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Distribution of Phosphorus & Organic Carbon in the Nearshore Sediments of Goa

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Samples collected from sediment water interface from the inner shelf region of Goa coast are examined for their phosphorus and organic carbon, which indicate the geochemical environment under which the present day deposits are laid down. As the colour, texture and lithology of the sediment varies considerably from north to south, so also the degree of concentration of organic carbon and phosphorus varies suggesting that they are in direct relationship with each other. Organic carbon is low (0·85%) at 5-10 m depth, but it is over 5% at 10-20 m depth with a few patchy areas of high and low values beyond and up to 50 m depth. Similarly, phosphorus is low (0-0·1%) at 0-10 m depth, but it is high (0·4-0·98%) at the mouths of the rivers. Both organic carbon and phosphorus are delineated into 2 zones (of high and low concentrations) along Marmugao Head (up to Tiracol river transect). Though organic carbon and phosphorus are related with each other, their variability fluctuates in terms of pre and postmonsoon periods in the region. The organic carbon has a proportional relationship with the clay fraction of the sediment. Higher concentration of phosphorus noticed in postmonsoon periods is considered to be due to a large supply of the terrigenous apatite brought in by the rivers; this is, in addition to contributing factors like organic productivity, upwelling and pollutants in the region. Since the sediment in the region falls within the zone of 0·5-5·0% P_2O_5, it can be considered to be 'phosphate bearing'.

PHOSPHORUS and organic constituents in sediments (ancient or modern) indicate the geochemical conditions under which the deposits were laid down. While a study of the successive deeper layers of the deposits of a region presents varying environmental conditions of the past, a study of the samples collected at the sediment-water interface, across the same region, reflects (i) the prevailing conditions under which the deposition is taking place, and (ii) the relationship of the sediment with the overlying water mass, which in turn, is subject to movement of currents, oxygen content, upwelling, organic productivity, etc.

The area under investigation is a part of the central west coast of India, and the present study is restricted to the inner shelf region (0-50 m) of the Goa shelf. Surface samples (42) were collected (using a Peterson grab) along 6 transects between 15°05'27"N: 73°39'08"E in the south (off Sol river) and 15°43'00"N: 73°39'30"E in the north (off Tiracol river) at 5-10 m interval (Fig. 1). The sampled localities and station locations are shown in Figs. 1 and 2. This report presents the results of the analyses done of total phosphorus and organic carbon content in the different types of sediments encountered in this region in relation to the environment in which they are present as well as the nature of the overlying water mass.

Methods

Total phosphorus present in the sediment was determined using the technique adopted by Rochford[1]. Extinctions were measured at 700 nm using the 'Speckol' spectrophotometer. Total phosphorus estimated includes all forms of phosphorus such as interstitial phosphate, adsorbed phosphate, organic phosphate, and also the insoluble organic phosphate. Using El-Wakeel and Riley's[2] method, organic carbon content in the sediment was determined and the values thus obtained were multiplied by the factor of 1·724 to obtain an estimate of organic matter present in the sample. However, the organic content here is discussed in terms of carbon ($C_{org.}$).

Results

Sedimentology — The colour, texture and lithology of sediment in the study area vary considerably from north to south (from Tiracol to Sol river region) and horizontally, depth-wise (0-20-50 m). Along the Tiracol transect, the sediment up to 0-5 m is fine sand (being up to 5% shelly), which is followed by silty clay up to 50 m depth. Along the Chapora transect the sediment is largely black, fine sand containing nearly 10-15% organic debris in it. This is followed by silty sand up to 10 m; at 15 and 40 m clayey silt; at 20-30 m sansicl; but at 50 m, it is chiefly silty clay. At Aguad transect, it is very similar to the above (Chapora) except at 5 m, it is medium sand (having a tinge of red) and clayey silt at 10 m, and silty sand at 15 m depth. Along the Baina transect, it is medium sand with a greyish colour containing 15-20% shell fragments in it (at 15 m depth) followed by silty clay up to 50 m depth. Off Colva, at 0-5 m, the fine sand has a high percentage of foraminifera and other microorganisms. This is immediately followed by sansicl at 10 m, silty clay at 15-40 m, and clayey silt at 50 m. Along the Sol river transect, at 5-10 m, it is sansicl, but it is silty clay from 15-50 m depth.

