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Studies on Calcium, Magnesium & Sulphate in the Mandovi & Zuari River Systems (Goa)

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Distribution of calcium, magnesium and sulphate have been examined in the tide-dominated Mandovi and Zuari river systems. Calcium and magnesium appear to take some part in the bio-geochemical cycles of the rivers and behave as semi-conservative parameters. Sulphate, however, behaves in a purely conservative manner and remains in a steady state in the rivers. A 'Simple mixture' relationship is applied to calculate the dilution and mixing processes in the rivers using calcium, magnesium and sulphate as indicators, it has been observed that the percentages of sea water in the estuarine region of Mandovi vary from 88 - 92 during premonsoon, 12 - 23 during monsoon and 78 - 79 during postmonsoon. Similar figures for Zuari are 94 - 99, 27 - 43 and 79 - 91 during the 3 seasons. The possibility of loss of calcium and magnesium due to precipitation as their insoluble phosphates in the upper reaches of the rivers is discussed.

Several physical, chemical and biological characteristics of the rivers Mandovi and Zuari in Goa have been examined, but most of them pertain to estuarine regions and are conducted during specific seasons of the year[1]. The most important findings of these studies are that the estuarine system is tide-dominated and remains almost an arm of the sea for most of the year, except during the monsoon months June to September when, due to river runoff, a shallow stratification develops up to some distance from the mouth.

During 1977-78, an extensive survey was undertaken in the 2 rivers to prepare a master plan for pollution control. In this survey 26 components of the water were regularly monitored over 12 hr tidal cycles, at 9 stations in either river at monthly intervals. Relevant physical characteristics were also studied during the representative periods of the year. Detailed analyses of data on a number of physical, chemical and biological parameters were reported[2]. The present paper deals specifically with major species like calcium, magnesium and sulphate together with their relations to chlorinity.

Description of Area

Mandovi-Zuari river systems are located between lat. 15°09′ and 15°33′N and long. 73°45′ and 74°14′E (Fig. 1). Both rivers are influenced by sea water (marked by 1 $^{0}/_{00}$ salinity) up to considerable distances upstream—11 - 65 km in the Mandovi and from 20 - 65 km in the Zuari—the maximum occurring during the peak summer month of May and the minimum during the peak monsoon month of July[2]. The average annual freshwater runoff has been estimated as 16 km^3 for the Mandovi and 9 km^3 for the Zuari[3].

Both rivers are perennial and originate from the Western Ghats. The Mandovi runs up to a stretch of about 75 km and the Zuari about 70 km before joining the Arabian Sea. The width at the mouth of the Mandovi is about 3.2 km and that of Zuari about 5.5 km. Upstream, the former narrows down to < 0.25 km and the latter to about 0.5 km.

The average annual rainfall in the 2 river basins (mostly during June-September) varies from 300 cm downstream to 373 cm at their uppermost reaches. The Mandovi has a basin area of 1530 km^2, a catchment

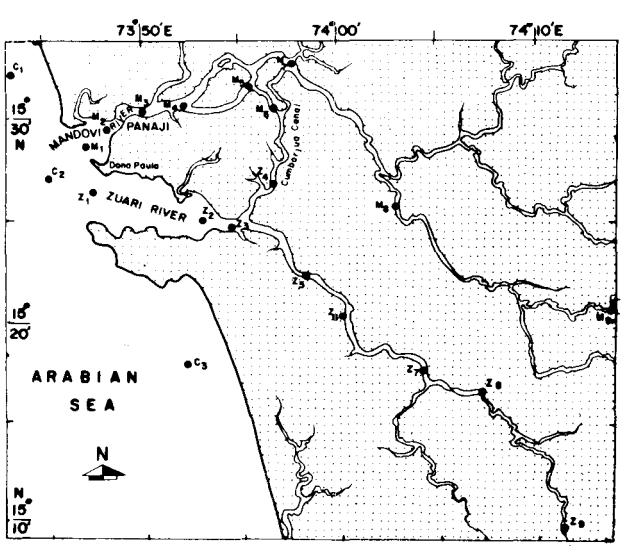

Fig. 1—Network of observation stations

area of 1150 km^2 and on its way to the sea meets a large tributary system and has a number of islands, narrow bends and shallow depths. The Zuari has a basin area of 973 km^2, a catchment area of 550 km^2 but a much smaller tributary system, as compared to the Mandovi. The basin areas of these 2 rivers together constitute about 70% of the total land area of the Union Territory of Goa. Due to scanty freshwater discharge during periods, other than the monsoon, the flow in these rivers is almost totally regulated by tides of semi-diurnal type (M_2) having a spring range of 2.3 m.

In the estuarine regions the 2 rivers are linked by the Cumbarjua Canal (Fig. 1). This canal is 14 km and 11 km away from the respective mouths of Mandovi and Zuari. The Canal is about 17 km in length and 0.5 - 0.7 km wide. The Canal along with the 2 rivers demarcates the island of Panaji in between. Although not of natural origin, the Cumbarjua Canal is an interesting example of two estuaries interacting dynamically through a common channel.

Though the flow in the 2 rivers is tide-dominated, there is always a longitudinal variation in salinity at almost all the depths from the mouths of the rivers upstream. The seaward flow always appears to be on the right, looking downstream, while the compensating flow is always on the left. There always exists a horizontal salinity gradient from the left to the right banks of the 2 rivers. During the monsoon, due to large influx of freshwater, a compensatory flow of salt water occurs below the freshwater in the form of a salt wedge up to short distances from the mouths[2]. This gives rise to a shallow stratification in the water column.

Thus, the Mandovi-Zuari estuarine system can be classified as a tide-dominated coastal plain estuary with vertical homogenity but lateral variation in salinity.

Materials and Methods

Eight observation stations were fixed on either river covering a distance of 43 km in the Mandovi and 45 km in the Zuari; sts M9 and Z9 at the uppermost approachable reaches served as reference or control for observations at places completely free from sea water intrusion (Fig. 1).

