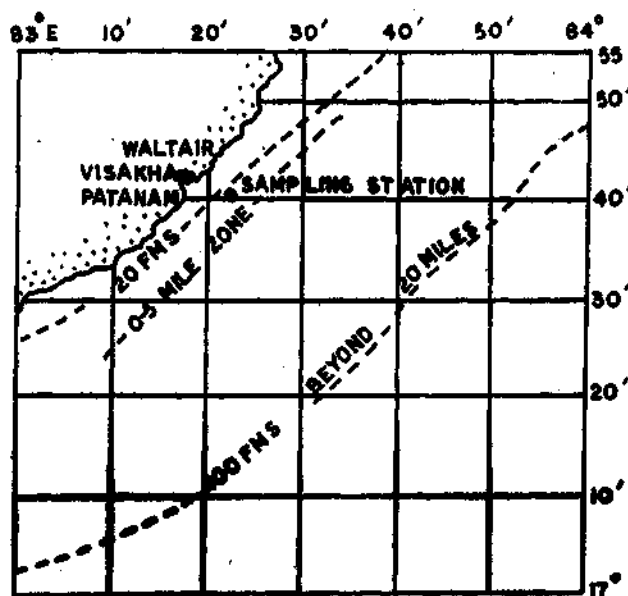


Fig. 1. Location of the sampling station for weekly collections.

A clean polythene bucket was lowered from the boat with the help of a cotton rope. The bucket was rinsed twice with the sea water sample and a bucketful of surface sea water was collected. The sea water sample was immediately dispensed into a 5 litre polythene carboy provided with screw cap and the sample was preserved with chloroform. Normally the samples were collected between 0730 hrs and 0800

hrs and brought back to the laboratory and were frozen at -10°C in polythene bottles and were analysed on succeeding days.

Sea water samples from different depths and from various regions in the Bay of Bengal (Fig. 2) were collected on board R. V. *ANTON BRUUN* by an all plastic 'dazzler' sampling bottle of 4 litre capacity and on certain occasions by 'Vandorn' plastic sampling bottle. The samples were frozen at -15°C in polythene bottles and were analysed later on a Unicam Sp. 600 Spectrophotometer.

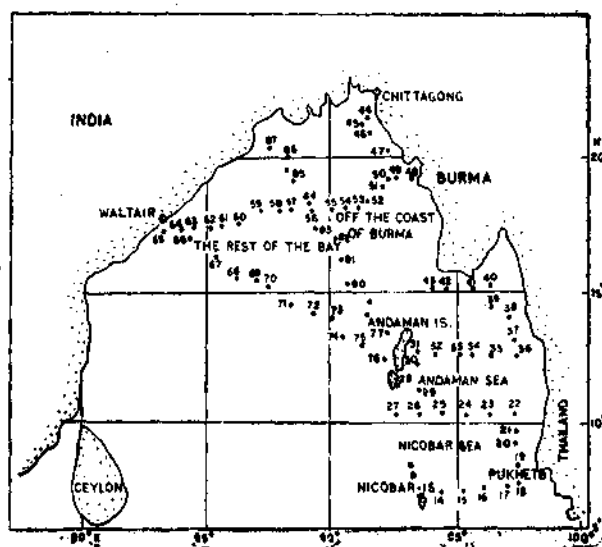


Fig. 2 Location of Stations during the first Cruise of 'Anton Bruun' in the Bay of Bengal.

Total iron was estimated by the method of Armstrong (1957) using 1:10 phenanthroline in the presence of hydroxylamine. Copper was estimated by the method of Strickland and Parsons (1960) treating the sample with sodium diethyl dithiocarbamate and extracting copper with carbon tetrachloride. Manganese was estimated by the method of Koroleff (1947) described by Barnes (1959) in which alkali was added to sea water and the precipitate which contains the manganese was dealt with by the periodate method. Cobalt in sea water was analysed using nitroso-R-salt according to Sandell as modified by Thompson and Laevastu (1960).

TOTAL IRON

Seasonal variation of the monthly average values of total iron in the surface waters off the coast of Waltair during 1961 and 1962 :

The monthly mean values of iron in the surface waters off the coast of Waltair during 1961 (Fig. 3) showed a variation from $72\ \mu\text{g/l}$ in August to $15.5\ \mu\text{g/l}$ in January, thus showing a range of $56.5\ \mu\text{g/l}$. The average value for iron for this year was

[3]

37 $\mu\text{g/l}$. From January to February the values showed an increase, followed by a fall in March. There was again a rise in April and values remained steady in May. From June through August, the values gradually increased and reached the maximum concentration in the latter month. The values had fallen by 50% in September and increased during October and November. From November to December the values registered considerable fall. A comparison of the data obtained in 1961 with that of 1962 would reveal that the average concentration and the trend in variation are

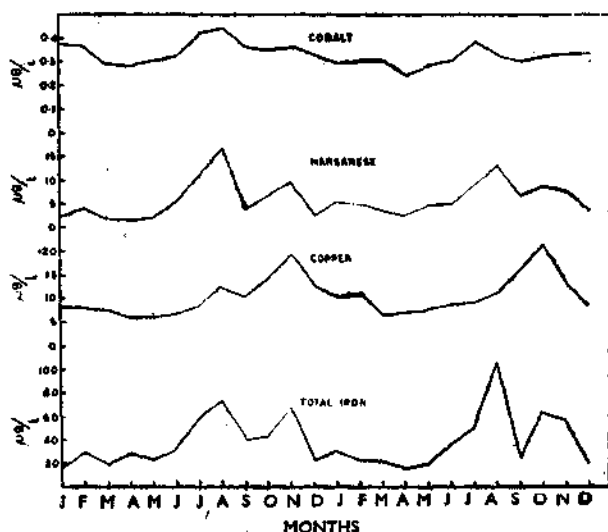


Fig. 3 Monthly average values of Iron, Copper, Manganese and Cobalt in the surface waters off the coast of Waltair during 1961 and 1962

identical in both the years. However, it may be pointed out that the values during 1962 did not show quick variation between month to month but showed a gradual decrease from January to April touching the lowest value in April (15.2 $\mu\text{g/l}$). Thereafter, the values showed a gradual increase till July and reached the highest value in August (104.0 $\mu\text{g/l}$). The low average in the premonsoon period and high average value of the monsoon period (July-November) agree with the values of 1961.

