

Studies on organic carbon, nitrogen and phosphorous in the sediments of Mandovi estuary, Goa

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Sediment organic carbon, total nitrogen, total phosphorous and hydrography of the overlying waters of the estuarine region in Mandovi estuary have been studied. The relationship of carbon and nutrients with sediment characteristics indicated a significant linear variation with clay and silt. The organic carbon varies from 1.04 to 32.77 mg.g⁻¹ and the total nitrogen and total phosphorous varies from 3.81 to 32.71 mg.g⁻¹ and from 0.46 to 6.74 mg.g⁻¹ respectively. A highly significant correlation between the phosphorous and nitrogen in sediments indicated a common source for both. The significant variations of the N/P ratios exhibiting high monsoonal ratios indicated low phosphorous content. The other ratios of C/P and C/N and their variations are discussed.

In an aquatic system, the sediments act as the storage reservoir of nutrient materials in water. The replenishment of these nutrients in times of need and their consequent removal, greatly helps in the biological cycle of the system. Such an exchange of nutrients depends upon the characteristics of the sediments and the hydrographic features of the estuary¹. Various systematic studies on nutrients and organic carbon in the estuarine sediments have been carried out along the east coast of India^{2,3}. However, along the west coast, very few such studies have been carried out in selected estuaries⁴⁻⁷. In the present study an attempt is therefore made to understand the spatial and seasonal variations of carbon, nitrogen and phosphorous in sediments along with hydrography of the overlying waters in the Mandovi estuary along the west coast of India. The aim is to assess the nutrient flow across the sediment-water interface and the impact of sediment characteristics on this flow.

Materials and Methods

Sediments and the water samples from the surface and bottom levels were collected from 4 stations in the estuarine region of Mandovi estuary (Fig. 1) during monsoon (July-Sept. 1994) and post-monsoon (October and January, 1994) seasons. Water samples were collected by the Niskin samplers fitted with a reversing thermometers and the sediments by the van Veen grab. Soon after collection, the samples were preserved at 4°C till analyses.

The pH of the water samples was measured in the laboratory using Centron Dynamic pH meter. The salinity of the samples was measured by the Autosal salinometer and the DO by the Winkler's method while the nutrients were analysed by the standard methods^{8,9}. In sediments, the organic carbon was analysed by the wet oxidation method¹⁰, nitrogen by the Kjeldhal method¹¹, and the phosphorous by the method of Rochford¹². Grain size were determined by the sieving and pipette analyses¹³ and the nomenclature based on the sand-silt-clay ratio was followed from the model given by Shepard¹⁴.

Results and Discussion

The floor of Mandovi estuary exhibit sediments of different textural types with sandy sediment at st. M1

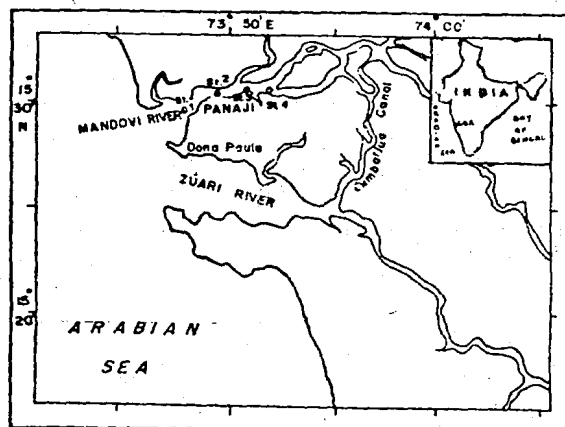


Fig. 1—Map showing the location of stations

and a mixture of sand, silt and clay of different combinations at other stations (Fig. 2). Such differing combinations of sediment observed are mainly due to the transport of sediments from one place to another and back associated with the tidal currents¹⁵. Such a transport of the bed load material becomes more pronounced during the monsoon which shows varying types of sediments compared to that of the postmonsoon. The sediments of the sand-silt-clay type and the still finer ones indicate the prevailing low energy conditions as reported in the Visakhapatnam shelf sediments¹⁶. While, the presence of sandy sediments at sts. M1-M3 during monsoon and at sts. M1 and M2 during the postmonsoon indicate high energy zone associated with high turbulence.

