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# Stable carbon and radiocarbon isotope compositions of particle size fractions to determine origins of sedimentary organic matter in an estuary

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## Abstract

Stable and radioactive carbon isotopic compositions of particle size fractions of a surface sediment from the Ems-Dollard estuary vary considerably with particle size. The organic material in the fine fractions (< 20 µm) has considerably higher <sup>14</sup>C values (<sup>14</sup>a~80%) than that in the coarse fractions (52%) and has higher δ<sup>13</sup>C values (average of -23‰ and -25.6‰, respectively). This shows that OM in the fine and the coarse fractions has different sources. The organic carbon in the fractions with particle sizes < 20 µm is mainly imported from the North Sea. The contribution of material from the Ems river appears negligible. The carbon isotopic composition of the coarse fractions points to a terrestrial contribution. Discrete organic fragments are found of both terrestrial and marine/estuarine origin. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

An important part of the global organic carbon cycle is the flux of terrigenous organic carbon from the continents to the oceans (e.g. Hedges and Keil, 1995). Estuaries form an important interface between marine and fluvial water masses where fluvial water is flowing into the sea and complex processes affect the transported substances (e.g. Burton and Liss, 1976).

A major organic carbon pool in estuaries is particulate organic matter (POM), both suspended in the water column and in sediments. POM in estuaries has several sources: marine, autochthonous and fluvial primary production and terrestrial detritus discharged by rivers. It can cycle between the sediment and the water column

by repeated settling and resuspension (Eisma, 1993). To estimate the relative contributions of these sources, measurements of the stable carbon isotopic concentrations (expressed as δ<sup>13</sup>C relative to a standard) in POM are frequently used based on the assumption that marine organic matter in general has a higher <sup>13</sup>C concentration than organic matter derived from terrestrial plants using the C3 carbon fixation pathway (e.g. Keil et al., 1997; Goñi et al., 1997, 1998; Laane et al., 1990; Fry and Sherr, 1984; Salomons and Mook, 1981).

Particulate matter is, however, not homogeneous in terms of particle size or chemical characteristics (Keil et al., 1994; Mayer, 1994; Bergamaschi et al., 1997). Furthermore, the organic component consists of a wide range of compounds with potentially different sources, characteristics and stability. Certain biochemicals such as polysaccharides and proteins are more labile than other compounds (Laane, 1982; Laane et al., 1987; Benner et al., 1987). Moreover, different classes of compounds from the same source have different δ<sup>13</sup>C

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values, as a consequence of their biosynthetic pathway. For example, polysaccharides and proteins have significantly higher  $\delta^{13}\text{C}$  values than lipids (Deines, 1980; Hayes, 1993; Schouten et al., 1998). Thus, selective degradation of the more labile components [e.g. (poly)saccharides and proteins] over time can change the stable carbon isotopic composition of POM drastically (Laane et al., 1990; Benner et al., 1987).

The normalized  $^{14}\text{C}$  abundance ( $^{14}\text{a}$ ; Mook and van der Plicht, 1999), however, is only dependent on the age of the material, because by definition a correction is made for isotopic fractionation, based on the generally known relation that fractionation of  $^{14}\text{C}$  is twice that of  $^{13}\text{C}$  (e.g. Mook and Streurman, 1983). In this way, using both  $^{13}\text{C}$  and  $^{14}\text{C}$  data, a distinction can be made between fresh and old organic matter present in estuarine POM (Raymond and Bauer, 2001; Masiello and Druffel, 2001; Megens et al. 2001). Mook and Tan (1991) suggested that  $^{14}\text{C}$  could be a useful tracer of the origin of POM in coastal waters because they assume that in general POM discharged by rivers originates from eroded peat or soil and therefore is relatively old. However, radiocarbon data show that POM in the Amazon river is rather fresh (Hedges et al., 1986). Trumbore (1993) showed that organic matter in soils in the drainage basin of the Amazon river has a very short residence time in the soil, but in soils of temperate regions the residence time is much longer.