A comparison of the average value from January to May (premonsoon period) with the average value from June to November (South west and North west monsoon period) would reveal that the average value of iron in the latter period is more than double the value of the January-May period, the figures being 51.3 $\mu\text{g/l}$ and 22.4 $\mu\text{g/l}$ respectively.

The higher values of iron during July-August period may be due to contribution from the small storm channels and rivers draining a rich iron and manganese ore area situated North of Waltair. The rise in the value in November can be ascribed to the river waters brought down the east coast of India from near the head of the Bay by the Southerly current. Gran (1933) suggested that the high iron concentration in the inshore areas may be due to their being washed out with humus compounds from the soil. From the success of his culture experiments with soil extracts, he

[4]

pointed out that the humic acids have the ability to maintain the iron in an available form. Armstrong (1957), and Laevastu and Thompson (1958) also suggested the possibility of higher values of iron due to land drainage. Goldberg (1954) remarked that high values of iron in the surface water may be due to turnover of iron within the marine biosphere. As a result of interaction between the biosphere and the hydrosphere with respect to iron, upper waters may act as a reservoir.

Since the quantity of iron involved in the present observation was rather high, it appears that contribution from land is significant and may be the principal cause for high iron values during these months.

Values of iron showed a reduction in the months of March and September. The low value in March coincided with high phytoplankton production. The utilisation of iron by the diatom populations seems to be responsible for the reduction of iron content in the surface waters during this period. Several authors have shown decrease and even exhaustion of iron content in the surface water during the period of high phytoplankton production (Cooper, 1935; Seiwel, 1935; Thompson and Bremner, 1935; Harvey, 1937; and Goldberg, 1952). It is also possible that particles of ferric hydroxide collect on the surface of diatom and in consequence of the round of events in the sea, may be carried downwards (Harvey, 1955).

Distribution of iron in the various regions of the Bay of Bengal during March-April 1963:

Nicobar Sea : The iron concentration in the surface waters of the Nicobar Sea fluctuates between $5.3 \mu\text{g/l}$ and $11.5 \mu\text{g/l}$, thus showing a range of $8.2 \mu\text{g/l}$. The average value for this region is $8.7 \mu\text{g/l}$. The values of iron near the Thai Coast are in general higher than the values near the Nicobar islands.

Andaman Sea : The iron values in the surface waters of this area vary from $5.8 \mu\text{g/l}$ to $21.3 \mu\text{g/l}$, showing a range of $15.5 \mu\text{g/l}$. The average iron concentration in the Andaman Sea is $13.0 \mu\text{g/l}$, which is higher than the average content in the surface water of the Nicobar Sea. In general the values at off-shore stations are low when compared to high values observed in the nearshore waters. Iron values are seen to increase in a South to North direction along the Thai and the Burmese Coasts.

Off the coast of Burma : Variation of iron in the surface waters off the coast of Burma shows values from $8.2 \mu\text{g/l}$ to $33.2 \mu\text{g/l}$, with a range of $25.0 \mu\text{g/l}$. The average value for these waters is $14.9 \mu\text{g/l}$. A high concentration of $33.2 \mu\text{g/l}$ has been observed at station 45 in the Northernmost part of the Burmese Coast, whereas values away from the coast indicate decreasing iron content.

The rest of the Bay : A great variation of iron in the surface waters of this area with values between $5.5 \mu\text{g/l}$ and $72.0 \mu\text{g/l}$, showing a range of $66.5 \mu\text{g/l}$ has been noticed. The average value of iron in the surface waters is $26.9 \mu\text{g/l}$.

Horizontal distribution of iron in the Bay of Bengal during March-April 1963:

It may be noticed (Fig. 4) that the iron concentration in the waters immediately below the head of the Bay (between 87° - 91°E meridian and along the 18°N parallel) is rather low when compared to the rest of the Bay. From this area, towards the

coast of India the values increase. The iron values show an increase in a South-west direction towards the Andamans from the East Coast of India. The values of iron are also high to the waters north of Andamans. It is interesting to note that the highest iron concentration of $72 \mu\text{g/l}$ in the surface water of this region which is also the highest value recorded for the whole area investigated during this period, comes from one deep station far away from the land. However, the value recorded at station 87 at the mouth of the Hooghly river is also comparatively high with a value of $52 \mu\text{g/l}$.

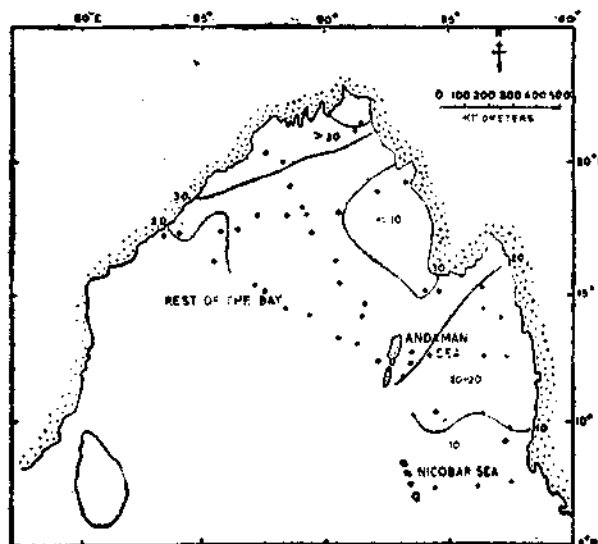


Fig. 4 Horizontal distribution of total Iron in $\mu\text{g/l}$ in surface waters in the Bay of Bengal.

A comparison of the iron values in the surface waters of the 4 regions investigated during March-April period indicates a gradual increase, both in the range, in variation and average values, in a South to North direction from the Nicobar sea towards the head of the Bay.

It is also a point of interest that, at stations situated close to river mouths, both on the coast of Burma and the Indian Coast, high values of iron have been noticed. Apparently, iron particles must have been carried along with silt and other suspended matter in the river waters. It may also be pointed out that there is a possibility of considerable quantity of dissolved organic compounds brought down by river waters which tend to form soluble iron organic complexes thereby facilitating greater contribution of this element to the sea water.

Vertical distribution of iron in the Bay of Bengal during March-April 1963 :

The vertical distribution of iron presents different trends in the various regions (Table 1).

