

# Humic substances in Baltic Sea sediments

Baltic Sea  
Superficial sediment  
Humic substances  
Humic acids  
Fulvic acids  
Mer Baltique  
Sédiment superficiel  
Substances humiques  
Acides humiques  
Acides fulviques

Sugandhini Naik \*, Eeva-Liisa Poutanen

Institute of Marine Research, P.O. Box 33, SF-00931 Helsinki 93, Finland.

\* Present address: National Institute of Oceanography, Dona-Paula-403004, Goa, India.

Received 16/11/83, in revised form 7/3/84, accepted 15/3/84.

## ABSTRACT

Humic substances in sediment samples from some of the oxic and anoxic basins in the Baltic Sea were studied. The humic material constituted 30-55% of the organic matter and had a higher content of fulvic acids than humic acids. The >300 000 molecular weight fraction was found to constitute the major portion of the humic acids, whereas the fulvic acids were mainly composed of two mol. wt groups >300 000 and <10 000.

Data on the elemental analysis, functional groups and IR absorption characteristics suggest that the humic material is formed from a similar type of organic matter in the Gulf of Bothnia, the Baltic Proper and the Gulf of Finland, and is of mixed origin (autochthonous and allochthonous). This may be a characteristic of partially or semi-enclosed basins.

*Oceanol. Acta*, 1984, 7, 4, 431-439.

## RÉSUMÉ

### Substances humiques dans les sédiments de la Mer Baltique

Les substances humiques ont été analysées dans des échantillons de sédiment prélevés dans des bassins oxiq ue et anoxique de la Mer Baltique. le matériel humique constitue 30 à 50% de la matière organique, avec une teneur plus élevée en acides fulviques qu'en acides humiques. La fraction de poids moléculaire supérieure à 300 000 constitue l'essentiel des acides humiques, tandis que les acides fulviques se composent principalement de deux groupes de poids moléculaires respectivement supérieur à 300 000 et inférieur à 10 000.

Les données de l'analyse élémentaire, les groupements fonctionnels et les caractéristiques de l'absorption suggèrent que le matériel humique provient du même type de matière organique dans le Golfe de Bothnie et le Golfe de Finlande, et que son origine est mixte (autochtone et allochtone), ce qui pourrait être une caractéristique des bassins partiellement ou semi-fermés.

*Oceanol. Acta*, 1984, 7, 4, 431-439.

## INTRODUCTION

Organic matter in natural waters and marine sediments can be composed of terrigenous material (allochthonous) and can be produced by aquatic organisms (autochthonous). Whereas the bulk of the organic matter in many recent marine deposits is derived from local biomass, organic matter of terrigenous origin is confined to river estuaries and in shoreline organic material

(Degens, Mopper, 1976; Pocklington, Leonard, 1979). The diagenetic transformation of organic matter yields humic material which accounts for about 60-75% of the total organic matter in marine deposits (Schnitzer, 1978). Humic material is known to enhance the reactivity of the sediments and of overlying water by facilitating the movement of water nutrients and trace elements. It is also known to form complexes with metal ions and hydrous oxides, and to interact with clay

minerals and organic chemicals that may be toxic pollutants. Humic substances, which are of great ecological, geological and economic importance, as discussed by Jackson (1975), have thus received considerable attention in recent years.

Humic substances comprise a group of high molecular weight polymers, acidic in nature and yellow to brown in colour. It has been reported that they are formed in differing marine environmental conditions, oxic as well as anoxic. Degens *et al.* (1964) reported that the humic acids in the basin off Southern California were of continental origin. The humic acids found in areas of the Central Atlantic away from the continent are reported to be mostly autochthonous (Bordovskiy, 1965). However, there seems to be general agreement that humic substances can be formed from the degradation products of organic matter derived from marine plankton (Nissenbaum, Kaplan, 1972; Kasatochkin *et al.*, 1968). This finding is further supported by the occurrence of large quantities of humic and fulvic acids in organic-rich marine surface sediments underlying areas of high productivity (Cronin, Morris, 1982; Poutanen, Morris, 1983).

The mechanisms of formation and the characteristics of these substances have been studied in many marine deposits in shelf zones and the organic-rich areas of the oceans of the world (Schnitzer, Khan, 1972; Chen *et al.*, 1978; Cronin, Morris, 1982; Calvert, Price, 1971; Calvert, Morris, 1977; Pempkowiak *et al.*, 1976). The major components of humic substances are differentiated into acid insoluble humic acid (HA) and alkali as well as acid soluble fulvic acid (FA) components. HA and FA occur in varying concentrations and the nature of these organic acids in natural waters and sediments shows marked geographical variability (Jackson, 1975). However, Schnitzer (1977) has shown that HA and FA from soils exhibit similar analytical characteristics and chemical structures, irrespective of the geographical and environmental conditions.

This study was undertaken to determine the nature and distribution of humic substances in the sediments of some of the oxic and anoxic basins of the Baltic Sea. Another aim of the study is to determine the effect of oxic/anoxic conditions on the nature of the humic substances. The concentration, molecular size distribution, functional groups and IR-spectroscopic characteristics of humic and fulvic acids have been studied in order to delineate their origin, nature and the mechanism of formation.

## MATERIALS AND METHODS

### Sampling

Core samples were collected from the topmost sediment layer at 5 stations covering the Gulf of Bothnia, the eastern part of the Gulf of Finland and the northern Baltic Proper, as shown in Figure 1. Samples collected in the Gulf of Bothnia (CVI, BO-3 and EB-1) were from oxic basins, whereas those collected in the Gulf of Finland (XV-1) and in the northern Baltic Proper

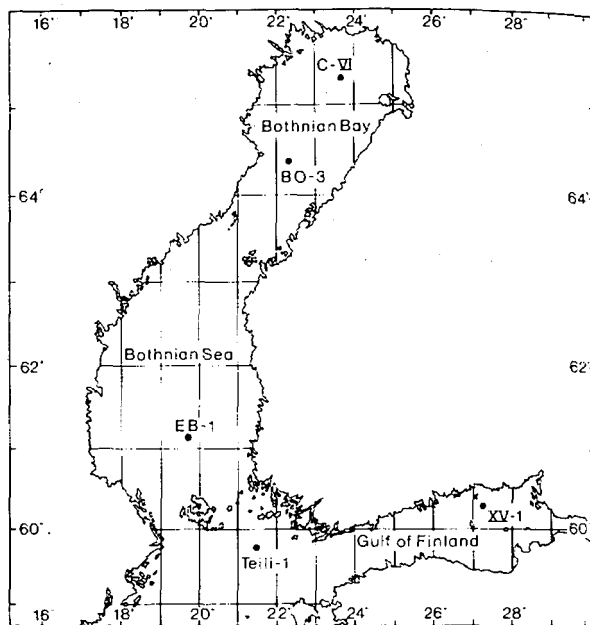


Figure 1  
Location of sampling sites in the Baltic Sea.

