

## A STUDY OF FLUORIDE, CALCIUM AND MAGNESIUM IN THE NORTHERN INDIAN OCEAN

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### ABSTRACT

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Estimation of fluoride in the Northern Indian Ocean gives an average concentration of  $1.31 \pm 0.01$  mg/l and a F/Cl ratio of  $(6.84 \pm 0.01) \cdot 10^{-5}$ . The Ca/Cl ratio in the area is  $0.02229 \pm 0.000005$  with an average calcium concentration of  $432 \pm 5$  mg/l. In the Bay of Bengal this ratio is influenced by river runoff while in the Arabian Sea the outflow from the Red Sea increases the ratio. The Mg/Cl ratio is observed to be  $0.06631 \pm 0.00003$  with an average magnesium concentration of  $1281 \pm 14$  mg/l. Neither the river runoff nor the Red Sea outflow has any influence on this ratio. Similarities or differences of these values spatially and with reference to literature data are discussed.

### INTRODUCTION

A large volume of chemical oceanographic data has been collected during the International Indian Ocean Expedition (IIOE), 1960–65, and a number of publications on the nutrients and oxygen and their spatial and temporal variations have appeared. Most of these have been issued in the form of collected reprints by UNESCO. Subsequent cruises to the Indian Ocean region followed mostly the same pattern of data collection. In assessing the literature and the records available from data centres it was found that few observations had been made of the concentrations of the major ions of the area.

Calcium, magnesium and fluoride are generally considered to be major ions in the oceans. Being conservative or semi-conservative properties of seawater, their concentrations or their relations with chlorinity may be useful in delineating the characteristics of different water bodies.

The northern part of the Indian Ocean is an area influenced by a large volume of river runoff which can be expected to modify significantly the characteristics of the upper layers in the Bay of Bengal and the Arabian Sea. The present report is a study of fluoride, calcium and magnesium concen-

trations, and their behaviours vis-à-vis chlorinity in the area, from observations carried out during a cruise of I.N.S. "Darshak" in March–April 1975.

#### MATERIAL AND METHODS

Samples were collected from standard hydrographic casts, at stations in Fig.1, using transparent TPN samplers (Hydro Bios, Kiel, F.R.G.) and stored in well-cleaned sealed polythene bottles. At each station samples were so collected as to cover the entire water column and analyses for all the elements were carried out several weeks later in the shore laboratory.

*Fluoride* was analysed by applying the lanthanum-alizarin complexone method of Greenhalgh and Riley (1961), after filtering the samples through Whatman No.1 filter papers, using a spectrophotometer.

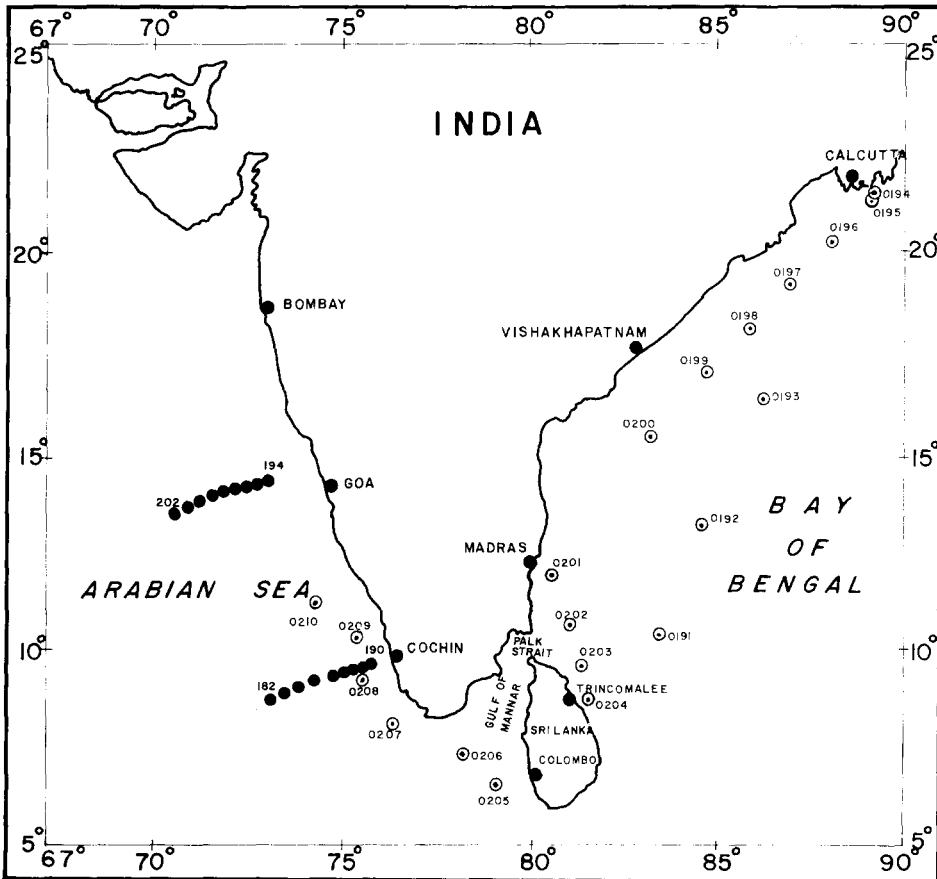


Fig.1. Network of observation stations.  $\odot$ , I.N.S. "Darshak" 1975;  $\bullet$ , R. V. "Meteor" 1964–65.

