ELSEVIER

Marine Geology 243 (2007) 169 – 179

MARINE GEOLOGY
INTERNATIONAL JOURNAL OF MARINE GEOLOGY, GEOCHEMISTRY AND GEOPHYSICS

www.elsevier.com/locate/margeo

Provenance of organic matter and nutrient conditions on a river- and upwelling influenced shelf: A case study from the Portuguese Margin

U. Alt-Epping [a,*], M. Mil-Homens [b], D. Hebbeln [a], F. Abrantes [b], R.R. Schneider [c]

[a] *DFG-Research Center Ocean Margins, University of Bremen, PO Box 330440, 28334 Bremen, Germany*
[b] *Department of Marine Geology, Instituto Nacional de Engenharia, Tecnologia e Inovação (INETI), Estrada da Portela, 2721-866 Alfragide, Portugal*
[c] *Department of Geosciences, Christian-Albrecht University Kiel, Ludewig-Meyn-Str. 10, 24118 Kiel, Germany*

Received 4 July 2006; received in revised form 22 March 2007; accepted 29 April 2007

Abstract

Organic matter contained in surface sediments from four regions on the western Portuguese shelf, which are influenced by coastal upwelling and fluvial input, was analysed with respect to elemental organic carbon (C_{org}) and nitrogen (N_{total}) content and isotopic carbon and nitrogen ratios ($\delta^{13}C_{org}$, $\delta^{15}N$). C_{org}/N_{total} weight ratios and $\delta^{13}C_{org}$ values are interpreted in terms of terrigenous or marine organic matter sources, supported by $CaCO_3$ content. Organic matter in the shelf sediments is mainly of marine origin, with increasing terrigenous components only close to rivers and estuaries. In the northern shelf region the data indicates significant terrigenous supply by the Douro River. North of the Nazaré Canyon organic matter composition implies a mainly marine origin, with a higher terrestrial influence close to the canyon head. Organic matter composition in the central shelf region, which is dominated by the Tagus Estuary and the Tagus prodelta, reveals a change from a continental-type signature within the estuary to a more marine-type signature further to the west and south of the estuary mouth. In the southern region near Cape Sines the geochemical properties clearly reflect the marine origin of sedimentary organic matter.

Sedimentary $\delta^{15}N$ values are interpreted to reflect various degrees of assimilation of seasonally upwelled nitrate, in relation to the upwelling centres. In the estuarine environment, inputs of agriculturally influenced dissolved inorganic nitrogen are reflected in the sediments. No evidence for N_2-fixation or denitrification is found. On the central shelf north of the Nazaré canyon, sedimentary $\delta^{15}N$ values are close to marine $\delta^{15}NO_3^-$ and thus indicate a complete NO_3^- assimilation and N-limitation of marine production. Light $\delta^{15}N$ values in distal sediments off the Douro River mouth and in samples south of C. Sines reflect high NO_3^- supply and a close proximity to the seasonal upwelling centres. Particularly in sediments form the Sines region, light $\delta^{15}N$ values in southern samples reflect stronger upwelling further south.

Keywords: organic matter provenance; upwelling pattern; $\delta^{15}N$, $\delta^{13}C_{org}$, C/N ratio; Portuguese margin

1. Introduction

The stable carbon isotope ratio ($\delta^{13}C_{org}$) and the C_{org}/N_{total} weight ratio of sedimentary organic matter has often been used as a first provenance proxy to distinguish between a marine or terrestrial organic

* Corresponding author. Tel.: +49 421 21865671.
E-mail addresses: alt-epping@uni-bremen.de (U. Alt-Epping), mario.milhomens@ineti.pt (M. Mil-Homens), dhebbeln@uni-bremen.de (D. Hebbeln), fatima.abrantes@ineti.pt (F. Abrantes), schneider@gpi.uni-kiel.de (R.R. Schneider).

0025-3227/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.margeo.2007.04.016

matter source (e.g. Sackett and Thompson, 1963; Bordovskiy, 1965; Fontugne and Jouanneau, 1987; Middelburg and Nieuwenhuize, 1998). The basic assumption for this approach considers organic matter to comprise a particular range of $\delta^{13}C_{org}$ and C_{org}/N_{total} ratios (e.g. Craig, 1953, Redfield et al., 1963), which depends on a variety of metabolic and environmental parameters (e.g. Sackett et al., 1965; Fontugne and Jouanneau, 1987; Altabet and Francois, 1994). Terrestrial organic matter typically has a $\delta^{13}C_{org}$ between −26‰ and −28‰, if C3 plants are the dominating organic constituents, or around −13‰, if C4 plants are prevailing (Peters et al., 1978; Middelburg and Nieuwenhuize, 1998). Typical terrestrial C_{org}/N_{total} ratios are > 10, with the exact ratio depending on the specific organic material (Smith and Epstein, 1971; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998). Terrigenous C_{org}/N_{total} values may be lowered by the adsorption of N to clay minerals, in which NH_4^+ substitutes for K^+. This effect occurs preferentially on land, as the high K^+ abundance in the marine realm prevents the substitution (Schubert and Calvert, 2001). Marine organic matter has a $\delta^{13}C_{org}$ of around −22‰ (e.g. Fontugne and Duplessy, 1981; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998), depending on water temperature, which controls dissolved CO_2 levels in surface waters (Sackett et al., 1965; Fontugne and Jouanneau, 1987). The cited value is valid for the mid-latitudes. C_{org}/N_{total} ratios of marine organic matter are around 6–7, but may be significantly lower, if protein rich organisms (e.g. bacteria) dominate (Redfield et al., 1963; Bordovskiy, 1965).

