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Original Research Paper

Studies on Distribution of Calcium and Magnesium in Coastal Waters of Gopalpur, Bay of Bengal

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ABSTRACT

The seasonal variability in the concentration of calcium and magnesium in coastal waters of Gopalpur, Bay of Bengal has been studied from March 2007 to February 2008. Salinity ranged between 19.48 and 34.44 ppt with an average value of 30.13 ppt. The calcium concentration varied from 0.313-0.451 g/kg with an average of 0.386 g/kg, and magnesium from 0.673-1.423 g/kg with an average 1.132 g/kg. The Ca/Cl ratio and Mg/Cl ratio ranged from 0.019-0.038 and 0.057-0.078 respectively. The concentration of calcium and magnesium was found to be higher in bottom water than the surface water. The ratio of Ca and Mg with chlorinity is proximity to the oceanic range. They were found to be lower in bottom water than the surface due to low saline surface water. The low range of variability of these in coastal waters indicates the insignificant inputs from extraneous sources. The average concentration of calcium and magnesium does not show much variability which reflects on the water quality parameters of Gopalpur coast.

INTRODUCTION

Major ions are defined as those elements whose seawater concentration is greater than 1 ppm. The main reason for this definition to be used is because salinity is reported to ± 0.001 ppt or 1 ppm. Thus, the major ions are those ions that contribute significantly to the salinity. According to this definition there are 11 major ions present in seawater. Amongst all the alkaline earths occur in seawater, magnesium and calcium are the major constituents, which play an important role in biogeochemical processes in sea. The behaviour of major elements in seawater all over the world was reported by Marcet (1819) and they bear nearly the same proportion to each other. Culkin (1965) and Wilson (1975) reported that the Ca/Cl and Mg/Cl ratios of seawater are used to assess the existing chemical and biological processes.

They further stated that input of calcium and magnesium is largely independent of salinity and varies from place to place where they accounted for the local circumstances such as (i) abundance of life forms, (ii) presence of rivers, and (iii) geological and meteorological conditions. The biological processes account for the uptake of calcium and magnesium by organisms and their removal from seawater is very pertinent to geochemical processes. Though, the distribution of calcium and magnesium and their ratios to chlorinity in Indian seas have been studied by several workers (Naik 1978, Naronha et al. 1981, Sen Gupta et al. 1978), limited information is available for Bay of Bengal. Tripathy et al. (1990) in their studies on distribution of Ca and Mg in the Rushikulya estuary of Orissa, observed strong positive correlation between chlorinity and calcium ($P>0.01$) and chlorinity and magnesium ($P>0.01$) confirming the conservative behaviour in a more general way.

Apart from the above, very little efforts have been made on the distribution of calcium and magnesium in coastal and offshore waters of this country. Due to influx of pollutants and freshwater, the variation of the major ions as well as salinity affect the ratio of the ions to chlorinity. Making a study on the major ions and their ratios with chlorinity will give an index of coastal water pollution. In view of this, the present work was undertaken for a period of one year (March 2007-February 2008) in the near shore waters of Gopalpur Port.

STUDY AREA

The study area of Gopalpur falls on 19°6' lat. N and 84°55' long. E., where three transacts were selected as shown in Fig. 1. The water samples were collected both from surface and bottom during monsoon (June-September), post-monsoon (October-February) and pre-monsoon (March-May) periods. Gopalpur on the south Orissa coast is endowed with marine resources, which fetch good financial earning to the state. The coastal sand is famous for its rich rare earth minerals, and there is an operational public limited company called Orissa Sands Complex (Indian Rare Earth Limited) to tap the resources like monazite, ilmenite, rutile, etc. There is a caustic soda producing unit named Jayshree Chemicals Ltd. on the bank of Rushikulya river near the estuary. This area also houses large patches of salt producing fields at

