Organic carbon and humic acids in sediments of the Arabian Sea and factors governing their distribution

Organic carbon
Humic acids
Arabian Sea
Surficial sediments
Environmental factors

Carbone organique
Acides humiques
Mer d'Oman
Sédiment superficiel
Paramètres environnementaux

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ABSTRACT

Organic carbon and humic acids in the sediments of the Arabian Sea show distinct regional variations to the south and north of 15°N latitude. Significant variations are also observed from the shelf to the slope regions. Organic carbon and humic acids are enriched on the slope compared to the inner and outer shelf. While upwelling, primary productivity and redox conditions at the bottom are known to influence organic matter accumulation in sediments, bacterial population and sediment texture also contribute to the preservation of organic matter and humic acids. A positive correlation ($r = 0.716$) between total organic carbon and humic acid content in the sediments indicates fairly favourable conditions for the humification of organic matter. The C/N ratio indicates more terrigenous matter on the shelf, whereas organic matter of planktonic origin seems to dominate the slope region.

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RÉSUMÉ

Répartition du carbone organique et des acides humiques dans les sédiments de la mer d'Oman

Le carbone organique et les acides humiques dans les sédiments de mer d'Oman présentent des variations régionales au sud et au nord du parallèle de latitude 15°. Des variations significatives sont également observées entre le plateau et le talus continental. Les teneurs en carbone organique et en acides humiques sont plus élevées sur le talus continental que sur le plateau. Pendant l'upwelling, la productivité primaire et les conditions redox, la population bactérienne et la texture du sédiment paraissent aussi liées à la préservation de la matière organique et des acides humiques. Une corrélation positive ($r = 0{,}716$) entre le carbone organique total et les acides humiques dans les sédiments indique des conditions favorables à l'humification des matières organiques. Le rapport C/N indique une influence plus grande des matières terrigènes sur le plateau continental, tandis que la matière organique dérivée du plancton semble dominer sur le talus.

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INTRODUCTION

Primary productivity, upwelling, rate of decomposition, redox conditions in the sediments, rate of sedimentation and sediment texture all influence the content of organic matter in sediments. Although the humification process is not directly related to the organic matter content of the sediments, it is largely controlled by the same environmental factors as those responsible for organic matter accumulation. Earlier studies on humic substances in different regions of the world oceans (Cronin and Morris, 1982; Poutanen and Morris, 1983; Bordovskiy, 1965 *a* and *b*) have indicated the influence of differing environmental conditions on the humification process. Relatively little work has been done on humic substances in the Arabian Sea, which is influenced by the monsoon. This event causes seasonal reversals in the surface circulation in the Northern Indian Ocean (Wyrtki, 1971). In the Arabian Sea the result is an upwelling phenomenon of varying intensity all along the coast of the western continental margin of India (Sharma, 1976). Upwelling of deep nutrient-rich waters enrich the surface layers along the southeast coast, thereby increasing primary productivity. Upwelling along the western continental margin of India is a seasonal phenomenon and has been studied by Ramamirthan and Jayaraman (1960), Varadachari and Sharma (1964), Reddy and Sankaranarayanan (1966) and Sharma (1976). These studies revealed that upwelling commences at deeper depths and upwelled waters gradually reach the surface layers. However, there is a time lag in the upwelling phenomenon, accompanied by a decrease in intensity, from south to north. Upwelling starts early in the south during the monsoon and progressively shifts to the north with decreased intensity. The cessation of upwelling takes place by September/October. This intense coastal upwelling in the southeastern region of the Arabian Sea makes it one of the highly productive regions of the world oceans.

Humic compounds constitute a large fraction of organic matter in marine ecosystems and, being heterogeneous in character, play a key role in the biogeochemistry of the marine environment. The present study reflects the author's endeavour to examine the influence of environmental factors - which favour or inhibit the accumulation of organic matter - on the humification process and the state of humic acid accumulation in relation to organic matter under the varied environmental conditions prevailing on the continental margin of India.

MATERIALS AND METHODS

Surface sediment samples were collected along the continental margin of India from the Gulf of Kutch in the north to Cape Comorin in the south as shown in Figure 1, during different cruises of R.V. *Gaveshani* and ORV *Sagar Kanya*. Samples were collected by Peterson's grab or snapper and stored in precleaned plastic bags and frozen until analysis.