The significant changes in the chemical constituents of this estuary is brought about by the variations in hydrographic features associated with the SW monsoon (Table 1). It is therefore, the salinity of the estuarine water varies widely from 0.02 to 35.45×10^{-3} and shows a decrease towards upstream. The extreme drop in salinity with nearer freshwater conditions observed during monsoon is due to the dilution by large freshwater influx while the

differences in the surface and bottom salinity is due to the outflowing riverine water giving a two layered structure¹⁷.

The distribution of DO depends upon salinity and indicate inverse relation with high salinity water showing low DO. The range of variation in DO shown by the estuarine water at sts. M1-M4 is from 2.90 to 5.04 ml l^{-1} with increase towards upstream due to decreasing salinity (Table 1). The high DO at surface

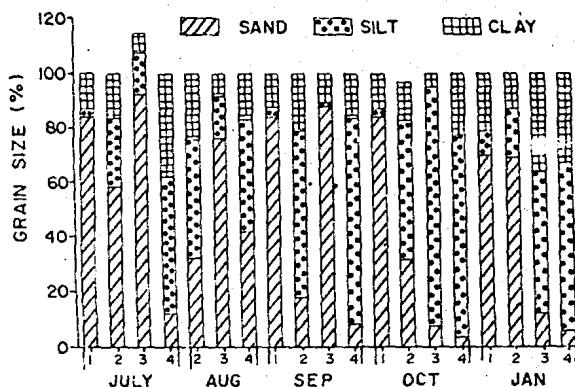


Fig. 2—Texture and grain sizes of sediments at st. M1-M4

Table 1—Pooled values of salinity, dissolved oxygen, pH and nutrients at stations M1-M4 in seawater

	Salinity ($\times 10^{-3}$)	DO (ml l^{-1})	pH	PO ₄ -P ($\mu\text{M dm}^{-3}$)	NO ₃ -N ($\mu\text{M dm}^{-3}$)	NO ₂ -N ($\mu\text{M dm}^{-3}$)
Monsoon (July-Sept.)						
St. M1						
Surface	10.13	4.82	7.13	1.95	14.69	1.51
Bottom	17.78	4.00	7.32	2.86	9.09	1.80
St. M2						
Surface	9.99	4.11	7.21	2.10	16.85	1.69
Bottom	14.99	4.03	7.32	3.30	8.25	2.50
St. M3						
Surface	8.30	4.36	7.22	1.88	11.97	2.34
Bottom	14.42	4.03	7.27	2.59	8.14	2.88
St. M4						
Surface	3.33	4.48	7.37	1.88	12.01	3.46
Bottom	10.86	4.37	7.77	2.60	14.10	4.00
Postmonsoon						
St. M1						
Surface	3.25	3.94	7.45	0.38	0.84	0.18
Bottom	3.44	3.82	7.62	0.59	0.94	0.41
St. M2						
Surface	3.29	3.79	7.63	0.73	1.09	0.35
Bottom	3.32	3.49	7.69	0.61	0.90	0.32
St. M3						
Surface	2.38	3.99	7.73	0.61	2.68	0.49
Bottom	3.04	3.47	7.63	0.51	1.60	0.56
St. M4						
Surface	1.51	3.78	7.79	0.63	3.83	0.73
Bottom	1.62	3.69	7.70	0.69	4.16	0.77

relative to bottom is due to the direct contact of the surface layer of water with the atmosphere, that enhances the dissolution of oxygen in water¹⁷.

As the DO is functionally involved in the biological processes of the estuary, its utilization and release (photosynthesis and respiration), indirectly affects the pH of estuarine water¹⁸. This give the range of pH of the estuarine water at sts. M1 and M4 from near acidic to alkaline (6.65-7.92). However, all these parameters play a very important role in the recycling of nutrients between water and sediments of the estuary.