TABLE I. Distribution of Iron, Copper, Manganese and Cobalt in various regions of the Bay of Bengal during March-April 1963*

R. V. ANTON BRUUN Stn. No	Depth metres	Iron $\mu\text{g/l}$	Copper $\mu\text{g/l}$	Manganese $\mu\text{g/l}$	Cobalt $\mu\text{g/l}$
<i>Nicobar Sea</i>					
26	1	10.1	7.1	10.0	not done
	100	31.2	4.5	8.2	"
	300	11.7	5.0	5.5	"
	600	15.6	2.3	4.1	"
<i>Andaman Sea</i>					
28	1	21.3	10.3	4.5	"
	25	11.4	9.2	4.8	"
	50	5.0	7.4	5.2	"
	75	5.0	3.2	5.5	"
32	1	20.5	9.5	3.1	"
	100	9.0	5.8	3.9	"
	300	8.0	6.4	4.8	"
	500	11.0	8.2	5.2	"
	1000	14.0	13.0	5.7	"
<i>Off the coast of Burma</i>					
51	1	10.7	5.0	2.6	"
	100	15.7	7.5	3.4	"
	200	32.1	7.8	4.9	"
	500	12.1	11.0	5.1	"
<i>The rest of the Bay</i>					
57	1	5.8	2.5	5.4	"
	100	11.7	not done	not done	"
	250	11.7	2.8	5.8	"
	500	11.0	4.3	7.2	"
	1000	13.5	5.0	6.4	"
60	1	31.2	2.5	3.0	0.25
	50	22.4	25.8	4.0	"
	250	11.1	33.0	4.8	"
61	500	10.5	10.7	5.2	"
	1	13.5	8.8	3.6	"
	250	17.4	33.0	4.8	"
67	850	15.0	21.4	6.8	"
	1	15.6	3.6	5.9	0.27
	100	11.7	2.6	4.2	"
71	250	17.4	1.3	4.8	"
	500	18.0	4.2	6.2	"
	1	22.4	2.3	3.3	0.22
75	100	35.1	2.3	3.8	"
	250	19.5	2.3	5.2	"
	500	29.1	4.0	5.8	"
	1	33.0	17.0	10.2	0.27
76	100	9.7	17.8	5.2	"
	250	27.3	21.2	6.2	"
	500	11.7	22.4	6.8	"
	1	29.4	13.4	5.8	"
76	100	19.0	11.1	6.4	"
	250	9.3	15.4	6.8	"
	500	15.6	18.2	7.7	"

*Only stations from where depth-wise data have been obtained are included here.

R. V. <i>ANTON BRUUN</i> Sta. No.	Depth metres	Iron $\mu\text{g/l}$	Copper $\mu\text{g/l}$	Manganese $\mu\text{g/l}$	Cobalt $\mu\text{g/l}$
79	1	37.10	9.8	4.8	0.27
	100	19.7	9.5	5.2	"
	300	15.0	7.2	5.2	"
	1000	11.7	10.5	5.8	"
80	1	72.0	10.5	4.0	0.22
	100	36.9	7.5	4.4	not done
	250	24.2	5.0	5.2	"
	500	22.4	4.3	6.2	"
	1025	29.3	11.3	6.0	"
	1775	14.8	6.3	2.2	"
81	2425	8.5	10.7	0.9	"
	1	31.0	19.8	6.4	"
	100	22.0	19.0	4.8	"
	500	11.0	11.8	5.5	"
84	1000	19.2	10.6	5.8	"
	1	24.2	8.2	4.8	0.28
	100	21.4	6.3	5.0	"
	250	69.2	8.2	5.5	"
	500	15.4	6.4	5.8	"
	1020	19.2	10.4	6.4	"
	2035	11.2	10.1	1.4	"

In the Nicobar Sea (station 26) the values increase at 100 metres and beneath that depth, the values fall. In the Andaman Sea (station 28) the iron content in surface water is high with $21.0 \mu\text{g/l}$ and the values gradually decrease to the bottom at 75 metres and show iron concentration of only $5.0 \mu\text{g/l}$. At another station (32) in the same region, the surface value is high and the values fall upto 300 metres. From 300 to 1000 metres, the values show an increase.

In the waters off the coast of Burma (station 51) the iron concentration is low in the surface water, increase upto 200 metres and thereafter decreases.

The distribution of iron in the rest of the Bay shows that in the area north of Andamans there is some uniformity in the depth distribution. The values are high in the surface consistently at all stations (75-84) and low at about 1000 metres. Though in general there is a decreasing trend in the values with increasing depth, at some of the depths certain discrepancies are observed. At other stations in the Bay, the depth distribution of iron is rather erratic, showing occasionally higher values at depths of 500 metres.

It may be noticed that the general vertical distribution of iron in the Bay of Bengal is somewhat erratic. Erratic variation of iron with depth was also recorded at a number of positions near Plymouth and in the Bay of Biscay by Armstrong (1957) based on his observations during 1955-56. The erratic distribution of iron in sea water seems to be mainly due to its particulate nature.

COPPER

Seasonal variation of monthly average values of copper in the surface waters off the coast of Waltair during 1961 and 1962:

Monthly average copper content in the surface waters off the coast of Waltair showed a seasonal variation. Highest value of $19.5 \mu\text{g/l}$ occurred in November

and the lowest value of 5.8 $\mu\text{g/l}$ in April during 1961, thus showing a range of 13.7 $\mu\text{g/l}$. The average copper concentration during this year was 9.9 $\mu\text{g/l}$ (Fig. 3).

The values of copper showed a gradual decrease from 8.2 $\mu\text{g/l}$ in January to 5.8 $\mu\text{g/l}$ in April. The values remained steady from April to May. From May to August the values increased from 5.8 $\mu\text{g/l}$ to 12.4 $\mu\text{g/l}$. From August to September the values registered a slight fall. From September through November, copper concentration increased considerably and attained the maximum value (19.5 $\mu\text{g/l}$) in November for this year. The values decreased from November to December.

During 1962, the copper values decreased from January to March from 10.2 $\mu\text{g/l}$ to 6.4 $\mu\text{g/l}$. Thus, it may be noticed that the minimum copper concentration during 1962 was observed a month earlier than in 1961. From April, the values exhibited an increasing trend till October, when the highest value of 21 $\mu\text{g/l}$ was touched. Incidentally, the highest value also appeared a month earlier in 1962 than in 1961. From October through December, the values showed a fall. But for this slight shift in the time of occurrence of the maximum and minimum concentrations, there is a close similarity in the trend of variation of copper during both the years. The average concentration and the range in variation during 1962 is not far from the value obtained in 1961.