Sedimentary $\delta^{15}N$ values are strongly determined by the isotopic composition and assimilation of N-containing nutrients. In oligotrophic ocean regions bacterial fixation of atmospheric N_2 is an important NO_3^- source, resulting in particulate $\delta^{15}N$ values around 0‰. The primary nitrogen source in upwelling regions is marine NO_3^- with a typical $\delta^{15}N$ between 5–6‰ (Liu and Kaplan, 1989). As organisms assimilate preferentially ^{14}N, the remaining nitrate pool is gradually enriched in ^{15}N. This enrichment is finally reflected in the sediments (Altabet and Francois, 1994; Freudenthal et al., 2001), leading to a temporal $\delta^{15}N$ gradient of increasingly heavier $\delta^{15}N$ values during the course of a bloom as well as to a spatial $\delta^{15}N$ gradient of heavier $\delta^{15}N$ with increasing distance to the upwelling centre (e.g. Freudenthal et al., 2001).

The spatial distribution of geochemical parameters for organic matter in the surface sediments along the Portuguese margin is evaluated and their elemental composition and isotopic C_{org} signature is attributed to the mixing or exclusive supply of organic matter from marine and terrestrial sources. Nitrogen isotope ratios are used to evaluate possible nitrogen sources, such as deep water NO_3^- or agriculturally affected dissolved inorganic nitrogen (DIN), as well as the degree of marine NO_3^- utilisation. For this purpose geochemical parameters (C_{org}, N_{total}, $CaCO_3$ content, $\delta^{13}C_{org}$, $\delta^{15}N$ and C_{org}/N_{total} ratio) of surface sediments from four different regions along the western Portuguese margin are mapped (Fig. 1). Two of these areas are located in front of river mouths, the Douro and Tagus Rivers, with the latter region including a large estuary. Here a large continental and estuarine influence on sedimentary properties can be expected, especially in estuarine samples. The Nazaré sampling region is located close to the Nazaré Canyon, away from major rivers and thus under primarily marine influence, but possibly including laterally advected terrigenous material. On the southern shelf, organic sediment properties are expected to be of entirely marine origin, as any lateral input of terrigenous sediment is intercepted by canyons north and south of the sampling region and riverine inputs are largely absent. In case of regularly re-occurring upwelling patterns, the spatial distribution of NO_3^- supply is expected to be reflected in sedimentary $\delta^{15}N$ values.

Table 1
Compilation of minimum, maximum, mean and standard deviation (SD) of elemental and isotopic C and N data as well as $CaCO_3$

	C_{org} (%)	N_{total} (%)	C_{org}/N_{total}	$\delta^{13}C_{org}$ (‰)	$\delta^{15}N$ (‰)	$CaCO_3$ (%)
Douro samples						
Minimum	0.4	0.06	6	−25.0	4.1	3
Maximum	1.3	0.12	10.6	−23.2	7.9	6
Mean	0.8	0.09	8.7	−24.2	5.4	4
SD	0.4	0.03	1.6	0.6	1.3	1
Nazaré samples						
Minimum	0.2	0.02	4	−23.4	4.5	5
Maximum	1.4	0.19	9	−21.9	5.5	49
Mean	0.7	0.1	7.4	−22.7	5.2	26
SD	0.4	0.05	1.4	0.6	0.3	18
Tagus samples						
Minimum	1.2	0.11	7.6	−26.2	5.3	3
Maximum	1.9	0.2	12.9	−22.9	7.1	15
Mean	1.6	0.16	9.6	−24.6	6.0	7
SD	0.2	0.03	1.5	0.9	0.5	4
Sines samples						
Minimum	0.2	0.04	5.5	−22.2	3.6	24
Maximum	0.9	0.15	8.0	−21.3	5.4	52
Mean	0.5	0.08	6.6	−21.8	4.4	38
SD	0.14	0.03	0.8	0.2	0.6	8