Humma and Sorol near Rushikulya and Bahuda estuarine areas respectively. The study area is not only manifested by different resource types, but also important to the tourist point of view, and occupies a prominent status on the fishing ground of the state. Gopalpur-on sea is a major tourist resort in the study area and its scenic beauty attracts the tourists from all over the country. Other tourist spots include Potagarh, an archaeological site near the Rushikulya estuary; Arjipalli, the widest bathing beach; Dhabaleswar and Mantridi, religious spots, and Sonepur for bathing beach and scenic beauty. The northern part of the coast shows a conducive environment for breeding and mass nesting of Olive Ridley (*Lepidochelys olivacea*) sea turtles, which come in thousands to lay eggs on the beach near Purunabandh village at Rushikulya estuary. This area is increasingly getting attention by the environmental lobbyists to declare as a marine sanctuary by the State Government. In regard to the anthropogenic activities, the coastal waters exhibit variability in the physico-chemical characteristics of the water and account for a divesting effect to the marine ecosystem. The seasonal variation of some selected major elements (calcium, magnesium, chloride) were assessed from the coastal water of the coast.

MATERIALS AND METHODS

The surface water samples were collected in polythene bucket, while bottom water samples were collected using shallow water sampler. The samples were filtered through Whatman filter paper. Before filling; the acid cleaned polythene bottles were rinsed 2-3 times with respective sample water. These filled polythene bottles with leak proof stoppers were preserved in a refrigerator till analysis, which was completed within a month from the date of collection. Generally, the samples preserved in refrigerator will not allow change in ionic concentration even after one month of storage.

Determination of chlorinity was made by Knudsen's titrimetric method (Grasshoff 1976). Calcium and magnesium were determined after titrating the samples to the photometric end point with EDTA solution. Complexometric titration with EDTA and Eriochrome Black T indicator yielded combined concentrations of calcium and magnesium concentration.

RESULTS AND DISCUSSION

The seasonal variability of the water characteristics of near shore waters depends on the freshwater discharge and associated inflow of saline water into the area. In the present study, the near shore waters of Gopalpur receive a significant influx of freshwater from the River Rushikulya on its north and the Bahuda on its south apart from other creeks contributing to some extent. The water discharge is regulated predominantly by the regime of rainfall.

Salinity: The data on level of salinity in seawater are given

Fig. 1: Map showing the sampling locations.

in Table 1 and Fig. 2. The surface values of salinity vary from 30.98 to 33.15 ppt during premonsoon, 32.92 to 29.04 ppt during monsoon and 27.94 to 30.48 ppt during postmonsoon periods at Station-1; from 31.56 to 33.18 ppt during premonsoon, 33.10 ppt during monsoon and 28.08 to 30.52 ppt during postmonsoon at Station-2; and from 31.16 to 33.12 ppt during premonsoon, 32.52 to 28.96 ppt during monsoon and 22.09 to 22.09 ppt during post monsoon at Station-3. The bottom values varied from 31.04 to 33.34 ppt during premonsoon, 33.44 to 29.48 ppt during monsoon and 28.71 to 30.95 ppt during postmonsoon at Station-1; from 32.78 to 33.38 ppt during premonsoon, 33.22 to 30.16 ppt during monsoon and 28.98 to 30.99 ppt during postmonsoon at Station-2; and from 31.33 to 33.32 ppt during premonsoon, 33.13 to 29.16 ppt during monsoon and 22.38 to 29.16 ppt during post monsoon at Station-3. The high values of salinity were recorded during the premonsoon months and also in June. The first sign of dilution was noticed during August and September , which gradually decreased to minimum in the month of October. But there was a sudden increase during November.

During premonsoon period, the monthly variation of salinity at surface waters is lower than the bottom waters and also high in June due to maximum evaporation and the influx of freshwater. In the month of February the water slowly begins to recover from the dilution. On an average, the surface values were lower than the bottom values because of continuous exchange of freshwater through adjacent creek. High salinity at Gopalpur is attributed to the onset of high salinity associated with northward flowing coastal current.

