

Calcium, Magnesium & Fluoride Concentrations in the Andaman Sea

R J NORONHA, CAROLINE MORAES & R SEN GUPTA
National Institute of Oceanography, Dona Paula, Goa 403 004

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Ca, Mg and F^- concentrations and the corresponding chlorinity ratios have been determined in waters of the Andaman Sea. The data indicate that the freshwater runoff into the sea exerts a significant influence on the chlorinity ratios.

As part of studies recently initiated on the chemical oceanography of the Andaman Sea¹, sea water samples were analysed for Ca, Mg and F^- contents. Since the Andaman Sea receives a considerable input of freshwater from the Salween and Irrawaddy rivers², it was of interest to find out the effects, if any, of this influx on the elemental concentrations in relation to chlorinity.

Materials and Methods

Sea water samples were collected from standard hydrographic depths during the 51 and 52 cruises of *R V Gaveshani* (Jan.-Feb. 1979). For the analysis of Ca and Mg a total of 120 samples were obtained from 6 stations (●, Fig. 1). F^- was determined in 150 samples from 14 stations (▲, Fig. 1).

Lanthanum-alizarin complexon method described by Greenhalgh and Riley³ was used for the shipboard determination of F^- in unfiltered samples. Methods described by Culkin and Cox⁴ were employed for the determination of Ca and Mg. Zincon Zn-EGTA served as an indicator in fixing the endpoint in the photometric titration of Ca with EDTA solution. Eriochrome Black-T indicator was used to find the photometric endpoint in the complexometric titration of Mg with EGTA solution.

Chlorinity and dissolved oxygen were determined by standard methods⁵.

Sigma-t values were utilized to convert mg/litre values of Ca and Mg into mg/kg in the calculation of chlorinity ratios.

Results and Discussion

Calcium—Average Ca concentration and the corresponding Ca/Cl ratio, determined in samples collected from 6 stations in the Andaman Sea (●, Fig. 1) are 421 ± 1.76 mg/kg and 0.02224 ± 0.000045 respectively. The Ca/Cl value is in close agreement with the mean value (0.02229) reported⁶ for the Bay of Bengal, Gulf of Mannar and Arabian Sea. However, these values are higher than those reported by

others^{4,7,8} for all oceans. The present higher ratio suggests the effect of dilution due to river runoff into the Andaman Sea.

Average Ca concentration at the surface of the stations on the eastern side of the Andaman Island is 400 ± 7 mg/kg, the average chlorinity being $17.8 \pm 0.19\%$. This results in a Ca/Cl of 0.02245, which is higher than the average Ca/Cl at different depth intervals (Table 1) for the 4 stations lying along $93^\circ 30'E$ (Region A). Since the Ca/Cl for river water is much higher than that of sea water⁹, the higher ratio in the surface waters of the Andaman Sea suggests the effect of runoff from rivers in Burma and Thailand.

The mean value of Ca/Cl (0.02229 ± 0.0009) for the 2

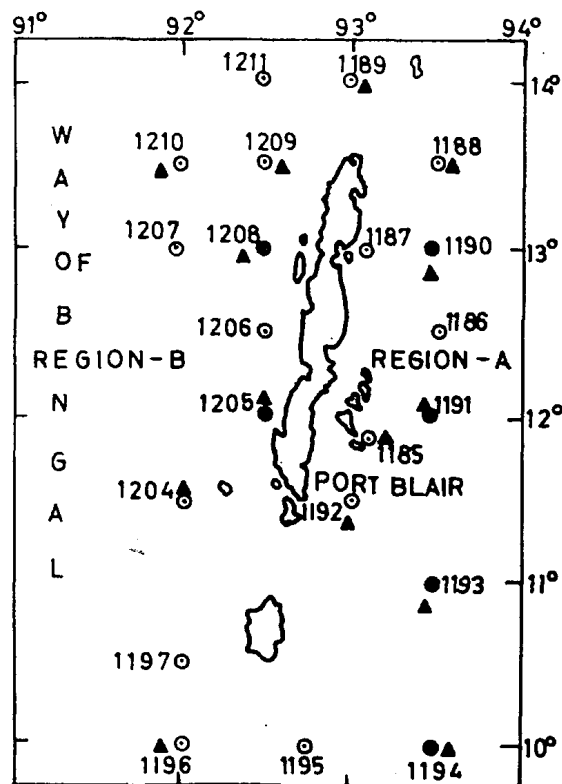


Fig. 1—Study area [●, stations samples for Ca and Mg ▲, for F^-]