Organic carbon content was determined by wet oxidation with chromic acid by the method of El Wakeel and Riley (1956). Total nitrogen content was determined by alkaline persulphate oxidation of sediments which yields NO_3-N as the sole nitrogen product (Smart *et al.*, 1983). The resultant nitrate-nitrogen was estimated by the method of Morris and Riley (1963)

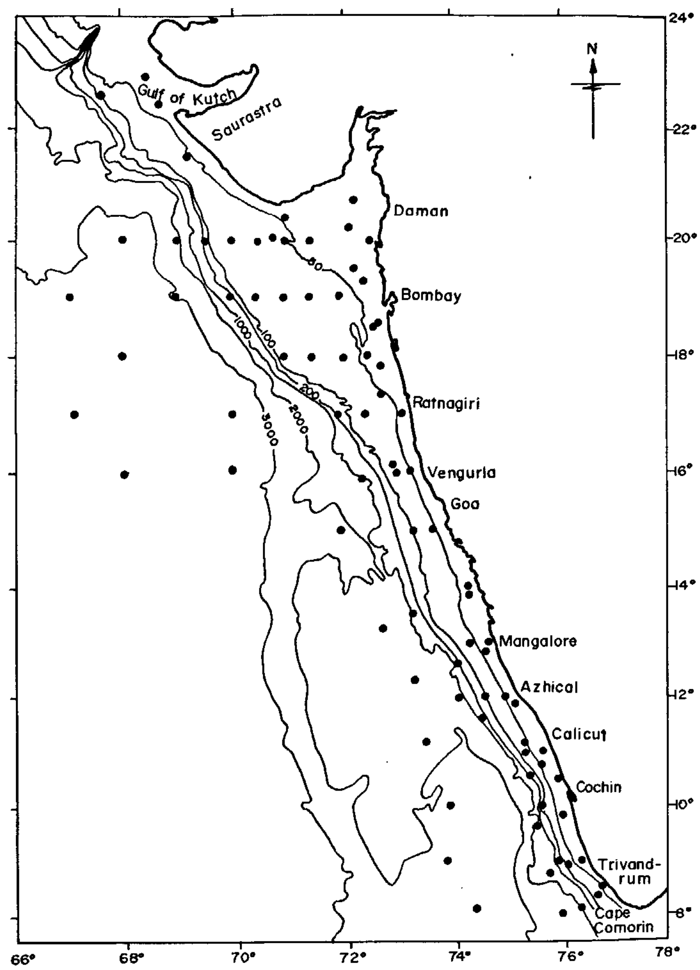

Figure 1

Map showing station locations.

Humic acids were extracted from 10 g of the dried sediment by 0.5 M NaOH and acidified with 6 N HCl to pH 2. The precipitate was then washed three to four times alternately with 95 % ethanol and water (Hair and Basset,1973), dried and weighed.

TOPOGRAPHIC CHARACTERISTICS OF THE WESTERN CONTINENTAL MARGIN OF INDIA

The Arabian Sea is surrounded by arid land masses to the west and north and by the coastal highlands of western India with a fairly high rainfall (50-250 cm) to the east. The Indus river in the north, which drains the Himalayas and the arid regions of Pakistan and India, and which discharged 400 million tons of suspended sediments annually until dam construction reduced the input to less than 45 million tons (Milliman *et al.*, 1984), has been the major fluvial source for the Arabian Sea. Despite the high rainfall, only small rivers and streams drain into the Arabian Sea from western India, and of these, only the Narmada and Tapti rivers are of any sedimentological significance, together contributing about 60 million tonnes of suspended matter every year (Borole *et al.*, 1982), most of which is retained on the inner shelf of India.

The continental margin shows diverse topographic as well as sedimentological characteristics all along the west coast. The continental shelf off Bombay is about 280 km wide. Here the inner shelf is composed of detrital sands and this zone grades rather sharply into a silty clay/clayey silt facies extending from about 40 to 60 m depth between the Gulf of Kutch and Bombay. The outer shelf sediments consist of predominantly carbonate material comprising oolites, shell fragments and algal debris in various proportions (Kidwai and Nair, 1972) The topographic features and sediment types of the region between Vengurla and Mangalore have been studied by Nair *et al.* (1978). In this area the continental shelf has an average width of 80 km. The inner shelf (40-50 m) is smooth and featureless. The shelf break between Vengurla and Mangalore is gentle; its depth varies between 90 and 120 m.