Calcium: The data on level of calcium in seawater are given in Table 3 and Fig. 3. The values of calcium in surface waters varied from 0.406 to 0.401g/kg during premonsoon, 0.375 to 0.4 g/kg during monsoon and 0.421 to 0.371 g/kg at Station-1; from 0.357 to 0.369 g/kg during premonsoon, 0.375 to 0.410 g/kg during monsoon and 0.411 to 0.333 g/kg during postmonsoon at Station-2, and from 0.403 to 0.394 g/kg during premonsoon, 0.396 to 0.350 g/kg during monsoon and 0.381 to 0.373 g/kg during postmonsoon at Station-3. The bottom water values ranged from 0.446 to 0.395 g/kg during premonsoon, 0.390 to 0.415 g/kg during monsoon and 0.421 to 0.358 g/kg during postmonsoon at Station-1, from 0.373 to 0.401 g/kg during premonsoon, 0.385 to 0.395 g/kg during monsoon and 0.415 to 0.393 g/kg during postmonsoon at Station-2, and from 0.345 to 0.393 g/kg during premonsoon, 0.396 to 0.375 g/kg during monsoon and 0.383 to 0.429 g/kg during postmonsoon at Station-3. The average concentration of Ca in bottom water was higher than the surface water. Lowering of Ca in surface waters may be due to the biological utilization, degradation of dead animals, precipitation of Ca and its carbonates, and settling through the particulate matter. The maximum concentration of calcium was observed during the months of March and April. The reason may be the less biological utilization and insignificant influx of freshwater.

During August, September and October, there was high concentration of Ca due to maximum influx of freshwater. During postmonsoon season, the Ca concentration was comparatively lower. Table 2 gives values of chlorinity and Table 4 describes the monthly calcium to chlorinity ratio at the three stations. Calcium to chlorinity ratio in surface waters vary from 0.02009 to 0.02723 at Station-1, 0.01964 to 0.02593 at Station-2, and 0.01943 to 0.03822 at Station-3. In the bottom waters, the ratio varies from 0.01967 to 0.02649 at Station-1, 0.01958 to 0.02611 at Station-2, and 0.01924 to 0.03327 at Station-3. During monsoon months, in most of the cases, the ratio for surface water was higher than the bottom water. In October month Ca/Cl ratios show higher values for all the stations, typically confirming that the dilution effect during these months play a significant role in Ca/Cl ratio. Station-3 values confirm this condition in a more regular sense. The Ca/Cl ratio for the surface water is higher than the bottom during the monsoon months and October due to the process of dilution. Its effect during these months plays a significant role in variation of Ca/Cl ratio.

Magnesium: The data on level of magnesium in seawater are given in Table 5 and Fig. 4. The surface values of magnesium varied from 1.120 to 1.244 g/kg during pre monsoon, 1.186 to 1.172 g/kg during monsoon and 0.943 to 1.148 g/kg during post monsoon at Station-1; from 1.030 to 1.230 g/kg during pre monsoon, 1.208 to 1.217 g/kg during monsoon and 0.900 to 1.170 g/kg during post monsoon at Station-2; and from 0.872 to 1.118 g/kg during premonsoon, 1.238 to 1.302 g/kg during monsoon and 1.240 to 1.148 g/kg during postmonsoon at Station-3. The bottom values varied from 1.172 to 1.251 g/kg during premonsoon, 1.223 to 1.208 g/kg during monsoon and 0.968 to 1.163 g/kg during postmonsoon at Station-1; from 1.001 to 0.913 g/kg during premonsoon, 1.268 to 1.216 g/kg during monsoon and 1.230 to 1.223 g/kg during postmonsoon at Station-2; and from 0.799 to 1.251 g/kg during premonsoon, 1.349 to 1.221 g/kg during monsoon and 0.894 to 1.194 g/kg during postmonsoon at Station-3. In general, the values were relatively higher in bottom waters compared to surface waters. The high concentration of Mg in bottom waters is due to remineralization taking place from the calcite skeletons containing high Mg content. The adsorption of Mg through suspended matter is one of the reasons for the decline in the surface water concentration. However, lower values observed during the monsoon and postmonsoon months were due to

Table 1: Salinity (ppt) of near-shore waters of Gopalpur.

Seasons	Station 1		Station 2		Station 3	
Months	Surface	Bottom	Surface	Bottom	Surface	Bottom
Premonsoon						
March	30.98	31.04	31.56	32.78	31.16	31.33
April	33.60	34.44	34.35	34.22	33.96	34.12
May	33.15	33.34	33.18	33.38	33.12	33.32
Monsoon						
June	32.92	33.44	33.10	33.22	32.52	33.13
July	31.48	32.16	31.81	32.44	31.55	31.94
August	29.78	30.18	30.03	30.68	28.56	29.14
September	29.04	29.48	33.10	30.16	28.96	29.16
Postmonsoon						
October	27.94	28.71	28.08	28.98	22.09	22.38
November	30.13	30.32	30.06	30.25	29.48	29.79
December	26.58	27.82	26.54	26.94	19.48	19.78
January	29.67	29.67	29.91	29.99	24.59	25.06
February	30.48	30.95	30.52	30.99	22.09	29.16

Table 2: Chlorinity (ppt) of near-shore waters of Gopalpur.