Coarse and fine particles are usually not transported in the same way (Eisma, 1993). Coarse particles are mainly transported via bottom currents (saltation) while finer particles can be reintroduced into the upper water column and transported as suspended matter. This difference in transport behaviour can be the cause of a difference in origin of the fine and coarse particles. Also the minerals differ, causing different absorption characteristics of organic compounds. For example amino acids have a high affinity for clay minerals (e.g. Wang and Lee, 1993). These differences between coarse and fine particles might be reflected in the composition and in the stable and radioactive carbon isotopic characteristics of the organic matter in different size fractions of POM (Bergamaschi et al., 1997; Keil et al., 1994).

Therefore, to trace its origin, we have investigated the relations between particle size and stable and radioactive carbon isotope ratios in POM of a surface sediment from the Ems-Dollard Estuary, bordering the Netherlands and Germany.

## 2. Materials and methods

### 2.1. Sampling area

The Ems-Dollard estuary (Fig. 1) receives fresh water inflow from the river Ems (40–350  $\text{m}^3/\text{s}$ ) and a smaller

inflow from the Westerwoldse Aa (ca. 30  $\text{m}^3/\text{s}$ ; Helder and Ruardij, 1982). The total length of the estuary is ca. 100 km with an area of 600  $\text{km}^2$ . In the inner part (the Dollard) ca. 80% of the area consists of tidal flats, in the outer part 40–50%. The tide in these waters is semi-diurnal with a diurnal inequality and has an amplitude from 2.5 m in the outer estuary and 3 m in the Dollard. It is fully mixed over much of the estuary and partially mixed only at low salinities in the Ems and the Southern part of the Dollard. There is a net input of particulate matter from the North Sea as a result of an accumulation mechanism. Suspended matter transported inward by the flood current starts to sink when the current decreases. Since it takes time for the particles to sink, they continue to be transported inward to a point where they can not be resuspended again by the ebb current (Postma, 1954, 1961).

The North Sea is estimated to contribute  $\sim 9 \times 10^5$  tons of particulate matter per year to the estuary, compared with a river input of ca.  $1.4 \times 10^5$  tons per year (Laane and Ruardij, 1988). The surface sediment studied here was collected in the “Bocht van Watum”, one of the two main tidal channels in the middle part of the estuary, close to the town of Delfzijl at a water depth of 4.5 m at low tide (Fig. 1).  $^{210}\text{Pb}$  profiles of sediments from the area are homogeneous in the upper part, and do not allow calculation of sedimentation rates, indicating strong mixing of the sediment (unpublished results RIKZ (National Institute for Coastal and Marine Management)). The average salinity at this location is 16‰.

### 2.2. Samples

The surface sediment sample from the Ems-Dollard Estuary (about 40 kg) was collected in February 1994 by the RIKZ with a grab sampler, sampling the upper 10–15 cm of the sediment. This sample was originally collected and size fractionated to study different grain size correction procedures for the determination of organic micropollutants and heavy metals using various size fractionation methods (cf. Klamer et al., 1990). Later, this fractionated sample was used in this study of carbon isotopic composition. The sample was stored in a 50 l PE container at 4 °C until further processing. An aliquot of 6 kg of this sample, taken from the top of the container, was passed through 2 mm nylon netting to remove large fragments. This resulting sample (hereafter named ‘total sample’; fraction 1, see Fig. 2) was size fractionated by wet sieving and settling according to the scheme shown in Fig. 2, based on the work of Klamer et al. (1990). Sieves consisted of polycarbonate with nylon netting. The water used for sieving and decantation was pre-filtered sea water mixed with deionised water to a salinity of 16‰. The water was first equilibrated with a small portion of sediment in an ultrasonic bath for 20