2. Regional setting

2.1. Shelf sediments

The northern and central parts of the western Portuguese shelf are between 30 and 50 km wide and covered dominantly by sandy sediments (Dias and Nittrouer, 1984). Mesozoic and Cenozoic rock outcrops on the shelf off the Douro River act as traps for fine sediment, resulting in the formation of a mud belt northwest of the Douro River mouth at about 100 m water depth. This mud belt covers an area of about 500 km^2 with a sediment layer of 2 to 5 m thickness (Drago et al., 1999). Lateral sediment transport between the northern and central shelf is intercepted by the Nazaré Canyon, which cuts the central shelf and removes laterally transported sediments into the deep sea (van Weering et al., 2002) (Fig. 1). Off the Tagus Estuary mouth a mud belt developed, which covers an area of 560 km^2 with maximal 15 m thick silty sediments (Jouanneau et al., 1998). South of the Tagus mud belt the shelf is incised by the Lisbon and Setubal Canyons, which deliver a significant amount of river discharged sediment towards the Tagus Abyssal Plain. Nevertheless sedimentation dominates on the shelf, resulting in sedimentation rates around 0.2 cm/yr (Jouanneau et al., 1998). The southern part of the western shelf is ca. 20 km broad, separated from the central part by the Setubal Canyon and bordered southwards by the S. Vicente Canyon. Sediments are dominated by calcareous marine sands and lack significant riverine contributions.

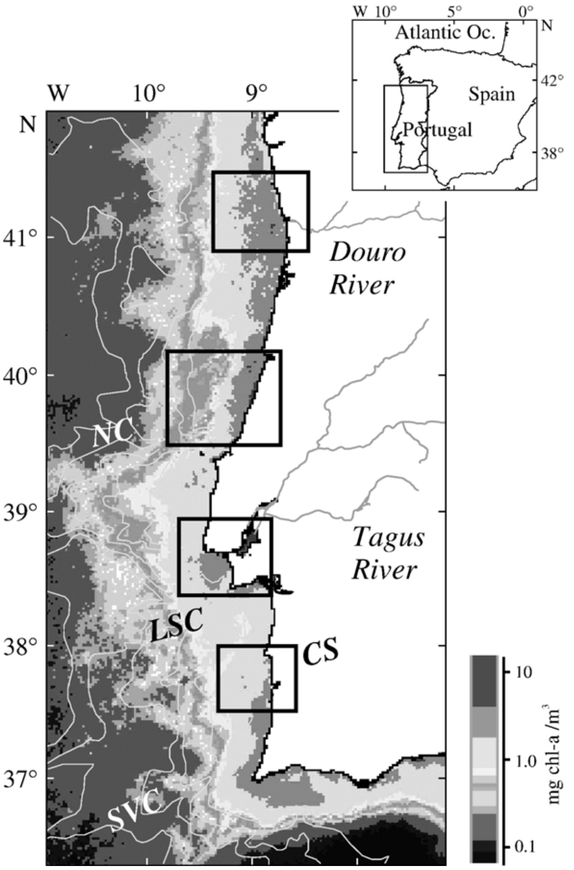

Fig. 1. Average chlorophyll-a concentration during August 2002 (SEAWIFS), showing the typical pattern of upwelling related marine productivity along the Portuguese western margin. Sampling regions are shown by rectangles. Centres of upwelling are north of the Nazaré Canyon, off the Tagus Estary mouth and around C. San Vicente. Major morphological features are indicated: NC — Nazaré Canyon, LSC — Lisbon and Setubal Canyons, CS — Cape Sines, SVC — St. Vicente Canyon. Fluvial sediment input is expected to occur mainly through the Douro and Tagus rivers.

2.2. Marine productivity

Northerly winds, caused by the periodic relocation of the Azores high-pressure system closer to the Iberian coast, generate seasonal upwelling along the Portuguese margin between May and September (Fiúza, 1983). Cold and nutrient rich waters, upwelled from depths between 60 and 120 m, form ca. 50 km wide bands along the coast (Fiúza, 1983), occasionally extending offshore some hundred kilometers through filaments. Upwelling enhances marine productivity, which can reach 60 to 90 g C/m^2 yr (Fiúza, 1983; Abrantes and Moita, 1999). A less pronounced upwelling also occurs around January and February (Dias et al., 2002), resulting in a phytoplankton bloom along the Portuguese Margin, which is fertilised by the input of river derived nutrients. Therefore, a persistently high productivity, evidenced by high chlorophyll concentration, is observed off the Tagus River (Moita et al. 2003). Upwelling off the Douro River is characterised by a large offshore extend (Fig. 1), while in the Nazaré region upwelling shows a high interannual variability. Generally, upwelling north of the Nazaré Canyon is relatively strong. South of C. Sines upwelling is restricted to a narrow band close to the coast, becoming stronger southward and reaching a maximum around Cape S. Vicente (Fig. 1).

2.3. Fluvial supply

The Douro River is the main source of terrigenous sediments on the northern shelf (Dias and Nittrouer, 1984), draining 95,700 km^2 of mountainous hinterland. The mean river discharge is about 420 m^3/s (Oliveira et al., 2002), showing a strong seasonality. Sediment discharge is estimated to be around 1.8 * 10^6 t/yr through the Douro River, compared to a total riverine sediment supply to the northern shelf of ca. 2.25 * 10^6 t/yr (Oliveira et al., 1982). Hence, the contributions of other rivers along the northern coast are minor (Dias et al., 2002).