Seasons	Station 1		Station 2		Station 3	
Months	Surface	Bottom	Surface	Bottom	Surface	Bottom
Premonsoon						
March	17.13	17.18	17.47	17.59	17.25	17.34
April	18.61	19.06	09.01	18.93	18.79	18.89
May	18.36	18.46	18.37	18.48	18.32	18.45
Monsoon						
June	18.23	18.52	18.32	18.38	18.01	18.33
July	17.42	17.79	17.60	17.96	17.47	17.67
August	16.47	16.70	16.62	16.98	15.80	16.11
September	16.07	16.30	16.45	16.69	16.03	16.13
Postmonsoon						
October	15.46	15.89	15.54	16.04	12.22	12.38
November	16.68	16.77	16.63	16.73	16.31	16.49
December	14.71	15.39	14.68	14.90	10.78	10.94
January	16.42	16.42	16.55	16.60	13.60	13.86
February	16.87	17.13	16.89	17.15	15.86	16.15

Table 3: Concentration of calcium (g/kg) of near-shore waters of Gopalpur.

Seasons	Station 1		Station 2		Station 3	
Months	Surface	Bottom	Surface	Bottom	Surface	Bottom
Premonsoon						
March	0.406	0.446	0.357	0.393	0.381	0.429
April	0.430	0.451	0.389	0.424	0.425	0.399
May	0.401	0.395	0.369	0.401	0.403	0.383
Monsoon						
June	0.375	0.390	0.375	0.385	0.350	0.375
July	0.350	0.350	0.389	0.380	0.340	0.340
August	0.400	0.386	0.400	0.402	0.420	0.380
September	0.400	0.415	0.410	0.395	0.396	0.396
Postmonsoon						
October	0.421	0.421	0.411	0.415	0.394	0.393
November	0.372	0.379	0.402	0.406	0.380	0.384
December	0.358	0.395	0.357	0.389	0.412	0.364
January	0.331	0.393	0.324	0.325	0.313	0.401
February	0.371	0.358	0.333	0.373	0.373	0.345

Table 4: Calcium to chlorinity ratio in near-shore waters of Gopalpur.

Seasons	Station 1		Station 2		Station 3	
Months	Surface	Bottom	Surface	Bottom	Surface	Bottom
Premonsoon						
March	0.02369	0.02596	0.02044	0.02234	0.02209	0.02474
April	0.02312	0.02366	0.02046	0.02245	0.02262	0.02112
May	0.02185	0.02140	0.02008	0.02170	0.02200	0.02076
Monsoon						
June	0.02058	0.02106	0.02047	0.02095	0.01943	0.02046
July	0.02009	0.01967	0.02210	0.2116	0.01946	0.01924
August	0.02427	0.02311	0.02407	0.02368	0.02658	0.02359
September	0.02489	0.02546	0.02492	0.02367	0.02470	0.02455
Postmonsoon						
October	0.02723	0.02649	0.02593	0.02587	0.03224	0.03174
November	0.02230	0.02260	0.02417	0.02427	0.02330	0.02329
December	0.02434	0.02567	0.02432	0.02611	0.03822	0.02227
January	0.02016	0.02393	0.01964	0.01958	0.02301	0.02893
February	0.02199	0.02090	0.01972	0.02175	0.02352	0.02136

Table 5: Concentration of magnesium (g/kg) of near-shore waters of Gopalpur.

Seasons	Station 1		Station 2		Station 3	
Months	Surface	Bottom	Surface	Bottom	Surface	Bottom
Premonsoon						
March	1.148	1.172	1.170	1.223	1.148	1.194
April	1.238	1.309	1.262	1.303	1.294	1.304
May	1.244	1.251	1.230	1.230	1.240	1.251
Monsoon						
June	1.186	1.223	1.208	1.216	1.302	1.349
July	1.325	1.423	1.224	1.299	1.225	1.226
August	1.267	1.306	1.106	1.137	1.232	1.240
September	1.172	1.208	1.217	1.268	1.238	1.221
Postmonsoon						
October	0.943	0.968	0.900	0.913	0.872	0.894
November	1.011	1.074	1.108	1.100	1.178	1.186
December	0.918	0.986	0.942	0.902	0.673	0.705
January	0.982	1.016	1.012	1.018	0.780	0.799
February	1.120	1.163	1.030	1.001	1.118	1.138

Table 6: Magnesium to chlorinity ratio in near-shore waters of Gopalpur.

