

Letter Section

FIELD OBSERVATIONS OF THE ISOTOPIC COMPOSITION OF PARTICULATE ORGANIC CARBON IN THE SOUTHERN NORTH SEA AND ADJACENT ESTUARIES

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ABSTRACT

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The carbon isotopic composition of the organic matter in fluvial sediments and in fluvial suspended matter falls in the range valid for continental organic matter (-25 to -28‰). The $\delta^{13}\text{C}$ values in sediments from marine sedimentation areas and in marine suspended matter varies between -20 and -25‰ . The rather low mean values for the deposited sediments of -13.2‰ suggest the presence of relatively large amounts of continental organic matter. This may be a direct supply by the present-day rivers and/or organic matter derived from the erosion of peat layers, even in the marine environment. A distinction between these two sources of detrital continental organic matter is not possible with stable isotopes studies.

In the estuaries studied the organic matter contents decrease and the $\delta^{13}\text{C}$ values of the organic matter increase in the seaward direction. These changes are primarily caused by the mixing of fluvial and marine sediments.

INTRODUCTION

Recent argillaceous sediments from Western Europe (Fig. 1) are composed of quartz, clay minerals, feldspars, carbonates and organic matter in varying proportions. The main sources for the marine sediments in the southern North Sea are (1) material carried by the net sea current from the English Channel in a northerly direction along the Belgian and Dutch coast, (2) material eroded from coastal and shallow-water clay deposits, and (3) suspended matter transported by the various rivers (McCave, 1973). The overall transport of suspended matter in the coastal areas of Belgium and The Netherlands is directed to the north. The origins of the carbonates, clay minerals and trace metals in these sediments have been discussed in a number of recent publications (Salomons, 1975; Salomons et al., 1975;

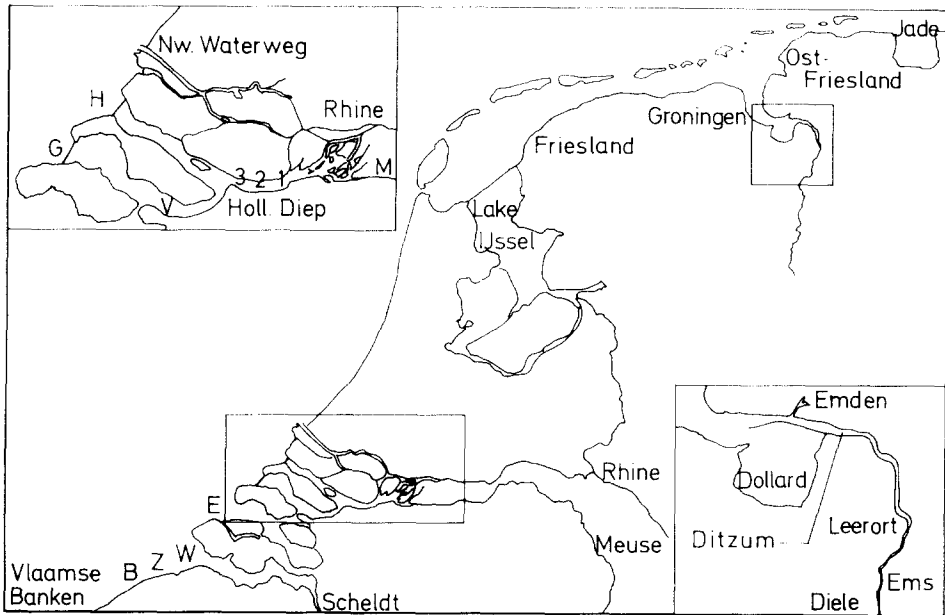


Fig. 1. Map of the Netherlands showing the sampling localities.

Salomons and Mook, 1977; Salomons and De Groot, 1978). It was found that the carbonates and clay minerals of Wadden Sea sediments are for less than 20% derived from the rivers Rhine and Meuse. A mixing process was observed of marine and fluvial sediments in the estuaries of the rivers Rhine and Ems. The origin of organic carbon in sediments is more difficult to determine; organic carbon is partly of detrital, partly of authigenous origin. Furthermore, the terminology used in the literature is often not consistent (e.g. there is a difference between organic matter found in marine sediments and marine organic matter). In Table I an attempt has been made to differentiate between various sources of organic matter in sediments found in the marine and fluvial environments.

According to Postma (1973), the primary production in the southern North Sea exceeds the fluvial input of organic carbon by a factor of 14. Other sources for detrital organic matter are the ancient peat deposits at present being eroded in the marine environment. However, direct information on the ratio of marine to continental (source) organic matter in sediments and suspended matter is not available.