(Teili I) represent anoxic sediment samples. The samples were taken with a box corer, cut immediately after sampling into 5 cm-thick subsamples and stored deep-frozen in precleaned polythene bags until analysed.

A separate sediment sample was collected at each station using a gravity corer for soft sediments as described by Niemistö (1974). The cores were cut into 8 mm subsamples, which were stored in plexiglass sheets until the redox measurements were made. The subsamples were then dropped into Petri dishes and stored at  $-25^{\circ}\text{C}$  until analysis for moisture content, organic carbon, nitrogen, hydrogen and carbohydrates. Subsamples were also taken for microscopical analyses.

### Methods

The samples for redox measurements were kept at room temperature for 30 min. and then measured according to the method described by Bågander and Niemistö (1978).

The sediments were freeze-dried, ground in an agate mortar and run on a CHN-Analyzer (Hewlett-Packard, F and M 185). Carbohydrates were estimated by the phenol-sulphuric acid method described by Artem'yev *et al.* (1971). The coefficient of variation observed for carbon, nitrogen and hydrogen analyses was 8% and for carbohydrates 5% as determined for three analyses. Several methods have been employed for the extraction of humic substances from sediments. Templeton and Chasteen (1980) have summarized the different extraction and fractionation procedures employed by different workers.

In the present study the marine humic and fulvic acids were extracted under nitrogen first with distilled water, then with a mixture of 0.05 M NaOH and  $\text{Na}_4\text{P}_2\text{O}_7$

and then repeatedly with 0.05 M NaOH until the extract was colourless. This was followed by extraction with 0.5 M NaOH until the extract was colourless and finally the residue was refluxed with 0.5 M NaOH under nitrogen for 20 hours. After separation from the residual sediments by centrifugation, all extracts were pressure-filtered through GF/C glass fibre filters and fractionated before HA and FA separation using ultrafiltration membranes (Amicon ultrafiltration cell and Diaflo ultrafiltration membranes XM-300, XM-100, PM-30 and PM-10). The extraction of marine humic substances and the fractionation and purification of humic and fulvic acids have already been reported in detail (Poutanen, Morris, 1982; Poutanen, Morris, 1983). Purified fulvic and humic acid fractions were then freeze-dried and weighed to determine the amount of the respective fractions.

The ash content of some of the major humic and all the fulvic acid fractions was determined by igniting a small amount of the sample for four hours at 800°C. Functional group analyses were carried out following the procedure outlined by Schnitzer and Khan (1972). Total acidity was determined by treating the sample with NaOH instead of Ba(OH)<sub>2</sub>, and then back-titrating the excess NaOH with HCl. The carboxyl group was estimated using calcium acetate and titrating the acetic acid formed with NaOH. The phenolic hydroxyl group was estimated from the difference between the total acidity and the carboxyl group values. The elemental analyses (C, H and N) were carried out using a Hewlett-Packard CHN analyzer.

Infrared spectra were recorded from about 1 mg of material pelleted with about 300 mg KBr using a Perkin-Elmer (Model 457) spectrophotometer.

## RESULTS AND DISCUSSION

Sediment samples taken from different sites in the Baltic Sea differed markedly from each other. The Bothnian Bay (CVI) sediment consists of brown to greyish brown mud with some remains of phytoplankton (*Navicula* sp.). A very loose, brown-coloured sediment sample with more consolidated sharp, darker brown bands was obtained at the sampling site BO-3. The phytoplankton debris was dominated by diatoms (predominantly species of *Achnanthes taeniata*, *Synedra* sp., *Actinocyclus octonarius*, *Melosira arctica*, *Thalassiosira baltica* and *Chaetoceros holsaticus*). Sediment sample EB-1 consists of very fine-grained material, with only a few diatoms. In the northern Baltic Proper, a small sedimentation basin (Teili I) is a sink for material transported from large non-deposition areas, and probably even erosion areas around it, as well as for material of the autochthonous primary production. The sediment recovered was black, very fine grained and with a very high H<sub>2</sub>S content. It consisted of large amounts of phytoplankton remains (predominantly *Chaetoceros holsaticus*, *Actinocyclus octonarius*, *Melosira arctica*, *Ebria tripartita*). The sample from the eastern part of the Gulf of Finland was dark in colour, very soft clay and with high H<sub>2</sub>S content, and consisted of phytoplankton

remains (predominantly species of *Thalassiosira baltica*, *Achnanthes taeniata*, *Tabellaria fenestrata* and *Melosira arctica*) and amorphous organic matter.

Table 1 shows the redox potential, the percentage of dry matter, and the percentages of organic carbon, nitrogen and hydrogen in each 8 mm thick layer through the sediment down to a depth of 5 cm at each station together with their average values. The percentage of dry matter was found to decrease from the station in the Bothnian Bay to that in the Bothnian Sea. The percentage of dry matter in the anoxic basins is low with a minimum value of 8.6% at station Teili-I. The redox potential data suggest that highly oxidising conditions prevail at all the stations in the upper few centimetres layer of the sediment in the oxic basins, and a decreasing trend below this depth. Of the two anoxic basins, Teili-I appears to be more anoxic than XV-I.

The preservation of organic matter in the anoxic basins is also indicated by a relatively higher percentage of organic carbon, nitrogen and hydrogen at station Teili-I and XV-I in the Northern Baltic Proper and the Gulf of Finland than at stations in the Gulf of Bothnia. Niemistö and Voipio (1981) studied the rate of sedimentation at some of these stations in the Baltic Sea. They observed a sedimentation rate of 2.4 mm y<sup>-1</sup> at station EB-I, and 2.2 mm y<sup>-1</sup> at station Teili-I. The maximum sedimentation rate of 7.4 mm y<sup>-1</sup> was found at station XV-I. Recent studies on sedimentation rates (Voipio, personal communication) have indicated a slightly lower rate of sedimentation (1.3 mm y<sup>-1</sup>) at station CVI and 2.0 mm y<sup>-1</sup> at station BO-3. It is established (Gross, 1966) that the accumulation of organic matter is greatest where the rate of sedimentation is highest. The high rate of sedimentation, together with the depletion of oxygen, may explain the high percentage of organic carbon, nitrogen and hydrogen in these basins.