Seasons	Station 1		Station 2		Station 3	
Months	Surface	Bottom	Surface	Bottom	Surface	Bottom
Premonsoon						
March	0.06704	0.06816	0.06697	0.06947	0.06655	0.06886
April	0.06656	0.06868	0.06644	0.06878	0.06887	0.06903
May	0.06785	0.06777	0.06696	0.06656	0.06769	0.06780
Monsoon						
June	0.06515	0.06604	0.06588	0.06616	0.07224	0.07359
July	0.07606	0.07993	0.06955	0.07227	0.06525	0.06938
August	0.07694	0.07838	0.06661	0.06702	0.07791	0.07697
September	0.07287	0.07417	0.07398	0.07597	0.07729	0.06200
Postmonsoon						
October	0.06093	0.06092	0.05792	0.05686	0.07144	0.07221
November	0.06001	0.06404	0.06663	0.06575	0.07216	0.07192
December	0.06241	0.06400	0.06431	0.06658	0.06252	0.06444
January	0.06017	0.06181	0.06115	0.06133	0.05735	0.05765
February	0.06639	0.06783	0.06098	0.05837	0.07055	0.07034

Table 7: Average values of chlorinity, calcium, magnesium and their ratios in Gopalpur, Andaman Sea and Visakhapatnam Harbour waters.

		Chlorinity (ppt)	Calcium (g/kg)	Magnesium (g/kg)	Ca/Cl	Mg/Cl
Observed in the present study		16.925	0.388± 0.006	1.163± 0.0008	0.02305± 0.0009	0.06799 ± 0.000172
Reported values	*	17.8± 0.19	0.421± 0.00503	1.268± 0.000176	0.02224± 0.000045	0.06655
	**	17.54	0.385 ± 0.007	1.203± 0.0011	0.02198± 0.000008	0.06856± 0.000008

*Values for Andaman Sea (Bay of Bengal); ** Values for Visakkhapatnam Harbour

the freshwater influx from rivers and creeks to the near shore water.

Table 6 shows the monthly variation of magnesium to chlorinity ratio at all the stations. For surface water the ratio ranged from 0.06001 to 0.07694, 0.05792 to 0.07498 and 0.05735 to 0.07791, and for the bottom water from 0.06092 - 0.07993, 0.05686-0.07597 and 0.05765 to 0.07697 for Station-1, Station-2 and Station-3 respectively. The bottom water ratios were, in general lower than the surface water, which may be attributed to the presence of comparative low salinity in surface waters.

The variations in both calcium and magnesium concentrations are observed in the present investigation but statistically not significant. Similarly, surface to bottom difference is also not significant and the minor differences noticed in the present study may be due to some removal mechanisms for surface waters. Bottom values are always higher than surface. Extraction of calcium by living organisms from surface water leading to lower calcium level in the surface water and precipitation of calcium carbonate at bottom region could result in increased calcium concentration in bottom water. Comparing the calcium and magnesium levels during the three seasons, it is observed that the values are always lower in the postmonsoon season than the premonsoon with an intermediate value during monsoon. These conditions in the postmonsoon may be related to the biogeochemical processes prevailing in different locations. The lowering of the levels of calcium in coastal waters during the monsoon months is obviously due to dilution effect. Freshwater run-off as a result of monsoonal rains could account for the lowering of the calcium and magnesium concentration. Naik (1978) also described a similar situation in near shore water of Goa. Higher concentrations during premonsoon season appear to be largely due to recovery of calcium for gradual attainment of normal oceanic conditions and almost constant values of the concentration of calcium at all the stations may be due to the attainment of stable equilibrium conditions in the waters (Naik 1978). Sen Gupta et al. (1978) reported that maximum recovery of calcium occurs during premonsoon season which is more comparable to oceanic ones.