A number of studies demonstrated the value of stable isotope geochemistry to differentiate between marine- and land-derived (continental) organic carbon in sediments (Nissenbaum and Kaplan, 1972; Newman et al., 1973; Aizenstat et al., 1973; Schultz and Calder, 1976; Gearing et al., 1977; Tan and Strain, 1979). To obtain a first overall picture on the origin of organic matter in Recent sediments and relate its origin to other sedimentary com-

TABLE I

Sources of organic matter found in fluvial and in marine sediments

	Sources	$\delta^{13}\text{C}$ (‰)
Organic matter found in fluvial sediments	Autochthonous organic matter (e.g. algal production in the river system)	-31 ± 2
	Detrital organic matter (e.g. erosion of soils)	-27.5 ± 1
Organic matter found in marine sediments	Fluvial organic matter	-27 ± 2
	Eroded ancient peat deposits	-27.5 ± 1
	Autochthonous organic matter (e.g. derived from organic products in the marine environment)	-19 ± 2

ponents (e.g. clays and carbonates) studied in two earlier investigations (Salomons, 1975; Salomons et al., 1975) we have determined the isotopic composition of the organic carbon in a large number of sediments from the southern North Sea and in fluvial and estuarine deposits (Fig. 1).

It should be noted, however, that from stable carbon isotopes it is not possible to distinguish between different sources of continental organic matter (e.g., fluvial organic matter and peat being eroded in the marine environment).

EXPERIMENTAL METHODS

The dry sediment samples were first treated with dilute hydrochloric acid to remove carbonates. After washing and drying, the residues were combusted to CO_2 in a small combustion system (Mook, 1968). The carbon dioxide samples were analysed for $^{13}\text{C}/^{12}\text{C}$ with a Varian M86 mass spectrometer. The results are reported relative to the PDB standard as:

$$\delta^{13}\text{C}_{\text{PDB}} = (^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{PDB}} - 1 \quad (\times 10^3 \text{ ‰})$$

The calibration is based on $\delta^{13}\text{C}_{\text{PDB}}(\text{NBS20}) = -1.06\text{‰}$ and on well-calibrated laboratory standards [$\delta^{13}\text{C}_{\text{PDB}}(\text{NBS21}) = -28.19\text{‰}$].

RESULTS

Content and isotopic composition of organic carbon in sediment samples from one locality

The organic carbon content of sediment samples from one locality varies

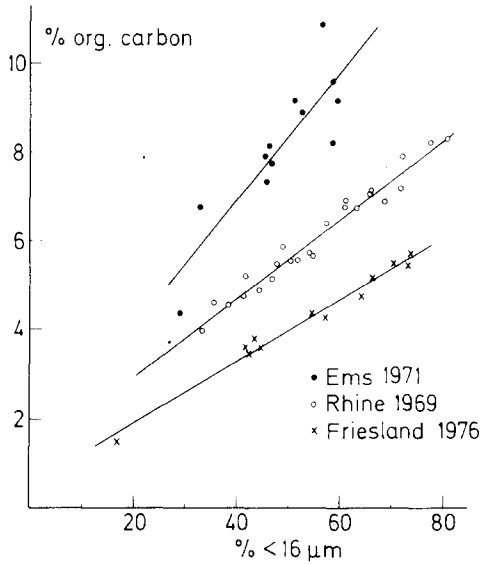


Fig. 2. Correlation between the organic carbon contents and the % < 16 μm in sediment samples from the same locality.

TABLE II

Isotopic composition of organic carbon in sediment samples from the same locality along the Ems estuary, with differences in grain size distribution (% < 16 μm)

Sample nr.	% < 16 μm	Organic carbon (%)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)
<i>Diele</i>			
63(1971)	29.3	4.4	-26.1
66(1971)	33.1	6.7	-27.4
70(1971)	58.9	8.2	-28.0
71(1971)	45.9	7.3	-28.0
73(1971)	58.9	9.6	-27.3
<i>Leerort</i>			
88(1971)	57.9	5.2	-26.6
90(1971)	68.5	6.0	-26.6
92(1971)	32.7	3.5	-26.9
93(1971)	45.4	4.6	-26.8
97(1971)	19.9	2.7	-27.0
<i>Ditzum</i>			
75(1971)	84.2	5.7	-25.2
78(1971)	83.0	5.5	-24.8
79(1971)	75.7	4.8	-26.0
81(1971)	80.7	5.2	-25.0
83(1971)	40.4	4.8	-25.0

widely. The content correlates positively with the amount of finely grained particles, as expressed by the percentage of particles less than 16 microns in diameter (Salomons and De Groot, 1978; Fig. 2).