All the sediments of Mandovi estuary from sts. M1-M4 are enriched in C,N,P and show spatial and temporal variability in their distribution. This variability is mainly related to the grain sizes of sediments influenced by other hydrochemical factors. This is observed from the significant relationships of sediment C,N and P with finer fractions of the sediments. The sediment organic carbon content that varies from 1.04 to 32.77 mg.g⁻¹, indicates peak values at sts. M2 and M4 in July and at st. M3 in September during monsoon (Fig. 3). However, these values fairly agree with those reported earlier for Mandovi estuary⁶. The observed peak values of organic carbon in these months could be attributed to the influx of land runoff containing a considerable amount of terrigenous organic matter. When the organic production of Mandovi estuary is considered, it is observed that during postmonsoon, the high planktonic production of the Mandovi estuary¹⁷ leaves behind large amount of dead planktonic matter due to the grazing by zooplankton. As this dead matter sinks to the bottom, it gets

oxidised and on settling its decomposition releases organic carbon into the interstitial water, part of which is then diffused into the overlying water¹⁹.

The phosphate in sediments varies from 0.46 to 6.74 mg.g⁻¹ and generally indicates low values during monsoon in contrast to its increasing values from 3.65 to 6.79 mg.g⁻¹ in postmonsoon (Fig. 4). During monsoon, however, the overlying water show high values of dissolved phosphate (Table 1). The low values of sediment phosphates in monsoon can be attributed to the leaching of phosphate from sediments to the overlying water that gives relatively high values of dissolved phosphate in the overlying bottom water. The postmonsoon season shows increases in sediment phosphate with a corresponding decrease in dissolved phosphate in the overlying water. The decrease in dissolved phosphate is mostly related to the organic production of the overlying water. The intense photosynthetic activity during postmonsoon¹⁷ utilizes dissolved phosphate and decreases their concentration thereby giving low values of dissolved phosphate in these water from October to January. However, the increase in sediment phosphate is due to the dead organic matter settling from top and is related to the permeability of the sediments. During the non-monsoon months the mud permeability is very low due to high silt content²⁰ and it retains large quantities of phosphate in sediment interstices.

The relationship between phosphate in sediments and the grain sizes indicated a significant correlation with silt, indicating its affinity for silt fraction of the sediments. Rajagopal & Reddy⁵ observed high phosphate in clayey-silt type sediments in Mandovi

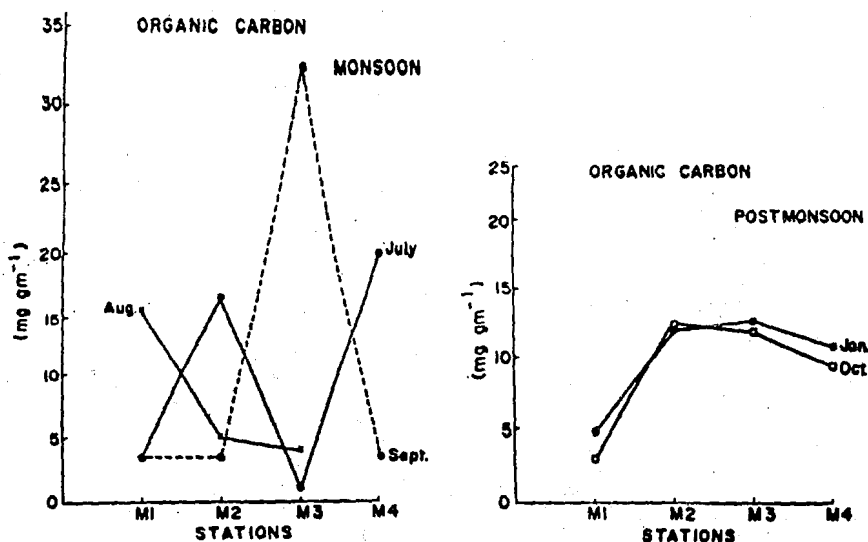


Fig. 3—Variation in org. Carbon in sediments at st. M1-M4 during monsoon and postmonsoon

estuary. Subsequent investigations revealed that the orthophosphate removal from water is due to the adsorption onto mud substrates²¹ while the adsorption-desorption studies of phosphorous²² in sediments indicated maximum adsorption at pH 4-7.