In general, the organic carbon content of the anoxic sediments (6.5-7.2%) was on the same level as in the open Baltic Proper (Niemistö, Voipio, 1981), but the carbon content of the oxic sediments (3.1-3.6%) was below this level. Lassig *et al.* (1978) have reported an annual phytoplanktonic primary production of carbon of about 15-30 g m<sup>-2</sup> in the Bothnian Bay, about 60 g m<sup>-2</sup> in the Bothnian Sea and about 100 g m<sup>-2</sup> in the Baltic Proper and the Gulf of Finland, the variation being chiefly caused by differences in nutrient levels and the length of the growing period. We also observed a similar trend for the variation in the percentage of organic carbon in the sediment samples in these different zones of the Baltic Sea (Tab. 1). However, the organic carbon content is high in comparison with the rate of primary production, which suggests an additional source of organic carbon at all the stations besides plankton.

The C:N ratios do not show any regular trend for the variation with the depth of the sediment core. In the topmost 5 cm it varied from 2.6 to 11.5 at station CVI, from 4.8 to 13 at BO-3, from 8.5 to 11.3 for EB-I, from 9.5 to 15.6 for Teili-I and from 5.9 to 8.6 for station XV-I. The mean value varied from 7.2 to 10.8, the minimum value being at BO-3 and the maximum at station Teili-I. The organic carbon to nitrogen ratio

Table 1

Redox changes and the content of dry matter, carbon, nitrogen and hydrogen (percents of dry matter) in the uppermost 0.8 cm thick subsamples in the five sediment cores.

Sample mm	C VI* 0-10 cm							BO <sub>3</sub> 0-5 cm						
	Dry matter %	Redox mv	C %	N %	H %	C:N	C:H	Dry matter %	Redox mv	C %	N %	H %	C:N	C:H
8	17.6	486	4.2	0.5	0.8	8.4	5.2	9.5	508	5.0	0.5	1.5	10.0	3.3
16	22.1	473	3.7	0.4	0.9	9.2	4.1	12.9	287	5.1	0.6	1.4	8.5	3.6
24	29.3	479	3.4	0.3	1.5	11.3	2.2	19.9	149	3.6	0.5	1.0	7.2	3.6
32	31.3	415	-	-	-	-	-	29.8	271	3.1	0.5	1.0	6.2	3.1
40	33.4	330	3.2	0.8	0.8	4.0	4.0	31.0	276	3.2	0.5	1.2	6.4	3.6
48	35.5	207	2.3	0.2	0.6	11.5	3.8	29.5	209	2.9	0.6	0.8	4.8	3.6
56	37.4	214	2.1	0.8	0.5	2.6	4.2	28.4	150	2.6	0.2	0.8	13.0	3.2
64	40.9	135	1.9	0.4	0.5	4.7	3.8							
72	44.0	89	1.8	0.1	0.4	18.0	4.5							
80	44.2	139	2.3	0.9	0.5	2.5	4.6							
88	39.5	61	2.0	0.6	0.5	3.3	4.0							
96	40.7	60	1.9	0.2	0.4	9.5	4.7							
104	37.7	86	2.0	0.3	0.6	6.6	3.3							
$\bar{X}$ (0-5 cm)	32.8	-	3.1	0.5	0.9	7.8	3.9	23.0	-	3.6	0.5	1.1	7.2	3.3
$\bar{X}$ (5-10 cm)	41.0	-	2.0	0.4	0.5	7.4	4.1							

Dry matter %	Redox mv	C %	N %	H %	C:N	C:H	EB <sub>1</sub> 0-5 cm					Teili-I 0-5 cm				
							Dry matter %	Redox mv	C %	N %	H %	Dry matter %	Redox mv	C %	N %	H %
20.0	536	3.3	0.3	1.0	11.0	3.3	5.4	-121	7.8	0.5	1.7					
22.2	524	3.3	0.3	1.1	11.0	3.0	7.1	-163	8.5	0.8	1.8					
24.3	500	3.4	0.4	1.1	8.5	3.0	8.0	-144	7.8	0.8	1.7					
26.3	492	3.8	0.4	1.2	9.5	3.1	8.0	-143	6.7	0.7	1.6					
27.8	334	3.4	0.3	1.1	11.3	3.0	8.4	-144	5.7	0.6	1.5					
28.0	193	3.1	0.3	1.0	10.3	3.1	10.9	-166	4.9	0.5	1.3					
28.8	171	2.9	0.3	0.9	9.7	3.2	12.8	-163	4.0	0.4	1.2					
25.3	-	3.3	0.3	1.0	10.2	3.1	8.6		6.5	0.6	1.5					

Sample mm	Teili-I 0-5 cm			XV-I 0-5 cm					
	C:N	C:H	Dry matter %	Redox mv	C %	N %	H %	C:N	C:H
8	15.6	4.6	6.0	-69	12.2	1.5	2.6	8.1	4.7
16	10.6	4.7	9.8	-136	8.4	1.0	1.9	8.4	4.4
24	9.7	4.6	11.2	-129	7.6	1.0	1.9	7.6	4.0
32	9.5	4.2	12.2	-113	5.6	0.7	1.6	8.0	3.5
40	9.5	3.8	14.3	-106	5.9	1.0	1.6	5.9	3.7
48	9.8	3.7	12.7	-109	5.7	0.7	1.5	8.1	3.8
56	10.0	3.3	13.4	-125	5.2	0.6	1.6	8.6	3.2
$\bar{X}$ (0-5 cm)	10.8	4.3	11.4	-	7.2	0.9	1.8	8.0	4.0

Data up to ~ 10 cm.

has been used as an indicator of terrigenous addition to marine sediments. This is based on the observed enrichment of carbon over nitrogen atoms in terrestrial, as compared to marine organic matter. According to the average values for the C:N ratio in the topmost 5 cm layer, it appears that the terrigenous addition is smaller in the Bothnian Bay than at the other stations studied, although it should be remembered that small variations in the C:N ratio may also be due to analytical inaccuracies. It is worth mentioning here that the Gulf of Finland and the northern Baltic Proper, where stations XV-I and Teili-I are situated, receive the maximum amount of river inflow (Mikulski, 1970; 1972). Bordovskiy (1965) attributes a similar type of variation in the C:N ratio in the shallows of closed and partly closed basins to the mixed nature of the organic matter. Thus comparison of the C:N ratios of the recent muds taken from different sites in the Baltic Sea indicates

that at least part of the organic matter is of autochthonous origin.