The distribution of sediment, from the north to the south, thus presents an irregular pattern of

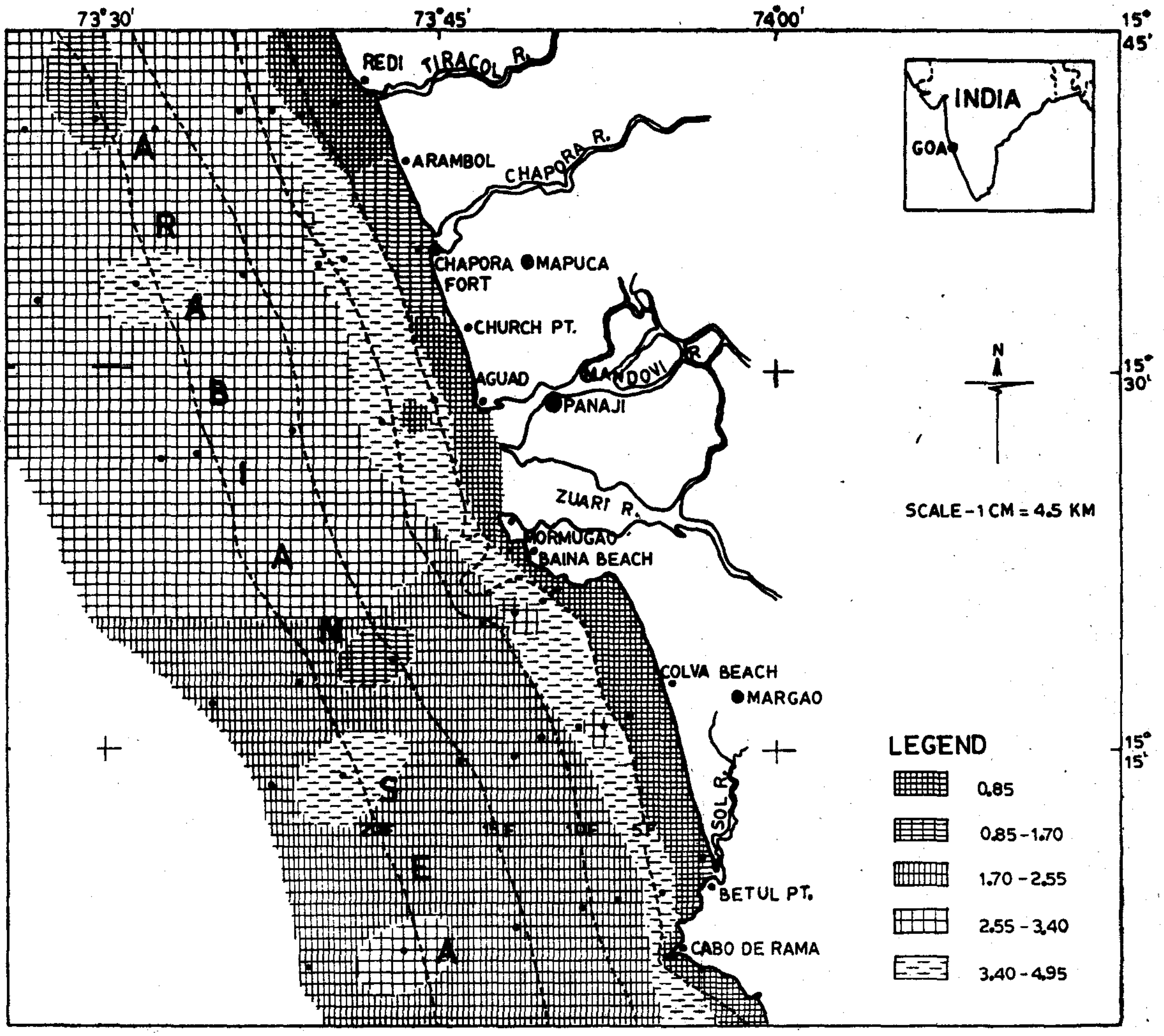

Fig. 1 — Station locations and distribution pattern of organic carbon in the nearshore sediments of Goa coast

differing sediments and size fractions. Therefore, it is envisaged that there is a variation in the degree of concentration of organic carbon, carbonate, phosphorus, iron and other elemental components in the sediment. Apatite grains are found to be present as detrital mineral primarily in the silty fractions of all the transects. This apatite seems to be derived from the quartzites, schists, diabases and gneisses which form the coastal rocks in the area.