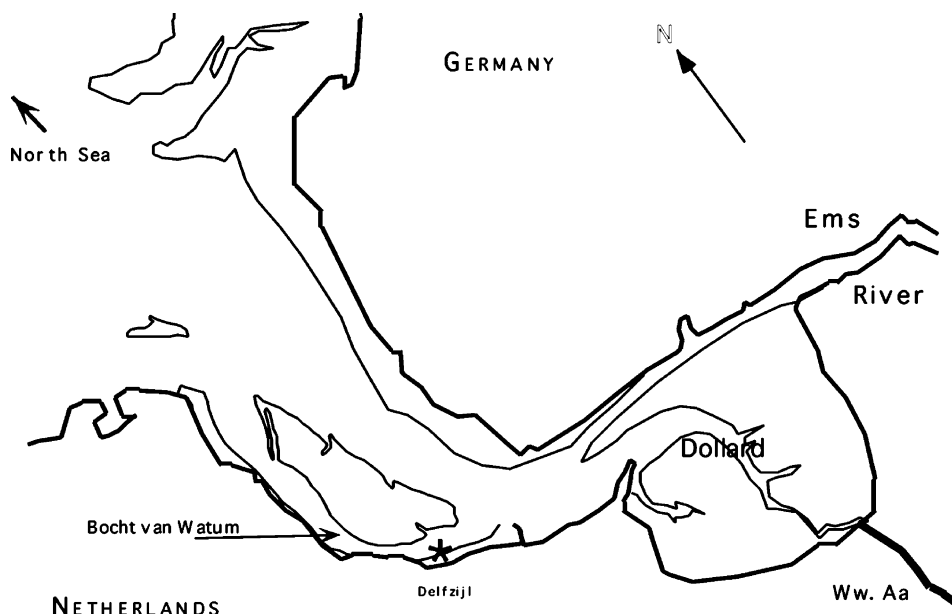


Fig. 1. Map of the Ems-Dollard estuary. Thin lines denote tidal flats. The sampling location is indicated by an asterisk.

min, and thereafter stored overnight at 4 °C to allow the particles to settle. The decantate was used for sieving. An aliquot of sample was put on a sieve placed over a collector dish on a vibrating table and precooled (4–10 °C) water was pumped onto the sieve. The water with the particles that passed through the sieve was led from the collector dish to a thermostated (10 °C) centrifuge with a flowthrough rotor, rotating at 22,000 *g*. The outflowing water was used for sieving again.

Four subsamples were obtained by using 20 and 63  $\mu\text{m}$  sieves respectively (fractions 2, 3 and 4, 5 respectively; see Fig. 2).

All fractions were freeze dried in containers covered by a lid with a small hole to avoid contamination by diffusion. The freeze dried fractions were homogenized in a Retsch ball mill. This did not affect particle sizes.

### 2.3. Particle size determination

Particle size fractions were determined according to the Dutch norm NEN 5753 (NNI, Delft, The Netherlands). Briefly, organic matter is digested with boiling hydrogen peroxide, and carbonates are removed by addition of dilute hydrochloric acid. In the remaining mineral sample the fraction  $>63 \mu\text{m}$  is determined by wet sieving. In the sample passing the sieve the  $<2 \mu\text{m}$  and  $<16 \mu\text{m}$  fractions are determined by the so-called “pipette method”. In a glass cylinder the sample is homogeneously suspended in water containing sodium pyrophosphate to prevent aggregation. At defined settling time and depth, calculated according to Stokes law, samples are taken from the waterphase by means of

a volumetric pipette. The particle weight determined by evaporation and corrected for the amount of sodium pyrophosphate is a measure for the specific fractions  $<2 \mu\text{m}$  and  $<16 \mu\text{m}$ .

### 2.4. Microscopy

A number of samples were studied using optical light microscopy. Aliquots in glycerol/water were used to prepare standard palynological slides. The material was examined using magnifications at 100 $\times$ , 400 $\times$  and 1000 $\times$  to determine the identity of the various recognizable particles (Fragments  $<10 \mu\text{m}$  can still be identified).