Organic carbon contents are high in clay-rich samples and low in sandy samples. In order to compare the composition of sediments from different sedimentation areas, the concentrations at $50\% < 16 \mu\text{m}$ will be used. These values are obtained by analysing a large number of samples from each separate locality and constructing curves as shown in Figure 2. In order to determine whether also the isotopic composition of the organic carbon depends on the grain-size distribution, samples from the Ems-estuary and from some marine sedimentation areas have been analysed (Table II). Although differences in the isotopic composition of sediment samples from one locality do occur, these appear not to be related to the grain-size distribution. In most cases the spread in these values is rather small. Therefore, we did not analyse individual samples, but made representative averages by mixing a large number of samples. These were analysed in duplicate for the isotopic composition of the organic carbon. A number of localities have been sampled repeatedly. The largest difference in $\delta^{13}\text{C}$ of sediments from the river Rhine taken over the period 1957–1973 is about 1‰ ; similar variations are found in the Dutch Wadden Sea area. Our conclusion thus is that the temporal differences in $\delta^{13}\text{C}$ for sediments from one locality are small. Apparently the sources of the organic matter have a relatively constant composition.

Organic carbon in fluvial sediments

Fluvial sediments of the rivers Rhine, Meuse, Ems and Scheldt have been sampled in the fresh-water tidal areas. The organic carbon contents (at $50\% < 16 \mu\text{m}$) as well as the $\delta^{13}\text{C}$ values are given in Table III. The organic carbon content of the fluvial sediments varies between 5.5% (Scheldt) and 8.4% (Ems). The $\delta^{13}\text{C}$ values vary between -28 and -25‰ , which is the range valid for land-derived material, where $\delta^{13}\text{C}$ values of peat generally are $-27 \pm 1\text{‰}$.

The relatively low carbon-14-content of 65% (equivalent to an age of 3560 years) of a sediment sample from the river Rhine (1958) points to the presence of old and stable organic components in the sediment.

Organic carbon in coastal marine sediments

Coastal marine sediments have been sampled off the Belgian, the Dutch and the German coast (Fig. 1). Results of the analyses of the organic carbon contents and their stable isotopic composition are given in Table IV, some carbon-14 data are presented in Table VII.

Organic carbon varies between 2.3% (Vlaamse Banken) and 4.3% (Wadden Sea). Compared with the fluvial sediments, the organic carbon con-

TABLE III

The isotopic composition of organic carbon in fluvial sediments

The % organic carbon refers to the calculated value at 50% < 16 μm (e.g. each value represents about 10–15 analyses from one locality)

	Organic carbon (%)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)
Rhine 1958	7.0	-25.4
Rhine 1969 (june)	5.9	-25.3
Rhine 1969 (november)	6.3	-25.9
Rhine 1970 (october)	7.0	-25.6
Rhine 1971 (october)	7.4	-25.5
Rhine 1973 (may)	8.6	-25.0
Rhine 1973 (october)	7.9	-25.4
Meuse 1958	7.9	-25.2
Meuse 1969	6.5	-26.0
Ems 1971	8.4	-27.4
Scheldt 1973	5.5	-28.0

TABLE IV

The isotopic composition of organic carbon in marine sediments

The organic carbon contents refer to the values at 50% < 16 μm

	Organic carbon (%)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)
Vlaamse Banken 1960	2.3	-23.2
Blankenberghe 1959	2.4	-23.8
Zwarte Polder 1959	2.8	-22.2
Westerschelde 1974	2.7	-25.4
Oosterschelde 1973	3.0	-24.0
Grevelingen 1959	3.8	-22.7
IJmuiden 1960	3.8	-23.4
Friesland 1957	3.7	-24.6
Friesland 1970	4.3	-24.2
Friesland 1976	4.0	-23.2
Groningen 1957	3.3	-22.8
Groningen 1975	3.6	-22.3
Groningen 1976	3.9	-21.7
Dollard 1958	3.8	-25.3
Ost-Friesland 1969	3.8	-21.3
Jade 1969	3.0	-20.1

tent is considerably lower. The Wadden Sea sediments are richer in organic carbon than the marine sediments south of the Rhine–Meuse estuary.