The nitrogen in sediments varies from 2.81 to 32.71 mg.g⁻¹ and follows the pattern of phosphorous distribution indicating low values (2.81 to 22.43 mg.g⁻¹) during monsoon gradually increasing in the postmonsoon (Fig. 5). This distribution of sediment nitrogen is in contrast to that of nitrate in the overlying water (Table 1) which shows high values of NO₃-N during monsoon and low values during postmonsoon. The increasing values of nitrogen in sediments during postmonsoon are related to the oxidation of dead planktonic matter¹⁸ which has settled from the top layer; whereas the subsequent decrease of nitrate in the overlying water is due to the

utilization of nitrate by high planktonic production. The organic nitrogenous compounds produced from the degradation of organic matter gets adsorbed onto sediments depending upon the temperature, electrical conductivity of the interstitial water, the concentration of organic matter and the porosity of sediments²³⁻²⁵.

The significant correlation of sediment nitrogen with clay ($r = 0.56$; $n = 19$; $t = 3.02$) and silt ($r = 0.66$; $n = 19$; $t = 3.81$) indicated that the adsorption is mainly affected by the finer fractions of the sediments. However, a similar pattern of variation of nitrogen and phosphorous and the significant correlation ($r = 0.67$; $n = 19$; $t = 3.93$) between them revealed that the concentration of one is dependent on the other and indicated a common source for both. The correlation of organic carbon with nitrogen during the postmonsoon was also significant ($r = 0.65$; $n = 8$; $t = 2.1$).

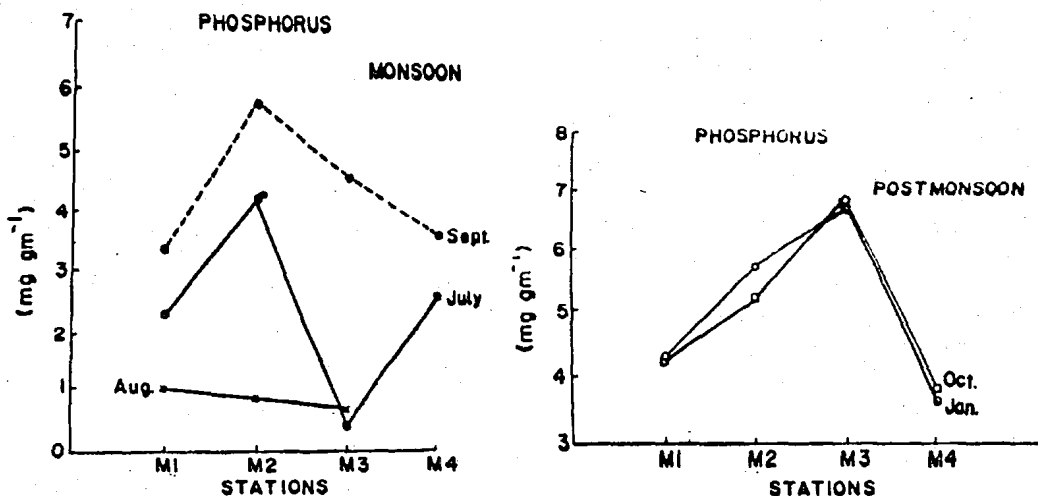


Fig. 4—Variation in phosphorous in sediments at st. M1-M4 during monsoon and postmonsoon