### 2.5. Organic carbon determination

Organic carbon concentrations were determined with a Carlo Erba elemental analyzer. Prior to analysis inorganic carbonates were removed by exposing the samples to hydrochloric acid vapour overnight.

### 2.6. Carbon isotope measurements

For carbon isotope analysis of the organic matter, aliquots of the fractions that contained ca. 1 mg organic carbon were acidified with dilute hydrochloric acid to remove inorganic carbonates, dried in vacuo over potassium hydroxide and combusted in an oven at 900 °C in a flow of oxygen. The combustion gases were led over silver in an oven at 400 °C to remove halogens and sulfur dioxide, an oven with copper oxide (800 °C)

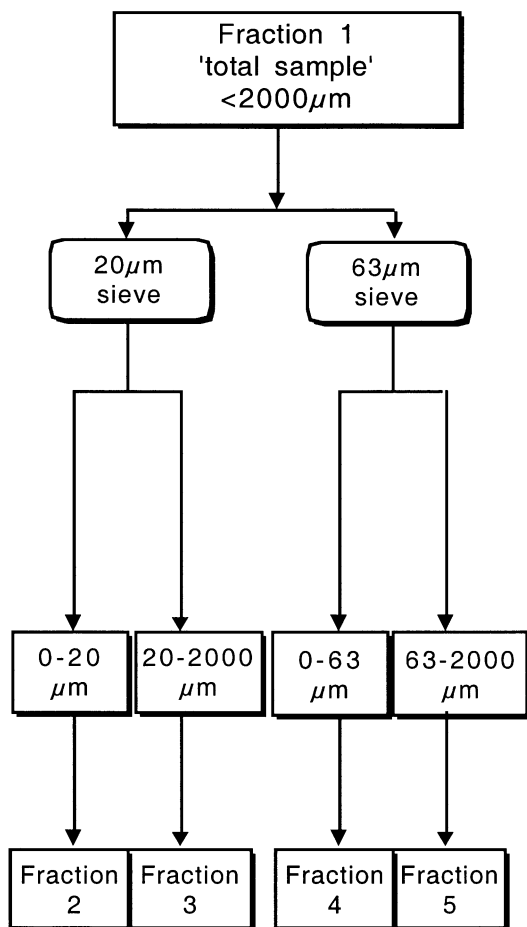


Fig. 2. Schematic representation of the sieving and settling procedure.

to oxidize carbon monoxide and through a cold trap (dry ice/ethanol) to remove water. The  $\text{CO}_2$  was collected in a cold trap in liquid air. After the oxygen was pumped away the gas was led over an oven with copper ( $600^\circ\text{C}$ ) to reduce nitrogen oxides. The  $\text{CO}_2$  yields were determined by expanding the gas in a known volume and measuring the pressure. The  $^{13}\text{C}$  concentrations of the purified carbon dioxide were measured with a VG SIRA isotope ratio mass spectrometer (IRMS) and expressed as  $\delta^{13}\text{C}$  relative to the V-PDB standard. Subsequently, the carbon dioxide was reduced to graphite with an iron catalyst at  $600^\circ\text{C}$  and a twofold excess of hydrogen (Aerts-Bijma et al., 1997). The  $^{14}\text{C}$  activity ( $^{14}\text{a}$ ) in the graphite was measured with the Groningen  $^{14}\text{C}$ -dedicated accelerator mass spectrometer (AMS; Gott dang et al., 1995). The  $^{14}\text{a}$  values are defined as the  $^{14}\text{C}/^{12}\text{C}$  ratio (corrected for fractionation using the  $^{13}\text{C}$  fractionation) in the sample relative to the same ratio in the oxalic acid standard and are reported in % (percent of modern carbon) (Mook and van der Plicht, 1999).