*Calcium* was determined according to the method of Culkin and Cox (1966) titrating the samples to the photometric end points with EGTA using Zincon Zn-EGTA indicator.

*Magnesium* was determined by the substitution method. Applying the method of Culkin and Cox (1966) samples were titrated complexometrically for Ca + Mg + Sr to the photometric end points against EDTA using Eriochrome Black T as indicator. Values for calcium were subtracted to obtain the magnesium concentrations.

*Strontium* was not taken into consideration in the calculations as it occurs in very low concentrations compared with calcium and magnesium [cf.,  $\text{Sr}^{2+}$  7.9 mg/kg,  $\text{Ca}^{2+}$  412.1 mg/kg,  $\text{Mg}^{2+}$  1290 mg/kg in a seawater of 35‰ salinity (Wilson, 1975)]. Sugawara and Kawasaki (1958) reported a strontium/chlorinity ratio of 0.000445 for the Indian Ocean while Turekian and Schutz (1965) and Culkin and Cox (1966) observed the same ratio as 0.000407 and 0.0004, respectively, in the same water body. Considering the wide differences in the concentrations of the alkaline-earth metals in seawater we decided to leave strontium out of our calculations, assuming that it would not affect the conclusions, at least at a first approximation. Moreover, a simple and suitable accurate analytical method for the determination of strontium in seawater is yet to be developed (Wilson, 1975).

A total of 275 samples from 20 stations were run for all the constituents. The precision of the analyses with the instruments and reagents at our disposal was determined from repeat analyses of several samples. The coefficients of variation are:  $\pm 0.8\%$  for fluoride,  $\pm 0.38\%$  for calcium and  $\pm 0.27\%$  for magnesium.

## RESULTS AND DISCUSSION

### *Fluoride*

Fluoride is generally considered to be a major component of seawater, being present in the oceans at a concentration of about 1.4 mg/l and bearing a ratio of approximately  $7 \cdot 10^{-5}$  to chlorinity. Recently it has been suggested (Brewer, 1975) that this lies on the borderline between major and minor constituents of seawater. It is currently a matter of some debate as to whether fluoride is a conservative component or is regulated by geochemical activities in the oceans (Greenhalgh and Riley, 1963; Riley, 1965; Brewer et al., 1970; Bowers, 1971; Kester, 1971; Warner, 1971; Bowers et al., 1973). Kullenberg and Sen Gupta (1973) observed that fluoride in the marine environment is regulated by evaporation, precipitation, settling particles, and accumulation as apatite, depending on the pH of the seawater. Moreover, variations in the fluoride concentration occur almost regularly in periodic anoxic basins. All these processes would naturally affect the F/Cl ratio in the sea. Therefore, we feel that it is more appropriate to describe fluoride as a semi-conservative rather than a fully conservative component of seawater.

Most of these conclusions on the properties of fluoride in seawater were drawn from studies elsewhere, in oceanic and semi-enclosed basins other than the Indian Ocean region. It was only during the International Indian Ocean Expedition 1960–65 that some measurements of fluoride concentrations were carried out during the cruises of R.V. "Meteor" to the Northwestern Indian Ocean (Dietrich et al., 1967) and only a part of these data has been published (Grasshoff, 1966). Greenhalgh and Riley (1963) carried out some measurements of fluoride concentrations in samples from the Indian Ocean in their global study of the F/Cl ratio in the seas. For all practical purposes it appears that ours is the first report of a somewhat more comprehensive study of fluoride and its relation to chlorinity in at least a part of the Indian Ocean.

To analyse the data we have divided the area of study into three regions: (a) Bay of Bengal, (b) Gulf of Mannar, and (c) Arabian Sea, and concentrated the detailed study only on the Bay of Bengal, since the major portion of the data was confined to this region.

The Bay of Bengal is an area of positive water balance. The average annual excess of precipitation over evaporation is about  $1500 \text{ km}^3$  (Venkateswaran, 1956) and about an equal amount is added by the rivers draining into it from India (Chopra, 1951). A similar amount can be expected to be added by the rivers of Bangladesh and Burma. The area of the Bay is  $2172 \cdot 10^3 \text{ km}^2$  (Hunt and Groves, 1965). This gives an annual dilution of 5.5% for the upper 25 metres, which can be assumed as the maximum depth of riverine influence in the Bay of Bengal (Dr. V. V. R. Varadachari, personal communication). This, of course, is a very rough assumption considering the large area of the Bay. The global average value of fluoride in river water is fairly well-defined at 0.1–0.2 mg/l (Livingstone, 1963) and the corresponding F/Cl ratios would be fairly high because of low chlorinity values ( $\sim 2 \cdot 10^{-2}$  — Dr. J. M. Bewers, personal communication). It has been observed (Kullenberg and Sen Gupta, 1973) that fluoride is removed by settling particles when river water meets the sea. The same authors observed a fluoride loss due to evaporation. These factors combined with the dilution factor may be the reason for the lower average of fluoride values in the group of stations nearer to the coast (stations 194–204) than those further offshore (stations 191–193) (Fig.2).

