

Characteristics of humic and fulvic acids in Arabian Sea sediments

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Received 30 November 1993; revised 14 June 1995

Humic and fulvic acids isolated from some of the shelf, slope and offshore sediments of the Arabian Sea were studied. The molecular weight, functional groups, elemental composition and infrared spectra were examined. Humic substances, dominated by humic acids contributed 22-53% of the sedimentary organic matter. The humic acids in turn are dominated by the high molecular weight fraction (> 300000). A major portion of fulvic acids was mostly present as < 10000 molecular weight fraction. The elemental composition ranges of HA and FA are C: 60.3-50.3%, H: 6.9-5.7% and N: 4.1-2.0% and C: 46.5-28.1%, H: 8.9-3.6% and N: 4.8-1.6% respectively. The C/N ratio points out to the dominance of terrigenous matter in the formation of humic substances. The infrared spectra of humic acids and fulvic acids although similar exhibited perceptible variations that could be interpreted in terms of changing phenolic, carboxylic and nitrogen contents.

The characteristics of humic substances differ significantly in varied depositional environments. The diagenetic transformation of organic matter into humic substances and the magnitude of humification depend upon the nature of the organic matter and several other environmental factors¹ such as the redox character, sediment texture, hydrodynamic conditions, topographic characteristics of the region etc. The proportion of humic substances to the organic matter of marine sediments also depends upon a number of geological, geochemical and depositional conditions¹.

Arabian Sea has a depositional environment influenced by arid land masses on the north and coastal highlands on the east, and is influenced by monsoonal rain, upwelling, depletion of oxygen, etc. The characteristics of the bulk sediments in this region are either silty clay, clayey silt or sand, silt and clay^{2,3}. The sediment texture in the marginal areas reflects higher inputs of both the coarse grained, terrigenous detritus and biogenic components (CaCO_3 and opal). The terrigenous sediments have been derived from the land through the rivers Indus, Narmada and Tapti and through the aeolian transport. The southerly deep areas far from these terrigenous sources have very fine grained clays⁴. Humic and fulvic acids isolated from some of these sediment types have been studied here through a combination of chemical and physical methods and are characterised with respect to their molecular weight, functional groups, elemental composition and infrared spectra. The influence of the Arabian Sea depositional

environment on their properties and diagenesis is also discussed.

Materials and Methods

The locations of the sediment sample are shown in Fig. 1. Stations 3464 and 29/22 lie in the inner and outer shelf of the northern region and sts 3695 and 37F8 lie in the inner shelf and slope region respectively of the southern Arabian Sea which is strongly influenced by upwelling during the monsoon. Station 44/11 lies in the offshore region of the central Arabian Sea. Surface sediments were collected by grab during the cruises of *R.V. Gaveshani* (March, October 1985) and *ORV Sagar Kanya* (January, November 1987 and August 1988) and preserved under frozen conditions until extraction.

Humic and fulvic acids were extracted from the sediments by the method described by Poutanen & Morris⁵. Briefly, a known quantity of the sediment sample was extracted under nitrogen first with a mixture of 0.05 M NaOH and 0.05 M $\text{Na}_2\text{P}_2\text{O}_7$ and then repeatedly with 0.05 M NaOH until the extract was colourless. All the 0.05 M NaOH extracts were combined. The residue was further extracted with 0.5 M NaOH under nitrogen and finally refluxed with 0.5 M NaOH for 20 hours. All the 0.5 M NaOH extracts were combined. The two extracts were separately pressure filtered twice through GF/C glass fibre filters. The extracts of samples from sts 29/22, 37F8 were directly fractionated into different molecular weight fractions using Amicon ultrafiltra-