Beyond the shelf edge the sea floor falls sharply to 1 000 m. The surficial sediments are comprised of clayey silt, silty sand and sand. The clayey silt forms a relatively narrow band confined to < 50 m water depth and within a distance of 25 to 35 km from the coast. Between 50 and 100 m the sediments are sands. Off Goa and north of Mangalore these sands extend to 200 m. The silty sands do not show any relation to water depth and are found from 40 to 200 m.

From Mangalore to Cochin, the inner shelf is relatively smooth up to 40 m depth; beyond this it is uneven due to exposure of sands. However, it is dominated by clayey silts. The outer shelf lies between 80 and 120 m water depth. The lower limit of 120 m is based on the shelf break. This region is almost entirely carpeted by sands. The upper slope region is mostly covered by clayey silts with patches of sands as off Mangalore and off Azhical, where coarse-grained sands are encountered (Paropkari, 1984).

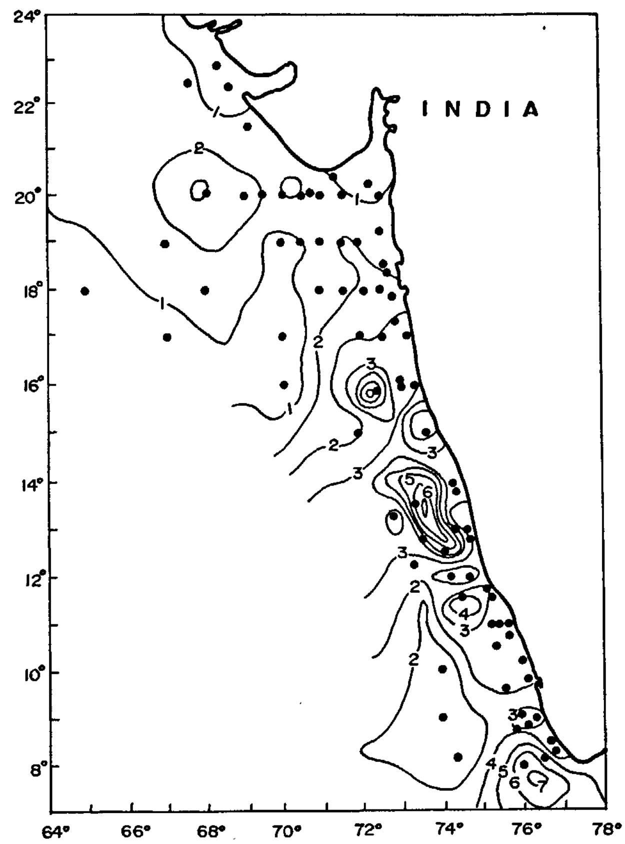

Figure 2

Map showing the distribution of organic carbon (weight %) along the western continental margin of India.

RESULTS AND DISCUSSION

Organic carbon

Figure 2 shows the distribution of organic carbon along the continental shelf, slope and offshore region from the Gulf of Kutch in the north to Cape Comorin in the south. In the region north of 15°N latitude, organic carbon concentrations are generally less than in the south. Patches of high concentration of organic carbon are observed in the shelf and slope regions in the southern zone. Table 1 *A* shows variations of organic carbon in different zones in the northern and southern regions of the continental margin. Paropkari *et al.* (1987) also observed marked regional trends along and across the shelf region towards the north of Ratnagiri (north of 17°N). The spatial and regional differences in the organic carbon content of the sediments are presumably due to high accumulation rates and to preservation of organic matter in the sediments which is enhanced by impingement of low-oxygen waters on the sea floor between 200 and 1 500 m water depth and by the high sedimentation rates (Kolla *et al.*, 1981). The latter also observed that the degree of preservation of organic matter along the Indian margin is about fifteen to eighty times higher than in the region off the Arabian peninsula. Pedersen and Calvert (1990) suggest through their review of the recent research that high primary productivity rather than oxygen-depleted conditions provides the first order control on the accumulation of organic-rich sediments in the modern oceans. In this study the conditions of other environmental parameters vis-à-vis organic matter accumulation and humic acid content in the sediments are also discussed.