The stations have been grouped together and averaged in order to reduce the number of values and to present a general picture of the region as the vertical profiles of the parameters are similar at each station. The interesting features which can be observed in Fig.2 are: maxima of fluoride at the thermocline ( $\sim 75 \text{ m}$ ) due to the accumulation of particulate matter and the gradual decrease of fluoride with decreasing oxygen concentrations, maintaining an almost constant value at the oxygen minimum. A minimum of fluoride is also observed at about 1000 m, which is the depth of the maximum oxidation intensity in the Indian Ocean (Sen Gupta et al., 1976). Below 1000 m fluoride increases with increasing oxygen concentration. It has been observed that fluoride can be removed in the presence of low oxygen which is redissolved when oxygen concentrations increase (Kullenberg

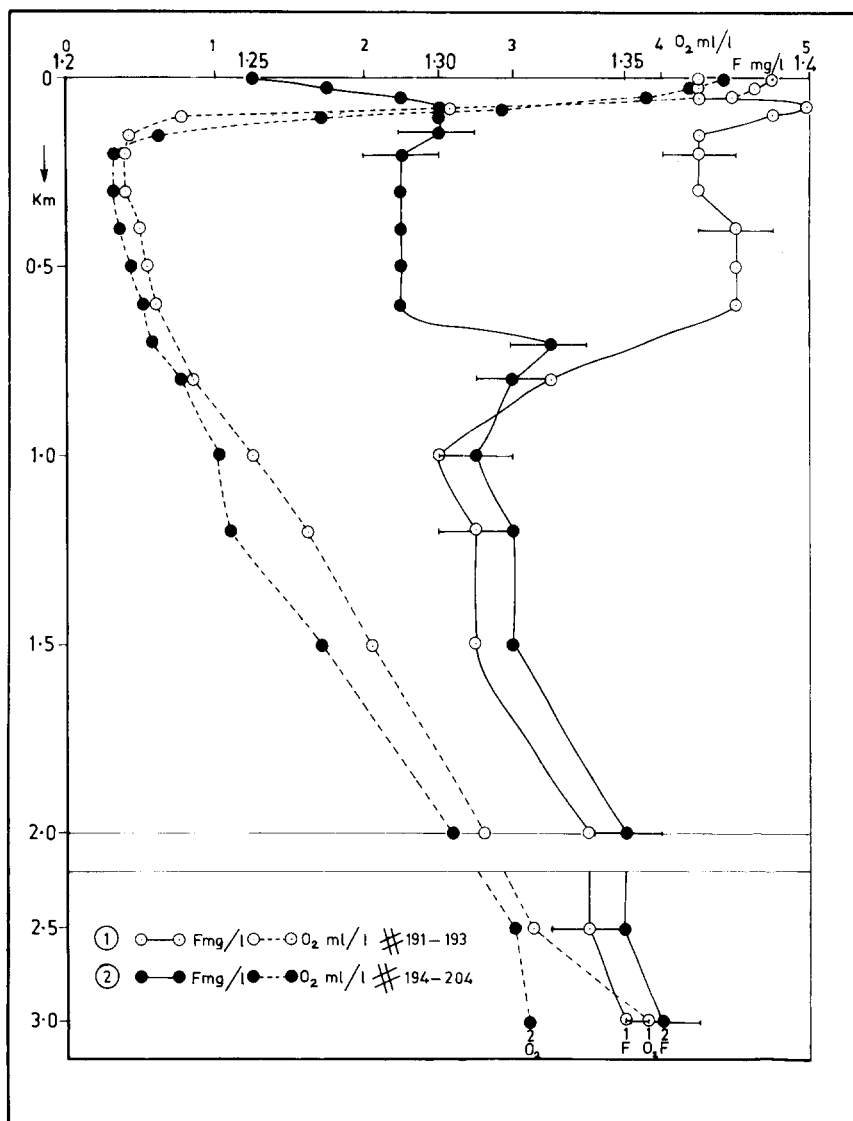


Fig. 2. Depth profiles of average values of fluoride (mg/l) and oxygen (ml/l) along two sections in the Bay of Bengal. Bars indicate range of error (0.8%).

and Sen Gupta, 1973). To check the validity of this assumption F, Cl‰ and F/Cl values are presented in Table I. It can be seen that Cl‰ values at the depth range of low oxygen, i.e., 150–600 m, do not differ significantly, ruling out the effect of the water masses on the ratio. It is very probable that this is the effect of some chemical process or maybe of the cumulative error in analyses. This appears to be one of the probable reasons for the vertical variations of fluoride in the Bay of Bengal.

TABLE I

Concentrations and fluoride/chlorinity ratios at different depths

Depth (m)	Stations 191—193			Stations 194—204		
	Cl(‰)	F (mg/l)	(F/Cl) · 10 <sup>-5</sup>	Cl(‰)	F (mg/l)	(F/Cl) · 10
1	18.61	1.36	7.31	18.20	1.25	6.87
25	18.90	1.36	7.20	18.80	1.27	6.76
50	18.97	1.36	7.17	19.08	1.29	6.76
75	19.05	1.40	7.35	19.19	1.30	6.77
100	19.24	1.39	7.22	19.32	1.30	6.77
150	19.35	1.37	7.08	19.35	1.30	6.72
200	19.40	1.37	7.06	19.43	1.29	6.64
300	19.50	1.37	7.03	19.52	1.29	6.61
400	19.44	1.38	7.10	19.54	1.29	6.60
500	19.44	1.38	7.10	19.52	1.29	6.61
600	19.49	1.38	7.08	19.52	1.29	6.61
700	—	—	—	19.50	1.33	6.82
800	19.47	1.33	6.83	19.50	1.32	6.77
1000	19.47	1.30	6.68	19.46	1.31	6.73
1200	19.47	1.31	6.73	19.47	1.32	6.78
1500	19.42	1.31	6.75	19.46	1.32	6.78
2000	19.37	1.34	6.92	19.42	1.35	6.95
2500	19.38	1.34	6.91	19.39	1.35	6.96
3000	19.30	1.35	6.99	19.35	1.36	7.03