In the central part of the shelf the Tagus River is the source for riverine input. With about 1000 km length it is the longest river of the Iberian Peninsula and drains a watershed of about 80 600 km^2, which is strongly influenced by agricultural activity and dominated by natural and cultured C3 plants. Therefore, an influence of agriculturally affected dissolved inorganic nitrogen (DIN) can be expected particularly in the estuarine sediments. The Tagus River feeds into the Atlantic Ocean through a 350 km^2 large, mesotidal estuary, which is characterised by a seasonally varying oxygen saturation of 60–130% (Ferreira et al., 2001). The course of the suspended matter carried by the Tagus Estuary outflow can be traced outside the estuary by a nepheloid layer, stretching over the Tagus mud belt and extending towards the Lisbon Canyon (Jouanneau et al., 1998).

On the southern shelf south of the Lisbon and Setubal Canyons large rivers are absent, thus fluvial contributions can be neglected.

3. Material and methods

All PO287, TV and TJ samples are surface samples. TV and TJ samples were collected with Van Veen and Shipeck sediment sampler. Plutur samples are taken from box core tops and the GeoB 8903 sample is a gravity core top. Locations of all sampling sites are compiled in the PANGEA database (www.pangea.de).

Measurements of elemental C and N content were performed following the procedure described by Müller et al. (1994), using an Elementar Vario-EL3 element analyser. All samples were freeze-dried, ground and homogenized. 25 mg of bulk sediment were filled into tin containers, folded and combusted in the analyser to obtain total carbon (C_{total}) and nitrogen (N_{total}) content, reported in wt.% (percent dry weight). Organic carbon (C_{org}) was measured on 25 mg sample material, that was filled into silver containers, treated with 1-molar HCl to remove carbonate and dried at 60 °C in an oven previous to combustion. Samples were not washed after treatment with HCl to prevent the loss of suspended material (Schubert and Nielsen, 2000). The analytical error, obtained by repetitive measurements, is 2% relative. Precision was ensured by continuous control measurements of a lab internal standard. The calcite content was calculated using the equation $CaCO_3 = 8.33 * (C_{total} - C_{org})$. The isotopic composition of organic carbon ($\delta^{13}C_{org}$) was measured on decalcified samples, following Müller et al. (1994). The material was combusted to CO_2 in an HERAEUS elementar analyser, cleaned in a trapping box system and measured with a FINNIGAN DELTA E mass spectrometer against an internal standard gas, that was calibrated against NBS19. The error of measurements is ± 0.1‰, based on long term calibration curves. Isotopic values are given in standard notation with reference to PDB. The nitrogen isotope ratio ($\delta^{15}N$) was measured by combustion of bulk sediment in a CARLO-ERBA elementar analyser to N_2, which was then led into the FINNIGAN DELTA E mass spectrometer in a continuous flow mode, using He as carrier gas. Precision is ± 0.2 to 0.3‰; internal calibration was performed the same way as for $\delta^{13}C$. Isotopic values are given in standard notation against $\delta^{15}N_{air}$ (= 0‰).

Grain sizes of TV and TJ samples were obtained at the Marine Geology Department of the INETI, by sieving and settling methods and are reported as fine fraction (< 63 μm), sand fraction (63 μm–2 mm) and gravel (> 2 mm). Grain sizes of PO287 samples were measured with a Coulter LS320 (Mil-Homens, 2006). Grain sizes of Plutur samples were determined by Jouanneau et al. (2004) and grain size of core GeoB 8903 was measured with a Coulter LS320 at the RCOM, Bremen, Germany. Except for the sediments from the Tagus region, grain sizes are expressed as fractions clay (< 4 μm), silt (4–63 μm), sand (63 μm–2 mm) and gravel (> 2 mm).

4. Results

4.1. Douro region

The surface sediments in the vicinity of the Douro river (Fig. 2a–f) contain 3–6 wt.% $CaCO_3$, with slightly higher values offshore. The C_{org} content is between 0.4 and 1.3 wt.% and the total N content is between 0.06 and 0.12 wt.% (not shown in figure). For both parameters, higher values are observed in offshore samples. C_{org}/N_{total} weight ratios range between 6 and 10.6. Lowest values are observed in the central part of the Tagus mud complex and closest to the Douro River mouth. The $\delta^{13}C_{org}$ values vary between − 23.2 and − 25‰ with lower values in the northern samples. $\delta^{15}N$ is between 7.9‰ closest to the Douro River mouth and 4.1‰ ca. 5 km away (Fig. 2). Offshore samples have about 2‰ lower $\delta^{15}N$ values than the four coastal samples (Table 1).