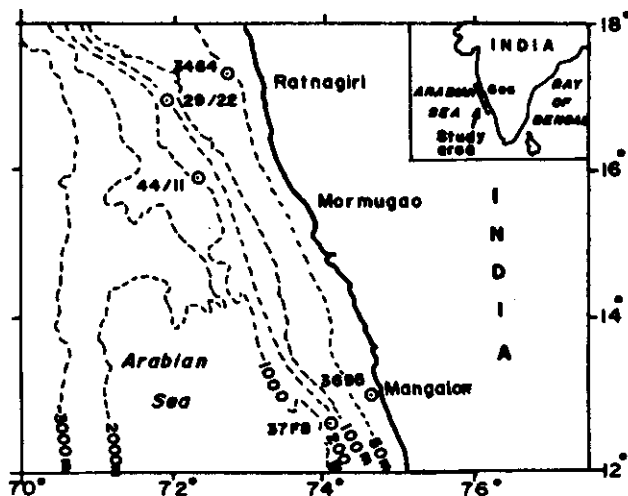


Fig. 1—Map showing stations position

tion cell and Diaflo ultrafiltration membranes XM-300, XM-100, PM-30, and PM-10. The extract of 44/11 sample was fractionated after dialysis. The different molecular weight fractions were then separated into humic and fulvic acids by acidification to pH 2 with 6 N HCl. The precipitate of humic acid was separated by centrifugation, dialysed against distilled water till neutral and freeze dried. The supernatant solution of fulvic acid was concentrated by rotary evaporation, dialysed till neutral and freeze dried.

Organic carbon⁶, total nitrogen⁷ and total acidity, carboxyl and phenolic hydroxyl groups⁸ were analysed. Total acidity was estimated by reacting a known weight of the humic material with an excess of NaOH solution. The NaOH, remaining after the reaction, was then back titrated with 0.5 N HCl solution to pH 8.4. The carboxyl group content was estimated treating the humic material with calcium acetate. The acetic acid liberated was then titrated with 0.1 M NaOH solution to pH 9.8. The phenolic hydroxyl group was calculated from the difference between the total acidity and the carboxyl group content. Elemental analyses were carried out using a Perkin-Elmer 240B CHN analyser. The dried samples were run for infrared spectra on a Pye Unicam (sp 1000) or Fourier transform IR spectrophotometer (model 1650) using KBr for pellets.

Results and Discussion

Table 1 shows the depth, textural characteristics, organic carbon, nitrogen and their ratios in the sediments at different stations. The highest percentage of organic carbon (5.6%) was found at st. 37F8, which lies in the upwelling region of the southern Arabian Sea. The percentage of organic

Table 1—Station depth, sediment texture, organic carbon, nitrogen (percentage of dry matter) and the C/N ratio in the sediments at different stations

St no.	Depth (m)	Sediment texture	C (%)	N (%)	C/N ratio
3464	60	Silt, clay	2.36	0.072	32.7
3695	26	Clay	2.13	0.023	92.6
29/22	220	Silt, clay	2.03	0.19	10.6
37F8	890	Clay	5.60	0.37	15.1
44/11	1121	Clay	4.80	0.27	17.7

carbon in the inner and outer shelf region varied from 2.03 to 2.36% whereas it was 4.8% at the offshore at 44/11. The C/N ratio at the stations located in the inner shelf region indicates that the organic matter is influenced by terrigenous source; whereas the stations in the outer shelf, slope and offshore region seem to be influenced partly by organic matter of marine origin.

Extraction efficiency and humification

Table 2 shows the extraction efficiency of humic and fulvic acids by 0.05 M and 0.5 M alkali solutions. The extractability of humic compounds from sediments by alkali solution varies depending on the environmental conditions under which the sediments were deposited and on the mineralogy of the sample. The variability in the extraction capacity of the alkali solution at different stations may be due to the organic matter being at different phases of diagenetic transformation into humics at different locations or the varied involvement of humics in the geochemical processes.

Sediments at sts 3464 and 29/22 (org. carbon 2.3 to 2%) showed 53% and 48% of organic matter bound to humics whereas at sts 3695 and 37F8 (org. carbon 2.13 to 5.6%) the percentage of organic matter bound to humics was much less (30% and 28% respectively). The area between Ratnagiri and Mangalore within which these stations lie is characterised by low productivity⁹ (0.25-0.5 gC/m²/day). The northern region of the Arabian Sea is characterised by oxic conditions and higher microbial activity¹⁰ which helps in the rapid mineralisation of organic matter while the slope region (st. 37F8) towards the southern parts of the area studied is characterised by higher organic carbon and oxygen deficient conditions¹¹. Higher yields of humic compounds were reported to be associated with oxic conditions and low rate of extraction were related to reducing environments¹². However, the other environmental factors like primary productivity, sediment texture

Table 2—Extraction efficiency of humic (HA) and fulvic (FA) acids by the two alkali solutions, percentage of humics in sediments and the estimated amount (%) of organic matter associated with humic material