The chemical characteristics of the 5-10 cm layer at station C-VI were also studied to determine whether there are any differences in the humic content between the topmost 5 cm layer and the underlying 5 cm layer. The sediment (5-10 cm) was found to be more consolidated, with a dry matter content of over 40%, and there is a sharp decrease in the redox potential from 214 mV at 5 cm to 60 mV at 10 cm. There is also a decrease in the percentage of organic carbon, nitrogen and hydrogen, with mean values of 2%, 0.4% and 0.5%, respectively.

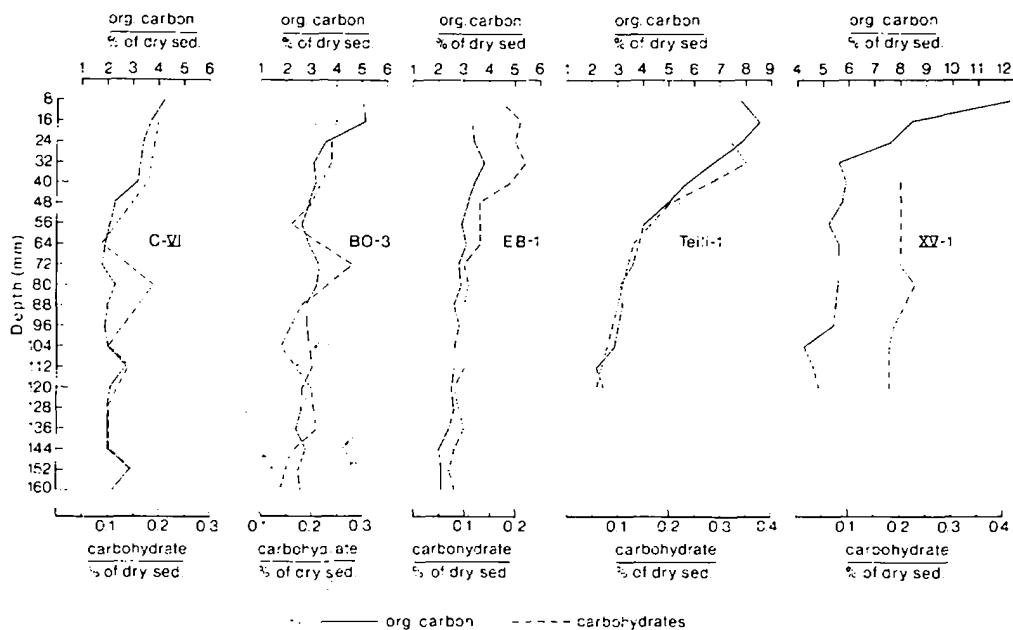
The carbohydrate content of the samples was estimated in order to study the origin of the organic matter and to determine whether there is any correlation between the carbohydrate content and the humic substances.

Carbohydrates are known to occur in marine environments as monosaccharides, oligosaccharides and polysaccharides (Swain, 1969). Only a few determinations of carbohydrates in marine sediments have been made so far because of the lack of sufficiently sensitive and precise method. Recent sediments from the Santa Barbara Basin, California, have been found to contain 2.2 mg carbohydrates  $g^{-1}$  of dry sediment at the surface, falling to very low levels below the seabed (Prashnowsky *et al.*, 1961). Carbohydrates were also detected in sediments from the San Diego Trough at a total concentration ranging up to 0.9 mg  $g^{-1}$  (Degens *et al.*, 1963). Relatively large amounts of carbohydrates have

whereas XV-I showed the highest concentration of humic substances. Our results are only tentative, and no conclusions can be drawn the basis of this data. The authors consider that more work should be done in this field.

The amount of total humic material extracted by different extractants and the percentage of organic matter associated with humic material are presented in Table 2. The extraction efficiency of 0.05 M NaOH ranges from 70 to 90% of total humics, the minimum value being obtained for station Teili-I and the maximum for station CVI. The percentage of organic matter associated with humic substances has been calculated

Figure 2  
Distribution of organic carbon (%) and carbohydrates (%) in the sediment cores (0-16 cm).



also been detected in anoxic Black Sea sediments (Stari-kova, Yobloková, 1972; Mopper *et al.*, 1978). Although Swain and Bratt (1978) were able to detect carbohydrate residues in north-western Atlantic sediments, they found no correlation between these residues and either depth or lithology.

The results obtained from our Baltic Sea sediments varied from one station to the next, the maximum being 3.5 mg  $g^{-1}$  and the minimum 0.5 mg  $g^{-1}$  of dry sediment (Fig. 2). The concentration of carbohydrates was found to decrease with depth in the upper few centimetres of the sediment. There is also a clear correlation with the carbon content. Various aspects of the biogeochemistry of carbohydrates in marine environment have been reviewed by Mopper (1973), who concluded that the origin of the carbohydrates could not be established unambiguously. For example, the carbohydrates in coastal sediments could have been derived from material having two different origins: allochthonous (terrigenous) and autochthonous, either in the water column or in the sediments themselves (Prashnowsky *et al.*, 1961). A comparison of our average carbohydrate content in the 5 cm layer sediment with that of humic substances did not show any significant correlation. The highest concentration of carbohydrates was found at the most anoxic station Teili-I,

Table 2

Extraction efficiency of humic (HA) and fulvic (FA) acids (g) by the distilled water and the two alkali solutions, and estimated amount (%) of organic matter associated with humic material.