Mid-depth sampling was done once in 4 hr over 12 hr tidal cycles at monthly intervals. Samples were pooled stationwise prior to analysis. This helped in eliminating the fluctuations with tides and to have only the residual tidal effect, which is normally the case in all tide-dominated estuaries. In addition 3 stations were operated 5 km off the coast of Goa.

Salinity was measured conductometrically by a salinometer (Model 8400 Autosal, S/n 40, 363). The values were divided by 1.80655 to obtain chlorinity. In samples of $< 5\ ^0/_{00}$ salinity the estimations were made by Mohr-Knudsen's titrimetric method as described elsewhere[4].

Calcium was determined according to the method of Culkin and Cox[5] by titrating the samples to the photometric end points with ethylene-glycol bis-(β-aminoethyl ether)-N-N′ tetra-acetic acid (EGTA) using Zincon Zn-EGTA as indicator.

Magnesium was determined by a substitution method[5] being titrated complexometrically to a photometric end point against ethylenediamine tetra acetic acid (EDTA) using Eriochrome Black T as indicator. Values for calcium were subtracted to obtain the magnesium concentrations. The values were further reduced by 1.6% to allow for the limitations of the analytical technique[5,6] and the strontium content of the water[7].

Sulphate was analysed gravimetrically as barium sulphate. The interferences of alkali and alkaline-earth metals were minimised by the addition of picric acid and hydrochloric acid[8].

Results and Discussion

Seasonal variability of different characteristics in a tide-dominated river system demands an understanding of the freshwater discharge into the system and out of it to the sea associated with the compensatory flow of saline water. In the Mandovi and Zuari river systems these features are predominantly regulated by the regime of rainfall during the southwest monsoon. Therefore, the year has been divided into 3 seasons, for analysing the data, viz. premonsoon (February-May), monsoon (June-September) and postmonsoon (October-January). Since these 2 rivers are mostly dominated by the incursion of sea water, at least for 8 months in a year, the parameters calcium, magnesium and sulphate are treated in the same way as for sea water where they are considered as conservative parameters with constant ratios to chlorinity.

Salinity/chlorinity—A detailed description of seasonal variation in salinity in the 2 rivers and its influence in regulating the dilutions through the 3 seasons has been presented by Qasim and Sen Gupta[2]. The diagrammatic variation, as presented in Fig. 2, has been reproduced from that paper to compare with the variations of the other parameters in order to study the influence of sea water incursion on them and to examine their behaviour, conservative or otherwise. Chlorinity values have been computed from salinity for the purpose of calculating the ratios.

Dilution factors were calculated using the relation $F = 1 - S_1/S_2$ (ref. 9). Applying the dilution factors the percentages of sea water in the 2 rivers during the 3 seasons were calculated (Table 1).

In this and other calculations, the entire estuarine region has been treated as one system. Some

longitudinal variations may exist from the mouth to the upper reaches of the estuary, but it is assumed that they may not be very significant as the estuary is tide-dominated and remains almost homogeneous vertically for a greater part of the year. In Mandovi, values at sts M1 to M6 and in Zuari those at sts Z1 to Z4 have been averaged, during different seasons for the calculation of dilutions and used as an approximation of the general conditions.

For sea water, values of sts C1 to C3, have been similarly averaged. The exception was in monsoon, which is represented only by September data, since navigation of small boats in the offshore region gets suspended. However, the salinity values in the open sea off these river mouths do not change appreciably from the average during the period June to September (MONEX 1979 - unpublished data) and such small volume of river runoff cannot be expected to dilute the sea water appreciably. Therefore, values during September may be taken as average for monsoon conditions, at least as a first approximation.

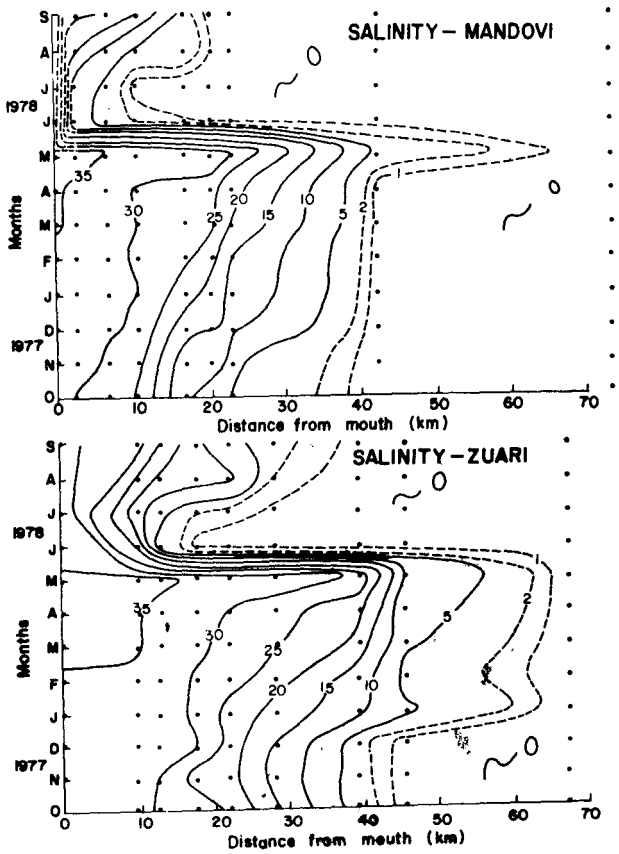

Fig. 2—Diagrammatic representation showing extent of salt water penetration from the mouth of Mandovi and Zuari rivers upstream in different months [—, salinity at 5‰ intervals; - - -, salinities of 2 and 1‰]

Calcium—Temporal and spatial variations of calcium in both the rivers are presented in Fig. 3. Concentrations decrease with increasing distance from the mouths. Slopes of the isopleths of calcium in Fig. 3 agree fairly well with those of the isohalines in Fig. 2. This clearly indicates that calcium concentrations in the 2 rivers are largely regulated by the salt water incursion. During monsoon, when the rivers get filled with fresh water almost to their mouths, calcium concentration decreases to zero or near-zero with decrease in salinity.