St no.	Extracting solution	Fraction	% of dry humic material	% of total humics extracted	Humics as % of org. matter
3464	0.05 M NaOH	HA	0.73	32.0	53.0
		FA	0.37	16.2	
	0.5 M NaOH	HA	0.90	39.5	
		FA	0.28	12.3	
3695	0.05 M NaOH	HA	0.64	54.7	30.6
		FA	0.09	8.0	
	0.5 M NaOH	HA	0.33	28.2	
		FA	0.11	9.4	
29/22	0.05 M NaOH	HA	0.17	16.4	48.0
		FA	0.07	7.2	
	0.5 M NaOH	HA	0.63	60.7	
		FA	0.16	15.6	
37F8	0.05 M NaOH	HA	0.56	19.8	28.1
		FA	0.37	13.0	
	0.5 M NaOH	HA	1.73	61.1	
		FA	0.17	6.0	
44/11	0.05 M NaOH	HA	1.26	65.5	22.2
		FA	0.09	4.8	
	0.5 M NaOH	HA	0.46	23.9	
		FA	0.11	5.7	

and microbial activity also play a significant role in the humification process¹³.

Humification of the organic matter depends on the physico-chemical and biological conditions of the environment which may promote or retard mineralisation, assimilation and polymerisation reactions¹⁴. These effects control the subsequent distribution and evolution of humic compounds. Thus the hydrodynamic conditions, the redox character, the sedimentation rate and temperature control humus formation and, in many instances, transform their physico-chemical properties.

Fulvic acids, a minor fraction of the humic substances in the Arabian Sea sediments did not show any regular variation in the extractibility by the two alkali solutions. Fulvic acids are believed to be the precursors of humic acids in the humification process. They were the major component in the Baltic Sea sediments¹⁵ but only a minor component in the Peru continental shelf, Arabian Sea and the Mediterranean Sea sediments^{5,16}.

Concentration of fulvic acids decrease with depth of the sediment core^{17,18} indicating that the associated anoxic conditions are favourable for

rapid transformation into humic acids. In surficial sediments, on the other hand, a higher content of fulvic acids is maintained as they are not easily diagenetically transformed into humic acids. Fulvic acids are also known to dominate in organic matter of an allochthonous source, e.g. through an estuary¹⁹.

Molecular weight fractions

The contents of humic and fulvic acids in different molecular weight fractions are given in Table 3. A major portion of humic acids were present as high molecular weight fraction (>300000), whereas the major portion of fulvic acids was generally present as <10000 molecular weight fraction.

Rashid & King²⁰ and Rashid & Prakash²¹ studied the molecular weight distribution of humic compounds isolated from shelf sediments, decomposed marine algae (*Fucus vesiculosus* and *Laminaria digitata*) and aquatic humus isolated from river waters. Their results indicate that the molecular weight of marine humic compounds is highly variable ranging from 700 to over 2000000. They observed higher degree of variability in humic acids than in the fulvic acids. Poutanen²² found significant differences in the molecular weight distribution of humic and fulvic acids in different sea areas and observed that high molecular weight fulvic acids dominated the organic matter in the Baltic Sea sediments, whereas humic acids of high molecular weight dominated sedimentary organic matter in all depth horizons of the Peru continental shelf and the Arabian Sea. Though considerable amount of work has been done by many workers on the molecular weight distribution of humic and fulvic acids is varying environmental and depositional conditions and in different types of sedimentary regions, it is difficult to correlate the abundance and characteristics of humic material with the type of depositional environment and for comparative purposes no two depositional environments can be found to be identical.

Functional groups and elemental composition

The total acidity in humic acids (Table 4) ranged widely from 3.2 to 12.1 meq/g; high molecular weight humic acids showing lower acidity. The carboxyl content ranging from 1.8-4.6 meq/g, was also higher in the low molecular weight fraction. The total acidity and carboxyl content of fulvic acids were in general higher than the corresponding high molecular weight humic acids indicating enrichment of oxygen content in the low molecular weight fulvic acid fractions.

Table 3—Distribution of humic and fulvic acids (mg/g of dry matter, ash free basis) in different molecular weight fractions in the two extracting solutions (mol. wt. fractions: A = > 300000, B = 300000-100000, C = 100000-30000, D = 30000-10000, E = < 10000)

St no.	Extracting solution	Humic material	Molecular weight fraction (mg/g of dry sediment)				
			A	B	C	D	E
29/22	0.05 M NaOH	HA	1.54	0.13	<0.10	<0.10	<0.10
		FA	0.18	0.10	<0.10	0.11	0.26
	0.5 M NaOH	HA	4.35	0.58	0.38	0.58	0.47
		FA	0.30	0.32	<0.10	0.12	0.79
37F8	0.05 M NaOH	HA	0.42	0.36	0.78	0.19	2.17
		FA	0.73	<0.10	0.16	0.18	2.55
	0.5 M NaOH	HA	13.90	0.41	0.41	1.60	1.00
		FA	0.36	0.84	<0.10	<0.10	<0.10
44/11	0.05 M NaOH	HA	11.70	0.25	0.48	0.13	<0.10
		FA	0.33	0.10	0.25	0.22	0.12
	0.5 M NaOH	HA	2.04	0.63	0.86	0.54	0.51
		FA	0.36	0.11	0.23	0.36	<0.10