Environmental factors

Primary productivity

Primary productivity plays an important role in the organic matter content of sediments. High organic matter is believed to be often associated with high productivity in the sea (Calvert, 1987; Pedersen, 1983; Pedersen and Calvert, 1990). The open ocean accounts for some 90 % of the total ocean surface but only 10 % of the overall production in the marine environment. The remaining 90 % is produced in coastal waters (Ryther, 1969). Other environmental characteristics such as oxygen concentration (redox conditions) in the deeper layers, the microbial population and the circulation pattern may limit the preservation of organic matter even in highly

Table 1

Variations of percentage or organic carbon (a) and humic acids (b) in different regions along the western continental margin of India.

A

Zone	Sediment texture	No. of samples	North of 15 °N		No. of samples	South of 15 °N	
			Range (%)	Average (%)		Range (%)	Average (%)
Inner shelf	Silt and clay	15	0.39-2.86	1.38 ± 0.97	15	0.64-3.75	1.88 ± 0.98
Outer shelf	Sand and silt	18	0.59-2.28	1.33 ± 0.38	7	0.98-1.24	1.14 ± 0.13
Upper slope	Clay	11	0.44-4.80	1.51 ± 1.26	16	0.85-8.04	3.03 ± 2.44
Overall average				1.42 ± 0.65			2.23 ± 1.82

B

Zone	North of 15 °N		South of 15 °N	
	Range (%)	Average (%)	Range (%)	Average (%)
Inner shelf	0.20-0.60	0.37 ± 0.16	0.10-2.00	0.70 ± 0.51
Outer shelf	0.10-1.00	0.54 ± 0.24	0.20-1.00	0.46 ± 0.28
Upper slope	0.06-1.72	1.03 ± 0.32	0.30-3.40	1.31 ± 0.90
Overall average		0.59 ± 0.34		0.95 ± 0.79

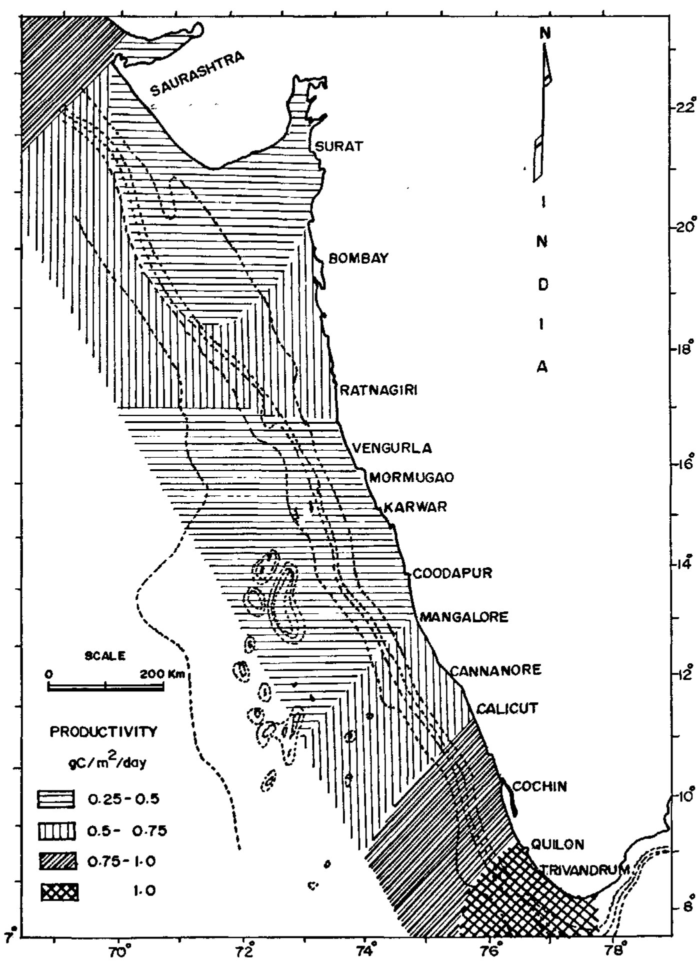

Figure 3

Map showing the primary productivity along the continental margin of India (Qasim, 1977).

productive coastal areas. Primary productivity along the western continental margin of India has been studied at several stations during different seasons (Radhakrishna *et al.*, 1978; Bhargava *et al.*, 1978). Qasim (1977) described the annual water column productivity in the region (Fig. 3). This varied from 0.25 to 1.0 g C/m^2/day and the area under study can be divided into high-, medium- and low-productivity regions (Fig. 3).