We tried to study the dilution in the rivers by deducing the following equations, based on the 'simple mixture' relationship of Carpenter *et al.*[10]:

$$A_1/A_2 = F/(1-F) \quad \ldots (1)$$

where $F=(X-X_2)/(X_1-X_2)$ and $F<1$ ... (2)

X_1 is the concentration of a component in solution 1 (sea water); X_2 is the concentration of the same component in solution 2 (river water at zero chlorinity); X is the concentration in the resulting mixture of solutions 1 and 2 (sample water); A_1 is the amount of solution 1 in the resulting mixture; A_2 is the amount of solution 2 in the same mixture; and F is a constant to be calculated for each season. Since zero or near-zero chlorinity was almost always observed throughout the year, applying the assumptions as stated under 'salinity' and values at sts M9 and Z9 as

Table 1—Seasonal Variation (%) of Sea Water in Estuarine Regions of Mandovi and Zuari (Calculated from Salinity Values)

Salinity ‰			F		Sea water %	
Sea	Mandovi	Zuari	Mandovi	Zuari	Mandovi	Zuari
			Premonsoon			
36.22	31.85	34.1	0.12	0.06	88	94
			Monsoon			
31.36*	7.09	13.52	0.77	0.57	23	43
			Post monsoon			
34.5	26.79	31.29	0.22	0.09	78	91

*Observation during September only

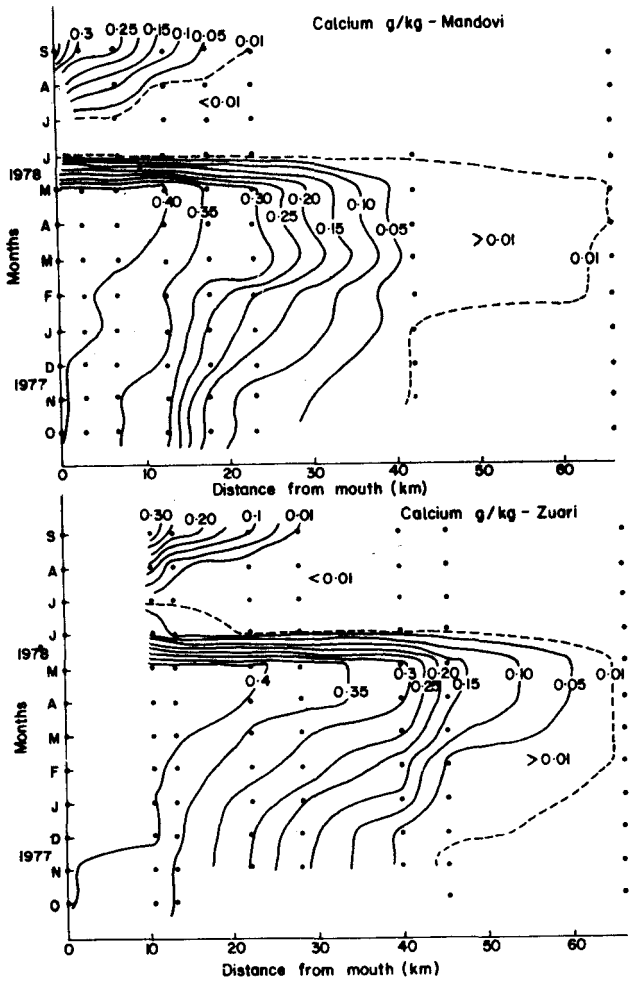

Fig. 3—Diagrammatic representation showing isolines of calcium concentration from the mouth of Mandovi and Zuari upstream in different months [—, concentrations at 0.05 g/litre intervals; ---, concentration of 0.01 g/litre]

representative for river water, the relevant factors have been calculated and presented in Table 2.

Eliminating F from Eq. 2, we can calculate the concentration of one component from the concentration of the others, using chlorinity as a reference element for the fraction of sea water present in the estuarine water sample. Chlorinity has been used as a reference element because it can be assumed as an index of conservative behaviour and there appears to be no evidence for halide ions behaving non-conservatively in estuarine waters[11,12]. Neglecting the chloride in river water, the resulting equation, as deduced by Carpenter *et al.*[10], has the following form:

$$X_{\text{sample}} = X_{\text{river}} + \frac{(X_{\text{sw}} - X_{\text{r}})}{\text{Cl}_{\text{sw}}} \text{Cl}_{\text{sample}} \quad \ldots (3)$$

In these calculations, all the stations from the mouth to the approximate distances of tidal influence are included (sts M1 to M7 in the Mandovi and Z1 to Z7 in the Zuari). The deviations between the measured and the computed values may give an idea of the nature of flow and mixing processes in the estuary. Ratios between the measured and the computed values of calcium to chlorinity were also similarly calculated in an attempt to study the influence of sea water (Table 3).

The calculated values of calcium (Ca_{calc}) are almost always lower than the measured values (Ca_{obs}) in both the rivers (Table 3). The same thing can be observed in their ratios to chlorinity (Ca_{calc}/Cl and Ca_{obs}/Cl). This lowering is due to low additions of calcium in river water. Global average of calcium in rivers is 15 mg/litre at 7.8 mg/litre chloride with Asian rivers having a mean of 18.4 mg/litre calcium at 8.7 mg/litre chloride[13]. Concentrations at st M9 varied from 4.6 to 10.3 mg/litre while at st Z9 the variation was 3.4 to 7.5 mg/litre. This is the reason for values for Ca_{calc} and Ca_{calc}/Cl in both the rivers being lower than the measured values.