It may be noticed that the average value of copper during the August-November period in both the years is nearly double the average for the January-June period.

Seasonal variations of the copper content in the surface waters of the sea have been ascribed to two important factors. One is the phytoplankton activity (Atkins, 1953) and the other contribution from the land drainage by the influx of river waters (Riley, 1937; Prytherch, 1934; Galtsoff, 1943; Chow and Thompson, 1954).

The fall in the copper values from February through April (1961) and from February to March (1962) may be due to active absorption of this element by the phytoplankton during its peak period. This utilisation of copper by phytoplankton is also noticed during the month of September 1961.

The increase in the concentration of copper in the surface water may be due to considerable amount of local drainage consequent on heavy rainfall during April through November on this coast. The high values of copper during October-November in 1961 and September-October in 1962 may be ascribed to the low salinity river waters that are brought down from near the head of the Bay along this coast. It may be pointed out that there are large deposits of copper ore of about 300 km long in the Singhbhum district of Bihar in North India. According to Dunn and Day (1937) the ores consist mainly of chalcopyrite, an important ore of copper which constitutes about 90% of the deposits. The soils over this belt consist of copper, nickel, cobalt, etc. in the following quantities (Rao, 1964; Personal communication).

Copper	300 to 3000 p.p.m.
Nickel	20 to 80 p.p.m.
Cobalt	20 to 30 p.p.m.

It is possible that the tributaries of the rivers Mahanadi and Ganges while traversing these orogenic areas carry considerable quantities of copper and empty those waters

into the Bay of Bengal. These copper rich waters are borne by the Southerly current along the east coast during June-November period. Though the minor phytoplankton peak appeared during October-November in both the years no indication of utilisation of copper by the phytoplankton is noticeable, since during this period, surface waters contain much copper contributed from the influx of river waters.

Horizontal distribution of copper in the surface water in the different regions of the Bay of Bengal during March-April 1963 (Fig. 5);

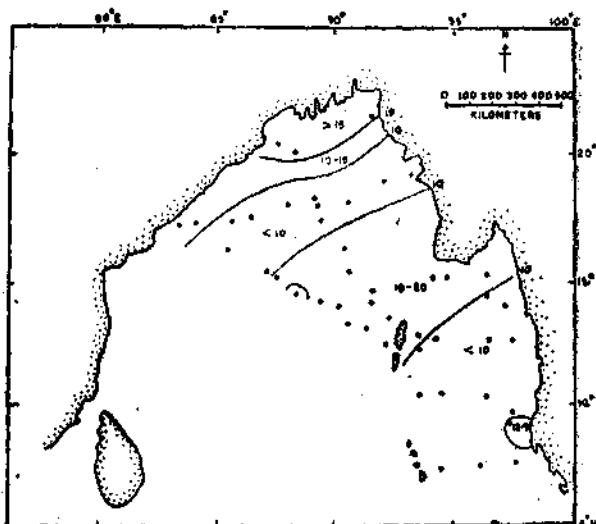


Fig. 5 Horizontal distribution of copper in $\mu\text{g/l}$ in surface waters in the Bay of Bengal.

Nicobar Sea : Copper content in the surface waters of this area varies from $12.9 \mu\text{g/l}$ to $4.4 \mu\text{g/l}$, thus showing a range of $8.5 \mu\text{g/l}$. The average value of copper for this region is $7.9 \mu\text{g/l}$. The values show an increase from the Nicobar Islands towards the Thai Coast.

Andaman Sea : The values of copper show a variation similar to that of the Nicobar Sea, from $4.0 \mu\text{g/l}$ to $12.8 \mu\text{g/l}$ showing a range of 8.8 and an average value of $7.3 \mu\text{g/l}$.

The values from the Thai Coast show a slight decrease westward towards the Andamans. But the values adjacent to the Andaman Islands are higher and they show a fall seaward towards the Southern part of the Burma Coast. Along this coast the values are rather very low.

The concentration gradually increases towards the South Burma Coast. In this region the values are high and are about $12.0 \mu\text{g/l}$.

In the waters near the North Burma Coast higher values upto $16.8 \mu\text{g/l}$ are encountered. The values exhibit a gradual fall away from the Burma Coast.

Rest of the Bay : The copper values increase towards the coast of Waltair as one proceeds from the Burmese Coast. The waters Southeast of the East Coast of India show on the average $6.0 \mu\text{g/l}$ and between $13.0 \mu\text{g/l}$ and $17.0 \mu\text{g/l}$ in the waters west of Andamans. The waters north of Andamans show on the average $10.0 \mu\text{g/l}$. The concentration of copper near the mouth of Hooghly is comparatively very high with values between $18.0 \mu\text{g/l}$ and $21.0 \mu\text{g/l}$.

Vertical distribution of copper in the Bay of Bengal during March-April 1963:

Data regarding the depth distribution of copper is available for one station in the Nicobar Sea, two stations in the Andaman Sea, one station off the Burma Coast and eleven stations in the rest of the Bay (Table 1). Though a detailed description of the vertical distribution of this element in the three regions on the eastern part of the Bay of Bengal is not possible with data from one or two stations only in each region, an attempt is made to point out the salient features of the trend in variation with depth in these areas.

Though stations 26 and 28 are grouped under two areas, the former in the Nicobar Sea and the latter in the Andaman Sea, they are indeed very close to each other and the copper distribution is very identical. At both the stations the values are high in the surface waters and fall with the depth. An interesting feature in the magnitude of fall is that at station 28 which is shallow it is seen that there is a difference of $6.8 \mu\text{g/l}$ between the surface value and bottom value at only 75 metres whereas at station 26, with a depth of 600 metres, the difference between the surface value of copper and the value at 600 metres is only $4.8 \mu\text{g/l}$. The vertical distribution of copper in the waters off the West Coast of Andamans is different from that on the East Coast. At two stations 75 and 76 which are situated in the vicinity of the West Coast of Andamans the values in the surface waters are high and showed a gradual increase with depth (though at station 76 a slight fall has been noticed from surface to 100 metres).