Sample	Fraction	H <sub>2</sub> O ext. (g)	0.05 M NaOH (g)	0.5 M NaOH (g)	Total amount of humics (mg/g dry sediment)	Organic matter associated with humics (%)
C VI	0-5 cm	—	0.15	0.03	1.4	30
	FA	—	1.79	0.17	15.6	
C VI	5-10 cm	—	0.73	0.09	3.9	47
	FA	0.02	2.19	0.52	13.0	
BO <sub>3</sub>	0-5 cm	0.01	0.58	0.03	6.2	38
	FA	0.10	1.33	0.43	18.7	
EB <sub>1</sub>	0-5 cm	<0.01	0.46	0.03	3.8	30
	FA	<0.01	1.52	0.36	14.2	
Teili-I	0-5 cm	0.01	0.18	0.03	7.6	39
	FA	0.02	0.72	0.36	38.3	
XVI	0-5 cm	<0.01	0.85	0.07	18.1	55
	FA	0.06	2.21	0.46	53.8	

using the approximate relation, organic matter =  $1.8 \times$  organic carbon, mg/g (Nriagu, Coker, 1980). The humic substances account for about 30-55% of the organic matter. Similar amounts of humic substances (33% of the organic matter) have been obtained from the sediments of the Gulf of Gdansk by Bojanowski *et al.* (1977). Humic material constituting more than 60% of the organic matter has been reported in the continental shelf sediments rich in organic material (Gershamovich *et al.*, 1976; Poutanen, Morris, 1983). The small amount of humic substances present in the sediments in this area is due to the low content of organic carbon as well as the low rate of primary production.

Organic matter is supposed to be most humified in areas where its concentration is highest and, irrespective of the particle size of the sediments, the degree of humification declines as the organic content decreases (Bordovskiy, 1965). We did not find a similar relationship between the humic content and the total organic matter. Considering the strong association of the fulvic acids with the inorganic material—which is evident from the high ash content (Table IV) of these fractions—it can be assumed that either a considerable amount of the humic substances is lost during purification (which involve a number of steps), or that some environmental factor may be limiting the humification process. Contrary to the findings of Poutanen and Morris (1983) and also of Bojanowski *et al.* (1977), we obtained

a higher value for the fulvic acids content than that for the humic acids in our sediment samples. Fulvic acids represented from 24 to 41.4% and humic acids from 3.4 to 13.6% of the organic matter.

A comparison of the contents of humic material at the two layers at station CVI reveals that there is an equal amount of humic substances  $g^{-1}$  of sediments, although the percentage of organic carbon is slightly higher in the upper 5 cm layer than in the lower one. It is also worth noting that the amount of humic acid increases while that of fulvic acid decreases on moving from the upper 5 cm to the lower 5 cm layer.

The distribution of humic and fulvic acids in the different molecular size fractions of the three extracting solutions is given in Table 3. Negligible amounts of humics are extracted by distilled water. The humic and fulvic acid fraction with a nominal molecular weight of  $>300\,000$  constitutes the major part of the humic material and most of it is extracted by 0.05 M NaOH. Significant amounts of FA, with a nominal molecular weight of  $<10\,000$ , are extracted by 0.05 M NaOH and also by refluxing with 0.5 M NaOH. The amount of FA fraction  $<10\,000$  extracted by 0.5 M NaOH suggests that there is a strong association between this fraction and the silicious inorganic material. The FA fractions with a nominal molecular weight of  $>100\,000$ ,  $>30\,000$  and  $>10\,000$  in the 0.05 M NaOH extracting solution, although small, are significant compared to

Table 3

Distribution of HA and FA (mg/g of dry sediment ash free basis) in different molecular weight fractions in the three extracting solutions.

Station	Extraction solution	Humic material	Fraction mg/g of dry sediment				
			$>300\,000$	$>100\,000$	$>30\,000$	$>10\,000$	$<10\,000$
C VI 0-5 cm	H <sub>2</sub> O	HA	—	—	—	—	—
		FA	—	—	—	—	—
	0.05 M NaOH	HA	0.7	0.2	$<0.1$	0.1	$<0.1$
		FA	11.9	0.6	0.4	0.4	0.9
	0.5 M NaOH 0.5 <sup>+</sup> M refl.	HA	$<0.1$	0.2	—	—	$<0.1$
		FA	0.1	0.2	$<0.1$	$<0.1$	0.9
C VI 5-10 cm	H <sub>2</sub> O	HA	—	—	—	—	—
		FA	0.1	—	—	—	—
	0.05 M NaOH	HA	2.9	0.2	0.1	$<0.1$	0.1
		FA	7.6	1.3	0.5	0.3	0.7
	0.5 M NaOH 0.5 <sup>+</sup> M refl.	HA	0.1	0.2	$<0.1$	0.1	$<0.1$
		FA	0.1	0.1	$<0.1$	$<0.1$	1.9
BO <sub>3</sub> 0-5 cm	H <sub>2</sub> O	HA	0.1	—	—	—	—
		FA	0.6	—	—	—	—
	0.05 M NaOH	HA	5.2	0.2	0.2	0.1	0.1
		FA	8.5	1.0	0.8	0.2	2.8
	0.5 M NaOH 0.5 <sup>+</sup> M refl.	HA	$<0.1$	0.1	0.1	0.1	0.1
		FA	0.1	0.2	0.2	$<0.1$	3.6
EB-I 0-5 cm	H <sub>2</sub> O	HA	$<0.1$	—	—	—	—
		FA	$<0.1$	—	—	—	—
	0.05 M NaOH	HA	3.2	0.2	$<0.1$	—	$<0.1$
		FA	6.9	1.8	0.4	0.3	2.0
	0.5 M NaOH 0.5 <sup>+</sup> M refl.	HA	$<0.1$	0.1	$<0.1$	$<0.1$	$<0.1$
		FA	0.1	$<0.1$	0.2	0.1	2.1
Teili-I 0-5 cm	H <sub>2</sub> O	HA	0.4	—	—	—	—
		FA	0.7	—	—	—	—
	0.05 M NaOH	HA	5.5	—	0.2	0.3	0.3
		FA	20.2	0.6	1.5	0.4	2.4
	0.5 M NaOH 0.5 <sup>+</sup> M NaOH	HA	0.2	$<0.1$	0.2	0.3	0.4
		FA	0.6	0.3	0.8	1.2	9.7
XVI 0-5 cm	H <sub>2</sub> O	HA	$<0.1$	—	—	—	—
		FA	0.4	—	—	—	$<0.1$
	0.05 M NaOH	HA	15.1	0.4	0.7	0.4	0.2
		FA	22.8	0.8	1.2	0.6	18.1
	0.5 M NaOH 0.5 <sup>+</sup> M refl.	HA	0.9	—	0.2	0.1	0.2
		FA	0.8	0.6	0.4	0.6	6.7

Table 4  
Functional groups (mg/g), elemental analysis (ash free basis) and ash contents (percents of dry matter) of HA and FA fractions.