The $\delta^{13}\text{C}$ values of the organic matter vary between -20.1‰ (Jade) and -25.3‰ (Dollard), comprising the whole range of values for continental (-25‰) to marine organic matter (around -20‰). The mean value for

the organic matter in the marine sediments studied is -23.2‰ . This rather low (negative) value suggests the presence of relatively (about 50% or more) large fractions of continental organic matter.

The contribution of relatively stable continental organic matter is further supported by the carbon-14 results, varying between 48 and 84% (Table VII). The high ^{14}C values in the Wadden Sea are observed for those sediments that have high (less negative) $\delta^{13}\text{C}$ values. Marine organic matter apparently is younger and less stable compared to continental organic matter.

Organic carbon in estuarine sediments

Estuarine sediment samples from the Rhine—Meuse estuary have been collected in 1957 and in 1958 before the closure of the Haringvliet and the Grevelingen. The Ems estuary was sampled in 1971. The sampling localities are shown in Fig. 1.

The main mud discharge in the Rhine—Meuse estuary was through the Haringvliet, whereas not more than 10% was discharged through the Volkerak (Terwindt, 1967). The freshwater boundary was located in the Hollands Diep. In the Ems estuary the limit of salt intrusion is located between Leerort and Ditzum.

In both estuaries the sedimentary organic carbon content decreases, the $\delta^{13}\text{C}$ values increase in the seaward direction. This is a consequence of the mixing of marine and fluvial sediments. The organic carbon content (12%) as well as the carbon isotopic composition (about -25.4‰) in the Hollands Diep sediments (Rhine—Meuse estuary) are similar to those ob-

TABLE V

The isotopic composition of organic carbon, inorganic carbon and clay minerals in the estuaries of the rivers Rhine—Meuse and of the Ems

Locality	Salinity (‰)	Organic carbon		Inorganic carbon	Clay fraction $\delta^{18}\text{O}_{\text{PDB}}$ (‰)
		%	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	
<i>Rhine—Meuse</i>					
Rhine	0.2	7.0	-25.5	-3.6	+16.6
Meuse	0.2	7.9	-25.8	-3.3	+15.8
Hollands Diep 1	0.2—4	7.1	-25.7	-2.0	+16.6
Hollands Diep 2	0.2—8	7.1	-25.4	-1.3	+17.2
Hollands Diep 3	0.2—12	7.1	-25.0	-1.2	+19.1
Haringvliet	2.0—25	4.8	-24.7	-0.6	+19.1
<i>Ems</i>					
Diele	0.2	8.4	-27.4	-5.0	+19.8
Leerort	0.2	4.9	-26.8	-0.6	+19.3
Ditzum	3	3.7	-25.2	-0.5	+19.3
Dollard	5—20	3.8	-25.3	-0.5	+19.5

served in the Rhine and Meuse sediments. Apparently the organic carbon is of continental origin.

The isotopic composition of the carbonates ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and clay minerals ($\delta^{18}\text{O}$), on the other hand, differ from those shown by the fluvial sediments (Table V). From the latter data we conclude that between 35 and 45% of these sedimentary components are derived from the North Sea. In the Ems estuary the carbonates and clay minerals collected at Leerort are mainly of marine origin (about 90%) (Salomons and Mook, 1977) whereas the organic carbon is mainly of continental origin.

Organic carbon in suspended matter

The last obvious step was to collect suspended matter from the North Sea and the Nieuwe Waterweg (October 1971) (Fig. 3). The samples have been taken at various depths. In some cases the amount of material allowed to determine both the isotopic composition of the organic and the inorganic carbon as well as the grain-size composition ($\% < 16 \mu\text{m}$). However, in a few cases it was necessary to combine two samples from one locality taken at different depths. In these cases, both depths are given in Table VI.

The grain-size distribution ($\% < 16 \mu\text{m}$) generally is close to the value used for characterizing the deposited sediments. Therefore, organic carbon contents from both the sediments and the suspended matter (Tables IV and VI) may be directly compared. The organic carbon content of marine suspended matter is higher compared to that in estuaries (compare localities A and B with E and G), contrary to the deposited sediments. The high $\delta^{13}\text{C}$

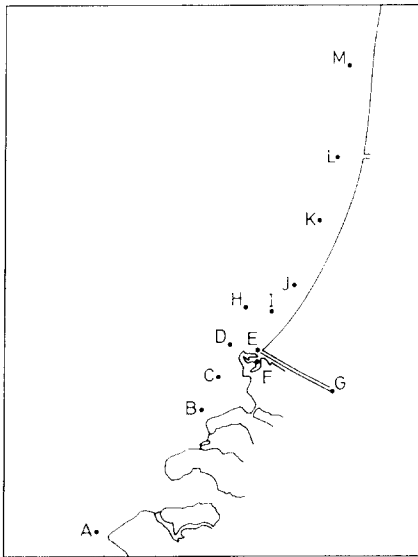


Fig. 3. The sampling localities for suspended matter along the Dutch North Sea coast.