At station 32 in the Andaman Sea, the copper values show a decrease from surface to 100 metres and below this level the values exhibit an increase upto 1000 metres.

At station 51 off the coast of Burma, the values are low in the surface waters and increase with increasing depth.

In the rest of the Bay the general trend in the depth distribution of copper is that the values decrease from surface to 250-500 metres and thereafter register an increase upto 1000 metres. Again from 1000-2000 metres the values show a fall. The only value available at 2400 metres at station 80 shows an increase from the previous depth of 1770 metres. In general, it may be pointed out that the concentration of copper below 100 metres in this region is *ca.* $10 \mu\text{g/l}$ or less. But stations 60 and 61 both of them located at the head of the Bay show abnormal concentrations for the 50 and 250 metre depths. The values are 25.8 and $33.0 \mu\text{g/l}$ at 60 and $33.0 \mu\text{g/l}$ at 250 metres at station 61.

In general, the distribution of copper in the surface waters of the Bay of Bengal during this period reveals higher values near the coasts probably due to discharge from the land and lower values away from the coast. Highest values are encountered near the river mouths both on the coast of Burma and on the coast of India and these values are assumed to be due to contribution from river waters. The latitudinal variation of average values of copper in the Bay of Bengal reveals nearly uniform

values (8.0-8.9) from 5° to 20° N parallel, but the values between 20° and 22° N parallel are double with an average of 17.9 $\mu\text{g/l}$.

MANGANESE

Seasonal variation of the monthly average values of manganese in the surface waters off the coast of Waltair during 1961 and 1962 :

Manganese values in the surface waters off the Waltair Coast during 1961 (Fig. 3) showed a variation from 1.5 $\mu\text{g/l}$ to 17.0 $\mu\text{g/l}$, thus showing a range of 15.5 $\mu\text{g/l}$. The average value for 1961 was 5.3 $\mu\text{g/l}$.

The values showed a fall from January to April from 2.5 to 1.5 $\mu\text{g/l}$, and from thence a gradual increase in May and June, and more than 2 to 3 times during July and August. The maximum value of 17.0 $\mu\text{g/l}$ was recorded in August. From August to September there was considerable decrease in the value, the concentration being 3.8 $\mu\text{g/l}$. During October and November, the manganese values again showed an increase (from 6.8 to 9.5 $\mu\text{g/l}$) followed by a considerable fall to 2.3 $\mu\text{g/l}$ in December.

The trend in the variation during the year 1962 follows almost a similar sequence as was noticed in 1961. The values varied from 2.2 $\mu\text{g/l}$ in April to 13.0 $\mu\text{g/l}$ in August, with a range of 10.8 $\mu\text{g/l}$. The average value for 1962 was 5.9 $\mu\text{g/l}$. Thus, the range in variation and the average in concentration during 1962 are easily comparable to the range and average during 1961. The values showed an increase from October to November in 1961, whereas a fall was noticed for the same period during 1962.

The average concentration of manganese in the inshore waters of this coast seems to be higher in general than the single value of 2.5 $\mu\text{g/l}$, reported from Bhavnagar (North of Bombay) (Kappanna *et al.*, 1962). No details are available regarding the time of the year when this value was recorded by the authors. A comparison with manganese values reported from temperate waters by Thompson and Wilson (1937), Harvey (1947), Goldberg and Arrhenius (1958) would reveal that the concentration of manganese is definitely higher on this coast.

The average value for the pre-southwest monsoon period during January-May is low when compared to the value during the southwest monsoon period and afterwards (June-December). The values are 2.3 $\mu\text{g/l}$ and 3.0 $\mu\text{g/l}$ (1961), 3.9 $\mu\text{g/l}$ and 7.5 $\mu\text{g/l}$ (1962) in the respective periods. It is interesting to note that high values are recorded during the months July through November in both the years when the east coast also gets the maximum rainfall from the South west and the North east monsoons. Situated about 50 km north of Waltair, there is an area of large iron and manganese deposits. The type of manganese ore occurring in this area is called Wad. This ore contains nearly 20% of MnO_2 and a good amount of cobalt (Rao, 1956 Doctoral thesis). During the period of heavy rains, two small rivulets the Nagavali and Vamsadhara flow through these areas and perhaps drain quantities of manganese into the Bay of Bengal. The coastal current during this period is Southerly and hence we may expect the manganese rich waters to be brought down along the coast.

Another important tributary of the Godavari, the Pranhita drains the Brandara area in the Madhya Pradesh containing rich manganese deposits. Similarly, a tributary of the Krishna crosses several bands of Dharwarians containing manganiferous

deposits. Draining Khondalitic formations of the Eastern Ghats, some important tributaries join these rivers before they debauch the plains. The Khondalitic suite of rocks is characterised by mineral content, rich in Mn. Chemical analysis of fresh Khondalite showed MnO ranging from 0.06 to 0.36% (Krishnan, 1934).

It may be concluded that the large influx of river waters rich in manganese into the Bay would in general be responsible for the high average values of manganese observed during the southerly current period (from June to December).

William (1960) pointed out that the existence of dissolved fatty acids in microgram concentrations as well as other organic compounds can give rise to strong organic complexes with metal ions. For example, Laevestu and Thompson (1958) postulated that the markedly high iron abundance in coastal waters are due to the formation of ferric organo complexes. One may expect therefore that the dilute coastal waters of salinity 21‰ during this period contain a good amount of dissolved organic compounds carried by the river waters and brought down by the southerly current. These dissolved organic compounds must have acted as solubilizers of these trace elements and formed trace-metal organo-complexes. The humic substances of fresh waters and the yellow organic acids of Shapiro (1957), Gelbstoff of Kalle (1949) and 'water-Humus' of Skopinstev (1959) are considered to perform the same function of trace metal solubilizers (Hill, 1963). It would appear that the large amount of river waters emptied into the Bay and brought down on the East Coast during October-November period may be characterised by dissolved organic compounds which act as trace metal solubilizers (It may be of interest to point out here that the dissolved organic nitrogen values during October-November period during 1961 and 1962 showed higher values). The occurrence of increased concentration of dissolved organic compounds may perhaps be also one of the factors influencing the higher values of manganese in the sea water during the flood season.