Station	Extraction solution molecular weight fraction	Functional groups meq/g of humic subst.			Elemental analysis			Ash. %	C:N Ash free	C:H Ash free
		Total acidity	COOH	Phenolic OH	%C	%N	%H			
CVI 0-5 cm	0.05 M NaOH									
	>300000 HA	2.7	1.5	1.2	47.3	3.9	6.2	16	12.1	7.6
	>300000 FA	17.4	3.2	14.2	38.0	1.9	6.3	49	19.4	6.0
	>100000 FA	3.7	2.9	0.8	49.0	3.4	5.8	25	14.2	8.4
	>30000 FA	—	4.8	—	51.4	4.8	8.0	30	10.6	6.4
<10000 FA	3.8	—	—	13.1	0.9	5.9	68	13.9	2.2	
CVI 5-10 cm	0.5 M NaOH									
	<10000 FA	2.7	—	—	10.4	1.5	7.7	74	6.8	1.4
	0.5 M NaOH									
	>300000 HA	3.5	1.8	1.7	44.9	4.1	6.3	6	10.8	7.1
	>300000 FA	7.1	3.0	4.1	30.4	1.7	6.3	49	17.3	4.8
>100000 FA	5.9	5.6	0.3	47.6	3.8	6.0	37	12.5	7.9	
>30000 FA	3.8	—	—	33.0	2.7	4.8	34	12.2	6.9	
<10000 FA	4.6	—	—	16.2	0.8	9.1	76	20.2	1.8	
BO <sub>3</sub> 0-5 cm	0.5 M NaOH									
	<10000 FA	3.1	1.9	1.2	3.8	4.2	8.8	74	0.9	0.4
	0.05 M NaOH									
	>300000 HA	3.9	1.7	2.2	46.5	4.1	7.3	3	11.3	6.4
	>300000 FA	5.5	3.3	2.2	42.6	3.3	8.2	55	12.9	5.2
>100000 FA	3.8	—	—	40.1	3.2	7.0	37	12.5	5.7	
>30000 FA	4.2	—	—	39.0	3.1	6.3	30	12.6	6.2	
<10000 FA	6.7	5.1	1.6	6.7	0.4	7.5	76	16.7	0.9	
<10000 FA	3.8	2.5	1.3	3.3	—	9.0	76	—	0.4	
EBI 0-5 cm	0.05 M NaOH									
	>300000 HA	3.1	2.4	0.7	33.4	3.1	5.0	0	10.7	6.7
	>300000 FA	6.4	2.6	3.8	26.2	3.0	4.0	60	8.7	6.6
	>100000 FA	3.7	2.2	1.5	32.1	—	—	3	—	—
	>30000 FA	6.1	—	—	66.7	7.1	10.2	55	9.4	6.5
<10000 FA	3.8	—	—	21.7	13.0	7.8	77	16.7	2.8	
<10000 FA	3.1	2.3	0.8	9.2	—	8.8	74	—	1.0	
Teili I 0-5 cm	0.05 M NaOH									
	>300000 HA	2.9	1.3	1.6	65.7	5.6	10.9	32	11.7	6.0
	>300000 FA	15.6	2.5	13.1	27.7	2.3	7.4	57	12.0	3.7
	>100000 FA	—	—	—	36.5	4.8	5.6	8	7.6	6.5
	>30000 FA	—	3.5	—	37.7	3.7	6.4	21	10.2	5.8
<10000 FA	4.7	—	—	—	—	—	77	—	—	
<10000 FA	3.7	—	—	—	—	—	76	—	—	
XV-I 0-5 cm	0.05 M NaOH									
	>300000 HA	3.7	1.4	2.3	43.3	4.1	7.3	2	10.6	5.9
	>300000 FA	4.4	2.9	1.5	23.5	1.8	6.9	55	13.3	3.4
	>100000 FA	—	—	—	34.5	5.1	6.3	43	6.8	5.5
	>30000 FA	2.5	—	—	29.3	5.2	6.6	44	5.6	4.4
<10000 FA	2.8	—	—	10.7	5.5	2.2	71	1.9	0.5	
<10000 FA	1.2	—	—	15.3	4.1	5.3	83	3.7	2.9	

the HA fraction. Considerable amounts of these fractions were also extracted by 0.5 M NaOH solution from sediments from stations Teili-I and XV-I. However, the fractions >300000 and <10000 comprise the major part of the fulvic acids.

The percentages of carbon, nitrogen and hydrogen in >300000 HA range from 33.4% to 65.7%, from 3.1 to 5.6% and from 5 to 10.9%, respectively (Table 4). The ranges of these elements in the corresponding FA fraction are from 23.5 to 42.6%, from 1.8 to 3.3% and from 4 to 8.2%, respectively. In general, humic acids have higher carbon, nitrogen and hydrogen percentages than the FA fractions. The minimum values for the content of these elements in both the HA and FA fractions were found in the sediments at station EB-I, whereas the HA and FA fractions at station Teili-I invariably have higher percentages of these elements.

The other major FA fraction (<10000) contains the lowest C and N content, ranging from 6.7 to 21.7% and 0.4 to 5.5% respectively with the exception of station EB-I which had a nitrogen content of 13%.

Examination of the ash content of the different humic fractions shows that the humic acid fractions are more loosely bound than the fulvic acid ones. Obviously some siliceous inorganic material is dissolved by the alkali during the extraction of humic substances and may be concentrated in the freeze-dried residues. However, the high ash content of fulvic acids—in spite of used treatments to lower the ash content—seems to be due to the strong association of fulvic acids with the inorganic materials. Fulvic acids in the molecular weight fraction <10000 had the highest percentage (68-83%) of this siliceous organic material. The C:N ratio of the major (>300000) HA fraction is lower at

all the stations than in the corresponding FA fraction. It varies within a narrow range of 10.6 to 12.1. The C:H ratio is higher in the major HA fraction than in the FA fraction and varies only slightly from one station to another (5.9-7.6).

**Total acidity**, which is a measure of the dissociable hydrogen atoms in aromatic and aliphatic carboxyl groups and phenolic and alcoholic hydroxyl groups, is lower in HA than in FA. It ranged from 2.7 to 3.9 meq g<sup>-1</sup> in HA and 4.4 to 17.4 meq g<sup>-1</sup> in FA fraction. A similar trend is also evident in the COOH and the phenolic OH groups. This is in accordance with the general observation that fulvic acids contain less carbon and nitrogen but more oxygen than humic acid fractions.