The phenolic hydroxyl content of humic acids lies between 0.47 to 5.4 meq/g (Table 4) except the high values of 10.7 and 7.1 in the two high molecular weight HA fractions at st. 44/11. The phenolic hydroxyl content of fulvic acids varies from 0.2 to 9.5 meq/g. The high values were mostly observed in the total fulvic acids and the high molecular weight fraction. As reviewed by Rashid & King²³ the phenolic hydroxyl content of soil humic compounds is 5-7 meq/g of humic material, whereas it is only 0.5 to 1.5 meq/g for marine humic compounds. Saito & Hayano²⁴ reported slightly higher values of 2.5 to 3 meq/g of organic matter. The present values are higher than those reported for marine humic compounds supporting the earlier observation (from C/N ratios) of predominance of terrestrial organic matter in sediments.

The ash content indicates that humic acids are more loosely bound to the clay mineral fractions than the fulvic acid fractions which show very high ash content even after employing several purification steps. However, it is interesting to note that the ash content of different fulvic acid fractions of sediments at st. 44/11 was minimum. This may be the effect of the pre-fractionation purification by dialysis carried out for the fulvic acids at this station. However, it seems likely that this method of purification reduces the low molecular weight fractions of fulvic acids.

From the elemental composition (Table 5), high molecular weight humic acids contained 60.3-50.3% carbon, 6.9-5.7% hydrogen and 4.1-2.0%

nitrogen. The ranges of these elements in the corresponding fulvic acid fractions were less at 46.5-28.1%, 8.9-3.6% and 4.8-1.6%. C/N ratios (Table 5) also point out to a dominance of terrigenous matter in the formation of humic acids. C/H ratios (Table 5) lying between 3-11 are much smaller than that of well developed and well aerated soils²⁵ (ratio: 16-21). Higher ratios indicate a high degree of condensation of organic matter, while aliphatic organic matter that constitute less aerated (marine) sediments is richer in hydrogen and hence the C/H ratios are lower.

IR spectral characteristics

The infrared spectra of some molecular weight fractions of humic acids HA extracted by different alkali solutions are shown in Figs 2 and 3. All the spectra of HA show prominent broad absorption from 3500 to 3150 cm^{-1} which probably arises from the O-H stretching vibrations of hydrogen bonded -OH group including -COOH group. In some cases -NH group may also contribute to a broad absorption in this region. The absorption at 2950 cm^{-1} and the shoulder at 2850 to 2875 cm^{-1} are related to -CH asymmetrical and symmetrical stretching mode of CH_2 and CH_3 groups. The presence of these groups in HA is supported by the presence of 1387 cm^{-1} absorption (C- CH_3) (Fig. 2). All the spectra are dominated to some extent, by absorption due to -COOH group at 1700 cm^{-1} . However notable variations exist in the absorption in different regions of different samples.

Table 4—Total acidity, carboxyl, phenolic hydroxyl groups (meq/g) and ash content (% of humic material) of humic (HA) and fulvic acids (FA) in different molecular weight fractions