Horizontal distribution of manganese in the Bay of Bengal during March-April 1963:

The horizontal distribution of manganese in the surface waters in different regions reveals certain interesting features (Fig. 6). The average values of manganese concentration are low at 4.6 $\mu\text{g/l}$ in the Nicobar Sea and increase in the waters north of it with values of 7.4 $\mu\text{g/l}$ in the Andaman Sea, 7.0 $\mu\text{g/l}$ in the waters off the coast of Burma, and 7.2 $\mu\text{g/l}$ in the rest of the Bay. Thus, it may be noticed that the values towards the mouth of the Bay (in the Nicobar Sea) are lower than the values at the head of the Bay. The range in variation of manganese values in the four areas also differs. In the Nicobar Sea, the values in surface waters vary from 2.2 to 10.0 $\mu\text{g/l}$ with a range of 7.8 $\mu\text{g/l}$; in the Andaman Sea from 3.1 to 15.0 $\mu\text{g/l}$ with a range of 11.9 $\mu\text{g/l}$; in the waters off the coast of Burma from 2.6 to 11.0 $\mu\text{g/l}$ with a range of 8.4 $\mu\text{g/l}$ and in the rest of the Bay from 3.0 to 17.0 $\mu\text{g/l}$ with a range of 14.0 $\mu\text{g/l}$. Thus, the highest range in variation of manganese has been recorded in the rest of the Bay.

In the Nicobar Sea, the values of manganese are seen to decrease towards the Thai Coast. The values at stations 18 and 28 which are very near the Thai and the Andaman Coasts respectively are low when compared to the offshore stations in this area. While the values off the Thai Coast are low, manganese concentrations increased in a northerly direction towards Burma.

The pattern of distribution of manganese in the rest of the Bay is rather interesting. The concentrations fall from the Burmese Coast towards the East Coast of India. A general increase in the values has been noticed in a south west direction

towards the Andaman Islands from the East Coast of India. The values of manganese North of Andamans towards the head of the Bay remain low between 4 and 6 $\mu\text{g/l}$. But at stations 86 and 87 situated very near the mouth of the Ganges, maximal

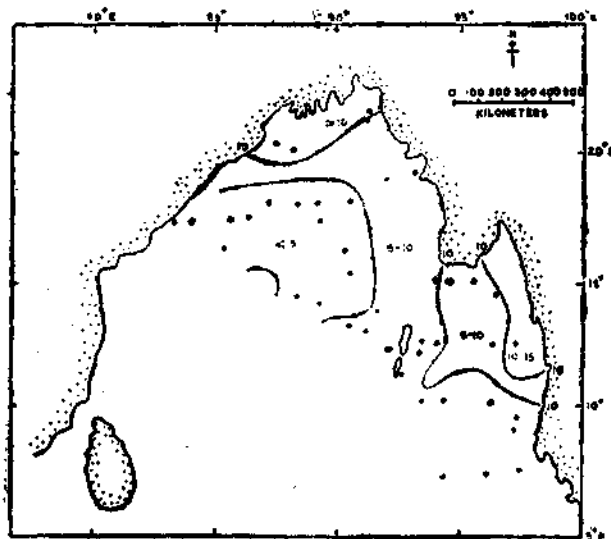


Fig. 6 Horizontal distribution of Manganese in $\mu\text{g/l}$ in surface waters in the Bay of Bengal.

concentration of manganese is recorded. The value is 17.0 $\mu\text{g/l}$ which is the highest value observed during this period of investigation. High values are also recorded at station 44 near Burma. These high values of manganese may be ascribed to the presence of considerable quantities of trace metal solubilizers received from the rivers in these areas.

Vertical distribution of manganese in the Bay of Bengal during March-April 1963:

The vertical distribution of manganese appears to present no significant variation in the different areas investigated (Table 2).

The general pattern of vertical distribution presents lower manganese values in the surface water. They gradually increase with depth and reach high values at about 1000 metres. The variation between the concentration of manganese in the surface water and at depths of 1000 metres is not more than 3 $\mu\text{g/l}$.

Data on manganese below 1000 metres is available only at two stations situated in the central Bay. The distribution below the 1000 metre level is almost identical at both the stations. The values exhibit a considerable fall by 5.1 $\mu\text{g/l}$ at station 80 (between 1025 and 2425 metres) and 5.0 $\mu\text{g/l}$ at station 84 (between 1020 and 2035 metres). There are two instances where the vertical distribution described above is not found. At station 26 near the east coast of Andamans, the manganese value in the surface water is high (10 $\mu\text{g/l}$). The concentration shows a decrease with depth

and attains 4.1 $\mu\text{g/l}$ at 600 metre level. At stations 67 and 75, both situated in the central Bay the values show a fall from surface upto 100 metres, but thereafter an increase with the depth has been noticed.

Latitudinal variation :

Average values of manganese in the surface water of the Bay of Bengal in the different latitudes shows an increase in a South to North direction, from 4.3 $\mu\text{g/l}$ between 5° - 10° N parallel to 6.1 $\mu\text{g/l}$ between 10° - 15° N parallel and from 6.2 $\mu\text{g/l}$ between 15° - 20° N to 9.9 $\mu\text{g/l}$ between 20° - 22° N parallel.

COBALT

Monthly average values of cobalt in the surface waters off the coast of Waltair during 1961-1962:

The monthly average values of cobalt in the surfacewaters off the Waltair Coast showed a slight seasonal variation both during 1961 and 1962 (Fig. 3). The values varied from 0.44 $\mu\text{g/l}$ in August to 0.28 $\mu\text{g/l}$ in March-April with a range of 0.16 $\mu\text{g/l}$ during 1961. During the year 1962, a variation from 0.38 $\mu\text{g/l}$ in July to 0.24 $\mu\text{g/l}$ in April with a range of 0.15 $\mu\text{g/l}$ was recorded. The average value of cobalt concentration during 1961 was 0.34 $\mu\text{g/l}$ whereas the average value for 1962 was 0.30 $\mu\text{g/l}$. Thus, it may be observed that the average concentration of cobalt in surface waters of the Waltair Coast does not show any appreciable difference between 1961 and 1962. The range in variation of this element during both the years was similar.

During 1961, the cobalt content in the surface water was similar in January and February. The values showed a fall from February to March and remained steady in April. During May and June also the values were steady showing only a variation of 0.02 $\mu\text{g/l}$. The cobalt content during July and August showed a considerable rise from the values in the preceding month and the values were 0.42 and 0.44 $\mu\text{g/l}$ respectively. From September onwards through November the cobalt concentration showed almost uniform values with a slight fall in December.