The average Ca/Cl ratio is 0.02305 ± 0.00009 with an average calcium concentration of 0.388 ± 0.0006 g/kg, the average chlorinity being 16.93 ppt (Table 7). The Ca/Cl values are high when compared to those reported for Andaman Sea (Bay of Bengal) and Visakhapatnam locality. Lower Ca/Cl values are mainly due to comparatively lower salinity (30.59 ppt) to that of reported values (Sen Gupta 1978, Sahu 1986). The average Mg/Cl ratio is 0.06799 ± 0.000172 with an average magnesium concentration of 1.153 ± 0.0008 (Table 7). Average concentration of magnesium is lesser than the reported values; whereas the ratio to chlorinity is higher than Andaman Sea and lower than Visakhapatnam waters.

The scattered plots between chlorinity versus calcium (Fig. 5) and chlorinity versus magnesium (Fig. 6) were drawn and the least square method was adopted to draw the regression lines. The regression equation computed for calcium with chlorinity is $y = 0.0015 x + 0.3613$, and magnesium with chlorinity is $y = 0.0041 x + 1.0023$. It appears from the calcium concentration graph (Fig. 5) that its concentration ranges from 0.313 to 0.510, and magnesium concentration from 0.673 to 1.423. The calcium versus chlorinity indicates that the low ranges of calcium concentration were caused due to the insignificant source of calcium, while the graph (Fig. 6) on magnesium versus chlorinity indicates the wider variations of magnesium concentration caused due to the biochemical activity as well as addition of magnesium from extraneous sources.

CONCLUSION

The major elements comprise of dissolved salts in seawater. These are very few in numbers and the major cations and anions play a significant role in seawater. These are conservative and bear a constant ratio with chlorinity. The conservative behaviour encountered was due to slight changes in physical properties of seawater. The salinity varied from 19.78 ppt to 34.35 ppt. The calcium and magnesium varied from 0.313 g/kg to 0.51 g/kg and 0.674 g/kg to 1.422 g/kg respectively. The concentration of calcium and magnesium is enriched with the influx of freshwater.

The scattered plots between chlorinity versus calcium and magnesium were drawn on regression lines. The calcium