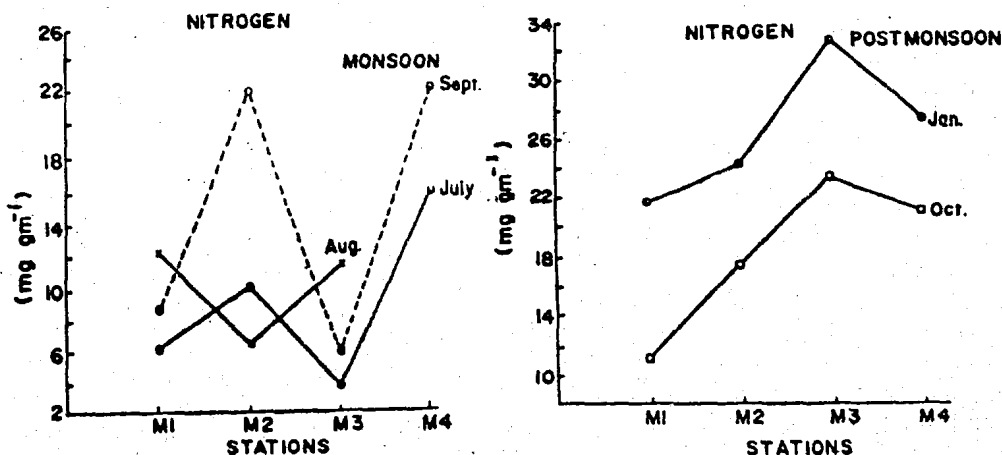


Fig. 5—Variation in nitrogen in sediments at st. M1-M4 during monsoon and postmonsoon

Muller²⁶, indicated that the total nitrogen in clayey sediments with carbon <0.5% can be affected by fixed ammonium which is normally bound to illites: In Mandovi estuary sediments, the illite was found to be the second abundant mineral after montmorillonite²⁷. However, the regeneration and mineralization processes at the sediment-water interface greatly enhance the primary production by releasing nutrients¹⁹. The regenerated nitrogen in sediments is then brought to the overlying water by diffusion or by churning of sediments due to the tidal force. This diffusion of nitrogen can be seen from the high values of NO₃-N in the overlying bottom water at most of the stations (Table 1).

An understanding of the extent of nutrient regeneration is based on the C/P, C/N and N/P ratios. The C/P ratios of these sediments from 1.53 : 1 to 38.5 : 1 (av. 8.24 : 1) indicate high values for monsoon (av. 10.6 : 1) and overlap those of the postmonsoon (av. 4.97 : 1). The lower ratios indicate an increase in phosphorous content of sediments whereas, the higher ratios particularly of the monsoon can be attributed to the cumulative effect of high organic carbon and low phosphorous content of sediments. The C/N ratios of these sediments of 0.2 to 2.0 are very low compared to those from the west coast of India (*R V Meteor*) having ratios of 1 to 8 and from the shelf sediments of the Arabian Sea with ratios of 2.48 to 37.5 and also of the sediments from the Cochin backwaters²⁸ (av. 6.4). Generally, the marine organic matter contains less nitrogen relative to the freshwater or the terrestrial organic matter²⁹. This probably leads to the low C:N ratios of the estuarine waters as observed in this study.

The N/P ratios of 2.92:1 to 37.51:1 (av. 12.36:1) indicate low ratios during the postmonsoon. Since every atom of phosphorous is matched by 15 atoms of nitrogen as nitrate giving the N:P ratio of 15:1, this ratio is not constant and was found to be 16.5:1 for phytoplankton and 15.1:1 for zooplankton (av. 16:1)³⁰. The high N:P ratios above the standard ratio (16:1), are observed in this study only during the monsoon and is shown by stations towards the upstream side of the estuary. These ratios decrease during the succeeding non-monsoon months and go very much below the normal ratio. The high ratios indicate low phosphorous content of the sediments. Usually, the contribution of phosphorous in sediments is from the organic matter as well as from the mineral matter. As seen from the texture of the sediments during monsoon, these sediments from sts. M1 to M4 are very rich in sand and are mostly sandy with little silt or clay (Fig. 2). However, during the other periods, the same stations show sediments

rich in clay or silt and are clayey or silty sediments. It therefore appears that apart from the organic matter, the contribution from the mineral phosphorous probably plays an important role in the variations of N:P ratios of these sediments.