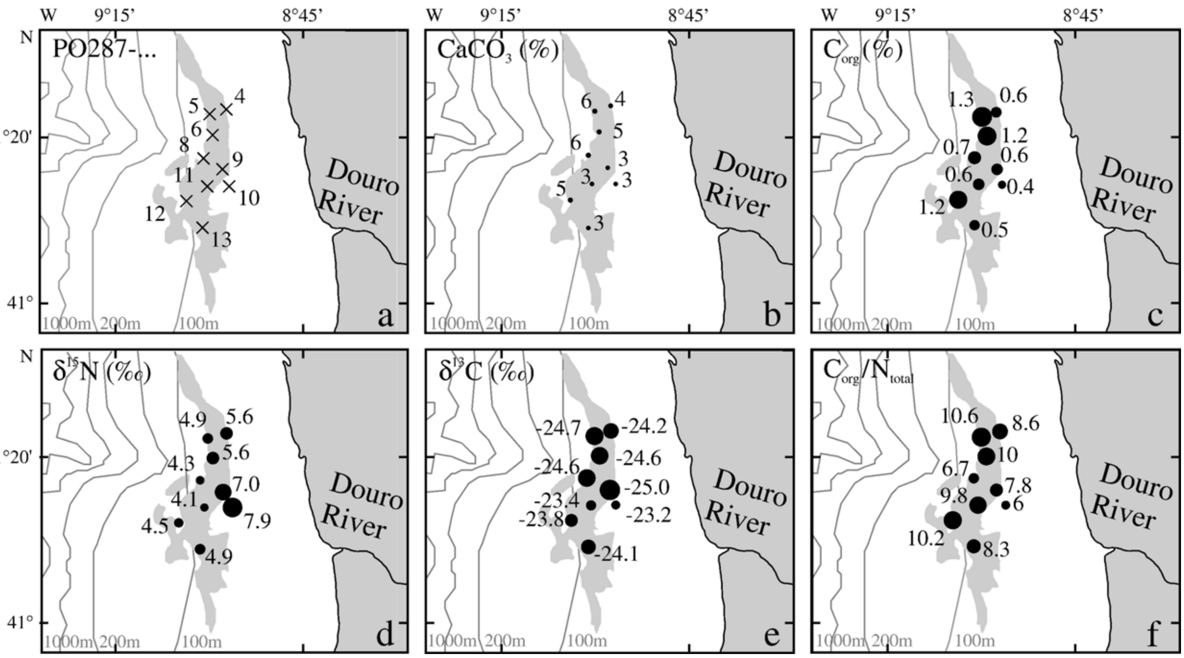

Fig. 2. Distribution of sediment properties in the Douro region. a) Sample name, b) $CaCO_3$ content, c) C_{org} content, d) sedimentary $\delta^{15}N$, e) $\delta^{13}C_{org}$, f) C_{org}/N_{total} ratio. Shaded area on the shelf indicates the limits of the Douro mud belt adapted from Drago et al. (1999).

The sediment texture is mainly silty, with a silt content between 34 and 74% and a sand content between 19 and 63% (Mil-Homens, 2006). The clay fraction reaches maximal 7%. C_{org} and N_{total} contents are higher in the fine fraction (R^2 = 0.9 for both). However, the correlation between C_{org}/N_{total} and fine fraction is statistically not significant (R^2 = 0.47), as the removal of only one data point leads to an R^2 below 0.3. Similarly, no significant correlation is evident between fine fraction and $\delta^{13}C_{org}$ or $\delta^{15}N$ (R^2 = 0.29 and 0.3, respectively) (Table 2).

4.2. Nazaré region

In the surface sediments close to the Nazaré Canyon (Fig. 3a–f) the $CaCO_3$ content varies between 49 and 5 wt.%, with higher values in the northwestern, distal samples. The C_{org} content ranges from 0.2 to 1.3 wt.% and the N_{total} content ranges from 0.02 to 0.19 wt.% (not shown in figure). Both parameters reach their highest value in the central sample, where the samples contain the highest fine-fraction contents, indicating the tendency of organic matter to accumulate with fine-grained material (Mil-Homens, 2006). Lowest values are found in the samples close to the coast. C_{org}/N_{total} weight ratios are between 4 and 9. $\delta^{13}C_{org}$ in the Nazaré samples varies between − 23.4‰ and − 21.9‰ an. That is close to typical marine $\delta^{13}C_{org}$ values. Samples in the south, close to the canyon head, are relative to the northern samples 0.6‰ lighter. $\delta^{15}N$ varies between 4.5 and 5.5‰, with slightly lower values close to the coast (Fig. 3, Table 1).

The grain size is highly variable, with a sand content between 14 and 86% and a silt content between 14 and 69% (Mil-Homens, 2006). Two samples were collected furthest offshore contain 15 and 18% gravel composed of shell fragments. The clay fraction can reach 17% but averages 8%. No significant correlation exists between grain size and C_{org}/N_{total}, $\delta^{13}C_{org}$ or $\delta^{15}N$ (Table 2).