Distribution of organic carbon — Table 1 presents the percentage distribution of organic carbon in the total sample and also in its clay fraction (in the case of all 6 transects) during the pre and postmonsoon periods.

Concentration of organic carbon is low (less than 0·85%) at 5-10 m depth all along the coast (north-south) with the exception of Chapora river transect (Fig. 1) where it is suddenly succeeded by a belt of very high levels (5%) immediately after (at 10-20 m). This belt is wide to the north of Marmugao Head, but it thins out to the south of it. However, there are small patchy areas of high and low values beyond and up to 50 m depth. Between 20 and 50 m the entire area appears to be divided along the Marmugao Head into areas of high (2·55 to 3·40%) concentration to the north and low (1·70-2·55%) concentration to the south of it.

The region is fed by small rivers which have their origin in the highlands having dense tropical vegetation. Therefore, it is considered that the high values of organic content in the sediments all along the coast beyond 10 m depth is the result of outflow of the rivers laden heavily with terrestrial organic detritus. The latter seems to be augmented by sewage and other pollutants discharged into the region derived from land and, the ships' movement in and out of the Marmugao Harbour, and the prolific fishing activity along the entire coast. Perhaps, this belt of highly concentrated organic carbon spreads into areas of weaker concentration in the deeper water region (20-50 m) in a desegregated and decomposed form. At the 40 m sampled locations along all the transects, except Aguad and Tiracol, high values of organic carbon are noticed which may be attributed to the decreasing grain size and consequent protective action of clay and porosity of sands[3].

It is implied, though not clearly, that the state of preservation of organic carbon undergoes decomposition during its transport in the river, at the mouth, and finally it finds its level of settlement at different depths in the inner shelf. This does not