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References

- 1 Pomeroy L R, Smith P E & Grant C M, *Limnol Oceanogr*, 10 (1965) 167.
- 2 Murty P S N & Reddy C V G, *Bull Natn Inst Sci India*, 38 (1968) 405.
- 3 Satyanarayana D, Panigrahy P K & Sahu S D, *Indian J Mar Sci*, 22 (1993) 235.
- 4 Sankaranarayanan V S & Panampunnaiyil S V, *Indian J Mar Sci*, 8 (1979) 27.
- 5 Rajagopal M D & Reddy C V G, *Indian J Mar Sci*, 13 (1984) 1.
- 6 Alagarsamy R, *Indian J Mar Sci*, 20 (1991) 221.
- 7 Jagtap T G, *Indian J Mar Sci*, 16 (1987) 103.
- 8 Strickland S C & Parsons T R, *A practical handbook of seawater analysis, Bulletin*, 167 (Fisheries Research Board of Canada, Ottawa) 1978, pp. 310.
- 9 Grasshoff K, in *Methods of seawater analyses*, edited by K Grasshoff, M Ehrhardt & K Krimling, (Verlag Chemie, Weinheim) 1976, 317.
- 10 El-Wakeel & Riley J P, *J du Con Int Expl du Mer*, 22 (1957) 180.
- 11 Anonymous, in *Manual of methods in aquatic environment research, Tech Paper No 137*, (FAO, Rome) 1975, 45.
- 12 Rochford D J, *Aust J Mar Freshwater Res*, 2 (1951) 1.
- 13 Folk R L, *Petrology of sedimentary rocks*, edited by R L Folk (Hemphills, Austin, Texas) 1961, 170.
- 14 Shepard F P, *J Sedim Petrol*, 24 (1954) 151.
- 15 Murty C S, Das P K, Nair R R, Veeryya M & Varadachari V R, *Indian J Mar Sci*, 5 (1976) 9.
- 16 Satyanarayana Murty P & Rao K S, *J Geol Soc India*, 13 (1959) 38.
- 17 Dehadrai R V & Bhargava R M S, *Indian J Mar Sci*, 1 (1972) 52.
- 18 Singbal S Y S, *Indian J Mar Sci*, 9 (1976) 27.
- 19 Martin D F, in *Marine chemistry*, Vol. 2, edited by D F Martin, (Marcel Dekker, Inc, New York) 1970, 267.
- 20 Ansari Z A & Rajagopal M D, *Mahasagar-Bull Natn Inst Oceanogr*, 7 (1974) 151.
- 21 Kimmel B L & Lind O T, *Texas J Sci*, 21 (1970) 439.
- 22 Furumai H, Kondo T & Okayaki S, *Water Res*, 23 (1989) 655.
- 23 Kamiyama K, Okuda S & Kawai A, *Japanese J Limnol*, 38 (1977) 100.
- 24 Kamiyama K, Okuda S & Kawai A, *Japanese J Limnol*, 39 (1978) 176.
- 25 Rosenfield J K, *Limnol Oceanogr*, 24 (1979) 356.
- 26 Muller P J, *Geochim Cosmochim Acta*, 41 (1977) 765.
- 27 Shirodkar P V & Kamat Dalal V N, *Mahasagar-Bull Natn Inst Oceanogr*, 21 (1988) 45.
- 28 Qasim S Z & Sankaranarayanan V N, *Mar Biol*, 15 (1972) 193.
- 29 Mantoura R F C, in *Marine organic chemistry*, edited by E K Duursma & R Dawson, (Elsevier, Amsterdam) 1981, 179.
- 30 Cooper L H N, *J Mar Biol Ass, UK*, 23 (1937) 181.