The Gulf of Mannar is a transitional zone between the Arabian Sea and the Indian Ocean proper. It is connected with the Bay of Bengal through the shallow sill of the Palk Strait (Fig.1). The Arabian Sea is an area of negative water balance, annual excess of evaporation over precipitation and runoff varying between 7 and 10 km<sup>3</sup> (Venkateswaran, 1956). We have divided the water masses of the areas studied according to their hydrographic characters (Rochford, 1964) as, an upper well-mixed layer (0—100 m), a layer in which oxidation of organic matter takes place (100—1000 m), the North Indian Ocean intermediate and deep waters (1000—2000 m) and Antarctic bottom water (below 2000 m). Average values of fluoride and the F/Cl ratios for the water masses in the regions are presented in Table II.

The low values in the upper layers of the Bay of Bengal are due to dilution. This effect is not very pronounced in the other two areas. Waters at the 100—1000 m levels in the Gulf of Mannar and the Arabian Sea are influenced by the outflows from the Red Sea and the Persian Gulf which have comparatively high concentrations of fluoride (Dietrich et al., 1967). Between 1000 and 2000 m, waters in the Northern Indian Ocean are mostly intermediate and deep waters originating near its equatorial region (Ivanenkov

TABLE II

Averages of fluoride concentrations and fluoride/chlorinity ratios at different depth intervals ( $n$  = number of samples)

Area	0-100 m		100-1000 m		1000-2000 m		2000-3000 m					
	$n$	F (mg/l)	$n$	F (mg/l)	$n$	F (mg/l)	$n$	F (mg/l)				
		(F/Cl) $\cdot 10^{-5}$		(F/Cl) $\cdot 10^{-5}$		(F/Cl) $\cdot 10^{-5}$		(F/Cl) $\cdot 10^{-5}$				
Bay of Bengal	59	1.31	6.68	104	1.32	6.77	28	1.32	6.78	6	1.33	6.87
Gulf of Mannar	8	1.33	6.90	18	1.35	6.96	5	1.33	6.84	—	—	—
Arabian Sea	19	1.34	6.91	19	1.37	7.02	—	—	—	—	—	—

and Gubin, 1960). This is evidenced from almost similar values of fluoride and the F/Cl ratios at this layer in the regions.

The averages of F (mg/l) and F/Cl with standard errors for the whole water mass in the three areas are presented in Table III.

Using the fluoride determinations made on board R.V. "Meteor", from stations in the vicinity of our stations in the Gulf of Mannar and the Arabian Sea (Fig.1), we calculate average fluoride values as 1.19 mg/l and F/Cl as

TABLE III

Overall averages with standard errors of fluoride conc. and fluoride/chlorinity ratio

Area	F(mg/l)	(F/Cl) · 10 <sup>-5</sup>
	average ± std. error	average ± std. error
Bay of Bengal	1.31 ± 0.01	6.81 ± 0.02
Gulf of Mannar	1.34 ± 0.01	6.92 ± 0.04
Arabian Sea	1.36 ± 0.01	6.97 ± 0.03

6.13. These values are rather low compared to our observations in the same area and the values on record from other regions. The analyses on board "Meteor" were carried out using a multi-channel autoanalyser system while we did ours manually, the colorimetric method being common to both procedures. We have no explanation for this discrepancy.

The overall average is 1.31 ± 0.01 for fluoride and 6.84 ± 0.01 for the F/Cl ratio. Vertical variations were noted at all the stations but no abnormal values were recorded.

From observations of fluoride concentrations from 0–20‰ chlorinity, Kullenberg and Sen Gupta (1973) deduced the following relation between the two parameters:

$$F(\text{mg/l}) = 0.166 + \text{Cl}^2 / (36.7 + 0.755 \text{Cl}^2) \quad (1)$$

To test our values we pooled the chlorinity values into averages in the ranges 18.5–19.0, 19.0–19.5, and 19.5–20.0, calculating the corresponding averages of fluoride concentrations. The values when fitted to eq. 1 gave the results in Table IV.

Except in the chlorinity range 18.5–19.0 our values fit almost perfectly with eq. 1. The effect of dilution by river runoff and the resulting removal of fluoride particles from the water column should always be felt most



TABLE IV

Observed and calculated values of fluoride conc. at different chlorinity ranges

Cl(‰) range	Cl(‰) average	F (mg/l) observed	F (mg/l) calculated	F <sub>calc</sub> - F <sub>obs</sub> (mg/l)
18.50-19.00	18.78	1.24	1.33	0.09
19.01-19.50	19.36	1.32	1.34	0.02
19.51-20.00	19.58	1.33	1.34	0.01

intensively in inshore waters. But these factors have already been taken into account while deducing eq. 1, where the river  $F^-$  mean has been calculated as 0.166 mg/l. This calculation was based on the  $F^-$  values in the rivers draining into the Baltic Sea. The closeness of  $F_{calc}$  and  $F_{obs}$  in the other two salinity ranges leads us to suggest that the Indian Ocean rivers have much lower  $F^-$  content than that used in eq. 1.

### Calcium

Measurements of calcium concentrations in the waters of the Indian Ocean are few and far between. We, therefore, did not find many data in the literature with which to compare our results. Data on calcium from the Arabian Sea were collected on board R.V. "Meteor" during the IIOE and we have compared our data with these, wherever applicable.

