

CALCIUM AND MAGNESIUM CONCENTRATION IN THE  
NEARSHORE WATERS OF GOA

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ABSTRACT

Calcium and magnesium concentrations have been estimated in the nearshore waters of Goa. These elements in the coastal waters show significant seasonal variation. Calcium concentration showed maximum variations in the post-monsoon season but the values are more or less constant in the pre-monsoon season and are comparable with normal oceanic ones. Magnesium showed significant variations in the pre-monsoon season but can be considered to be more or less a stable conservative element compared to calcium in the coastal waters. The average Ca/Cl ratio is 0.02131 with a std. error of  $\pm 0.00027$ . The average Mg/Cl ratio is 0.06641 with a std. error of  $\pm 0.00028$ .

Calcium and magnesium are two of the major constituents of sea water contributing significantly to the biological and geochemical processes in the sea. High concentrations of these elements in the sea, relative to their biogeochemical reactions tend to make them conservative elements especially in the open sea. However, in the coastal, estuarine and lagoon waters the concentration variations specially for calcium are quite significant due to land drainage, high rates of biological uptake, precipitation and dissolution processes characteristic of shallow systems. The formation of some of the economically important minerals like phosphorites, calcite and aragonite are intimately associated with these elements. Despite the well established importance of these elements practically very little effort has been made hitherto to investigate their distribution and variations in our coastal and offshore waters. To understand the distribution and the biogeochemical behaviour of these two major elements in our waters, the present paper relates to some of the observations made in the nearshore waters of Goa.

Locations wherein the samples were collected are shown in Fig. 1. Surface water samples were collected once a month in the nearshore region from station No. 1 to 3 during the pre and post-monsoon periods and water samples in the surf zone were collected during pre-monsoon period from stations Nos. 4 and 5. Samples were analysed for chlorinity, calcium and magnesium concentrations. Calcium was determined using the method of Culkin and Cox (1966). A 10 ml sample of sea water was photometrically titrated with 0.005M EGTA using EEL-titrator. Magnesium was determined by difference from the sum of magnesium, calcium and strontium as estimated by the Culkin and Cox method (1966) using EDTA as titrant. Strontium being in negligible quantities in comparison to the concentration of calcium and magnesium no correction has been applied for strontium in calculations. The EGTA and EDTA solutions were standardised against 0.01N calcium solution prepared from reagent grade calcium carbonate. Chlorinity was estimated by Mohr's Knudsen technique.

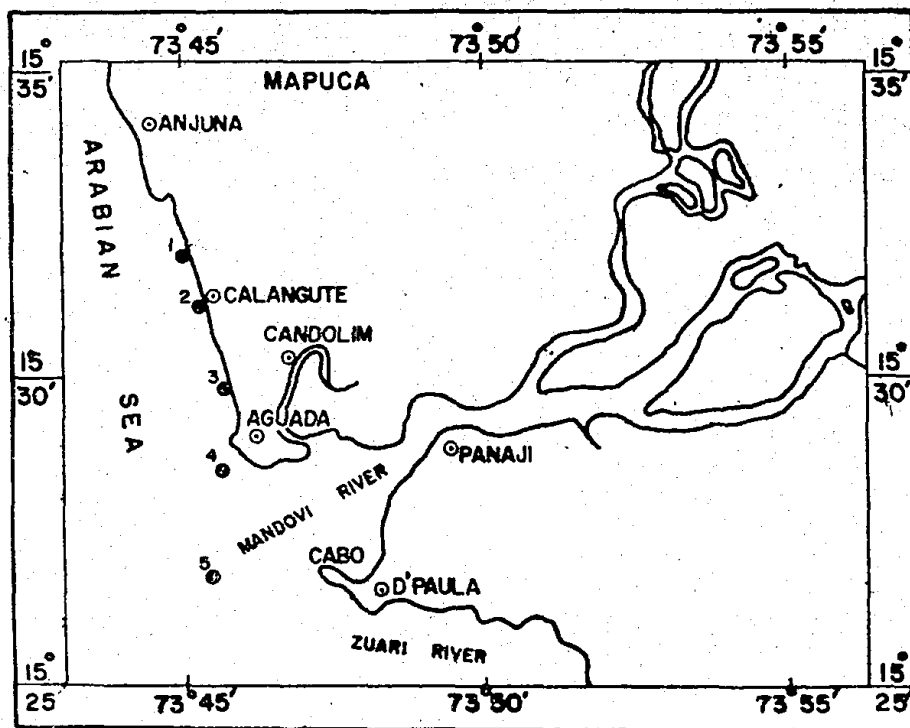


Fig. 1. Map showing the station position.