To test blank levels, the procedure was performed with a purified organic matter sample. No organic carbon was detected upon organic carbon determination using the Carbo Erba analyser. The instrumental error of the IRMS ( $^{13}\text{C}$ ) was 0.02 per mil; for the AMS this is 5 per mil. Repeated sample treatment and analysis showed that the total error for  $^{13}\text{C}$  was ca. 0.1 per mil in  $\delta^{13}\text{C}$ , and ca. 1% in activity  $^{14}\text{a}$  for  $^{14}\text{C}$ . Samples made from natural gas are used as background material; they have infinite age on the  $^{14}\text{C}$  timescale. Background activities for all AMS runs (including sample preparation) are very low, corresponding to ages of 45 ka (activities  $^{14}\text{a} \approx 0.4\%$ ). These background activities are subtracted from the activities of the samples.

### 3. Results

To study the effect of grain size distribution on the stable and radioactive carbon isotopes and the applicability of this combination of analytical methods, fractions obtained by size fractionation procedures from a surface sediment sample from a tidal channel in the Ems-Dollard estuary were analyzed. Results of the analyses are summarized in Table 1. The total sample contains ca. 20% material  $<20\ \mu\text{m}$  on a mass base. About 70% of the total sample was separated as the  $>63\ \mu\text{m}$  fraction (No. 3). Particle size analysis of the fractions showed that there is a considerable amount of mineral particles larger than  $63\ \mu\text{m}$  in the fractions obtained by sieving over the  $63\ \mu\text{m}$  sieve.

Organic carbon concentrations (%OC) are, as expected, much higher in the fine fractions than in the coarse fractions. Most of the organic carbon is associated with fine grained material. The organic carbon in the fractions obtained by sieving over  $20\ \mu\text{m}$  (Nos. 2 and 3) and over  $63\ \mu\text{m}$  (Nos. 4 and 5) is ca. 65% of the organic carbon in fraction 1 (No. 1).

There is a marked difference in the  $^{14}\text{C}$  activities of the fractions  $<20\ \mu\text{m}$  and  $>20\ \mu\text{m}$  (Fig. 3). The coarser fractions have a  $^{14}\text{a}$  value of around 50% and the fine fraction around 80%. The  $\delta^{13}\text{C}$  values of the fractions  $<20\ \mu\text{m}$  are ca.  $-23.0\%$ , the  $\delta^{13}\text{C}$  of the coarse fractions ranges from  $-24.9$  to  $-26.2\%$ . There is a clear correlation ( $r^2=0.80$ ) between the  $^{14}\text{a}$  and the  $\delta^{13}\text{C}$  values of the fractions (Fig. 4a). The correlation between the carbon isotopic composition and the organic carbon concentration is less significant (Fig. 4b).

Organic carbon mass balances can be calculated from  $\delta^{13}\text{C}$  and  $^{14}\text{a}$  values, since these parameters in a bulk sample are the weighted average of the same parameters in its components. For example, in a mixture consisting of component A and B, the fraction A ( $x_A$ ) in the mixture M can be calculated from the  $\delta^{13}\text{C}$  values of the fractions and the mixture by solving the equation:

Table 1  
Overview of measured and calculated data

No.	Description	Fm	> 63 $\mu\text{m}$	< 63 $\mu\text{m}$	< 16 $\mu\text{m}$	< 2 $\mu\text{m}$	CaCO <sub>3</sub> mass%	% OC	$\delta^{13}\text{C}$ (‰)	<sup>14</sup> a (%)	OC <sub>f</sub> /OC <sub>t</sub>	CB-13	CB-14
1	<2000 $\mu\text{m}$ upper part of sample	1.00	45.9	19.4	15.6	10.8	21.8	0.98	-23.91±0.07	70.9±1.0			
2	0–20 $\mu\text{m}$	0.18	0.5	59.2	57.4	38.5	17.9	2.91	-23.08±0.07	80.1±1.0	49.0	69	68
3	20–2000 $\mu\text{m}$	0.82	62.4	1.7	1.7	1.2	22.8	0.24	-25.60±0.07	51.7±1.0	15.7	31	32
4	0–63 $\mu\text{m}$	0.29	18.0	51.7	32.5	21.9	15.1	1.72	-23.47±0.07	74.2±1.0	54.0	74	86
5	63–2000 $\mu\text{m}$	0.71	68.3	1.3	1.3	0.9	23.4	0.14	-25.08±0.07	50.1±1.0	10.6	26	14