1) The area off the Gulf of Kutch and the region off the southwest coast of India are the regions of higher productivity (0.75-1.0 gC/m^2/day).

2) The area off the Saurastra coast and the region between Bombay and Ratnagiri and between Mangalore and Calicut are regions of intermediate productivity (0.50-0.75 gC/m^2/day).

3) The regions between the Gulf of Kutch and Bombay and between Ratnagiri and Mangalore are regions of lower productivity (0.25-0.50 gC/m^2/day).

Comparison of productivity variations with the distribution of organic carbon (Fig. 2) indicates that primary productivity has a considerable influence on organic carbon accumulation. High organic carbon content in the sediment is found in higher and intermediate productivity areas from Mangalore to the southern tip of India. Although the productivity is high and medium in some parts of the northern region, organic carbon concentrations are lower than in the southern region. Kumar *et al.* (1990) observed that the dissolved organic carbon concentration in sea water is higher in the southern region than in the northern region of the Arabian Sea, and attributed this to the recycling of the carbon in the water column in the northern region due to higher microbial activity. The dissolved organic matter aggregating into particles may be a dominant feature due to lower microbial activity in the southern region. High rates of biological consumption and bacterial decomposition may compensate the effect of a high rate of primary productivity and adversely affect the accumulation of organic matter in the sediments. Moreover, variations of productivity in the shelf and slope regions of the western continental margin are seasonal and are largely controlled by the seasonal upwelling.

Rate of sedimentation and sediment texture

A few quantitative estimates of the rate of sedimentation in the Arabian Sea made by Stakelberg (1972) and Zobel (1973) in the inner shelf region reveal that the maximum sedimentation rates are of the order of 15 to 19 mm ky^{-1}. The present day sedimentation rates in the Arabian Sea calculated from the total annual flux based on sediment trap studies are reported by Ramaswamy *et al.* (1991). They observed sedimentation rates of 8.6 to 15.06 mm ky^{-1} in the eastern Arabian Sea. Sedimentation rates nearest to this site in the eastern Arabian Sea (Zobel, 1973; station 205) are around 60 mm ky^{-1}. This is higher by a factor of 4 than that reported by Ramaswamy *et al.* (1991). They have attributed this to the reduced suspended discharge of the Indus river from more than 400 million tonnes to the present annual discharge of less than 45 million tonnes (Milliman *et al.*, 1984). Strong seasonality in the particle flux with peaks during the southwest and northeast monsoons in the Arabian Sea has been recorded by Nair *et al.* (1989).

Based on sediment texture, the area can be broadly divided into four regions: the inner shelf (0-50 m); the outer shelf (50-120 m); the upper slope (> 500 m); and the deep open-sea region (> 1 500 m). Studies on the distribution of sediments based on their texture such as clay, silty clay clayey silt, silt and sand have been carried out by Nair and Hashimi (1980); Hashimi *et al.* (1981) and Stakelberg (1972) and are reproduced in Figure 4. The figure shows that the fine-grained sediments such as clays, silty clays and clayey silts are deposited in the inner shelf region north of Quilon. South of Quilon the inner shelf is covered by terrigenous sands. Between the Gulf of Kutch and Cape Comorin, the outer shelf region consists of sands, silty sands and clayey sands. The entire shelf region north of the Gulf of Kutch is completely covered by fine-grained sediments. In the slope region, fine-grained sediments are again encountered, as on the shelf. In the deeper regions of the sea the sediments consist mostly of calcium carbonate deposits.

The distribution of sediments away from the coast suggests that the inner shelf is characterized by a more rapid rate of sedimentation than the outer shelf. The upper continental slope also has high rates of sedimentation, though not as high as in the coastal areas. The estimated rate of sedimentation in this zone is around 40 cm ky^{-1} (Zobel,1973). In the deeper regions the sedimentation rate is as low as 1.0 cm ky^{-1} (Stakelberg, 1972; Zobel,1973).