The precision of the analysis is  $\pm 0.22\%$  for calcium and  $\pm 0.48\%$  for magnesium. *Calcium*

Table I shows the monthwise variation in calcium concentration and the Ca/Cl ratio at different locations. Fig. 2 shows the average values of the calcium content of

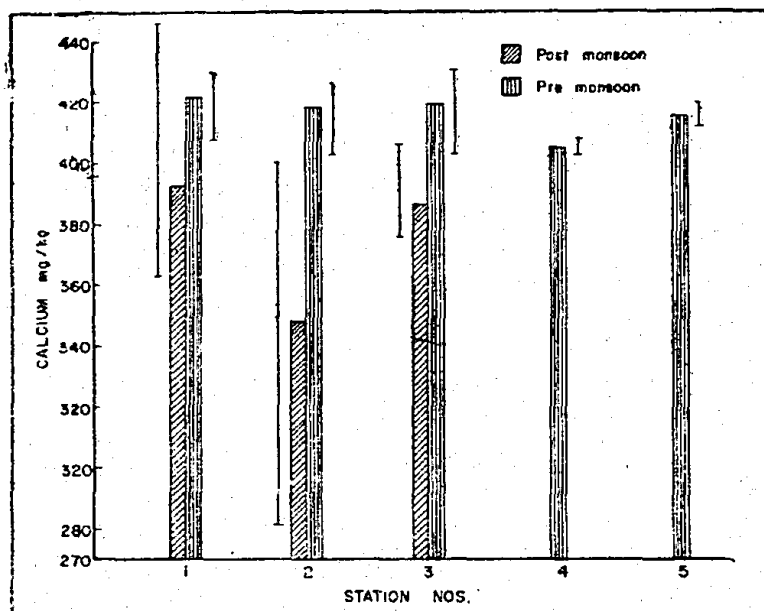


Fig. 2. The average calcium concentration (mg/kg) in the pre and post-monsoon seasons. The vertical line indicates the range of values.

*Calcium and magnesium concentration*

**Table I.** Monthwise variation in calcium concentration and the Ca/Cl ratio at different stations.

Month	Station I		Station II		Station III		Station IV		Station V	
	A	B	A	B	A	B	A	B	A	B
Oct.	445	0.02608	281	0.01542	378	0.02141				
Nov.	369	0.02011	400	0.02120	406	0.02148				
Dec.	362	0.01989	362	0.01900	375	0.01952				
Jan.	407	0.02207	402	0.02172	402	0.02192				
Feb.							402	0.02190	411	0.02172
March	427	0.02222	427	0.02239	424	0.02224	407	0.02164	428	0.02214
April										
May	429	0.02171	426	0.02164	430	0.02177				

A—Calcium—mg/kg

B—Ca/Cl ratio

water during post-monsoon (Oct, Nov and Dec) and pre-monsoon (Jan, March and May) seasons. An examination of the data indicate significant variations in the levels of the calcium concentration in different seasons as also with the locations. Maximum variation in the concentrations was found in the post-monsoon period while the values are more or less constant during the pre-monsoon period. Few observations made in the Zuari estuary in the month of July indicate that calcium concentration is very less suggesting that the calcium contribution from the river is negligible in this region. The lowering of the levels of calcium in the coastal waters during the monsoon months is obviously due to dilution effect. Higher concentrations in the subsequent seasons appear to be largely due to the recovery of calcium for gradual attainment of normal oceanic conditions. Comparing the calcium levels during the post and pre-monsoon seasons it can be seen that the values are always lower in the post-monsoon season than the pre-monsoon season. These conditions in the post-monsoon season might be related to the biogeochemical processes prevailing in different locations. Rao, Krishna Kumari and Dwivedi (1975) in their study of the breeding periodicity of the mussels which are found in abundance in this area observed that the post-monsoon season is the active growth period of the eyed larvae of these animals, suggesting active uptake of calcium during this period. The almost constant values of the concentration of calcium at all the stations might be due to the attainment of stable equilibrium conditions in the waters. Maximum recovery of calcium is observed during pre-monsoon season and the values are comparable with normal oceanic ones (Sen Gupta, Naik and Singbal, 1978).

The average Ca/Cl ratio for the entire period is 0.02131 with a standard error of  $\pm 0.00027$ . The Ca/Cl ratio is lower than that observed for the northern Indian Ocean ( $0.02229 \pm 0.000005$ ) which is an average value for the entire water column (Sen Gupta, Naik and Singbal, 1978). The low value of Ca/Cl ratio observed is due to the high chlorinity compared to calcium in this area. The high deviation in the value of standard error is due to the wide variations in the Ca/Cl ratio in different seasons (Table I). Thus calcium especially in the coastal waters behaves as a non-conservative element in view of its greater involvement in the biological and geochemical processes.