Values for Ca_{calc}/Cl compare quite well with the Ca/Cl ratios at the stations in the nearshore region. The difference between Ca_{obs}/Cl and Ca_{calc}/Cl can, thus, be attributed to riverine influence. Thus, it can be concluded that in the estuarine regions of Mandovi and Zuari, calcium concentration is regulated by the inflow of sea water. Positive values of the deviations, $Ca_{calc} - Ca_{obs}$ and $Ca_c/Cl - Ca_o/Cl$, would therefore, indicate dilution by fresh water influx, the magnitude of which is indicated by the magnitude of the difference. Whatever differences from sea water values at corresponding chlorinity and the seasonal variation of calcium concentrations occurring in these two rivers are due to the participation of this element in the estuarine biogeochemical cycle rendering its character as non-conservative or semi-conservative in the estuarine region. A similar phenomenon has been observed in the nearshore regions of Goa and the same explanation has been attributed for this[14].

Magnesium—Temporal and spatial variations of magnesium in both the rivers (Fig. 4) agree very well with isopleths of calcium (Fig. 3) than with the isohalines (Fig. 2). In both these figures, the salt water incursion during post and premonsoon along with fresh water runoff during monsoon can be identified clearly. Similarities in the variations and slopes of the isopleths indicate that calcium and magnesium in these 2 rivers should behave in a similar fashion.

Seasonal variation of sea water fractions in the 2 rivers using magnesium as indicator for these 2 rivers by applying Eq. 1 has been studied. Similar postulations and assumptions, as were used in case of calcium were applied in the case of magnesium also. Results obtained from these calculations are presented in Table 2.

Table 2—Seasonal Variation (%) of Sea Water in Estuarine Regions of Mandovi and Zuari (Calculated from Calcium, Magnesium and Sulphate Concentrations)

	Conc. g/kg				F		A_1/A_2		Sea water %	
Sea	Mandovi (estuary)	Mandovi (river)	Zuari (estuary)	Zuari (river)	Mandovi	Zuari	Mandovi	Zuari	Mandovi	Zuari
					CALCIUM					
					Premonsoon					
0.424	0.390	0.01	0.42	0.005	0.92	0.99	11.5	99	92	99
					Monsoon					
0.421	0.067	0.006	0.122	0.005	0.15	0.28	0.18	0.39	15	28
					Postmonsoon					
0.409	0.325	0.007	0.370	0.006	0.79	0.90	3.8	9	79	90
					MAGNESIUM					
					Premonsoon					
1.295	1.177	0.006	1.267	0.001	0.91	0.98	10.1	49	92	98
					Monsoon					
1.271	0.183	0	0.350	0	0.14	0.27	0.16	0.37	14	27
					Postmonsoon					
1.234	0.974	0.003	1.116	0.003	0.79	0.90	3.8	9	79	90
					SULPHATE					
					Premonsoon					
2.65	2.45	0.002	2.62	0.007	0.92	0.99	11.5	99	92	99
					Monsoon					
2.63	0.33	0.003	0.73	0.002	0.12	0.28	0.14	0.14	12	28
					Postmonsoon					
2.48	1.93	0.006	2.22	0.017	0.78	0.89	3.5	8.1	78	89

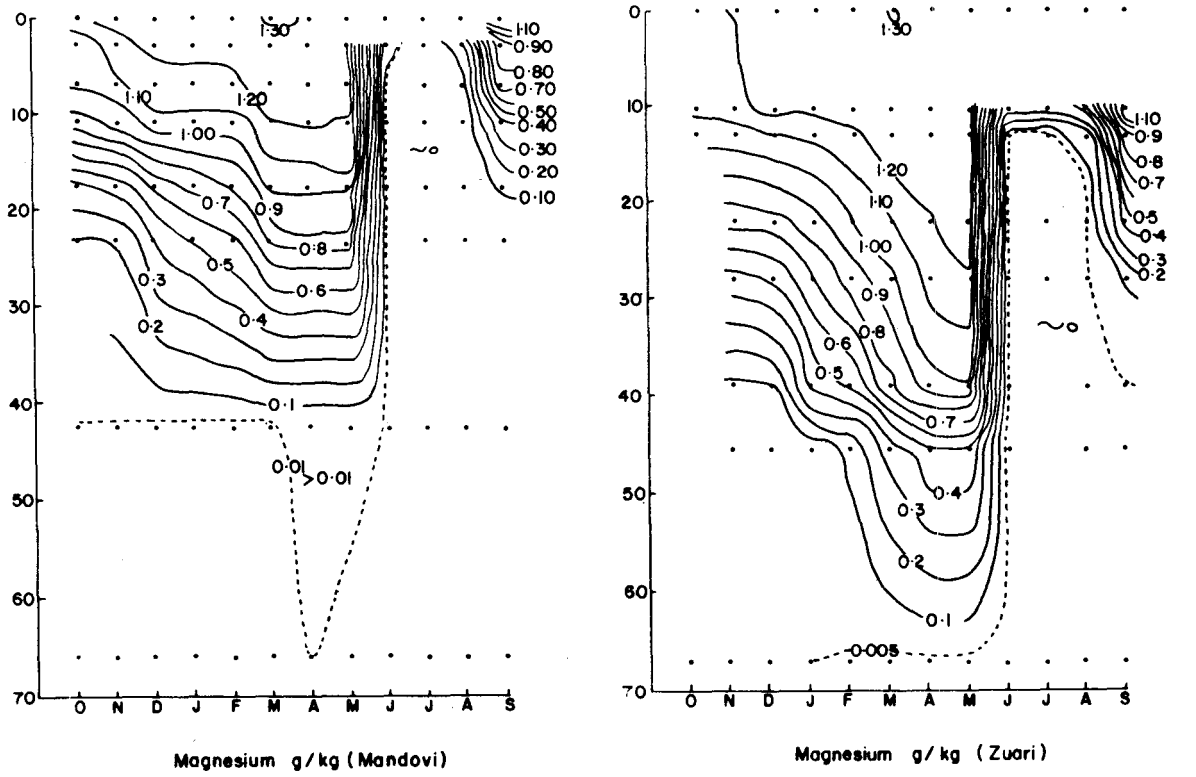

Fig. 4—Diagrammatic representation showing isolines of magnesium concentration from the mouth of Mandovi and Zuari upstream in different months [—, concentrations at 0.1 g/litre intervals, ---, concentration of 0.01 g/litre]