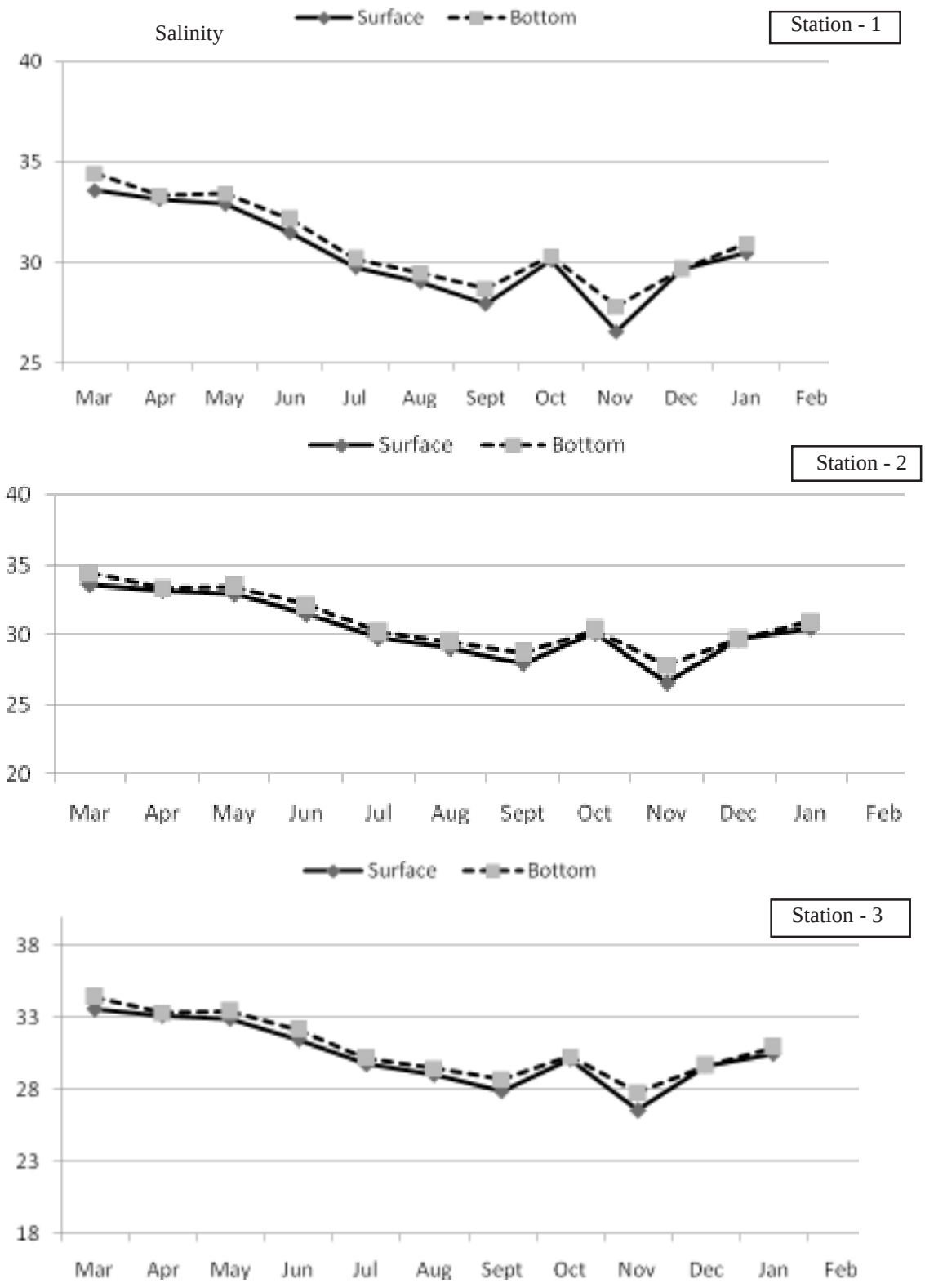

Fig. 2: Monthly distribution of salinity (ppt) of near shore water of Gopalpur Port at the three Stations from March 2007 to February 2008.

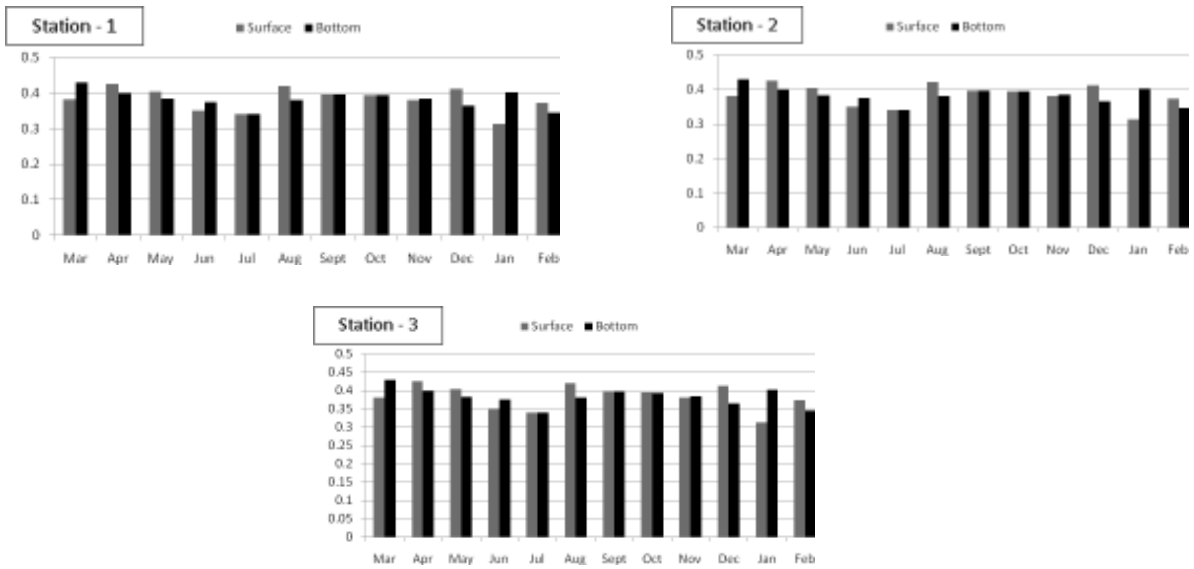

Fig. 3: Monthly distribution of calcium concentration of near shore water of Gopalpur at the three Stations from March 2007 to February 2008.