Comparison of the pattern of distribution of organic carbon (Tab. 1 *A*) with that of the sediment texture reveals that the organic carbon concentration is closely correlated with the texture of the sediment. The inner shelf and the upper slope regions are characterized by fine-grained sediments and are found to be associated with high concentrations of organic carbon (0.38 -8.04 %), whereas the sandier outer shelf region is characterized by comparatively lower concentrations of organic carbon

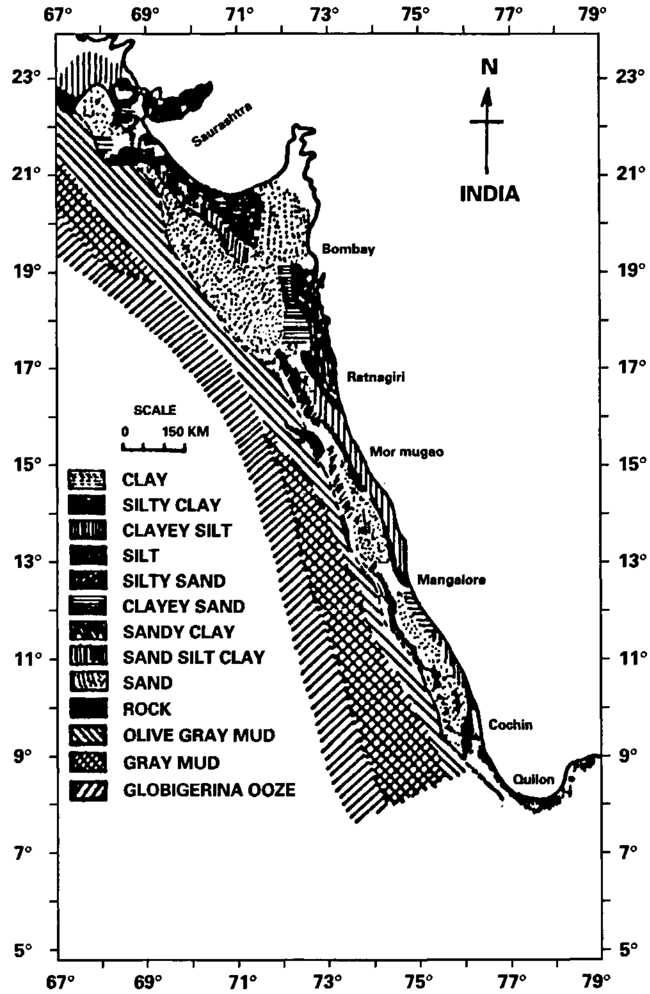

Figure 4

Map showing the distribution of sediments along the continental margin of India. (Nair and Hashimi, 1980; Hashimi et al., *1981; Stakelberg, 1972.)*

(0.59-2.28 %). The influence of other environmental parameters such as upwelling and primary productivity are also reflected in the distribution of organic carbon in the two regions described in Table 1 *A*.

Humic acids

Figure 5 depicts the distribution of humic acids from the coast to the offshore area. Patches of relatively high concentrations of humic acids are observed in the southern shelf and slope compared to the north. The lowest concentrations of humic acids are observed in the outer shelf region but the lowest concentration was observed in the inner shelf region in the northern Arabian Sea. This distribution is similar to the variations of organic carbon in the two regions.

Figure 6 shows the relationship between amounts of organic carbon and humic acids in the sediments. The linear correlation-coefficient of this relationship r = 0.716. This relationship is a function of the humification process; since the degree of humification is dependent on a number of geological, geochemical and depositional conditions, the concentration of humic acids may or may not be proportional to the concentration of organic matter at the bottom.