Table 3—Observed and Calculated Values of Calcium and Their Ratios with Chlorinity in Mandovi and Zuari

Months	Cl ‰	Ca g/kg		$Ca_{calc} - Ca_{obs}$	Ca/Cl		$(Ca_{calc}/Cl) - (Ca_{obs}/Cl)$
		obs	calc		obs	calc	
				Mandovi			
Feb.	15.31	0.335	0.328	−0.007	0.02188	0.02142	−0.00046
March	16.47	0.386	0.345	−0.041	0.02343	0.02137	−0.00206
April	16.56	0.389	0.352	−0.037	0.02349	0.02125	−0.00224
May	19.02	0.391	0.405	+0.014	0.02055	0.02129	+0.00074
June	1.27	0.02	0.031	+0.011	0.01575	0.02441	+0.00866
July	1.12	0.005	0.032	+0.027	0.00446	0.02857	+0.02411
Aug.	3	0.016	0.077	+0.061	0.00533	0.02567	+0.02034
Sept.	7.24	0.17	0.159	−0.011	0.02348	0.02196	−0.00152
Oct.	12.1	0.272	0.261	−0.011	0.02247	0.02157	−0.0009
Nov.	12.21	0.268	0.262	−0.006	0.02194	0.02145	−0.00049
Dec.	13.62	0.302	0.291	−0.011	0.02217	0.02136	−0.00081
Jan.	15.32	0.33	0.327	−0.003	0.02154	0.02134	−0.0002
				Zuari			
Feb.	15.17	0.338	0.328	−0.01	0.02228	0.02162	−0.00066
March	16.38	0.371	0.358	−0.013	0.02264	0.02185	−0.00079
April	16.94	0.405	0.361	−0.044	0.0239	0.02131	−0.00259
May	18.87	0.405	0.401	−0.004	0.02146	0.02125	−0.00021
June	2.04	0.029	0.055	+0.026	0.01421	0.02696	+0.01275
July	2.13	0.005	0.055	+0.05	0.00235	0.02582	+0.02347
Aug.	5.43	0.042	0.135	+0.093	0.00773	0.02486	+0.01713
Sept.	7.99	0.199	0.174	−0.025	0.0249	0.02177	−0.00313
Oct.	—	—	—	—	—	—	—
Nov.	12.31	0.266	0.264	−0.002	0.0216	0.02144	−0.00016
Dec.	13.47	0.281	0.287	+0.006	0.02086	0.0213	+0.00044
Jan.	14.30	0.312	0.306	−0.006	0.02181	0.02139	−0.00042

Ca_{obs}/Cl = 0.02237 ± 0.00028 (excluding June-August)
Ca_{calc}/Cl = 0.02150 ± 0.00006 (excluding June-August)
Ca/Cl = 0.02161 ± 0.00012 (At sts C1 to C3)
Ca/Cl = 0.02131 ± 0.00027 (nearshore Goa[14])

Similarity can be observed between values calculated from calcium and magnesium concentrations (Table 2). This would indicate that both calcium and magnesium originate from the same type of terrain and behave the same way in both the river systems, as has also been noted from similarities of their isopleths (Figs 3 and 4).

Mixing processes with the help of magnesium concentrations and also the influence of sea water on the magnesium/chlorinity ratios and their monthly variations in both the rivers have been studied. For these calculations, relations as given in Eq. 3 are applied. The results are presented in Table 4.

In contrast to calcium (Table 3) the calculated values of magnesium (Mg_{calc}) are higher than the observed values (Mg_{obs}) (Table 4). This would indicate that river water adds less magnesium as compared to calcium. Magnesium concentrations at st M9 ranged from 0 to 15.7 mg/litre and at st Z9 from 0 to 4.8 mg/litre with zero values appearing during 8 months of the year at both the stations, while for calcium no zero value was observed. Global average of magnesium in river water is 4.1 mg/litre at 7.8 mg/litre chloride, while the mean composition of Asian rivers is 5.6 mg/litre magnesium at 8.7 mg/litre chloride[13]. Although apparently Mandovi and Zuari contain, on an average, less calcium and more magnesium compared to global and Asian mean values, yet because of the influence of sea water, the difference cannot be evidenced. Averages of both calcium and magnesium in these 2 rivers are about 75% of these elements in the sea outside, but river calcium is more (1.1 to 3.2%) in the estuarine region than river magnesium (0 to 1.6%). This would imply that calcium takes more active part in the biogeochemical cycles in the rivers than magnesium.

As expected, Mg_{calc}/Cl and Mg_{obs}/Cl show the same type of variation as Mg_{calc} and Mg_{obs}. Maximum difference between the two is observed during

Table 4—Observed and Calculated Values of Magnesium and Their Ratios with Chlorinity in Mandovi and Zuari

Months	Cl ‰	Mg g/kg		$Mg_{calc}-Mg_{obs}$	Mg/Cl		$(Mg_{cal}/Cl)-(Mg_{obs}/Cl)$
		obs	calc		obs	calc	
				Mandovi			
February	15.31	1.070	0.998	−0.072	0.06988	0.06518	−0.00470
March	16.47	1.145	1.073	−0.072	0.06952	0.06514	−0.00438
April	16.56	1.146	1.086	−0.060	0.06920	0.06557	−0.00363
May	19.02	1.136	1.245	+0.109	0.05972	0.06545	+0.00573
June	1.27	0.037	0.092	+0.055	0.02913	0.07244	+0.04331
July	1.12	0	0.081	+0.081	0	0.07232	+0.07232
August	3.00	0.029	0.218	+0.189	0.00967	0.07267	+0.06300
September	7.24	0.479	0.474	−0.005	0.06616	0.06546	−0.00070
October	12.10	0.695	0.794	+0.099	0.05743	0.06561	+0.00818
November	12.21	0.800	0.801	+0.001	0.06552	0.06560	+0.00008
December	13.65	0.905	0.892	−0.013	0.06644	0.06549	−0.00095
January	15.32	0.973	1.008	+0.035	0.06351	0.06579	+0.00228
				Zuari			
February	15.17	1.006	0.993	−0.013	0.06631	0.06545	−0.00086
March	16.38	1.23	1.072	−0.051	0.06855	0.06544	−0.00311
April	16.94	1.176	1.109	−0.069	0.06942	0.06546	−0.00396
May	18.87	1.220	1.235	+0.015	0.06465	0.06544	+0.00073
June	2.04	0.068	0.148	+0.080	0.03333	0.07255	+0.03922
July	2.13	0	0.155	+0.155	0	0.07277	+0.07277
August	5.43	0.105	0.395	+0.290	0.01934	0.07274	+0.05340
September	7.99	0.666	0.523	−0.143	0.08335	0.06545	−0.01790
October	—	—	—	—	—	—	—
November	12.31	0.778	0.806	+0.038	0.06320	0.06547	+0.00227
December	13.47	0.840	0.882	+0.042	0.06236	0.06547	+0.00311
January	14.30	0.931	0.937	+0.006	0.06510	0.06552	+0.00042