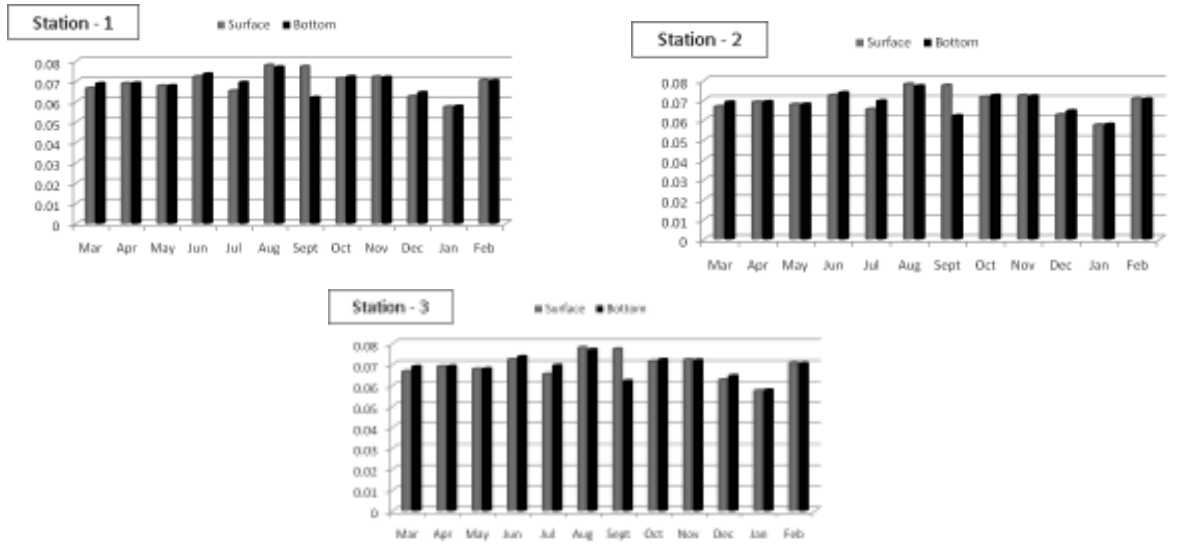

Fig. 4 : Monthly distribution of magnesium concentration of nearshore water of Gopalpur Port at the three Stations from March 2007 to February 2008.

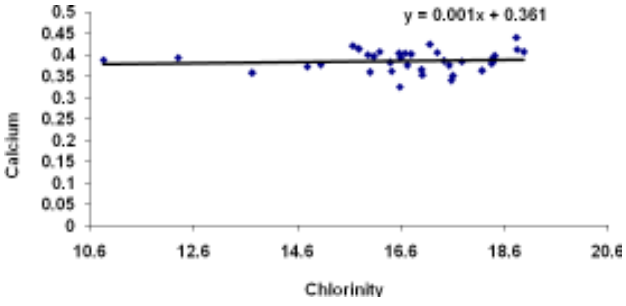

Fig. 5: The seasonal linear relationships of Ca with chlorinity.

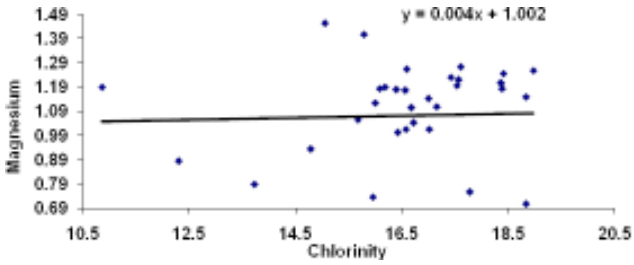

Fig. 6: The seasonal linear relationships of Mg with chlorinity.

versus chlorinity indicated a low range of variability in concentration of calcium, and magnesium indicated a wider range due to biochemical activity of organisms. Hence, the findings of the present study indicate that there is monthly variation from time to time. The conservative behaviour of ions (Ca^{++} and Mg^{++}) does not show a deviation from the Marcets principle of conservative behaviour of major ions in seawater which reflects on the water quality of Gopalpur coast.

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