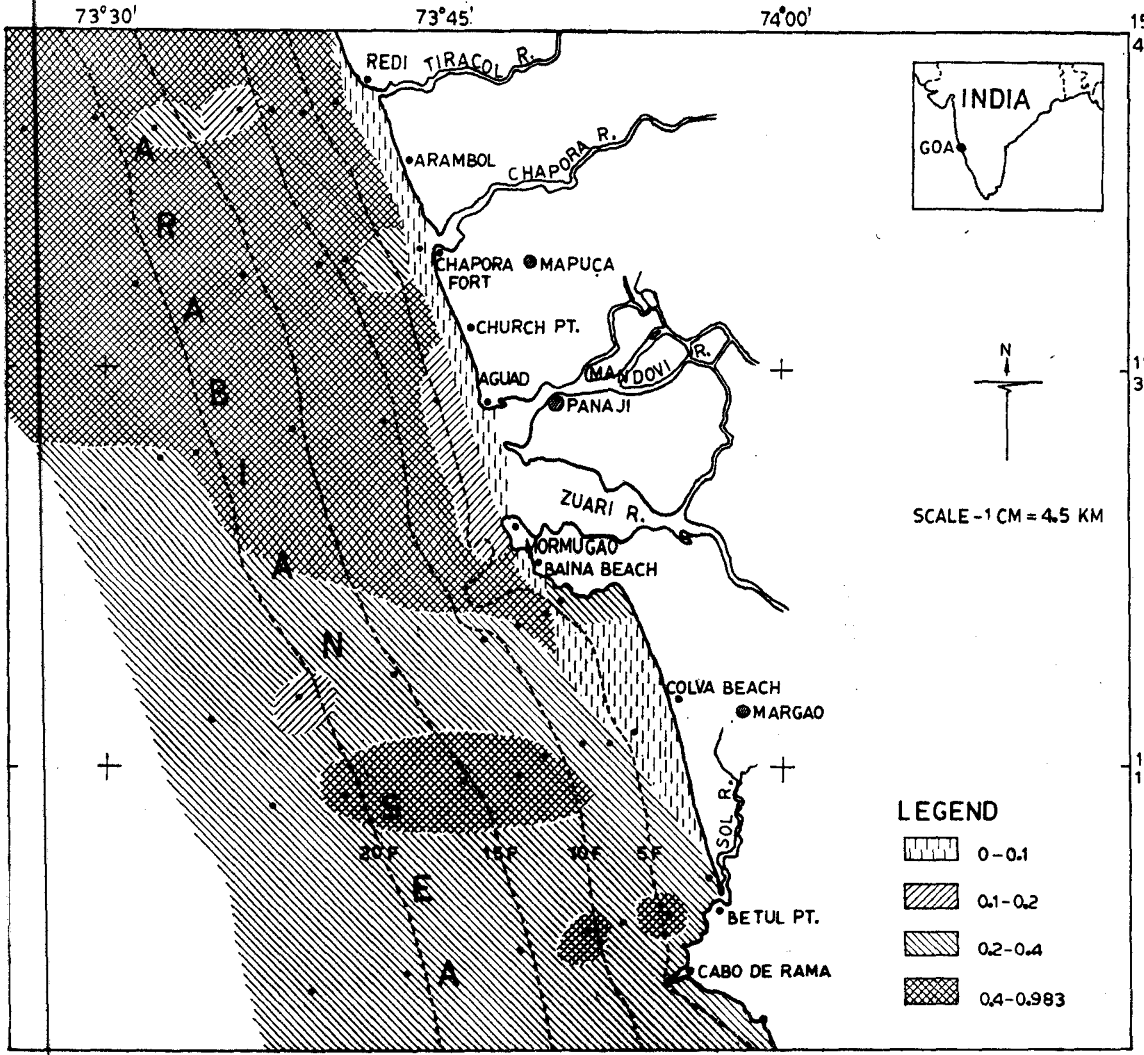

Fig. 2 — Station locations and distribution pattern of phosphorus in the nearshore sediments of Goa coast

preclude further addition or enrichment of organic carbon through biological productivity of the overlying waters. Though the activities of micro-organisms, bacteria, burrowing animals and other feeding and scavenging types result in the degradation of some compounds, but at the same time, synthesis of others continues unabatedly with the result that the organic carbon in the sediment is quite high due to cumulative increase. The horizontal distribution of organic carbon into areas of high and low are apparently controlled by the outflow of the rivers, and the movement, direction and force of the longshore currents in the region.

The percentage of organic carbon is high in the clayey fraction of the sediment (Table 1). However, it is noticed that the substrate in the region is highly clayey also. Therefore, the grain size of the clayey fraction is considered to retard the organic carbon from rapid decomposition.

Distribution of phosphorus — Fig. 2 presents the general distribution of phosphorus as a constituent (P_2O_5) in the sediment. The variation in percentage of P_2O_5 (on carbonate free basis) is not appreciable (0 to 0·983%). The pattern of distribution indicates very low values (0 to 0·1%) all along the beach to an approximate depth of 10 m, but it shows a spurt of high values (0·2-0·4%) at the mouth of the Sol river. Similarly, at the mouths of the rivers Chapora, Mandovi and Zuari the percentage values are high. This is obviously related to the character of the sediment off these mouths of rivers. The very low concentration zone (0 to 0·1%) is followed by a sudden very high level zones (0·2-0·4 and 0·4-0·98%). The delineation into 2 areas of low and high regions takes place along the Marmugao Head or along the Baina transect — the northern zone being richer (0·4-0·98%) while the southern zone being poorer (0·2-0·4%). There are a few isolated patches in this area where high and low values are noticed. In general, the organic carbon and total phosphorus values appear to correlate with each other. However, the presence of a belt of very high organic carbon running along north-south appears to be unique.