Weight portions relative to the total sample (Fm) and results of mineral particle size analysis of the fractions after removal of OM and carbonates. Calcium carbonate content, organic carbon content,  $\delta^{13}\text{C}$  values (vs. V-PDB) and <sup>14</sup>C normalized relative abundance (<sup>14</sup>a) of the organic carbon. In the last three columns the distribution of organic carbon over the respective fractions calculated from weight portions and organic carbon percentage (OC<sub>f</sub>/OC<sub>t</sub>; OC<sub>f</sub> is %OC \* Fm of the fraction and OC<sub>t</sub> is the OC concentration of sample 1, the 'total sample'),  $\delta^{13}\text{C}$  values (CB13) and <sup>14</sup>a values (CB14). Absolute errors in CB13 and CB14 are approximately ±10%.

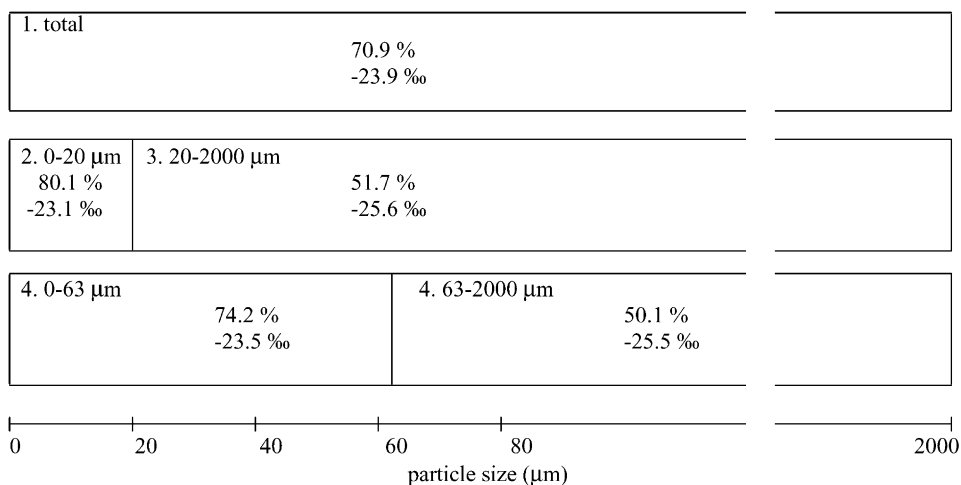


Fig. 3. Carbon isotopic compositions of OM in fractions obtained by sieving of the surface sediment. Numbers in bold are the fraction numbers (corresponding to those in Fig. 2). The upper number is the <sup>14</sup>C activity <sup>14</sup>a (in%), the lower number is the  $\delta^{13}\text{C}$  (in ‰).

$$x_A \cdot \delta^{13}\text{C}_A + (1 - x_A) \cdot \delta^{13}\text{C}_B = \delta^{13}\text{C}_M$$

Comparison of organic carbon mass balances calculated from %OC and weight fraction,  $\delta^{13}\text{C}$  and <sup>14</sup>a thus gives an indication of the quality of the analyses and separation procedure. The carbon mass balance calculations based on  $\delta^{13}\text{C}$  and <sup>14</sup>a (with an absolute error of ca. 10%) are in reasonable agreement with the balance calculated from the weight portions and the organic carbon concentrations (Table 1). The calculations based on  $\delta^{13}\text{C}$  and <sup>14</sup>a show that 70% of the total organic carbon is associated with particles smaller than 20  $\mu\text{m}$  and 90% with particles smaller than 63  $\mu\text{m}$ .