St no.	Extracting solution/ mol. wt. fraction	Functional groups meq/g of humic material						Ash(%)	
		Total acidity		Carboxyl		Phenolic hydroxyl		HA	FA
		HA	FA	HA	FA	HA	FA		
3464	0.05 M NaOH	7.9	11.3	2.6	3.5	5.3	7.8	1.9	73.3
	0.5 M NaOH	6.8	12.2	2.3	3.8	4.5	8.4	3.1	71.6
3695	0.05 M NaOH	7.9	5.1	2.6	3.4	5.3	1.7	1.4	53.2
	0.5 M NaOH	10.1	3.8	—	3.0	—	0.8	6.0	66.4
29/22	0.05 M NaOH								
	> 300000	6.1	11.2	3.5	—	2.6	—	5.7	55.9
	> 10000	—	—	—	4.4	—	—	—	13.3
	< 10000	—	2.9	—	1.4	—	1.5	—	61.3
	0.5 M NaOH								
	> 300000	3.7	8.8	2.2	5.7	1.5	3.1	1.7	85.9
> 100000	4.7	—	2.9	—	1.8	—	Nil	53.2	
> 30000	4.8	—	3.3	—	1.5	—	Nil	15.6	
> 10000	6.4	—	4.0	7.3	2.4	—	9.4	69.8	
< 10000	—	6.1	—	3.7	—	2.4	—	36.8	
37F8	0.05 M NaOH								
	> 300000	4.6	3.5	2.6	3.3	2.0	0.2	Nil	29.0
	> 100000	5.1	—	2.1	—	3.0	—	Nil	33.1
	> 30000	5.8	—	2.5	2.9	3.3	—	Nil	23.3
	> 10000	5.1	—	2.2	—	2.9	—	1.0	30.1
	< 10000	4.6	4.5	3.1	2.7	1.5	1.8	Nil	51.6
0.5 M NaOH	> 300000	3.2	8.2	1.8	2.5	1.4	5.7	Nil	53.2
	> 100000	3.4	9.2	2.5	7.5	0.9	1.7	Nil	32.0
	> 30000	7.3	—	2.9	—	4.4	—	Nil	22.5
	> 10000	3.8	—	3.2	—	0.6	—	5.7	52.5
	< 10000	6.6	3.7	3.5	3.0	3.1	0.7	4.6	41.6
	44/11	0.05 M NaOH							
> 300000		4.5	11.1	2.1	1.6	2.4	9.5	3.3	Nil
> 100000		12.1	—	1.4	—	10.7	—	4.2	Nil
> 30000		9.5	7.7	2.4	1.5	7.1	6.2	7.5	Nil
> 10000		5.0	5.6	4.6	1.0	0.5	4.6	Nil	1.1
0.5 M NaOH									
> 300000	4.2	2.3	—	2.0	—	0.3	4.8	8.1	
> 100000	4.1	—	1.8	—	2.2	—	Nil	Nil	
> 30000	3.8	6.6	2.3	2.7	1.5	3.9	Nil	Nil	
> 10000	5.6	—	2.7	—	2.9	—	1.7	Nil	
< 10000	8.0	—	2.6	—	5.4	—	5.3	Nil	

Table 5—Elemental analysis of different molecular weight humic and fulvic acids fractions

St no.	Extracting solution/ mol. wt. fraction	Elemental analysis					St no.	Extracting solution/ mol. wt. fraction	Elemental analysis					
		% C	% H	% N	C/N	C/H			% C	% H	% N	C/N	C/H	
3464	0.05 M NaOH						44/11	0.5 M NaOH						
	HA	55.1	5.7	4.0	13.7	9.6		> 300000 HA	50.3	6.9	2.5	20.1	7.3	
	FA	46.3	3.6	—	—	—		> 100000 HA	55.2	6.2	—	—	8.9	
	0.5 M NaOH	HA	58.5	6.6	4.1	14.2		8.8	> 30000 HA	53.6	5.9	—	—	9.1
		FA	45.1	4.0	2.5	18.0		11.3	> 10000 HA	35.6	6.0	2.4	14.8	5.9
	3695	0.05 M NaOH							> 300000 FA	43.0	8.9	1.6	26.8	4.8
HA		55.9	6.3	2.0	27.9	8.8		> 100000 FA	42.5	7.2	—	—	5.9	
FA		44.7	5.7	2.2	20.3	7.8		> 30000 FA	44.1	6.9	—	—	6.4	
0.5 M NaOH		HA	52.6	5.9	2.8	18.8		8.9	> 10000 FA	26.7	6.3	—	—	4.2
		FA	43.2	4.2	2.0	21.6		10.3						
29/22		0.05 M NaOH							0.05 M NaOH					
	> 300000 HA	54.3	6.4	2.7	20.1	8.5		> 300000 HA	53.3	6.1	2.0	26.6	8.7	
	> 300000 FA	46.5	4.2	—	—	11.0	> 100000 HA	51.4	7.4	2.3	22.3	6.9		
	0.5 M NaOH	> 300000 HA	60.3	6.9	2.8	21.5	8.7	> 30000 HA	49.7	6.4	4.8	10.3	7.7	
		> 100000 HA	56.2	6.4	2.1	26.7	8.8	> 10000 HA	37.7	5.6	3.7	10.2	6.7	
	> 30000 HA	53.2	5.8	1.8	29.5	9.2	> 300000 FA	39.5	6.9	1.9	20.8	5.7		
	> 10000 HA	58.7	6.2	1.8	32.6	9.4	> 30000 FA	29.3	6.6	3.3	8.8	4.4		
	< 10000 HA	54.5	5.5	2.3	23.7	9.9	> 10000 FA	10.4	2.2	1.5	6.9	4.7		
	> 10000 FA	39.8	4.7	3.6	11.0	8.4								
	< 10000 FA	36.8	3.9	2.5	14.7	9.4	0.5 M NaOH							
	37F8	0.05 M NaOH						> 300000 HA	48.2	5.8	3.7	13.0	8.3	
		> 300000 HA	53.6	6.3	2.2	24.3	8.5	> 100000 HA	32.4	4.3	4.8	6.7	7.5	
> 30000 HA		54.2	6.4	3.2	16.9	8.4	> 30000 HA	26.2	3.7	2.3	11.4	7.1		
> 10000 HA		56.6	6.7	2.6	21.7	8.4	> 10000 HA	21.7	4.9	1.6	13.5	4.4		
< 10000 HA		51.9	5.5	3.5	14.8	9.4	< 10000 HA	16.9	4.0	1.9	8.9	4.2		
> 300000 FA		28.1	5.4	3.4	8.2	5.1	> 300000 FA	47.7	5.7	4.8	9.9	8.3		
> 100000 FA		25.9	4.6	—	—	5.6	> 30000 FA	36.5	6.5	3.7	9.8	5.6		
> 30000 FA		41.9	6.6	—	—	6.3								
> 10000 FA		20.6	7.4	3.7	5.5	2.8								
< 10000 FA		31.8	10.6	—	—	3.0								