The trend in the variation of the average monthly values of cobalt during 1962 was almost identical with that of 1961. The cobalt content in February, January and February was steady and about 0.3 $\mu\text{g/l}$ and declined in March and April to 0.28 $\mu\text{g/l}$. The values were seen to increase from May through August to 0.44 $\mu\text{g/l}$. However, in August 1962 the value showed a slight fall during 1962 (0.32 $\mu\text{g/l}$). There was not much variation in the values between September and December.

High cobalt values in the surface waters off the Waltair Coast recorded in July-August 1961 and July 1962 during both the years of observation happen to be associated with the period in which the inshore waters of this area are characterised by a considerable quantity of drainage of the rain water from land through a number of storm water channels. It was pointed out earlier, the iron and manganese ore belt, are situated north of Waltair and the composition of the manganese ore 'Wad' shows that it contains a good amount of cobalt (Rao, 1956; Doctoral thesis). These orogenic areas are drained by small rivulets which empty into the Bay of Bengal during this period. It is possible that the increased concentration of cobalt during July-August may be due to contribution from these waters. Further, a comparison of the average value 0.31 $\mu\text{g/l}$ of cobalt for the January-June period with the

average value $0.37 \mu\text{g/l}$ for the July-December period in 1961 and $0.28 \mu\text{g/l}$ and $0.33 \mu\text{g/l}$ in 1962 for the respective periods would reveal that the average value for July-December period in both the years is higher than the former period. These high values are attributed to contribution from the waters of the rivers Mahanadi and Ganges which traverse copper bearing areas before they open into the Bay of Bengal. The copper belt in the Bihar area was shown to consist of mainly Chalcopyrites, Pyrite and Pyrrhotite. On analysis (Rao, 1964; Personal communication) both Chalcopyrite and Pyrite were shown to contain cobalt ranging from 0.02 to 0.6 % and 0.009 to 0.8 % respectively. Besides, the soils over the copper belt in the same area gave an analysis of cobalt concentrations between 20 and 30 p.p.m. The high average value of cobalt content in the surface water of this coast during July-December period may in general be attributed to contribution from river waters.

The decrease in the cobalt concentration during April in both the years which coincides with the period of maximum phytoplankton production on this coast may perhaps be attributed to utilisation of this element by the phytoplankton.

Distribution of cobalt in the surface water in the Bay of Bengal during March-April 1963:

Sea water samples for the estimation of cobalt could not be collected in the different regions and from different depths of the Bay of Bengal during the *ANTON BRUUN* Cruise in view of the difficulty in storing (by deep freezing) a large volume of 5 litres of water for a single estimation. It was only possible to collect a dozen samples from the surface in the region off the east coast of India, freeze them at -15°C and analyse later.

The cobalt values obtained from the surface water in the rest of the Bay are seen to vary between 0.22 and $0.32 \mu\text{g/l}$ with an average of $0.25 \mu\text{g/l}$. The surface distribution of cobalt during March-April shows that slightly higher values are observed near the coasts as compared to the oceanic waters. For example, at stations 67, 75, and 87 situated near the coasts, the cobalt concentrations are 0.27, 0.27 and $0.32 \mu\text{g/l}$ respectively and at stations 70, 74 and 80 situated in the deep waters the values are 0.22, 0.23 and $0.22 \mu\text{g/l}$ respectively.

REFERENCES

- ARMSTRONG, F. A. J. 1957. The Iron Content of Sea Water. *J. Mar. Biol. Assoc.*, **33** : 383.
- ATKINS, W. R. G. 1953. Seasonal Variation of Copper Content of Sea Water. *Ibid.*, **31** : 493-494.
- BARNES, H. 1959. *Apparatus and Methods of Oceanography, Part I : Chemical*, Interscience Publishers Inc., New York, N.Y.
- BLACK, W. A. P. and R. L. MITCHELL, 1952. Trace Elements in the Common Brown Algae and in Sea Water. *J. Mar. Biol. Assoc.*, **30** : 575-584.
- CHOW, T. J. and T. G. THOMPSON 1952. The Determination and Distribution of Copper in Sea Water. *J. Mar. Res.*, **11** : 124-138.
- COOPER, L. H. N. 1935. Iron in the Sea and in Marine Plankton. *Proc. Roy. Soc., B.*, **118** : 419-438.
- DUNN, J. A. and A. K. DAY, 1937. *Geol. Survey of India*, p. 89.
- GALTSOFF, P. S. 1943. Copper Content of Sea Water. *Ecology*, **24** : 263-265.