The overall average calcium/chlorinity ratio in the areas sampled is 0.02229 with a standard error of  $\pm 0.000005$ . This is higher than the ratios reported from other regions. Lyakhin (1971) reported a Ca/Cl ratio of 0.02155 in the western part of the tropical Atlantic and an average Ca/Cl ratio of 0.02115 was obtained in the deep waters of the Antarctic Ocean by Tsunogai et al. (1971). Ca/Cl ratios of 0.02126 and 0.02128 were reported for all the oceans by Culkin and Cox (1966) and Riley and Tongudai (1967), respectively. The high Ca/Cl ratio obtained by us may be explained in the following way:

The mean salinity of the rivers of the world appears to be about 100 mg/l and their mean Ca/Cl ratio is 6.3 (Hutchinson, 1957). The annual dilution in the upper 25 metres of the Bay of Bengal is 5.5%. Seawater at 35‰ salinity contains 413 mg/l calcium (Culkin, 1965). Mixing of 5.5% of river water with 94.5% of seawater would result in a calcium concentration of 409 mg/l and a Ca/Cl ratio of 0.0223. Calcium concentration of 414 mg/l on average with a Ca/Cl ratio of 0.02245 can be recorded from our data from the surface waters of the Bay of Bengal. Therefore, the higher Ca/Cl ratio in the

Bay of Bengal may be caused by river runoff. Dilution effects of the rivers are very seasonal and are hardly perceptible throughout the year. There may be other factors as well. Considering the limitations of the calculation of the dilution factor, we may also presume this as due to the systematic error in the analyses and calculations.

From our data we obtained an almost identical value of 0.02242 with an average calcium concentration of 428 mg/l from the Gulf of Mannar and the Arabian Sea. "Meteor" values from stations in the vicinity of our observation stations in the Arabian Sea give an average Ca/Cl ratio of 0.02214 at an average calcium concentration of 431 mg/l. Waters at an intermediate layer in the Arabian Sea are considerably influenced by outflows from the Red Sea and the Persian Gulf. The former has an average calcium concentration of 456 mg/l (Dietrich et al., 1967) and an equal concentration can be expected to be contributed by the latter.

The depth profiles of the averages of calcium/chlorinity ratios in the Bay of Bengal and the Gulf of Mannar together with the Arabian Sea are plotted separately in Fig.3 in order to study their variations in the two areas. It can be noted from Fig.3 that the water masses in the Bay of Bengal can be broadly divided into three layers with respect to their Ca/Cl ratios. In the upper 50 m of the surface layer the Ca/Cl ratio decreases. Below this depth to about 200 m it remains approximately unchanged (0.02226 at 50 m to 0.02223 at 200 m).

An examination of Fig.4 reveals that the absolute calcium concentration increases gradually with depth to about 300 m together with increasing chlorinity. The decrease in the calcium/chlorinity ratio is the result of the increasing chlorinity in this layer relative to calcium. It has been observed (Koczy, 1956) that in the upper few hundred metres in the oceans optimal conditions for lime-secreting organisms seem to exist, but exceptions have also been observed (Sen Gupta and Pylee, 1968). Koczy's observation may be a contributing factor to the decrease in Ca/Cl ratio in the upper water column.

In the intermediate layer (200 m—1000 m) the calcium/chlorinity ratio remains essentially constant (0.02223 at 200 m to 0.02225 at 1000 m). In the deep and bottom layers (1000 m to 3000 m) the ratio gradually increases with a maximum value of 0.02247 at about 3000 m. This must be the effect of the dissolution of calcium carbonate at depths.

The depth profiles of calcium and Ca/Cl ratios in the Gulf of Mannar and the Arabian Sea are almost similar to those in the Bay of Bengal. The values, in general, are of a higher order in curves 2 in Figs.3 and 4 than those in curves 1. A maximum in calcium concentration at 800 m can be noted from curve 2 in Fig.4. This is obviously the effect of the Red Sea water which is known to find its own density level at about this depth in the Arabian Sea (Rochford, 1964). There is no increase, however, in the Ca/Cl ratio at this depth because of the higher salinity of the Red Sea water.