Mg_{obs}/Cl = 0.06648 ± 0.00135 (excluding June to August)
Mg_{calc}/Cl = 0.06547 ± 0.00003 (excluding June to August)
Mg/Cl = 0.06451 ± 0.00055 (at stations C1 to C3)
Mg/Cl = 0.06641 ± 0.00028 (nearshore Goa[14])

monsoon when magnesium concentration in river water is zero and, therefore, the differences between the ratios reach maximum positive values indicating maximum dilution effect.

From the positive deviations between Mg_{calc} and Mg_{obs} the possible dilution by fresh water can be calculated. As river water contains little or no magnesium the lowering in Mg_{obs} can be attributed entirely to the dilution effect. Thus, it can be concluded that Mandovi is influenced by fresh water runoff from 0.1 to 100% and Zuari from 0.6 to 100%, maximum values being attained in July. Similarly, negative deviations should be due to salt water incursion, maximum values in both the rivers being observed in March - April.

Using calcium concentration in a similar way, positive values in the range of 3.5 to 84.4 and 2.1 to 91 have been obtained for Mandovi and Zuari respectively, the highest being in July. Negative values showed maximum salt water incursion in March April.

Thus, using calcium and magnesium as indicators we get almost similar ranges of dilutions by freshwater run off and mixing by salt water incursion.

Sulphate—A general review of sulphate and chlorinity and their interrelationships in the rivers Mandovi and Zuari has been presented[2]. Temporal and spatial variations of sulphate in Mandovi and Zuari are presented here.

A remarkable similarity can be observed between the slopes of the isopleths of sulphate (Fig. 5) and isohalines (Fig. 2). The extension of the sulphate isopleths upstream is similar to the penetration of the isohalines inland, with zero or near-zero values at the last stations for both the components in both the rivers. It can, therefore, be assumed that sulphate concentrations in these 2 rivers can be used in the same way as the chlorinity values. Moreover, sulphate

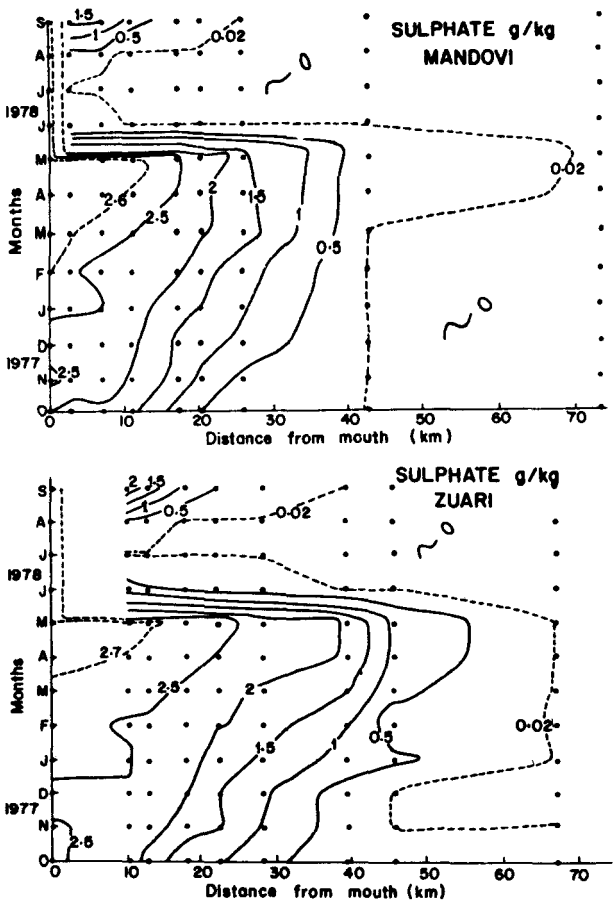

Fig. 5—Diagrammatic representation showing isolines of sulphate concentration from the mouth of Mandovi and Zuari upstream in different months [—, concentrations at 0.5 g/litre intervals; ---, at the top of the figure for Mandovi gives concentration of 2.6 g/litre and the same for Zuari gives 2.7 g/litre; - - -, at the bottom in both the figures indicate concentration of 0.02 g/litre]

hardly takes part in biogeochemical cycles in aerobic environments.

Following Eqs. 1 and 2 and the associated assumptions, as applied for calcium and magnesium, seasonal variations of sea water fractions in the 2 rivers were calculated using the average values of sulphate concentrations during the 3 seasons. Since the isopleths of sulphate matched with the isohalines much better than those for calcium and magnesium, it can be expected that the dilution values, calculated using sulphate as indicator, would be very close to the values obtained using salinity. Results, using sulphate, are presented in Table 2. Values for percentages of sea water during pre and postmonsoon (Table 2) compare quite well with the corresponding values for those in Table 1. However, this difference becomes quite appreciable for the monsoon season. We attribute this, partly, to the errors in the gravimetric estimation for low concentrations of sulphate.