Table 1—Averages of Ca and Mg Concentrations and Ca/Cl and Mg/Cl at Different Depth Intervals for 4 Stations (Region A) along 93°30'E

Depth m	n	Ca mg/kg	Ca/Cl	n	Mg mg/kg	Mg/Cl
0-100	17	407	0.02215	14	1240	0.06672
100-1000	27	428	0.02225	28	1306	0.06652
1000-2000	10	432	0.02242	10	1306	0.06658

n = Number of observations

Table 2—Ca Levels and Ca/Cl for 2 Stations along 92°30'E

Depth m	Ca (mg/kg)	Ca/Cl*
St 1205 (12°N; 92°30'E)		
0	408	0.02274
25	407	0.02255
50	413	0.02224
75	419	0.02224
St 1208 (13°N; 92°30'E)		
0	404	0.02193
25	410	0.02234
50	413	0.02233
75	421	0.02219

* mean, 0.02229 ± 0.0009

stations (Table 2) along 92°30'E (Region B) agrees well with the average Ca/Cl observed for the northern Indian Ocean by Sen Gupta *et al.*⁶ and also with the present value (0.02224), the total area covered, indicating the effect of river runoff.

A study has been made of enrichment of Ca in sub-surface waters with reference to the surface waters along 93°30'E meridian (Fig. 2). The northern part of this section is separated from the southern part by a shallow bank. Waters at 100-200 m depths are enriched by 5-10% with reference to the surface. The enrichment is 10% at 200 m on the Invisible Bank south of which this factor decreases. This enrichment is about an order higher than what it is in the Pacific, along 150°W and in the Sargaso Sea¹⁰. Hence, we believe this difference is due to the coralline bottom in the Andaman Sea and large volume of river runoff at the surface.

Magnesium—Mg the 2nd most abundant cation in sea water bears a concentration of 1209 mg/kg and a Mg/Cl of 0.0665 in sea water of 35‰ salinity¹⁰. Due to its conservative nature in sea water, its ratio to chlorinity is more or less constant, except in nearshore waters, where freshwater modifies the relationship between ions.

The average value of Mg (1268 ± 5.03 mg/kg) is lower than that reported by Sen Gupta *et al.*⁶ and 1290 mg/kg for ocean waters by Wilson¹⁰. The

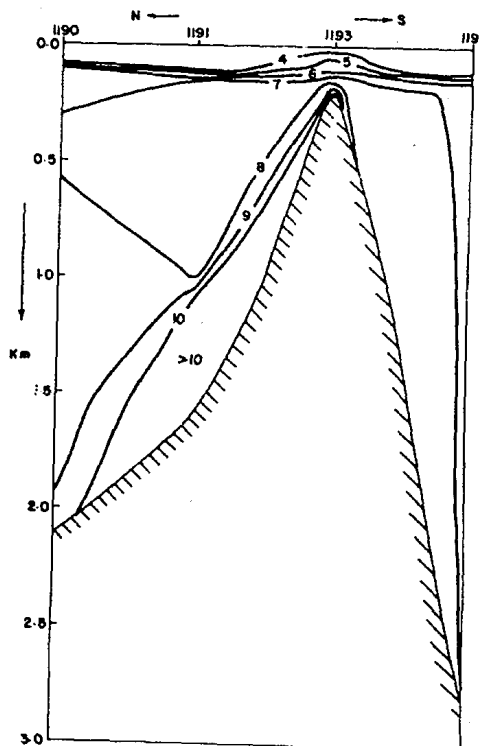


Fig. 2—Ca (mg/l) anomaly in the eastern region of the Andaman Sea

Table 3—Mg/Cl in Different Ocean Waters

Region	Mg/Cl
All oceans ⁴	0.06692*
Northern Indian Ocean ⁶	0.06631
All oceans ⁷	0.06692*
Atlantic ¹¹	0.06626
All oceans ¹²	0.06680
Pacific ¹³ (north eastern part)	0.06676
Tropical Atlantic ¹⁴ (western part)	0.06688
Andaman Sea (eastern part)	0.06655