The infrared spectra of the humic and fulvic acids are shown in Figure 3. The main absorption bands for humic acids (Fig. 3, c, d, e) were in the regions 3400 cm<sup>-1</sup> (hydrogen-bonded OH), 2900-2840 cm<sup>-1</sup> (aliphatic C-H stretch), near 2500 cm<sup>-1</sup> (very broad, hydrogen-bonded CO<sub>2</sub>H), 1730-1715 cm<sup>-1</sup> (very weak, C=O of CO<sub>2</sub>H, C=O of ketonic carbonyl), 1650-1630 cm<sup>-1</sup> (aromatic C=C, COO<sup>-</sup>, hydrogen-bonded C=O), and near 1500 cm<sup>-1</sup> (C=C of aromatic rings). In addition, there were broad bands in the 1250-1000 cm<sup>-1</sup> regions, possibly due to asymmetric stretching of alcohols and ethers.

The infrared spectra of fulvic acids (Fig. 3a, b) resemble those of humic acids (c, d, e). Only a few differences could be found. Bands at 2900-2840 cm<sup>-1</sup> were present in the spectra of all the humic acids but were absent from the spectra of fulvic acids, thus indicating the absence of large amounts of CH<sub>2</sub> and CH<sub>3</sub> groups. Bands near the 800 cm<sup>-1</sup> region were absent in the humic acids spectra, but the fulvic acids spectra exhibited strong absorption in this range. We believe that the bands near 1000-700 cm<sup>-1</sup> were most likely due silico-organic compounds. In general, the spectra of humic substances are very similar. This may indicate the presence of essentially similar chemical structures, the main difference being in the contents of functional groups.

## CONCLUSIONS

The process leading to the formation of humic substances from organic matter is a subject of considerable controversy among marine scientists, although much work has been done on the identification and nature of the organic matter from which those substances are derived. It is generally accepted that humic matter is a result of the diagenesis of carbohydrates and protein substances released into the sediments during the decomposition of plant or animal material, and that it is biochemically undegradable. Some scientists believe that it is formed through a chain of condensation and polymerisation reactions which progress from small molecules through fulvic acids, humic acids and finally to kerogen, becoming larger and more condensed as the diagenesis progresses (Nissenbaum, 1974; Welte, 1974). According to Ishiwatari (1971), the reaction in-

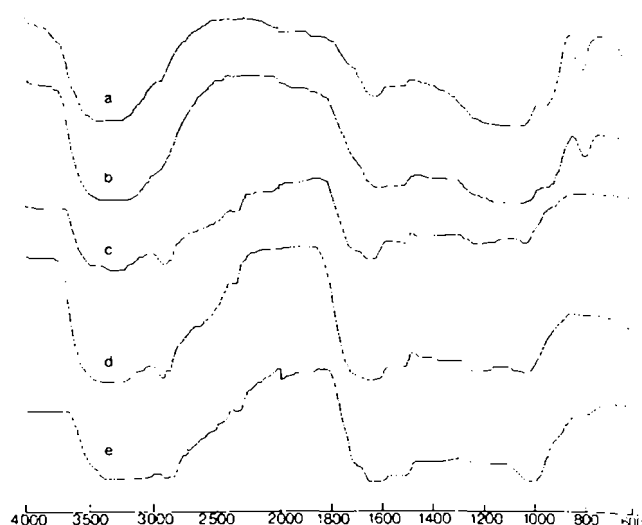


Figure 3

Infrared spectra of fulvic acid fractions > 300 000 at stations XI-1 (a) and C VI (b) and humic acid fractions > 300 000 at stations XV-1 (c), BO-3 (d) and C VI (e).

volves a transformation of the bio-polymers with small molecules becoming by-products rather than intermediates in the reaction, the final form of the transformation being the kerogen polymers.

Our results concerning the total acidity, contents of carboxyl groups and phenolic hydroxyl groups, which are almost constant in the major humic and fulvic acid fractions, and the close similarity in their IR spectra indicate that the humic material at different stations is formed from similar source of organic material and that humic acids are closely related to fulvic acids, the main difference being in the contents of functional groups. However, the amount and molecular weight distribution of humic substances which can be extracted from a surficial marine sediment depend on the redox conditions in the aquatic environment. Analyses of fulvic acids in anoxic sediments show that there is a sizable fraction with a low molecular weight (< 10 000), in addition to a large fraction with high molecular weight (> 300 000), whereas in the oxic sediments the major part of the fulvic acids were found in the molecular weight fraction > 300 000. Presumably the difference in redox conditions and microbial activity between oxidized and reduced sediments lead to differences in the humic content and molecular weight distributions as a result of differences in the decomposition of organic matter.

## Acknowledgements

We would like to thank Dr. A. Voipio for helpful discussions and Kaisa Kononen for advice on the smear slide analyses. Support from the Finnish Ministry of Education and the Government of India is gratefully acknowledged.