4.3. Tagus region

In surface sediments from the Tagus region (Fig. 4a–f) the $CaCO_3$ content varies between 3 and 15 wt.% and is considerably lower inside the estuary, compared to mud belt samples. The C_{org} content in the Tagus estuary and on the prodelta is between 1.2 and 2.2 wt.% and the N_{total}

Table 2
Correlation coefficients R^2 between fine fraction < 63 μm and C_{org}/N_{total}, $\delta^{13}C_{org}$ and $\delta^{15}N$ of the four sampling regions

	C_{org}/N_{total}	$\delta^{13}C_{org}$	$\delta^{15}N$
Douro	0.47	0.29	0.3
Nazaré	0.06	0.5	0.38
Tagus	0.79	0.16	0.01
Sines	0	0.16	0.09

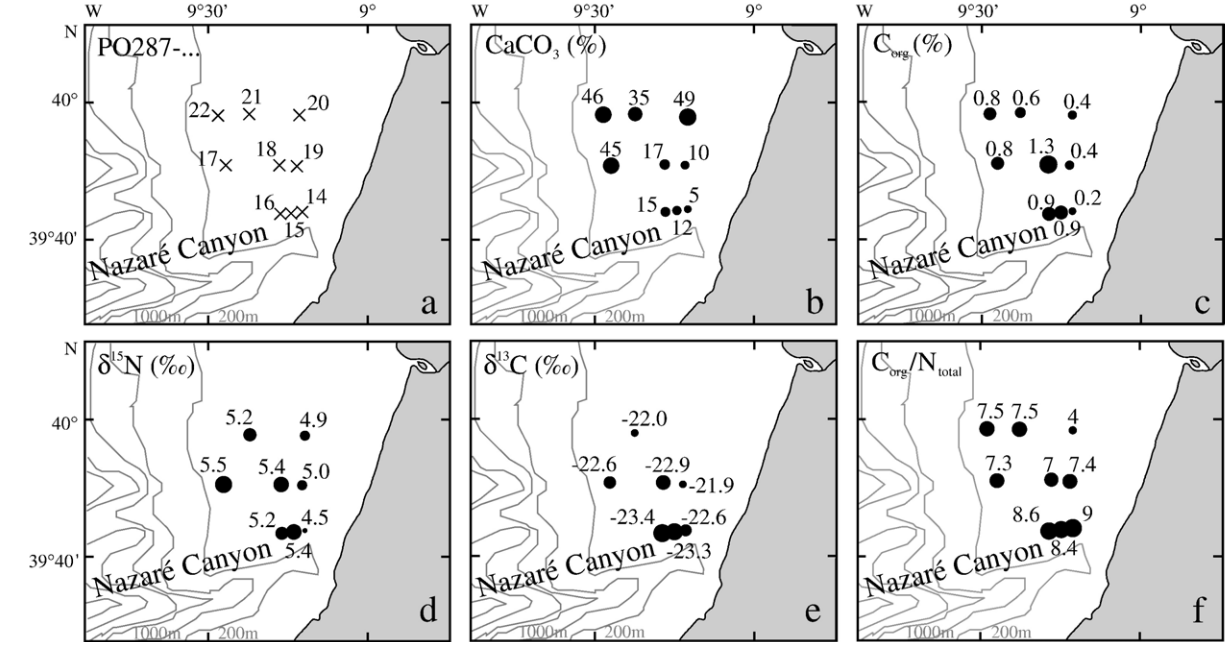

Fig. 3. Distribution of sediment properties in the Nazaré region. a) Sample name, b) $CaCO_3$ content, c) C_{org} content, d) sedimentary $\delta^{15}N$, e) $\delta^{13}C_{org}$, f) C_{org}/N_{total} ratio.

content ranges between 0.1 and 0.2 wt.% (not shown in figure). Both parameters have similar values inside and outside the estuary. C_{org}/N_{total} weight ratios range between 7.6 and 12.9. Values inside the estuary are generally higher, although also low values (8.1) are observed in the northeastern part of the estuary (Fig. 4). On the