Discussion

Table 1 shows a relationship between phosphorus and organic carbon on the one hand and on the other, refer to the fluctuation in organic carbon concentration in the type of sediment and also the variability of these three interconnected parameters in terms of pre and postmonsoon periods. Considered together phosphorus and organic carbon fluctuate almost parallelly with each other. However, it is

TABLE 1 — PERCENTAGE DISTRIBUTION OF ORGANIC CARBON AND TOTAL PHOSPHATE IN THE NEARSHORE SEDIMENTS OF THE GOA COAST DURING (A) PRE- AND (B) POSTMONSOON PERIODS

Sample No.	Station depth	Organic carbon, %		Total P_2O_5, %	
		Total sample	Clay fraction	Total sample	Clay fraction
		(A) PREMONSOON			
		OFF TIRACOL RIVER			
1	5	1·19	—	0·289	—
2	10	1·80	1·93	0·298	0·545
3	15	2·42	1·75	0·575	0·312
4	20	4·60	2·47	0·142	0·490
		OFF CHAPORA RIVER			
8	5	2·70	—	0·142	—
9	10	3·58	1·93	0·224	0·555
10	15	4·95	3·01	0·390	0·525
11	20	3·82	2·56	0·330	0·495
		OFF AGUAD FORT			
74	5	0·187	—	0·220	—
75	10	4·10	1·93	0·440	0·535
76	15	1·92	0·92	0·481	0·568
77	20	4·30	1·72	0·412	0·404
		OFF BAINA BEACH			
20	5	0·900	—	0·096	—
21	10	3·84	1·66	1·119	0·046
22	15	2·88	1·09	0·230	0·326
23	20	2·17	1·93	0·146	0·045
		OFF COLVA BEACH			
24	5	0·90	—	0·091	—
25	10	3·55	2·24	0·614	0·449
26	15	3·68	1·65	0·302	0·471
27	20	2·66	1·60	0·330	0·449
		OFF SOL RIVER			
28	5	0·725	—	0·123	—
29	30	4·23	2·80	0·540	0·297
30	15	3·30	2·95	0·293	0·517
31	20	3·12	1·62	0·559	0·375
		(B) POSTMONSOON			
		OFF TIRACOL RIVER			
					—
32	5	0·85	—	0·266	0·152
33	10	0·76	2·00	0·530	0·394
34	15	2·15	2·59	0·590	0·421
35	20	2·70	2·14	0·119	0·210
36	30	2·14	2·56	0·389	0·421
37	40	1·31	2·42	0·454	0·289
38	50	1·87	2·22	0·444	
		OFF CHAPORA RIVER			
39	5	1·01	—	0·096	—
40	10	3·66	2·80	0·312	0·100
78	15	4·95	2·90	0·500	0·156
41	20	3·46	2·58	0·450	0·147
42	30	2·70	2·35	0·505	0·295
43	40	3·80	2·96	0·524	0·298
44	50	3·17	2·79	0·570	0·257
		OFF AGUAD FORT			
45	5	0·51	—	0·305	—
46	10	3·88	2·02	0·137	0·279
47	15	1·62	1·52	0·581	0·399
48	20	4·20	2·72	0·983	0·299
49	30	3·02	2·63	0·476	0·282
50	40	3·14	2·28	0·445	0·282
51	50	3·30	2·77	0·390	0·408

TABLE 1 — PLRCENTAGE DISTRIBUTION OF ORGANIC CARBON AND TOTAL PHOSPHATE IN THE NEARSHORE SEDIMENTS OF THE GOA COAST DURING (A) PRE- AND (B) POSTMONSOON PERIODS — *Contd*