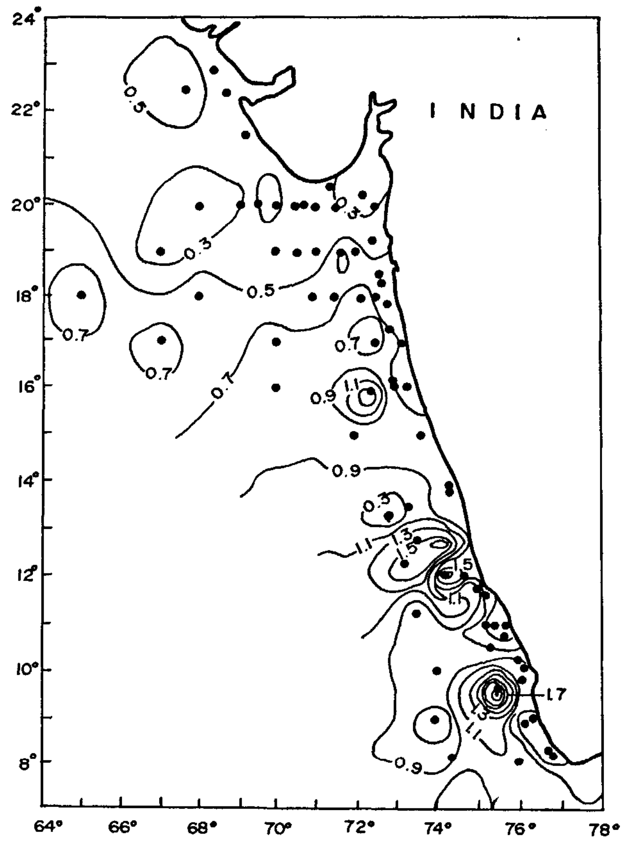

Figure 5

Map showing the distribution of humic acids (weight %) in sediments along the western continental margin of India.

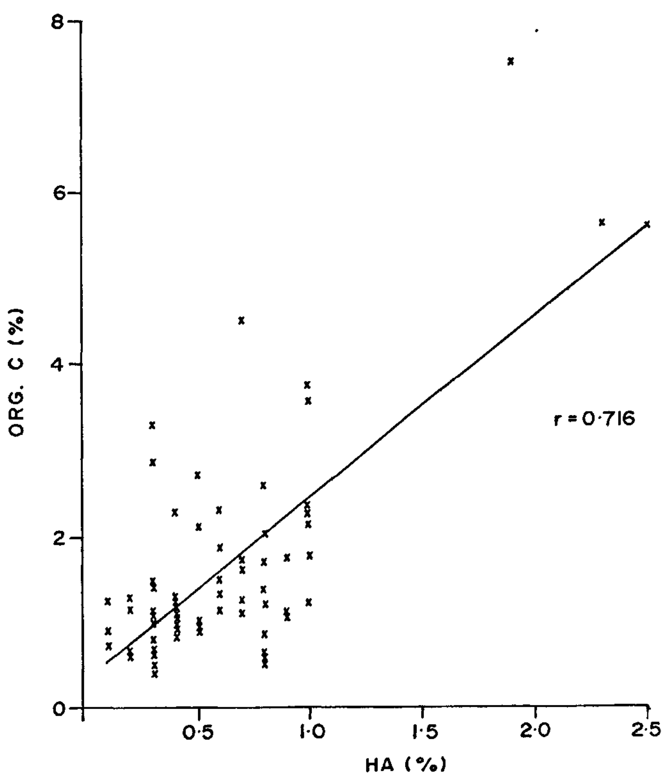

Figure 6

Relationship between organic carbon and humic acids (weight %) in the sediments of the western continental margin of India.

Data on humic acid concentration in the three zones from the coast to the offshore area are analysed for the northeastern and southeastern Arabian Sea, and presented in Table 1 . Similar to the variations of organic carbon, humic acids also show the highest concentration, from 0.06-1.72 %, in the upper slope region. The average concentrations are 1.03 % in the northern region and from 0.3-3.4 % in the southern region with an overall average concentration of 1.31 %. The averages for the northern and southern regions were 0.59 ± 0.34 % and 0.95 ± 0.79 % respectively.

Dissolved oxygen

The dissolved oxygen content of the waters over the continental shelf off Quilon, Cochin, Calicut and Mangalore has been studied by Sharma (1968). The distribution of dissolved oxygen in the slope waters was studied by Stakelberg (1972); Sen Gupta *et al.* (1975); Sen Gupta *et al.* (1976) and Sen Gupta and Naqvi (1984). The shelf waters are well oxygenated down to a depth of about 150 m, while the waters over the slope are oxygen-depleted. The low-oxygenated waters (< 0.5 ml/l) extend from a depth of 150 to 1 500 m. The oxygen concentration in the northern Arabian Sea has two minima, one at 150-500 m and the other between 1 000-1 500 m. These minima are pronounced to the north of 18°N latitude whereas to the south of 18°N only one minimum, that between 150-500 m, is present. A thick oxygen maximum is observed to the south of 10°N latitude. The depletion of oxygen in the northern region is attributed to the higher rate of oxidation of organic matter due to higher bacterial population, whereas in the southern region lower bacterial population limits the decomposition of organic matter.