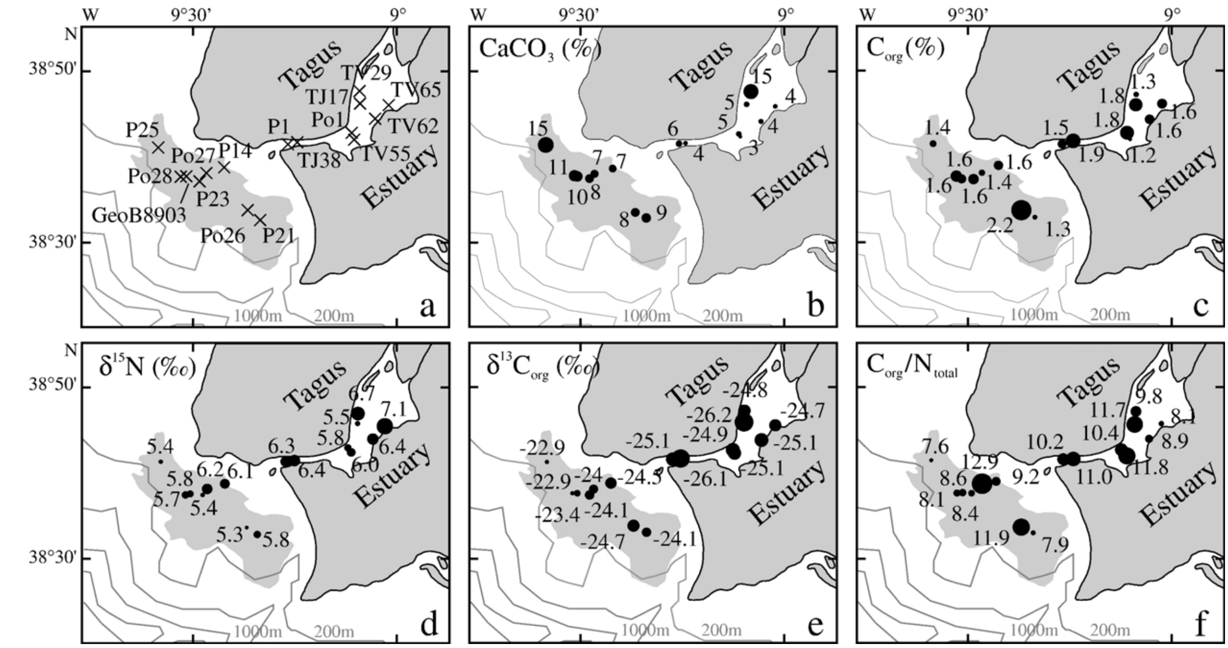

Fig. 4. Distribution of sediment properties in the Tagus region. a) Sample name (Pl = Plutur, Po = Po287), b) $CaCO_3$ content, c) C_{org} content, d) sedimentary $\delta^{15}N$, e) $\delta^{13}C_{org}$, f) C_{org}/N_{total} ratio. Shaded area on the shelf indicates the limits of the Tagus Prodelta mud belt adapted from Jouanneau et al. (1998).

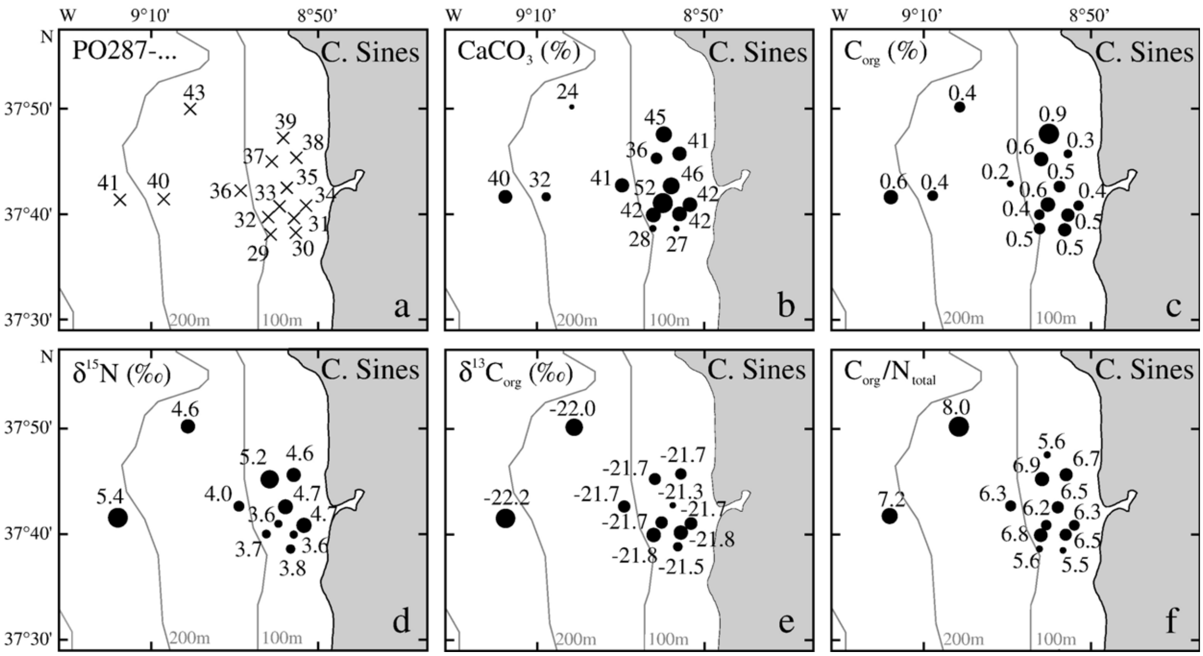

Fig. 5. Distribution of sediment properties in the Sines region. a) Sample name, b) $CaCO_3$ content, c) C_{org} content, d) sedimentary $\delta^{15}N$, e) $\delta^{13}C_{org}$, f) C_{org}/N_{total} ratio.

Tagus mud belt lowest C_{org}/N_{total} ratios below 8 occur at the western and eastern fringes of the mud belt and highest C_{org}/N_{total} ratios above 11 were measured in the central part. The $\delta^{13}C_{org}$ of sediments inside the estuary varies between − 26.2‰ and − 24.7‰. This is significantly lower, than $\delta^{13}C_{org}$ of mud belt samples, which range between − 24.7 and − 22.9‰. $\delta^{15}N$ values are between 5.5 and 7.1‰ inside the estuary and between 5.3 and 6.3‰ on the mud belt, where higher $\delta^{15}N$ and lower $\delta^{13}C_{org}$ values are found in the central part, compared to southeastern and northwestern values (Fig. 4, Table 1).