Using Eq. 3 monthly variations in sulphate concentrations and the sulphate/chlorinity ratios (S/Cl) in the 2 rivers were calculated with a view to studying the mixing processes and the eventual influence of biogeochemical cycles on these values. The same assumptions and limitations in these calculations, as stated under salinity, calcium and magnesium, will be valid in case of sulphate also. The results are presented in Table 5.

Similar to magnesium (Table 4), the calculated values of sulphate are higher than the observed values (Table 5). But in case of sulphate, excepting on 2 occasions during peak summer, the calculated values are almost always higher than the observed values. This would indicate either insignificant addition of sulphate by river water or its absolute non-participation in biogeochemical cycles indicating its strongly conservative character. Concentrations at st M9 varied from 0 to 19 mg/litre while those at st Z9 showed a variation from 0 to 22 mg/litre throughout the year. Global mean sulphate concentrations in rivers is 11.2 mg/litre while the mean for Asian rivers is 8.4 mg/litre[13]. This means that fresh water additions of sulphate in Mandovi and Zuari are not insignificant, as compared to global and Asian averages. Therefore, the other possibility of non-participation of sulphate in biogeochemical processes seems to be valid for these 2 rivers.

The same trend is also indicated by S_{calc}/Cl and S_{obs}/Cl ratios. Remarkable similarity between S_{obs}/Cl in the estuarine regions (Table 5) and S/Cl at sts C1 to C3 (0.1369 ± 0.0015) in the nearshore region of Goa indicates that the water flowing into the rivers from the sea outside does not lose its sulphate concentration as long as it circulates inside the river. Therefore, sulphate concentrations in Mandovi and Zuari are at a steady state, agreeing with an earlier conclusion[2].

Utilising the differences between S_{calc} and S_{obs} it has been calculated that the annual range of dilution by sea water varies from 1 - 97% in Mandovi and 2 - 98% in Zuari. These values do not fully agree with similar values calculated using calcium and magnesium concentrations as indicators. But the values for seasonal variation of dilution compare quite well between sulphate and salinity. This leads us to believe that both calcium and magnesium participate in the biogeochemical processes in the rivers while sulphate does not. This can also be seen from the differences between Ca_{obs}/Cl (Table 3), Mg_{obs}/Cl (Table 4) and S_{obs}/Cl (Table 5) and their corresponding values at sts C1 to C3. For Ca/Cl the difference is + 5%, for Mg/Cl it is − 3% while for S/Cl it is only − 0.5%, which is well within the range of scatter for oceanic S/Cl (0.4%).

Geochemical processes—Having studied temporal and spatial variations of the 3 components it is postulated that calcium and magnesium take part in the geochemical processes in the rivers and are

Table 5—Observed and Calculated Values of Sulphate and Their Ratios with Chlorinity in Mandovi and Zuari

Months	Cl ‰	Sg g/kg		$S_{calc}-S_{obs}$	S/Cl		$(S_{calc}/Cl)-(S_{obs}/Cl)$
		obs	calc		obs	calc	
				Mandovi			
February	15.31	2.10	2.14	+0.04	0.1371	0.1397	+0.0026
March	16.47	2.37	2.30	−0.07	0.1438	0.1396	−0.0042
April	16.56	2.41	2.32	−0.09	0.1455	0.1400	−0.0055
May	19.02	2.47	2.66	+0.11	0.1298	0.1398	+0.0100
June	1.27	0.09	0.19	+0.10	0.0709	0.1496	+0.0787
July	1.12	0.005	0.17	+0.165	0.0045	0.1518	+0.1473
August	3.00	0.014	0.46	+0.446	0.0047	0.1533	+0.1486
September	7.24	1.01	1.02	+0.01	0.1395	0.1408	+0.0013
October	12.10	1.63	1.87	+0.24	0.1347	0.1545	+0.0198
November	12.21	1.67	1.71	+0.04	0.1367	0.1400	+0.0033
December	13.62	1.82	1.90	+0.08	0.1336	0.1395	+0.0059
January	15.32	2.00	2.15	+0.15	0.1305	0.1403	+0.0098
				Zuari			
February	15.17	2.09	2.14	+0.05	0.1377	0.1410	+0.0033
March	16.38	2.30	2.29	−0.01	0.1404	0.1398	−0.0006
April	16.94	2.50	2.38	−0.12	0.1475	0.1404	−0.0071
May	18.87	2.55	2.64	+0.09	0.1351	0.1399	+0.0048
June	2.04	0.15	0.30	+0.15	0.0735	0.1470	+0.0735
July	2.13	0.005	0.33	+0.325	0.0023	0.1549	+0.1526
August	5.43	0.12	0.81	+0.69	0.0221	0.1549	+0.1328
September	7.99	1.20	1.12	−0.08	0.1501	0.1401	−0.0100
October	—	—	—	—	—	—	—
November	12.31	1.66	1.73	+0.07	0.1348	0.1405	+0.0057
December	13.47	1.70	1.88	+0.18	0.1262	0.1395	+0.0133
January	14.30	1.95	2.00	+0.05	0.1363	0.1398	+0.0035

S_{obs}/Cl = 0.1376 ± 0.0015 (excluding June to August)
S_{calc}/Cl = 0.1408 ± 0.0008 (excluding June to August)
S/Cl = 0.1369 ± 0.0015 (at sts C1 to C3)

probably lost to the sediments. Therefore, an attempt has been made to study the possible form(s) in which these 2 elements can be lost. Relations of calcium and magnesium with sulphate, silicate and phosphate have been examined. Sulphate and silicate did not show any regular pattern of relation. But a 2nd order fit could be approximated between calcium, magnesium and phosphate (Fig. 6). The curves for both calcium and magnesium tend to be asymptotic above a certain concentration of phosphate. From Fig. 6, it can be estimated excluding the values during the monsoon season at the lower part of the figures, that above 1.5 μg-at/litre phosphate-phosphorus in water, calcium and magensium would be removed from the system. The asymptotic relation or the convex formation of the curves at higher concentrations of phosphate-phosphorus may be due to either or both the processes of sedimentation and evaporation with more possibilities for the latter, as has been suggested by Kullenberg and Sen Gupta[15]. This type of relation may be expected beyond sts M5 and Z5, that is, at the upper reaches of both the rivers. These conclusions are very tentative and much work has to be done on the chemistry of suspended and particulate matter and sediments in Mandovi and Zuari to delineate a clear picture of the geochemical processes therein.