In Fig. 2 the presence of a distinct band at 1710 cm^{-1} due to carboxyl of the carboxylic acids in high molecular weight fractions occurs as a shoulder in other fractions where the carboxyl group is present mainly as carboxylate ion. The concentration of carboxyl increases gradually with decrease in molecular weight as evidenced by the broad absorption centred at 1630 cm^{-1} and 1400 cm^{-1} . The region $900\text{--}1200\text{ cm}^{-1}$ usually contains unsaturated including aromatic C—H out

of plane bending vibrations and C—O stretching as well as O—H deformation vibrations. They are of medium and low intensities in high and low molecular weight fractions respectively suggestive of different concentrations of aromatics. The spectra also give an indication of the presence of aliphaticity in all the samples, their concentration being high in the low molecular weight fraction as evidenced by the peak at around 1460 cm^{-1} due to methylene group.

Figure 3A (st. 44/11, 0.05 M NaOH HA) features a decrease in the associated $-OH$ stretching absorption centred at 3400 cm^{-1} accompanied by a decrease in the intensity at $1035-1060\text{ cm}^{-1}$ indicating dehydration. A gradual increase in the characteristic CO_2 absorption at 2360 cm^{-1} in fractions (a) and (c) suggested that decarboxylation of the carboxylic acid group also takes place as evidenced by the simultaneous decrease in the carboxyl carbonyl absorption at

1710 cm^{-1} . Fraction (b) also indicates decarboxylation but to a lesser extent. An increase in the intensity of carboxylate ion at 1388 cm^{-1} and $1620-30\text{ cm}^{-1}$ due to chelation is also observed.

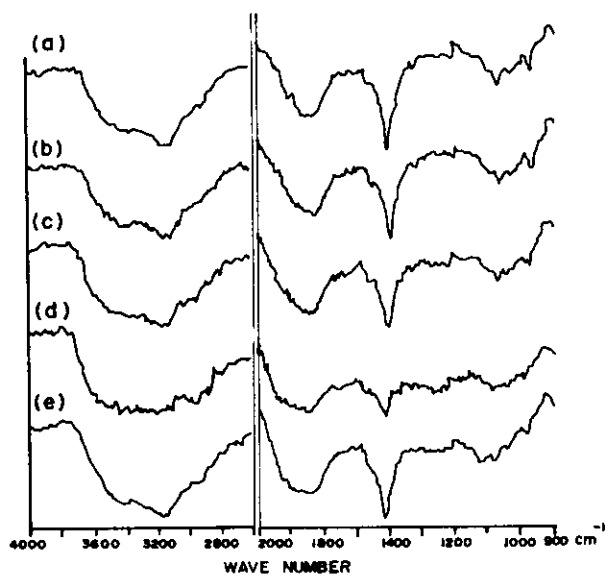


Fig. 2—IR spectra of (a) >300000 , (b) >100000 , (c) >30000 , (d) >10000 , (e) <10000 mol. wt. humic acids (0.5 M NaOH ext) at st. 37F8