* uncorrected values

corresponding Mg/Cl of 0.06655 suggests the closeness of the present value with those reported (Table 3). In obtaining the overall average of 0.06655 we applied a total correction of 1.6% to account for the error of Carpenter and Manella¹¹, in the titration endpoint detection of the estimation of alkaline earth metals by the method of Culkin and Cox⁴.

Average values for Mg and Mg/Cl at different depth intervals for 4 stations along 93°30'E (●, Fig. 1) are shown in Table 1. Except for the upper (0-100 m) layer, the intermediate (100-1000 m) and bottom (1000-2000 m) water layers exhibit overall constant values indicating the 'conservative' nature of this element.

Working in the same way, as mentioned under Ca, the average Mg concentration at the surface of the 4 stations on the eastern side of the Andaman Islands comes to 1185 ± 11 mg/kg at an average chlorinity of

17.8 ± 0.19‰. The corresponding Mg/Cl is 0.06652. The low Mg content in waters from the Irrawaddy and Salween rivers which discharge into this area, could account for the low level of Mg in the surface waters of the Andaman Sea.

Fluoride—In normal sea water, F⁻ is found to be a semi-conservative constituent, being present in the oceans at a concentration of 1.4 mg/litre and bearing a F/Cl of 7 × 10⁻⁵. Sen Gupta *et al.*⁶ reported a F⁻ and F/Cl of 1.31 mg/litre and 6.84 × 10⁻⁵ respectively for the northern Indian Ocean. In the Andaman region (▲, Fig. 1) 1.38 ± 0.01 mg/litre and (7.15 ± 0.05) × 10⁻⁵ for F⁻ and F/Cl respectively were obtained. Anomalous high concentrations of fluoride in sea water at a number of locations were reported^{3,15}. Warner¹⁶ gave a mean F/Cl of 6.75 × 10⁻⁵ for F⁻ determined in samples from Atlantic, Pacific Ocean and Caribbean Sea. Hence whether these differences in overall averages of F/Cl as reported are due to experimental uncertainties or whether some are real is not certain¹⁰.

Averages of F⁻ concentration and F/Cl, with standard error for whole of the water masses in the 2 regions (▲, Fig. 1) are presented in Table 4. It is of interest to note, that the F⁻ concentrations and F/Cl in Region A are higher than those values in Region B, and as such could be attributed to the tremendous

influx of fresh water from the Irrawady and Salween rivers. Since river water holds F⁻ in appreciable concentrations with very little or no chloride, mixing of river water with sea water will therefore increase the F⁻ concentration and the F/Cl.

It has been observed that F⁻ can be removed in the presence of low oxygen and can be redissolved when oxygen concentrations increase¹⁷. To check the validity of this assumption, depth-wise averages of O₂, Cl‰, F⁻ and F/Cl from both regions are presented in Table 5. Between 150 and 600m the zone of low oxygen concentrations, no depletion in F⁻ concentration is noted. On the contrary, the concentrations in both the regions remain fairly constant increasing slightly as we go down the water column. In deeper waters, below 600m, F⁻ and oxygen concentrations tend to increase much more in Region A than in Region B and this increase corresponds to the enrichment of Ca (Fig. 2). F⁻ can be lost to the bottom as its ion pair, higher values of both indicate that F⁻ is not precipitating in the Andaman Sea. Hence we believe that regions with coralline or rocky bottom will contain more dissolved F⁻ than that in regions with sandy or muddy bottoms, due to geological activities in the former region.