Higher quantities of humic and other organic compounds are found more often in soils and sediments enriched in clay minerals than in other types of sediments. To verify the enrichment of humic acids in the clay sediments over the other types of sediments, the sediments were classified broadly into three categories: clay, silt and sand. This classification is based on the dominant grain size of the sediment. The humic acid content and the percentage of organic matter associated with humic acids in each type was analysed and is shown in Table 2. The clayey sediments contain the highest concentration of humic acids compared to the silty and sandy sediments. Higher concentrations of organic matter associated with humic acids were also observed in the clayey sediments rather than the other two types. While this relationship is attributed to the high adsorption capacity of clay for organic compounds, experimental evidence suggests that clay minerals exert an indirect catalytic effect on the decomposition of organic matter and on the process of humification (Filip *et al.*, 1972 *a* and *b*).

Martin and Haider (1971) postulated that the presence of clay minerals has a marked effect on the growth and metabolism of microbes. The increased amount of humic polymers found in the presence of clay minerals indirectly reflects the effect of clays on microbial activity rather than a catalytic effect on the process of polymerization (Haider *et al.*, 1975).

Table 2

Percentage of organic carbon, humic acids and the organic matter associated with humic acids in different types of sediment.

Sediment type	Organic carbon (%)	Organic matter (%)	Humic acids (%)	% of organic matter associated with humics
Clayey	2.26	4.07	2.8	68.7
Silty	1.49	2.68	1.1	41.0
Sandy	1.27	2.28	0.9	39.5

Source of organic matter

Organic matter of both terrigenous and marine origin is present in different zones of the marine ecosystem. The relative proportions of these two types of organic matter, which are differentiated on the basis of their C/N ratios, depend upon the dominance of the source from which this matter is derived. C/N ratios < 10 are considered to be indicative of a marine source (Parsons, 1975) whereas a ratio 12 indicates a terrigenous source (Kukal, 1971). In the marine sediments the concentration of organic carbon and nitrogen of the organic matter derived from either source may be significantly altered by diagenesis, and thus there may not be a clear demarcation in the C/N ratio of the two types of organic matter. Also, the terrigenous matter coming from land drainage settles in the sea along with the organic matter produced *in situ*. Therefore the proportion of terrigenous to marine organic matter at a particular site cannot be determined with certainty. However, the dominant type can be identified on the basis of the C/N ratio. The C/N ratios of sediment samples from transects between 15°N and 20°N were examined from the inner shelf to the offshore region. On the inner shelf the ratio varied from 14.5 to 55.9; on the outer shelf, it varied from 11.3 to 28.8; and in the upper slope region it ranged from 6.5 to 17.5. On the inner shelf the terrigenous organic matter dominates while towards the outer shelf region the concentration of terrigenous matter decreases rapidly away from the coast. Kolla *et al.* (1981) found high inputs of quartz and feldspar in the coarse-grained low-carbonate sediments in the northeasterly areas of the Arabian Sea close to land. This reflects the significant terrigenous sediment influx from the Indus river and other sources. The carbonate content of sediments increases gradually from the northernmost areas to about 18°-21° N and reflects the waning influence of terrigenous sediment supply southwards. In the upper slope region the C/N ratio suggests the dominance of organic matter of planktonic origin.

CONCLUSIONS

The contents of organic carbon and humic acids in the Arabian Sea are influenced by environmental factors such as upwelling, productivity, sediment texture, sedimentation rate and bacterial activity. There seems to be a considerable difference in the organic carbon and humic acid accumulation in the northern and Southern Arabian Sea as well as in the different shelf and slope regions, which are controlled by changes in the environmental parameters caused by the monsoon.

The humic acid content closely follows the organic carbon variation pattern and shows fairly good correlation with organic carbon. The clayey sediments seem to adsorb higher contents of humic acids compared to silty and sandy sediments and consequently show higher concentrations in the slope region. Microbial activity also controls the preservation of organic matter.

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