It is seen from Fig.3 that the Ca/Cl ratios at the surface (~1 m) are almost

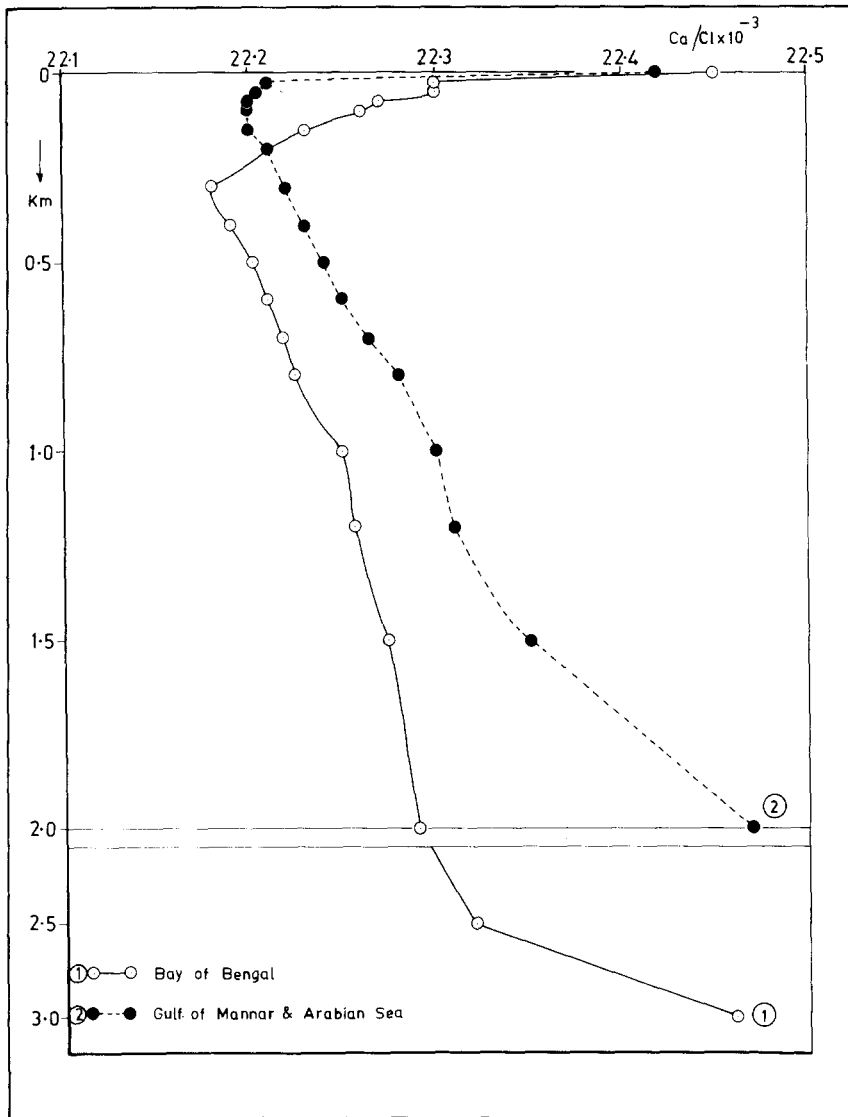


Fig.3. Depth profiles of average values of calcium/chlorinity ratio in the area of observations.

equal to those at the deepest sampling levels. Sillén (1961) suggested that surface water in the sea is saturated or super-saturated with respect to calcium carbonate. This factor affects the  $\text{Ca}/\text{Cl}$  ratio in the surface water. The deeper water is in a state of under-saturation with respect to calcium carbonate as a result of which more of it is dissolved from bottom sediments. In the intermediate water mass the  $\text{Ca}/\text{Cl}$  ratio is lower than those in the surface and the deep waters. Due to the degradation of organic matter,

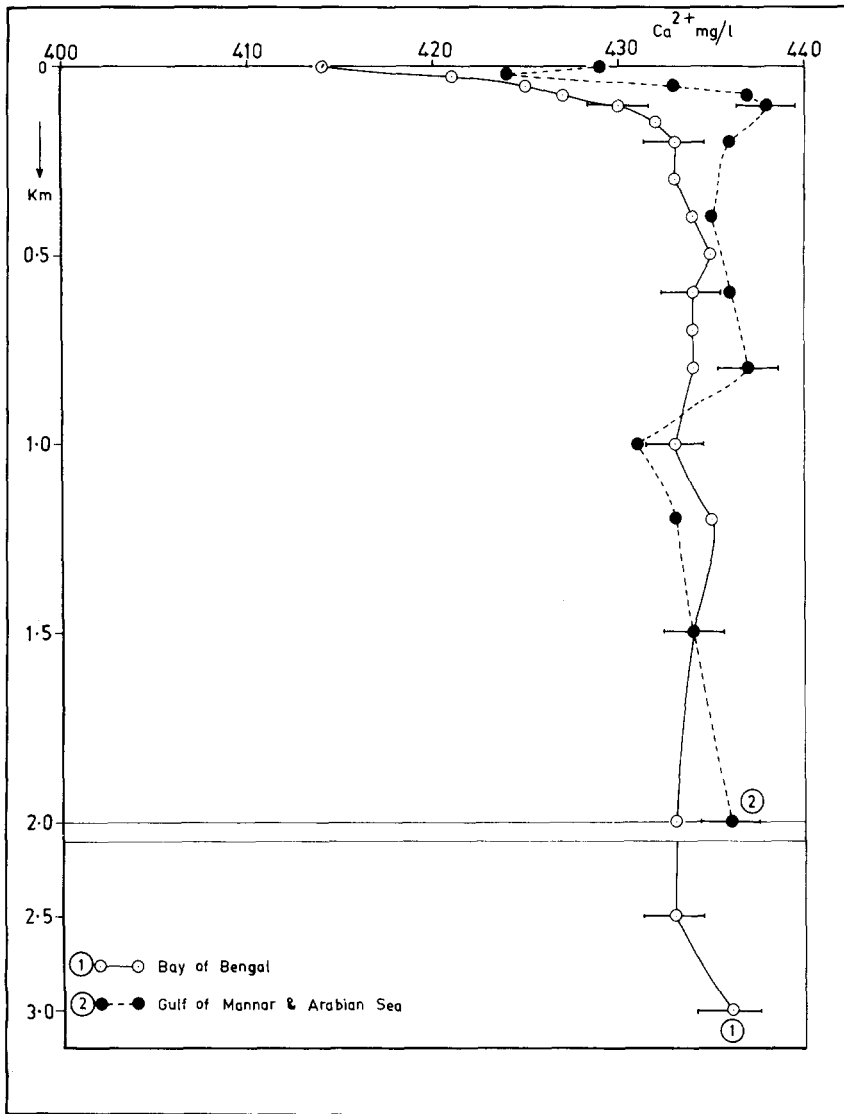


Fig.4. Depth profiles of average values of calcium concentration (mg/l) in the area of observations. Bars indicate range of error (0.38%).

calcium is released in this layer, as can be seen in the increasing concentration in Fig.4. However, the increasing chlorinity of the water inhibits the increase in the Ca/Cl ratio.