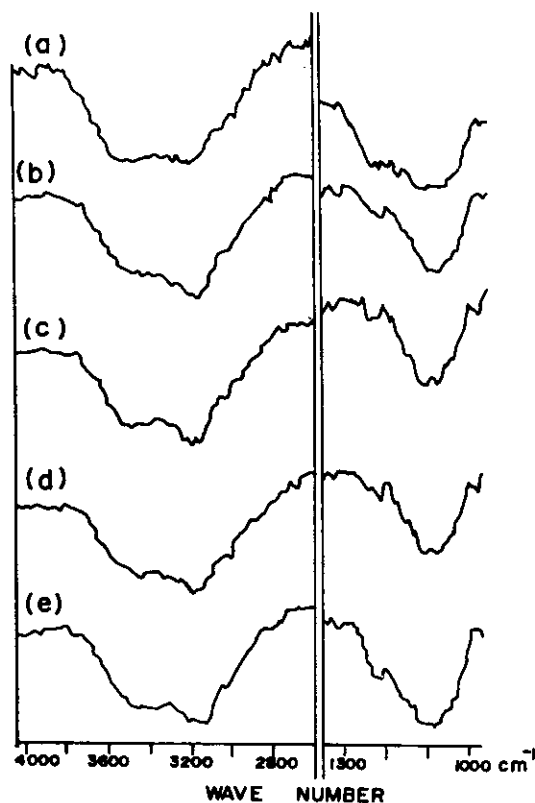


Fig. 4—IR spectra of (a) >300000 , (b) >100000 , (c) >30000 , (d) >10000 , (e) <10000 mol. wt. fulvic acids (0.5 M NaOH ext) at st. 37F8

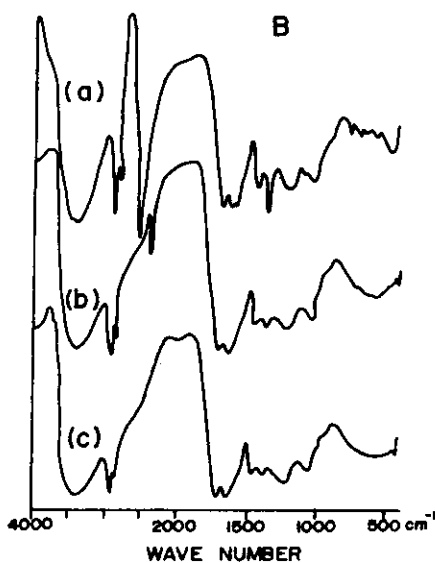
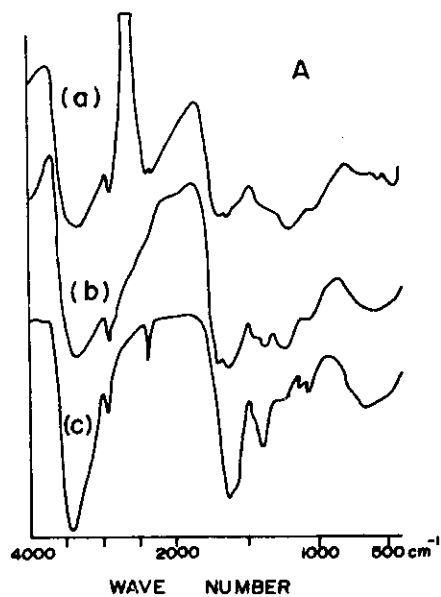


Fig. 3—IR spectra of (a) >300000 , (b) >30000 , (c) >10000 mol. wt. humic acids at st. 44/11. (A) 0.05 M NaOH ext, (B) 0.5 M NaOH ext