Sample No.	Station depth	Organic carbon, %		Total P_2O_5, %	
		Total sample	Clay fraction	Total sample	Clay fraction
		OFF BAINA BEACH			
52	5	0·52	—	0·295	—
53	10	3·64	2·22	0·055	0·184
54	15	2·66	2·03	0·271	0·153
55	20	1·94	2·12	0·220	0·170
56	30	1·62	1·51	0·193	0·275
57	40	2·25	1·77	0·305	0·275
58	50	1·76	1·66	0·280	0·248
		OFF COLVA BEACH			
59	5	0·405	—	0·041	0·228
60	10	3·380	1·84	0·380	0·293
61	15	3·59	1·94	0·338	0·206
62	20	2·28	2·64	0·535	0·334
63	30	2·53	1·66	0·476	0·256
64	40	4·08	3·18	0·495	0·274
65	50	3·44	2·64	0·342	0·192
		OFF SOL RIVER			
67	5	0·74	—	0·224	0·142
68	10	3·88	2·97	0·439	0·357
69	15	2·14	1·80	0·306	0·407
20	20	2·07	1·65	0·458	0·531
71	30	2·00	1·40	0·362	0·256
72	40	3·18	2·62	0·343	0·362
73	50	2·02	1·64	0·211	0·265

noticed that they show two different patterns to the north and south of the Aguad transect (or the Marmugao Head region). The Aguad transect shows a complete reversal of the pattern found in the southern part, but the values to the north of it show a definite increase of that pattern noticed here, until it reaches the Tiracol river transect where it presents another change. At 15 and 20 m depth along Aguad transect a sharp change of sediments has resulted in the low and high values of organic carbon which is in direct relationship to the texture of the sediments. Carrigy[4], from a study of Warnbro sediments, finds a similar relationship. However, the trend in the Tiracol transect which is considered to be least influenced by pollution is reversed.

It is observed that wherever phosphorus values are high, the organic carbon (C_{org}) values are also high and vice versa. According to Kaplan and Rittenberg[5] lack of iron under anerobic conditions to fix phosphorus as phosphate results in the low values for phosphate. The fine grain size of the calcareous or clastic clayey material increases the phosphate values as is seen presently in Aguad transect. Conversely, the coarseness of sediment inhibits the accumulation of organic carbon, hence it results in low values. But it is established that the high organic content in the sediment is also a consequence of luxuriant organic productivity in the overlying water mass and the nutrients brought up by upwelling. This relationship is explained by Trask[6] from a study of several areas in California, Panama and equatorial Africa. Phosphorus and organic carbon content in sediments of uppermost layers is very high whereas it decreases with depth as seen in cores from the Bombay-Saurashtra coast[7].

Further, it is noticed that the organic carbon content increases with the increasing clay fraction and decrease with the increasing grain size in the sediments. This suggests that carbon is predominantly adsorbed by the clay particles[8]. Thus there is a correlation between organic carbon and clay content which is qualified by the particle size of clay component, however, this is influenced by environmental factors[9]. The carbon value also decreases in an oxidizing environment during its settling and in regions where dissolved oxygen is exceptionally high, i.e. the bottom waters of the sea[10]. This pattern of proportionality of organic carbon with clay content of the sediments are noticed in Lakes Ontario, Erie and Huron[11], and Lake Manzalah and Egypt[12]. Therefore, it is well established that organic carbon concentration in a sediment is high in finer fractions than in coarser fractions; clayey sediments tend to hold more organic carbon than the other kinds. The north-south belt of high organic carbon along the coast in 10-15 m depth is an example in this respect.

The upwelling currents bring in enormous quantities of phosphorus to the shelf from beneath and considerable amounts are also carried by rivers from the hinterland. The cold water of the upwelling current moving upward from depth towards the surface is heated and, therefore, tends to lose CO_2 due to the release of pressure. This CO_2 is consumed by the photosynthesis of the phytoplankton in the zone. Thus, water, which becomes unusually rich in phosphorus moving into a region of high pH, results in the precipitation (inorganically) as calcium phosphate (apatite). Whether this results in the precipitation of calcium phosphate directly or indirectly through organisms or by rapid replacement of earlier formed calcium carbonate or tricalcium phosphate is still not very clear[13]. However, this can take place in the upper or middle parts of the shelf[14], i.e. at depths of 100 to ± 50 m. It is found that the modern phosphorites are being formed even today at depths greater than this as seen off California and Cape of Good Hope[15], and north-eastern Arabian Sea[7].