### *Magnesium*

Magnesium is the second most abundant cation in seawater, being about

0.05 *M* at 35‰ salinity. It does not appear to take part in the biological cycle and as such can be treated as a conservative element in seawater. Its ratio to chlorinity should, therefore, be more or less constant except in nearshore areas where fresh water modifies the relationship between these ions.

The magnesium/chlorinity ratio has been studied quite extensively in all the oceans except the Indian. Recent values for Mg/Cl ratio are 0.06688 for the tropical Atlantic (Lyakhin, 1971), 0.06676 for the NW Pacific (Tsunogai et al., 1968), 0.06667 (Riley and Tongudai, 1967) and 0.06692 (Culkin and Cox, 1966) for all the oceans. From our data we have examined the same relation in the Northern Indian Ocean.

From our uncorrected data, as obtained by the procedure outlined under Material and Methods, we calculated an overall average for Mg/Cl ratio of  $0.06764 \pm 0.00003$ . It has been suggested by Carpenter and Manella (1973) that the titration end-point in the method of Culkin and Cox (1966), which we applied for the titration of the total alkaline-earth metals in our samples, introduces a systematic overestimate of about 1% in the results. Both the concentration of strontium and its ratio to chlorinity are about 0.6% of the same properties of magnesium in seawater of 35‰ salinity (Wilson, 1975). We, therefore, reduced our values by 1.6% as we thought that would result in at least a fair first approximation of the magnesium concentrations and the Mg/Cl ratios. Our data, thus corrected, result in an overall average Mg/Cl ratio of  $0.06631 \pm 0.00003$ . The standard error, being only 0.05%, may be eliminated considering that the values for the ratio have been corrected by 1.6%. This compares quite well with the values of  $0.06626 \pm 0.00003$  of Carpenter and Manella (1973). The values of Riley and Tongudai (1967) and Culkin and Cox (1966), when corrected by the factors suggested by Carpenter and Manella (1973), result in Mg/Cl ratios of 0.06628 and 0.06625 respectively. The closeness of our corrected ratio with these confirms the similarities in the Mg/Cl ratios in all the oceans.

The depth profiles of magnesium/chlorinity ratios are shown in Fig.5. Tsunogai et al. (1968) found a constant magnesium/chlorinity ratio at all the depths in the Western North Pacific. Lyakhin (1971) also reported that the magnesium/chlorinity ratio was very constant both in deep and surface water samples in the western part of the tropical Atlantic. In our study we find that the magnesium/chlorinity ratio shows a gradual decrease with depth in the upper layers (0—ca. 200 m) whereas below this depth the variation, although slight (0.06659 at 600 m to 0.06631 at 3000 m), does not lie within the experimental error. Culkin and Cox (1966) reported a slight vertical increase of the ratio while Carpenter and Manella (1973) showed the reverse. We believe that this is the effect of the geographical variations in the characteristics of the water masses.

In Fig.6 the depth profiles of magnesium concentrations are plotted. It can be seen that the points are distributed over a wider range as compared to Fig.4 for calcium. This is because magnesium shows a wider vertical variation