### 3.1. Microscopy

Microscopic inspection of the coarse fraction > 63  $\mu\text{m}$  (fraction 5) shows that this fraction consists mainly of large mineral particles and large pieces of organic material which are identified as fragments of soft tissue of higher plants (parenchyma), copepod eggs, diatom fragments, *Pediastrum* (a fresh water alga) and cuticle fragments. The fine fraction (< 20  $\mu\text{m}$ ), fraction 2, is quite homogeneous, consisting mainly of mineral particles with brown entities attached (most probably organic matter). Recognizable discrete organic fragments include spores, pollen grains and possibly small algae.

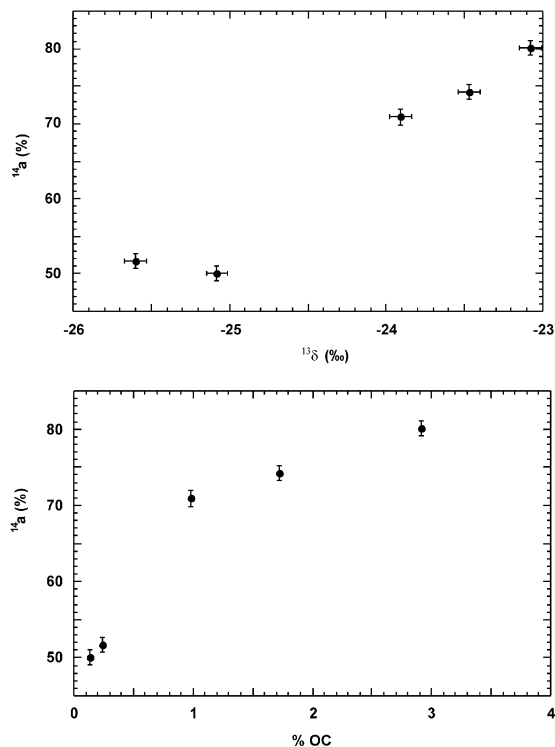


Fig. 4. a) relation between  $\delta^{13}\text{C}$  and  $^{14}\text{a}$  of OM in the fractions and (b)  $^{14}\text{a}$  vs. organic carbon concentration (%OC). Errors indicated are ca.1% for  $^{14}\text{a}$  and ca. 0.1‰ for  $\delta^{13}\text{C}$ , based on repeated analysis of samples (see materials and methods section).

#### 4. Discussion and conclusions

The carbon isotopic compositions of the size fractions within this single sediment sample show considerable variability. The fractions with particle size larger than 20  $\mu\text{m}$ , accounting for 30% of the total organic carbon, have  $\delta^{13}\text{C}$  values ranging from  $-25$  to  $-27\text{‰}$  and  $^{14}\text{a}$  values around 52%. The fractions finer than 20  $\mu\text{m}$  have  $\delta^{13}\text{C}$  values around  $-23\text{‰}$  and have considerably higher  $^{14}\text{a}$  values (78–84%). These fine fractions are similar in their carbon isotopic composition when compared to suspended organic matter at this site that has average  $\delta^{13}\text{C}$  values of  $-23.2 \pm 0.4\text{‰}$  and average  $^{14}\text{a}$  values of  $75 \pm 3\%$  (Megens, 2000) indicating the close relation between the small particles in the sediment and in the watercolumn as far as the organic matter is concerned (e.g. Eisma, 1981).

The  $\delta^{13}\text{C}$  value of organic carbon in the Ems river in surface sediments is about  $-27\text{‰}$  (Salomons and Mook, 1981) and in suspended matter it ranges from  $-25$  to  $-28\text{‰}$  (Eisma et al., 1983, 1991). Typical  $\delta^{13}\text{C}$  values of organic carbon in sediments and suspended matter in dutch coastal waters of the North Sea are around  $-23\text{‰}$

(Laane et al., 1990). The  $^{14}\text{a}$  values of suspended matter in the Dutch coastal waters ranges from 82 to 88%. Therefore, the organic matter in the fine fraction appears to consist entirely of material imported from the North Sea.