## REFERENCES

- Artem'yev V. Ye., Krayushkin L. N., Romankevich Ye. A., 1971. Determination of the total amount of carbohydrates in ocean sediments, *Oceanology*, **11**, 934-936.
- Bågander L. E., Niemistö L., 1978. An evaluation of the use of redox measurements for characterizing recent sediments, *Estuarine Coastal Mar. Sci.*, **6**, 127-134.
- Bojanowski R., Pempkowiak J., Kupryszewski G., 1977. Humic substances in the Baltic sediments, *Oceanology*, **7**, 105-120.
- Bordovskiy O. K., 1965. Accumulation and transformation of organic substances in marine sediments, *Mar. Geol.*, **3**, 1-114.
- Calvert S. E., Price N. B., 1971. Recent sediments of the Sout-West African shelf, in: *Geology of the East Atlantic continental margin*, edited by E. M. Delany, Institute of Geological Sciences Rep. 70/16, 171-185.
- Chen Y., Senesi N., Schnitzer M., 1978. Chemical and physical characteristics of humic and fulvic acids extracted from soil of the Mediterranean region, *Geoderma*, **20**, 87-104.
- Cronin J. R., Morris R. J., 1982. The occurrence of high molecular weight humic material in recent organic rich sediment from the Namibian Shelf, *Estuarine Coastal Shelf Sci.*, **15**, 17-27.
- Degens E. T., Mopper K., 1976. Factors controlling the distribution and early diagenesis of organic material in marine sediments, in: *Chemical oceanography*, edited by J. P. Riley and R. Chester, Academic Press.
- Degens E. T., Emery K. O., Reuter J. H., 1963. Organic materials in present and ancient sediments of Santa Barbara Basin, California. Part 3: Biochemical compounds in San Diego, California, *Neues Jb. Geol. Paläont. Mh.*, 231-248.
- Degens E. T., Reuter J. H., Shaw N. F., 1964. Biochemical compounds in offshore California sediments and sea water, *Geochim. Cosmochim. Acta*, **28**, 45-66.
- Gershamovich D. E., Verber V. V., Konyukhov A. I., 1976. *Studies of organic matter in recent and fossil sediments*, edited by N. B. Jassoevick and P. P. Timofeev, Nauka, Moscow, USSR.
- Gross M. G., 1966. Organic carbon in surface sediment from the Northeast Pacific Ocean, *Int. J. Oceanol. Limnol.*, **1**, 46-54.
- Ishiwatari R., 1971. Molecular weight distribution of humic acids from lake and marine sediments, *Geochem. J.*, **2**, 175-184.
- Jackson T. A., 1975. Humic matter in natural waters and sediments, *Soil Sci.*, **119**, 56-64.
- Kasatochkin V. L., Bordovskiy I. K., Larina N. K., Cherkinskaya K., 1968. Chemical nature of humic acids in Indian Ocean floor sediments, *Dokl. Akad. Nauk. SSSR*, **179**, 690-693.
- Lassig J., Leppänen J. M., Niemi A., Tamelander G., 1978. Phytoplankton primary production in the Gulf of Bothnia 1972-1975 as compared with other parts of the Baltic Sea, *Finn. Mar. Res.*, **244**, 101-115.
- Mikulski Z., 1970. Inflow of river water to the Baltic Sea in the period 1951-1960, *Nord. Hydrol.*, **4**, 216-227.
- Mikulski Z., 1972. The inflow of the river waters to the Baltic Sea in 1961-1970, *Proc. 8th Conf. Baltic Oceanogr. Copenhagen*, 3 p.
- Mopper K., 1973. Aspects of the biogeochemistry of carbohydrates in aquatic environments, *Ph. D. Thesis, Massachusetts Institute of Technology, Cambridge and Woods Hole Oceanographic Institution, Woods Hole*.
- Mopper K., Michaelis W., Gerrasi C., Degens E. T., 1978. Sugars, amino acids and hydrocarbons in Black Sea sediment from DSDP Leg 42B cores, in: *Initial Reports of the Deep Sea Drilling Project, 42B*, US Government Printing Office, Washington D.C., 696-705.
- Morris R. J., Calvert S. E., 1977. Geochemical studies of organic-rich sediments from the Namibian Shelf. I: The organic fractions, in: *A voyage of Discovery, George Deacon 70th Anniversary volume*, edited by M. Angel, 647-665.
- Niemistö L., 1974. A gravity corer for studies of soft sediments, *Merentutkimuslaitoksen Julk. Havsforkningsinst. Skr.*, **238**, 33-38.
- Niemistö L., Voipio A., 1981. Notes on the sediment studies in the Finnish pollution research in the Baltic Sea, *Cons. Int. Explor. Mar.*, **181**, 87-92.
- Nissenbaum M. A., 1974. The organic geochemistry of marine and terrestrial humic substances: implications of carbon and hydrogen isotope studies, in: *Advances in organic geochemistry*, 1973, edited by B. Tissot and F. Biener, Technip Ed., Paris, 39-52.
- Nissenbaum A., Kaplan I. R., 1972. Chemical and isotopic evidence for the *in situ* origin of marine humic substances, *Limnol. Oceanogr.*, **17**, 570-582.
- Nriagu J. O., Coker R. D., 1980. Trace metals in humic and fulvic acids from Lake Ontario sediments, *Environ. Sci. Technol.*, **14**, 443-446.
- Pempkowiak J., Bojanowski R., Kupryszewski G., 1976. Humic substances in the Baltic sediments, *Xth Conf. Baltic Oceanogr., Göteborg*, 1976.
- Pocklington R., Leonard J. D., 1979. Terrigenous organic matter in sediments of the St. Lawrence Estuary and the Saguenay Fjord, *J. Fish. Res. Board Can.*, **36**, 1250-1255.
- Poutanen E.-L., Morris R. J., 1982. A study of the formation of high molecular weight compounds during the decomposition of a field diatom population, *Estuarine Coastal Shelf Sci.* (in press).
- Poutanen E.-L., Morris R. J., 1983. The occurrence of high molecular weight humic compounds in the organic-rich sediments of the Peru continental shelf, *Oceanol. Acta*, **6**, 1, 21-28.
- Prashnowsky A., Degens E. T., Emery K. O., Pimenta J., 1961. Organic materials in present and ancient sediments of Santa Barbara Basin, California, Part 1, *Neues Jahrb. Geol. Paläontol. Monatsh.*, 400-413.
- Schnitzer M., 1977. Recent findings on the characterization of humic substances extracted from soils from widely differing climatic zones, in: *Soil organic matter studies*, International Atomic Energy Agency, Vienna II, 117-132.
- Schnitzer M., 1978. Humic substances. chemistry and reactions, in: *Soil organic matter*, edited by M. Schnitzer and S. V. Khan, Elsevier Scientific Publishing Company, 1-64.
- Schnitzer M., Khan S. V., 1972. *Humic substances in the environment*, Marcel Dekker, New York.
- Starikova N. D., Yoblokoval O. G., 1972. Carbohydrates in the Black Sea, *Oceanology*, **12**, 363-368.
- Swain F. M., 1969. Fossil carbohydrates, in: *Organic geochemistry, methods and results*, edited by G. Eglinton and M. T. J. Murphy, Springer-Verlag, Berlin and New York, 374-400.
- Swain F. M., Bratt J. M., 1978. Carbohydrate residues in Leg 44 core sample, in: *Initial Reports of the Deep-Sea Drilling Project, 44*, US Government Printing Office, Washington D.C., 653-654.
- Templeton III G. D., Chastee N. D., 1980. Evaluation of extraction schemes for organic matter in anoxic estuarine sediments, *Mar. Chem.*, **10**, 31-46.
- Welte D., 1974. Determinations of  $^{13}\text{C}/^{12}\text{C}$  isotope ratios of individual higher n-paraffins from different petroleum, in: *Advances in organic geochemistry*, 1973, edited by B. Tissot and F. Biener, Pergamon Press, Oxford, 269-278.