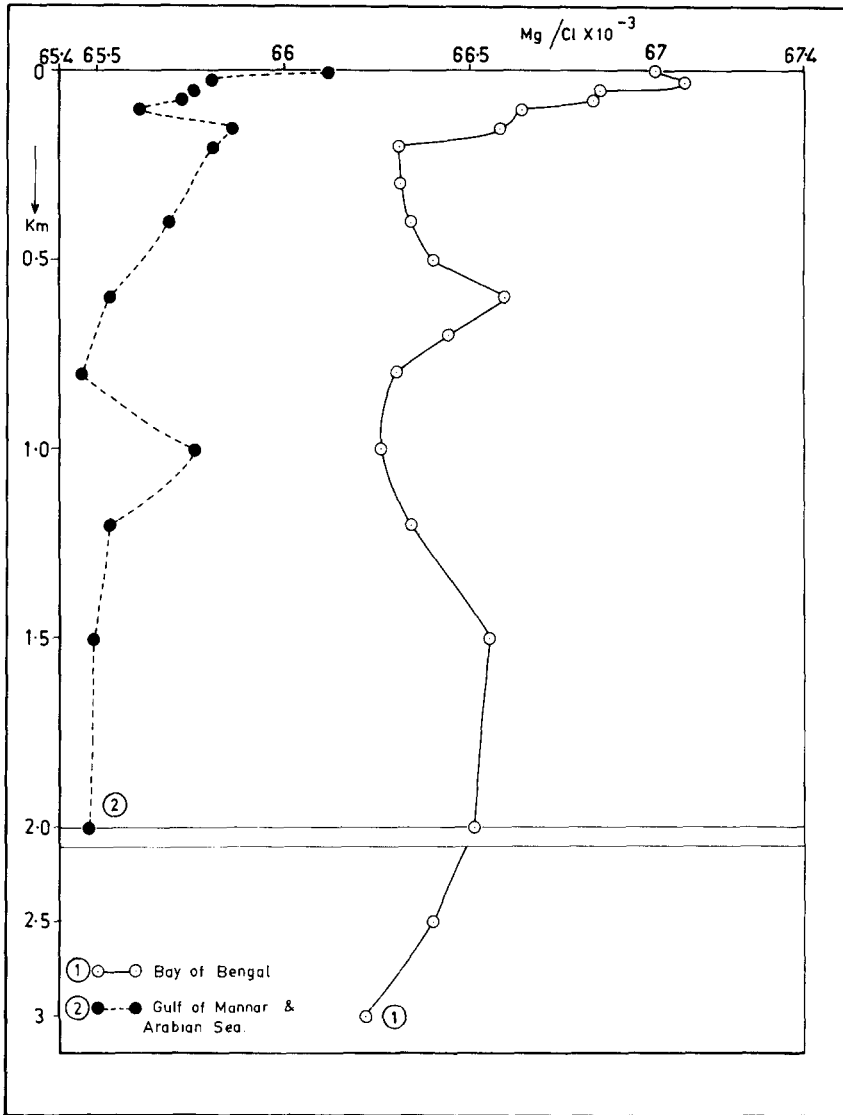


Fig.5. Depth profiles of average values of magnesium/chlorinity ratio in the area of observations.

than calcium. The range of variation in our magnesium values agrees well with similar characteristics in the values of Carpenter and Manella (1973). In both the areas of our observations the concentration of magnesium increases with depth reaching maxima at about 500 m in the Bay of Bengal and at about 150 m in the Arabian Sea and the Gulf of Mannar. Both the maxima appear at depths of oxygen minima. They may be due to the accumulation of

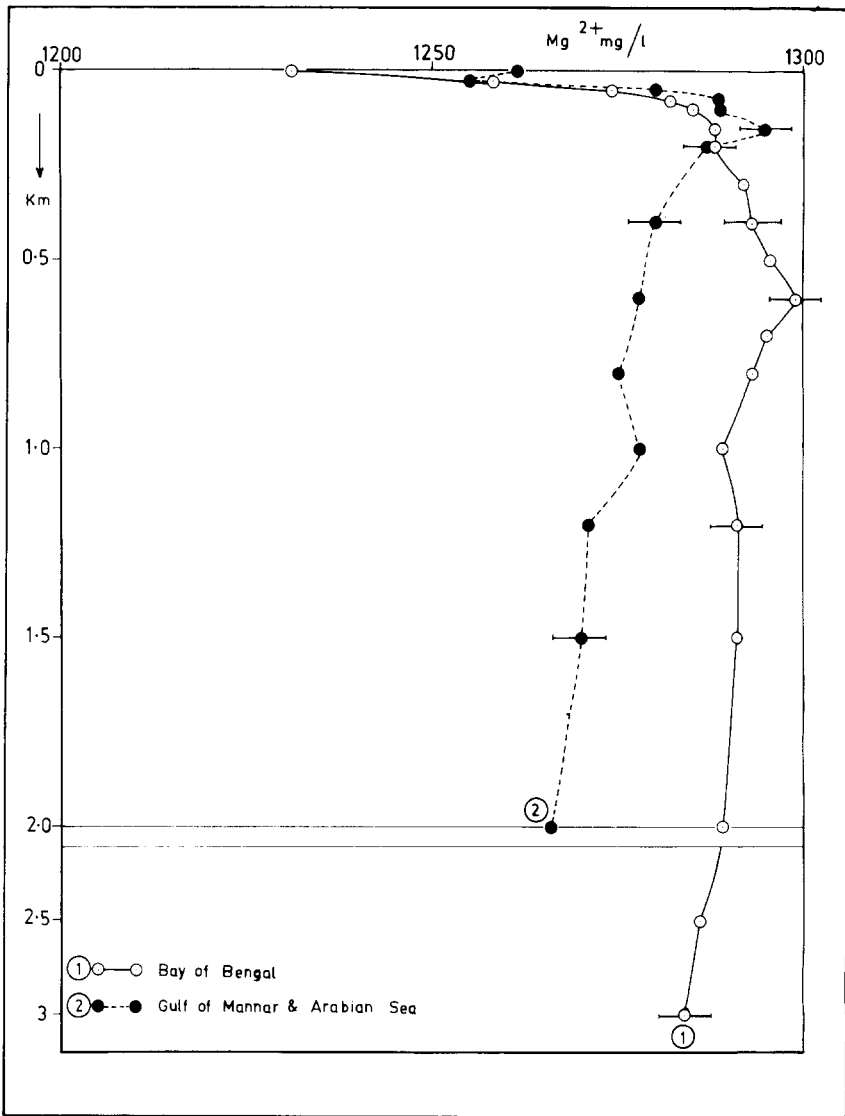


Fig.6. Depth profiles of average values of magnesium concentrations (mg/l) in the area of observations. Bars indicate range of error (0.27%).

particles in these layers caused by thermal gradients. A minimum in magnesium concentration is noted at a depth of about 800 m in the Arabian Sea and the Gulf of Mannar. This is the depth of flow of waters coming out of the Red Sea. A maximum in calcium concentration has been noted at around this depth (see earlier). It appears that the Red Sea water flowing into the Arabian Sea over the shallow sill at the Strait of Bab-el-Mandeb is

richer in calcium but depleted in magnesium. This water normally has a high salinity and this is the reason for the minimum of the Mg/Cl ratio at 800 m in curve 2 of Fig 5.

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