Kullenberg and Sen Gupta¹⁷ reported that F⁻ in the marine environment is regulated by evaporation, precipitation, settling particles and river runoff. They deduced the following relation between the 2 parameters:

Table 4—Overall Averages with Standard Errors of F⁻ Concentration and F/Cl

Area	F ⁻ mg./litre	(F/Cl)
Region A	1.43 ± 0.016	(7.36 ± 0.07).10 ⁻⁵
Region B	1.32 ± 0.013	(6.85 ± 0.06).10 ⁻⁵

$$F \text{ mg./litre} = 0.166 + \frac{Cl^2}{36.7 + 0.755 Cl^2} \dots (1)$$

Table 5—Concentrations of O₂, F⁻ and F/Cl at Different Depths in the Andaman Sea

Depth (m)	Region A				Region B			
	O ₂ mg./litre	Cl‰	F ⁻ mg./litre	(F/Cl) × 10 ⁵	O ₂ mg./litre	Cl‰	F ⁻ mg./litre	(F/Cl) × 10 ⁵
1	4.57	17.73	1.2	6.61	5.07	17.84	1.24	6.94
25	4.48	17.78	1.34	7.3	5.03	17.97	1.26	6.97
50	3.34	18.39	1.39	7.47	4.65	18.58	1.27	6.74
75	1.68	18.96	1.44	7.42	2.61	18.97	1.33	6.87
100	1.05	19.16	1.43	7.31	0.91	19.04	1.35	6.89
150	0.62	19.3	1.46	7.32	0.72	19.26	1.34	6.71
200	0.59	19.36	1.47	7.4	0.59	19.31	1.34	6.74
300	0.6	19.38	1.48	7.42	0.94	19.34	1.36	6.83
400	0.74	19.4	1.46	7.32	1.02	19.34	1.38	6.82
500	0.88	19.38	1.52	7.64	1.04	19.33	1.37	6.87
600	1.19	19.36	1.5	7.54	0.94	19.32	1.36	6.82
700	—	—	—	—	—	19.25	—	—
750	1.02	19.38	1.53	7.69	—	—	—	—
800	1.24	19.33	—	—	1.21	19.28	1.37	6.91
1000	1.49	19.32	1.54	7.76	1.36	19.24	1.34	6.8
1200	1.85	19.29	1.52	7.68	1.48	19.28	1.37	6.93
1500	1.92	19.3	1.51	7.62	—	—	—	—
2000	1.91	19.28	1.51	7.6	—	—	—	—
2750	1.99	19.28	1.54	7.68	—	—	—	—

Table 6—Observed (Av. of Regions 'A' + 'B') and Calculated Values (mg/l) of F⁻ at Different Chlorinity Ranges

	Chlorinity range			
	17.5-18	18.01-18.5	18.51-19	19.01-19.5
Cl‰	17.72	18.31	18.77	19.29
F _{obs} ⁻	1.24	1.36	1.34	1.42
F _{cal} ⁻	1.31	1.32	1.33	1.34
F _{cal} ⁻ - F _{obs} ⁻	0.07	-0.04	-0.01	-0.08

from observations of fluoride concentrations from 0-20‰ chlorinity. To test the present values chlorinity values were pooled into averages in the ranges 17.5-18, 18.01-18.5, 18.51-19 and 19.01-19.51. The average F⁻ values were also calculated in these ranges. The values when fitted into Eq. 1 gave the results as shown in Table 6. Except in the range 17.5-18 and 19.01-19.5 present values fit almost perfectly. The closeness of F_{cal}⁻ and F_{obs}⁻ in the next 2 chlorinity ranges indicate that the rivers draining into the Bay of Bengal have much lower F⁻ content than that used in Eq. 1. The difference between F_{cal}⁻ and F_{obs}⁻ at the lowest chlorinity range was 0.09 in an earlier study⁶ on Bay of Bengal F⁻. We obtained this difference as 0.07. This leads us to suggest that the rivers draining into the Bay of Bengal should have F⁻ concentration in the range 0.08-0.1 mg/litre. The effect of dissolution at or from the bottom in the deeper waters in the chlorinity range 19.01-19.5 may be the case of high F_{obs}⁻ value.

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