P_2O_5 content in the total sample of the sediment varies from 0·041 to 0·983% during postmonsoon and 0·119 to 0·559% during premonsoon periods between 0 and 20 m depth in the region. However, in the clay fraction itself, the percentage ranges from 0·142 to 0·531% during postmonsoon and 0·046 to 0·555% during premonsoon period. The low values of phosphorus during premonsoon period is due to decreased supply of terrigenous phosphorus into the region, through the rivers in the northern sector. But a slight increase in the phosphorus value in the premonsoon period is mainly due to settling of the fine sediments and the meagre supply by Sol river and others. However, higher concentrations of phosphorus are noticed in the sediments of the postmonsoon period in the northern sector, which is due to the settling of the sediment found in the region, and a larger supply of the terrigenous apatite brought in by the rivers in floods during the monsoon. The organic carbon in the clay fraction fluctuates even though the total organic carbon is slightly high, as compared

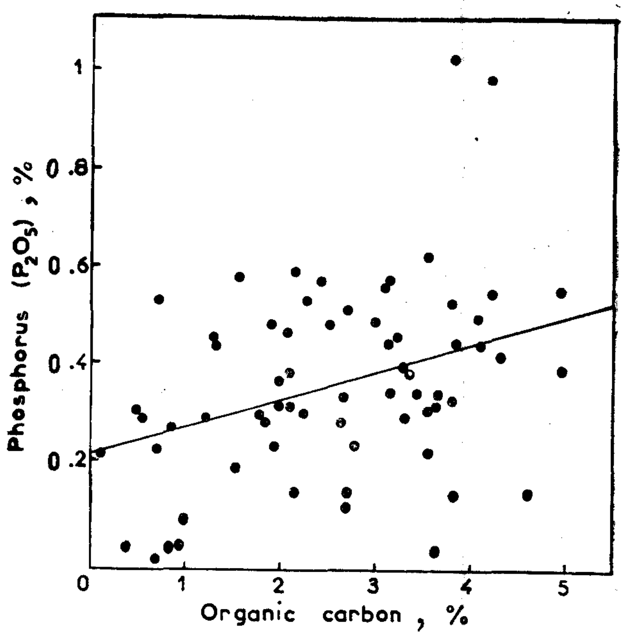

Fig. 3 — Scatter plot with least squares fit between organic carbon and total phosphorus

with lower value in the premonsoon period (Table 1).

Apatite is brought in by the rivers in silt size grade and seem to have been deposited beyond 5 m depth. This region shows a value of 0·4-0·98% P_2O_5 to the south of it. However, there are a few localized patches of high values in the southern region and low values in the northern region. This can be considered that apatite is practically absent at 0-5 m depths by its very low values (0-0·1%). Hirst[16] suggests from a study of Gulf of Paria sediments that the presence of 0·1-0·2% apatite accounts for 0·05-0·06% phosphorus. A lower biomass value of 0·11-1·33 g/m², suggests a meagre supply of phosphorus as calcium phosphate from the shell fragments and organisms in the region (Parulekar, personal communication). Correlation coefficient factor between phosphorus and organic carbon is $r = 0{\cdot}29$, which includes both pre and postmonsoon samples. It is found to be statistically significant to a level of 0·018 for 66 samples[17]. The functional relationship between phosphorus and organic carbon is shown in the scatter plot (Fig. 3) and the method of least squares is used to fit in the straight line between the two variables. This indicates that a significant amount of phosphorus is organically bound. Further, mineral studies indicate that the presence of apatite up to 1% in the sediment has contributed to a maximum of 0·5% P_2O_5. In view of this the phosphorus contribution in the fine sediments can be inferred to be the result of the presence of apatite in the sediments. This factor may be considered as an addition to the pollutants in the area. Therefore, it is noticed that upwelling in the region amounting to high phosphorus values as proposed by Sankaranarayanan and Jayaraman[18] may not be the chief cause of high phosphorus values here. According to the classification proposed by Gimmel'farb *et al.*[19] this sediment containing 0·5-5% of P_2O_5 can be considered as 'phosphate bearing'. However, given time for further phosphatization followed by enrichment it may well prove to contain higher percentages.

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