- GOLDBERG, E. D. 1952. Iron Assimilation by Marine Diatoms. *Biol. Bull.*, **102** : 242-248.
- 1954. Marine Geochemistry I. Chemical Scavengers of the Sea. *J. Geol.*, **62** : 249-265.
- 1961. Marine Geochemistry. *Annual review of physical chemistry*, **12** : 29-48.
- and G. O. S. ARRHENIUS 1958. Chemistry of Pacific Pelagic Sediments. *Geoch. et Cosmoch. Acta.*, **13** : 153-212.
- GRAN, H. H. 1933. Studies on the Biology and Chemistry of the Gulf of Maine. II : Distribution of Phytoplankton in August 1932. *Biol. Bull.*, **64** : 159-182.
- HARVEY, H. W. 1937. The Supply of Iron to Diatoms. *J. Mar. Biol. Assoc.*, **22** : 205-219.
- 1947. Manganese and the growth of Phytoplankton. *Ibid.*, **26** : 562.
- 1955. *The Chemistry and Fertility of Sea Water*. Cambridge Univ. Press., London.
- HILL, M. N. 1963. *The Sea*, Vol.2. The Composition of Sea Water Comparative and Descriptive Oceanography. Interscience Publishers, John Wiley and Sons, New York.
- ISHIBASHI, M., T. SHIGEMATSU, and Y. NAKAGAWA, 1951. Qualitative determination of Nickel and Cobalt in Sea Water. *Bull. Inst. Chem. Res.*, Kyoto, **26** : 68.
- KALLE, K. 1949. Fluoreszens und Gelbstoff in Bottnischen und Finnischen Meerbusen *Dent. Hydrogr.*, **2** : 117-124.
- KAPPANNA, A. N., G. T. GADRE, H. M. BHAVNAGARY and J. M. JOSHI 1962. Minor Constituents of Indian Sea Water. *Curr. Sci.*, **31** (7) : 273-274.
- KOROLEFF, F. 1947. Determination of Manganese in Natural Waters. *Acta. Chem. Scand.*, **1** : 503-506.
- KRISHNAN, M. S. 1934. Laterisation of Khondalities. *Rec. Geol. Sur. Ind.*, **63** : 395.
- KYLIN, A. 1945. The Nitrogen Sources and the Influence of Manganese on the Nitrogen Assimilation of *Ulva lactuca*. *Kgl. Fysiograf. Sällskap. Lund. Forh.*, **15** (4) : 27-35.
- LAEVASTU, T. and T. G. THOMPSON 1958. Soluble Iron in Coastal Waters. *J. Mar. Res.*, **16** : 192-198.
- LEWIS, G. J. and E. D. GOLDBERG. 1954. Iron in Marine Waters. *Ibid.*, **13** : 183-197.
- MALYUGA, D. P. 1945. Content of Copper, Nickel, Cobalt and Other Elements of the Iron Family in Native Waters. *Doklady. Akad. Nauk. USSR*, **48** : 113-116.
- NODDACK, I. and W. NODDACK, 1939. Die Häufigkeiten der Schwermetalle in Meerestieren. *Ark. Zool.*, **32A**, (4) : 1-35.
- PIRSON, A. 1937. *Z. Botan.*, **31** : 193-287.
- PRYTHERCH, H. F. 1934. The role of Copper in the Setting, metamorphosis, distribution of American oyster, *Ostrea virginica*. *Ecol. Monogr.*, **4** : 47-107.
- RAO J. S. R. K. 1956. Genesis of manganese ore deposits of Visakhapatnam and Srikakulam Districts of Andhra State, Doctorate Thesis, Andhra University, Waltair.
- RAO, K. K. 1964. Doctorate Thesis, Andhra University, Waltair.
- RILEY, G. A. 1937. The significance of the Mississippi River drainage for biological conditions in the northern Gulf of Mexico. *J. Mar. Res.*, **1** : 60-74.
- SEIWELL, G. E. 1935. Note on Iron Analysis of Atlantic Coastal Waters. *Ecology*, **16** : 663.
- SHAPIRO, J. 1957. Chemical and Biological Studies on the Yellow Organic acids of Lake Water. *Limnol. Oceanogr.*, **2** : 161-179.

- SKOPINTSEV, B. A. 1959. Organic Matter of Sea Water. *Preprints Intern. Oceanogr. Congress, A.A.A.S.*, 953-954.
- STRICKLAND, J. D. H. and T. R. PARSONS, 1960. A manual of Sea Water Analysis. *Bull. Fish. Res. Bd., Canada*, 125 : 135.
- THOMPSON, T. G. and R. W. BREMNER, 1935. The Occurrence of Iron in the Waters of the North-East Pacific Ocean. *J. Cons. Int. Explor. Mer.*, 10 : 39-47.
- , and LAEVASTU, T. 1960. Determination and Occurrence of Cobalt in Sea Water. *J. Mar. Res.*, 18: 189-193.
- , and T. L. WILSON, 1935. The Occurrence and Determination of Manganese in Sea Water. *J. Amer. Chem. Soc.*, 57 : 233.
- WILLIAMS, P. W. 1960. Organic Acids found in Pacific Ocean Waters. Thesis, University of California, La Jolla, California.

DISCUSSION

- T. N. V. PILLAI : It is a well known fact that the dissolved organic matters in the sea water do play the major role in keeping the trace elements in the sea water. Have you done any work to see in what forms these trace elements are present in the sea water?
- V. C. RAO : No please.
- B. L. K. SOMAYAJULU : Have your procedures taken care to see that all soluble part of Fe, Mn., etc. have been recorded in the analysis?
- V. C. RAO : The procedures adopted here for estimation of Fe, Mn, etc. take into account the total content of these elements.
- B. L. K. SOMAYAJULU : Several measurements exist in literature where enrichment of Pb, Be and other elements in large amounts. But when we looked into the radioactive isotopes Pb ²¹⁰, Be ⁷ of these elements we did not find any. Most probably enrichment of stable elements such as Pb, Be, etc. is from detrital fraction, but not from sea water.
- V. C. RAO : There is no data available on Pb and Be. So far as Iron, Copper, Manganese are concerned, there are a number of reports showing manifold concentration of these elements from sea water by different groups of organisms.
- K. C. PILLAI : I wonder whether you had any problem with contamination of trace metals from reagent chemicals used? I find some of the chemicals contribute high blank values. For example, Periodate gives high Mn, and Ammonia gives high Zinc value.
- V. C. RAO : Whenever high reagent blank values were obtained, a fresh lot of chemical was used.
- N. V. N. DURGA PRASAD RAO : In view of the major rivers debouching into the Bay of Bengal, draining through a variety of geological formations compared to the Mahanadi River, do you think that the Singbhum copper ores form the source of copper in the Bay of Bengal?
- V. C. RAO : Many other copper ore bearing areas also may be contributing to this.
- N. V. N. DURGA PRASAD RAO : As the particulate matter has not been separated from the water analysed for the trace elements, the vertical variations in the distribution of trace elements may as well be due to the difference in the content (vertical) of particulate matter and may not represent the actual variation of these elements in the sea water.
- V. C. RAO : The sea water samples were filtered through a Prefilter Pad (Millipore Corporation, U.S.A.).
- R. VISWANATHAN : The suggestion that trace elements originating from river run off are efficiently utilized by phytoplankton assumes that : i. either there is no precipitation *en route* and/or, ii. the trace elements are easily brought to surface for utilization by phytoplankton. This ignores differences in physical chemistry of trace elements in sea water.

- V.C.RAO : In spite of the occurrence of a minor phytoplankton bloom in November on the Waltair Coast, the high trace element concentration in surface water indicates positive contribution from river waters. One would expect some degree of precipitation *en route*, but it is possible that the high concentration of dissolved organic matter might have helped to keep the trace elements in a soluble state.
- R. VISWANATHAN : Regarding particulate Carbon and dissolved organic Carbon, extensive surveys have been carried out by Menzel and Ryther in the Arabian Sea. To this extent, dissolved organic matter estimations (reported in Abstract) cannot be considered 'unique'.