General remarks—Summing up the above results and discussions, we can draw the conclusion that in the tide-dominated Mandovi and Zuari river systems calcium behaves as a semi-conservative property while magnesium and sulphate behave as conservative properties of water, with sulphate being the most conservative of the 3. Properties of the water masses in these 2 rivers are regulated mostly by the inflowing sea water during pre and postmonsoon. Percentages of sea water that can be expected to be present in the estuarine regions of the rivers, calculated by using the 4 variables, salinity, calcium, magnesium and sulphate, are presented in Tables 1 and 2. The range of variation of per cent sea water in Mandovi is quite small and may be considered to be within the analytical and computational errors. However, in Zuari the

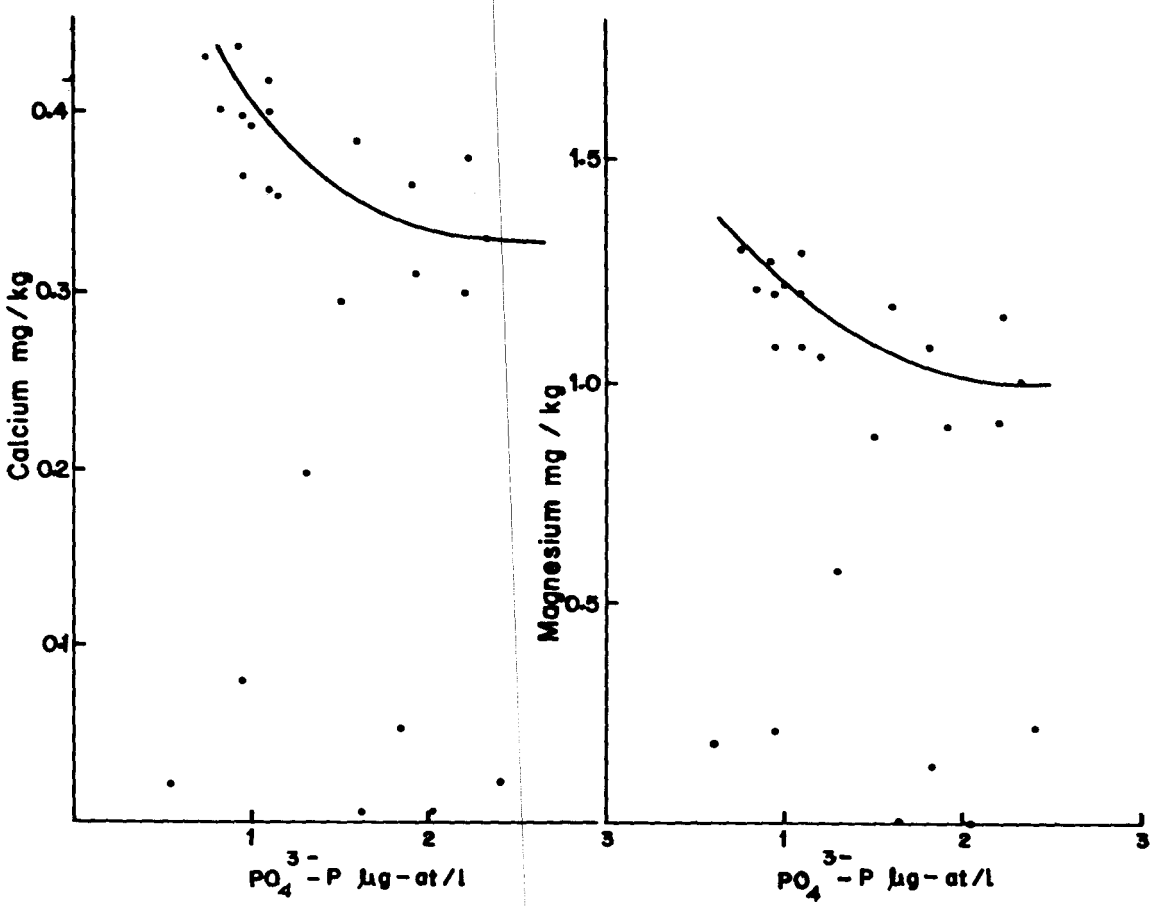

Fig. 6—Cumulative relations of calcium and magnesium with phosphate-phosphorus in both the rivers through the year [Curves have been extrapolated at higher concentrations]

differences are larger. This may be due to the fact that Zuari receives about half as much fresh water runoff as Mandovi and at any time contains more salt between the 2 rivers[2].

It has been observed that during mixing, the major ions sodium, potassium, calcium, magnesium and sulphate behave conservatively in rivers[12]. Calcium is the dominant exchange ion in fresh water; in brackish water sodium begins to occupy the exchange sites, as salinity increases, replacing calcium[16]. This means that uptake of one major cation should be replaced by that of another.

A conservative ion should have a linear relation with chlorinity. In fact, all the 3 ions in our study indicate the same type of relations with chlorinity when individual values are plotted against each other. However, higher values of Ca/Cl and Mg/Cl in the rivers as compared to the values from the inshore region indicate that both these elements do take part in biogeochemical processes. Differences between the observed and calculated values of calcium and magnesium and their ratios to chlorinity are higher than the accuracy of the analytical methods. This corroborates the above postulations.

However, sulphate appears to behave as a conservative element as the differences between the observed and calculated values and their ratios with chlorinity lie well within the analytical accuracy. Moreover, the rivers are well oxygenated throughout their entire stretches which precludes any sulphate reduction.

It is difficult to draw comparisons between different estuaries; distributions of the chemical species are regulated by fresh water runoff, sea water inflow, evaporation, precipitation and the nature of the catchment area[17].

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