Suspended POM from the Ems river has a similar  $^{14}\text{a}$  value (77%; Megens, 2000), but a lower  $\delta^{13}\text{C}$  value ( $-25.3\text{‰}$ , Megens, 2000;  $-25$  to  $-28\text{‰}$ , Eisma et al., 1991). Therefore the OM in this fraction is not a simple mixture of OM from the Ems and the North Sea. Based on mineralogical investigations it was determined that no small particles from the Ems reach this point (Eisma, 1981; Favejee, 1960). Thus, the older component probably does not originate from fluvia POM. Exchange with dissolved organic matter (DOM) has been proposed as an explanation for the lower  $^{14}\text{a}$  values in detrital aggregates at the deep ocean sea floor compared with sinking POM (Wang et al., 1996). Macromolecular DOM ( $> 1000$  dalton) from the Ems-Dollard has  $^{14}\text{a}$  values of 87% (Van Heemst et al., 2000), and is therefore not the source of the old component. The  $^{14}\text{a}$  of low molecular weight DOM in the Ems-Dollard is not known. At this stage it cannot be excluded that this fraction contains a small contribution of old, so-called black or fossil carbon (Hedges et al., 2000).

The lower  $\delta^{13}\text{C}$  values of the coarser fractions indicate, using the simple two end member mixing model of marine and terrestrial organic matter, a higher contribution of terrestrial organic matter to the coarse fractions than to the fine fractions. However, the  $\delta^{13}\text{C}$  values of phytoplankton in the estuary can cover a range from a marine value of  $-17\text{‰}$  to values around  $-30\text{‰}$ , due to the gradient of  $\delta^{13}\text{C}$  of dissolved inorganic carbonate (DIC) in the Ems-Dollard estuary, which ranges from  $-11\text{‰}$  in the river to  $+1\text{‰}$  in the sea (Megens, 2000). Therefore, the lower  $\delta^{13}\text{C}$  values could be related to upstream produced phytoplankton derived OM as well. The considerably lower  $^{14}\text{a}$  values (ca. 50%, corresponding to a  $^{14}\text{C}$  age of about 5500 yr BP) is an indication for a terrestrial source, because the Ems river flows through an area with large peat deposits that started to form ca. 7000 years ago (Dupont, 1986). The lower  $\delta^{13}\text{C}$ , however, can also indicate selective degradation of compounds with relatively high  $\delta^{13}\text{C}$  values like carbohydrates and proteins.

Microscopy showed the presence of remains of higher plant in these fractions, but also fresh water algae and discrete organic particles associated with a marine or estuarine environment. We did not determine how much these discrete organic particles contribute to the total organic carbon in these fractions. In total sediment usually less than 10% of the organic matter is present as discrete organic debris (Hedges and Keil, 1995), but in coarse fractions ( $> 38\text{ }\mu\text{m}$ ) of sediment from the delta of the Amazon river more than 60% was present as low density discrete organic particles (Keil et al., 1997).

Our study of the stable and radioactive carbon isotopic compositions of one size fractionated surface sediment from the Ems-Dollard estuary shows that large differences exist in the stable and radioactive carbon isotopic composition of OM in fractions of this sediment with particle sizes  $<20\ \mu\text{m}$  and  $>20\ \mu\text{m}$ . The average  $^{14}\text{a}$  (80%) and  $\delta^{13}\text{C}$  ( $-23\ \text{‰}$ ) values of the fine fractions are much higher than those of the coarse fractions (52% and  $-25.6\ \text{‰}$ ). The main and possibly only source of OM in the fine fractions of this sediment sample is POM from the North Sea. The OM in the coarse fractions appears to be mixture of terrestrial and estuarine or marine material. The low  $^{14}\text{a}$  and  $\delta^{13}\text{C}$  values in combination with the presence of fragments of soft tissue of higher plants indicate a contribution of eroded peat. The lower  $\delta^{13}\text{C}$  values can also be explained partly by the selective degradation of carbohydrates and proteins.

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