Table II. Monthwise variation in magnesium concentration and the Mg/Cl ratio at different stations.

Month	Station I		Station II		Station III		Station IV		Station V	
	A	B	A	B	A	B	A	B	A	B
Nov.	1268	0.0691	1285	0.0680	1297	0.0684				
Dec.	1295	0.0709	1293	0.0676	1329	0.0691				
Jan.	1232	0.0667	1241	0.0670	1260	0.0685				
Feb.							1218	0.0663	1253	0.0660
March	1304	0.0678	1282	0.0670	1276	0.0668	1263	0.0670	1298	0.0670
April										
May	1316	0.0665	1314	0.0667	1311	0.0663				

A—Magnesium - mg/kg (uncorrected)

B—Mg/Cl ratio (uncorrected)

### Magnesium

Table II shows the monthwise variation in magnesium concentration and the Mg/Cl ratio at different locations. The magnesium levels at all the five locations during the entire period (Fig. 3) show some variations which can be treated as significant relative to the general uniform concentration of this element in the sea. Maximum variations are found in the pre-monsoon season. This is in contrast with that of calcium which shows insignificant variations in the pre-monsoon season. Magnesium is not considered as a biologically active element (Sverdrup, Johnson and Fleming, 1942) and it is not disturbed by the activity of marine organisms and the only factor that alters the concentration is of geochemical nature. One of the removal mechanisms of magnesium from the sea is that the organisms which secrete carbonate skeletons incorporate varying amount of magnesium into the skeletons as magnesium calcite and aragonite. The extent of incorporation of magnesium varies from species to species and is also a function of tempe-

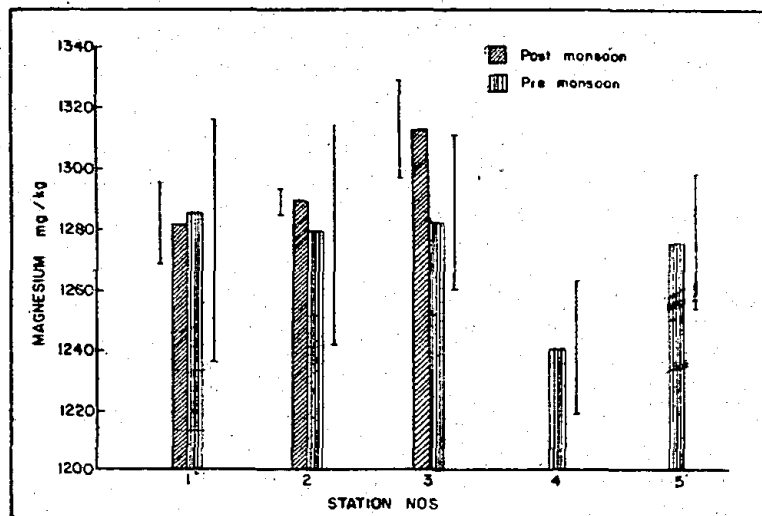


Fig. 3. The average magnesium concentration (mg/kg) in the pre and post-monsoon seasons. The vertical line indicates the range of values.

rature to which the organisms are exposed (Chave, 1954, cited by Drever, 1974). Ion-exchange process also plays a significant role in the removal of part of the magnesium from the medium. In the clay minerals calcium ion is largely replaced by magnesium and the cation exchange capacity of the clays vary with the salinity. The magnesium ions once replaced by calcium are no longer exchangeable by other ions and are considered as fixed (Drever, 1974). Even though magnesium is considered to be more or less a stable conservative element, which is more so perhaps in the deep sea, it does show significant variations in the coastal waters wherein the conditions of extraction of magnesium as mentioned above may be dominant.

In the present study the average Mg/Cl ratio is 0.0675 with a standard error of  $\pm 0.000205$ . Carpenter and Manella (1973) found that there is 1% error in the titration end point detection in the estimation of alkaline earth metals by the method of Culkin and Cox (1966). Strontium concentration when considered to be 7.9 mg/l (Wilson, 1975) it is about 0.6% of magnesium in sea water of 35‰ salinity. Thus, if total correction of 1.6% is applied; the average Mg/Cl ratio becomes  $0.06641 \pm 0.00028$  which is in close agreement with the value of 0.06631 observed for the north Indian Ocean (Sen Gupta, Naik and Singbal, 1978). This indicates the relative stability of the magnesium concentration in the coastal waters as compared to calcium.

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