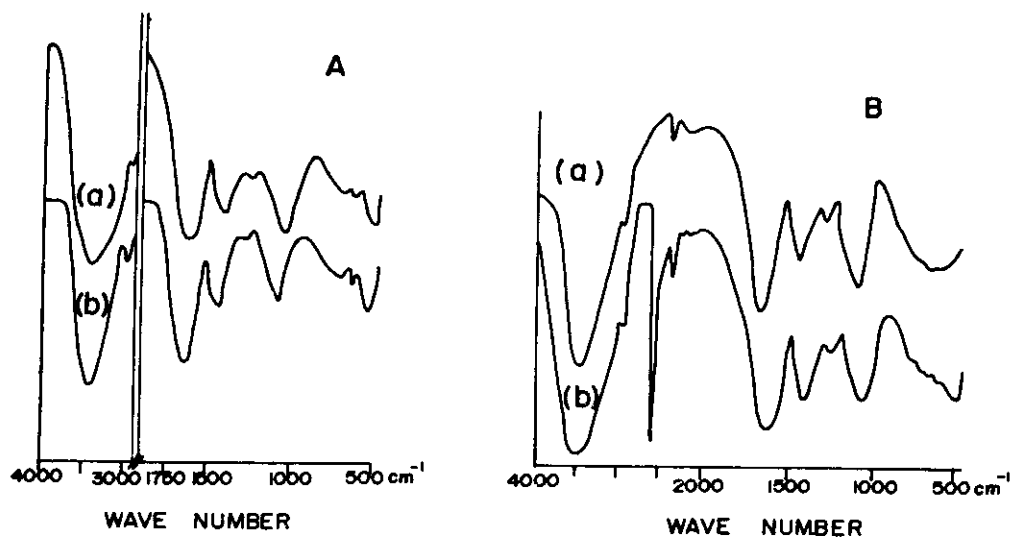


Fig. 5—IR spectra of (a) >100000 and (b) >30000 mol. wt. fulvic acids at st.44/11, (A) $0.05\ M$ NaOH ext, (B) $0.5\ M$ NaOH ext

Figure 3B (st. 44/11, $0.5\ M$ NaOH HA) indicates the presence of aliphaticity containing mainly $-\text{CH}_2-$, methylene group, their concentration being higher in >300000 molecular weight fraction and minimum in the low molecular weight fraction. The aliphaticity in these fractions is more than the $0.05\ M$ NaOH HA from the same station (Fig. 3A). The intensity of absorption at $1375\text{--}1377\ \text{cm}^{-1}$ decreases in the order of decreasing molecular weight indicating greater number of methyl groups which shows that the aliphatic component is highly substituted in high mol. wt. fraction.

The IR spectra of fulvic acids at different stations are shown in Figs 4 and 5. The fulvic acids have similar composition as the humic acids from the same locality and show similar kind of prominent bands as in the spectra of humic acids, except few differences.

In Fig. 4 the presence of maxima at $3380\ \text{cm}^{-1}$ in all the fractions implies the presence of H-bonded OH or $-\text{NH}$ groups whereas absorption towards lower wave numbers $3100\ \text{cm}^{-1}$ is consistent with H-bonded $-\text{OH}$ group characteristic of carboxylic acid. It could also be due to H bonded $-\text{NH}$ as indicated by low C/N ratio for fulvic acids (Table 5). The associated phenolic $-\text{OH}$ peak is more dominant in higher molecular weight fractions (mol. wt. >300000) and lowest fraction (<10000). This is further supported by the peak at $1250\ \text{cm}^{-1}$ whereas chelation is more in low molecular weight fractions.

There is not much difference in the spectra of FA's of st. 44/11 (Fig. 5). Both the spectra show

an absorption at $2922\ \text{cm}^{-1}$ indicative of the presence of $-\text{CH}_2-$ methylene groups of all types including asymmetric stretching of $-\text{CH}_3-$ groups attached to aromatic rings.

The intensity of the peak at $1400\ \text{cm}^{-1}$ and at $1050\ \text{cm}^{-1}$ in case of FA spectra at st. 44/11 is higher than in humic acid spectra of the same locality indicating higher concentration of carbonyl group in fulvic acids. Similarly, the IR spectra of HA (Fig. 3) and FA (Fig. 5) at st. 44/11 show striking differences in the region at $1717\ \text{cm}^{-1}$ and $1650\ \text{cm}^{-1}$. The absorption at $1717\ \text{cm}^{-1}$ is very strong in the case of HA but it is not seen in case of FA. The absence of absorption at this wavelength in case of FA may be related to the involvement of the $-\text{COOH}$ group in the formation of metal complexes²⁶. FA seems to be richer in carboxylate (COO^-) than the corresponding HA from the same locality as evident from the intensity of $1636\text{--}1670\ \text{cm}^{-1}$ band.

In conclusion, the concentration of humic compounds in the Arabian Sea is variable and depends upon biogeochemical and oceanographic factors. The environmental factors like primary productivity, sediment texture, redox conditions as well as microbial activity play significant role in the humification process. The elemental and functional group characteristics point out to the dominance of allochthonous source of organic matter. However, the presence of aliphaticity in the IR spectral characteristics also indicate the presence of marine source component in the formation of humic compounds.

Acknowledgement

Author thanks Drs R Sen Gupta, S N D'Sousa and Solimabi Wahidullah for reviewing and making valuable suggestions.

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