TABLE VI

Isotopic composition of organic and inorganic carbon in suspended matter from the North sea and the Nieuwe Waterweg (Rotterdam Harbour)

Locality	Depth (m)	% < 16 μ m	Organic carbon		Inorganic carbon		
			%	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	%	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)
A	0	—	6.6	-21.9	—	—	—
	2+4	44.5	6.4	—	—	—	—
	6+8	—	6.6	-22.2	17.8	-0.2	-3.2
B	0	—	7.8	-21.0	—	—	—
	2+4	—	8.7	-21.0	11.4	-0.5	-4.4
	6+8	43.1	6.0	-22.0	—	—	—
C	0+2	—	7.6	-24.2	—	—	—
	4+6	—	6.6	-24.6	22.2	-0.2	-3.4
E	0	51.5	5.5	-26.4	21.5	-0.8	-4.3
	4	51.4	5.9	-26.6	18.3	-0.8	-5.0
	8	50.5	5.0	-26.4	19.5	-0.6	-4.6
	10	48.9	5.4	-26.3	19.6	-0.7	-4.6
	14	50.9	5.0	-25.8	20.5	-0.7	-4.4
G	0	43.2	5.9	-27.2	18.3	-1.0	-5.3
	8	32.7	4.6	-27.0	15.3	-0.9	-5.2
	12	48.0	6.8	-26.8	16.6	-1.1	-5.6
	16	34.2	4.7	-27.1	16.1	-0.8	-4.7
I	0	—	9.2	-15.2	16.7	-0.6	-4.0
J	0+4	—	12.6	-20.6	—	—	—
K	0	—	9.8	-20.1	—	—	—

E = Europoort and G = Botlek.

values at the localities A, B, J and K show that the high organic carbon contents are caused by the presence of marine organic matter. In general, the amount of marine organic carbon in the suspended matter is higher than that in the sediments. It should be noted, however, that the marine contribution to the suspended matter is seasonally dependent; a survey in February showed much less variation in $\delta^{13}\text{C}$ (-22 to -24‰). The mean values of 16 samples was $-23.2 \pm 0.6\text{‰}$.

The organic carbon in the Nieuwe Waterweg, Europoort and Botlek is mainly continental: the $\delta^{13}\text{C}$ values vary between -26 and 27‰ (Table VI). The $\delta^{13}\text{C}$ values of the suspended inorganic carbonate vary between -1.1 and -0.2‰ . The estuarine values (-1‰) differ from those observed in fluvial sediments (-2.6‰). This can be explained by a mixing of marine and fluvial carbonates in the estuaries, as has been described for the deposited sediments (Salomons, 1975).

The influence of fluvial carbonates on the composition of the carbonates in marine suspended matter is rather limited. Only close to the mouth of the river Rhine (locality I) can the presence of fluvial carbonates be detected. Apparently, the amount of suspended matter transported by the Rhine to the North Sea is small as compared to the amount of suspended matter already present. These data, therefore, confirm the conclusions derived from an earlier examination of the isotopic composition of carbonates and clay minerals (Salomons, 1975; Salomons et al., 1975) in the deposited sediments.

TABLE VII

The carbon-14 content of the organic carbon in a number of marine (*m*), fluvial (*f*) and estuarine (*e*) sediment samples
The ^{14}C content is given in percentages of modern carbon ($0.95 \times$ spec. act. of NBS oxalic acid)

Number	Locality	Carbon-14 (pmc)	
GrN	Ost-Friesland	83.9 ± 0.7	m
GrN-6754	Friesland	48.0 ± 0.6	m
GrN-6797	Groningen	66.6 ± 1.2	m
GrN-7046	Grevelingen	55.9 ± 1.0	m
GrN-5669	Biesbosch (Rhine) 1958	65.1 ± 0.6	f
GrN-7047	Biesbosch (Rhine) 1969	91.4 ± 1.3	f
GrN-7045	Europoort	66.9 ± 0.8	m
GrN-7048	Rijnhaven (Rotterdam Harbour)	58.2 ± 0.7	e

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