The amount of material finer than 63 µm is between 41 and 98%, with an average of 82% (Jouanneau et al., 2004). Lima (1971) identified illite as the dominant clay mineral in this area, varying between 34 and 62% of the clay fraction. No relation between fine fraction (< 63 µm) and C_{org}, $\delta^{13}C_{org}$ nor $\delta^{15}N$ exists in the Tagus surface samples. Fine sediments however have lower C_{org}/N_{total} ratios (R^2 = 0.79), which is caused by a higher N_{total} content in finer sediments (R^2 = 0.78) (Table 2).

4.4. Sines region

The $CaCO_3$ content in Sines surface samples ranges from 24 to 52 wt.%. C_{org} content ranges from 0.2 to 0.6 wt.% and the N_{total} content varies between 0.04 and 0.15 wt.% (not shown in figure). C_{org}/N_{total} weight ratios are very low, ranging from 5.5 to 8. $\delta^{13}C_{org}$ values range between − 21.3‰ and − 22.2‰ and $\delta^{15}N$ values are low, with values between 3.6 to 5.4‰, which slightly increase northwards (Fig. 5, Table 1).

Surface sediments from the Sines region contain between 49 and 88% sand (average 77%) and between 7 and 41% silt (average 18%) (Mil-Homens, 2006). The clay content does not exceed 10% and the gravel content is maximal 5%. In the Sines surface samples, no correlation between fine fraction and C_{org}, N_{total}, C_{org}/N_{total}, $\delta^{13}C_{org}$ or $\delta^{15}N$ is observed, as all R^2 values are below 0.2.

5. Discussion

5.1. Organic matter sources

Although sedimentary $\delta^{13}C_{org}$ and C_{org}/N_{total} values do not always reflect organic matter provenance (Miltner et al., 2005), the clear relation between $CaCO_3$ content, which is regarded as of marine origin, and $\delta^{13}C_{org}$ values implies, that $\delta^{13}C_{org}$ values can be interpreted in terms of organic matter provenance (Fig. 6).

Discrete C_{org}/N_{total} and $\delta^{13}C_{org}$ values for each organic matter source are needed, in order to quantify the fraction of terrigenous organic material. Defining terrigenous organic matter to have a C_{org}/N_{total} ratio of

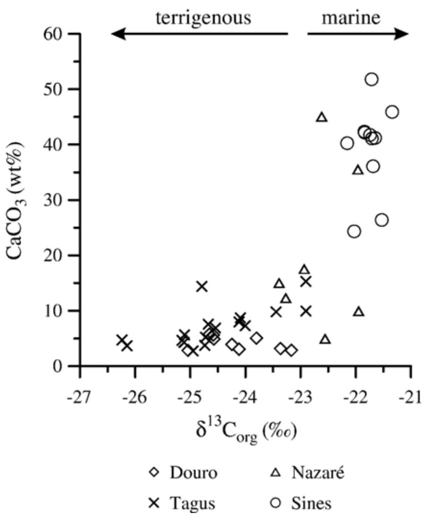

Fig. 6. $\delta^{13}C_{org}$ versus $CaCO_3$ content, showing the dependence of $\delta^{13}C_{org}$ values on sediment provenance.

15 and a $\delta^{13}C_{org}$ value of −27‰, and marine organic matter to have a C_{org}/N_{total} ratio of 6 and a $\delta^{13}C_{org}$ value of −22‰ (e.g. Middelburg and Nieuwenhuize, 1998) allows the calculation of the terrigenous organic matter fraction, assuming conservative and linear mixing, by

$$f_t = \left[\delta^{13}C_{org} - \left(\delta^{13}C_{mar}{*}f_m\right)\right]/\delta^{13}C_{terr}$$

with f_t and f_m as terrigenous and marine organic matter fractions, respectively, $\delta^{13}C_{org}$ as measured value and $\delta^{13}C_{terr}$ and $\delta^{13}C_{mar}$ as terrigenous and marine $\delta^{13}C$-endmember values.

Generally, the range of C_{org}/N_{total} and $\delta^{13}C_{org}$ values in the four sampling regions indicate a dominantly marine origin of organic matter, except in the close vicinity of the Douro and Tagus river mouths. The marine endmember is represented by sediments from the Sines region, where $\delta^{13}C_{org}$ and C_{org}/N_{total} values indicate a fraction of only 5% terrigenous organic matter (Fig. 5). In the Nazaré region 10–15% of the sedimentary organic matter is of terrigenous origin (Fig. 3), whereas in the Douro region as well as on the Tagus Prodelta a terrigenous fraction of 30–40% is calculated (Figs. 2 and 5). As expected, highest terrigenous contributions of 50–65% are reconstructed inside the Tagus Estuary. Slightly increased C_{org}/N_{total} ratios and lowered $\delta^{13}C_{org}$ values in prodelta samples southwest of the estuary mouth indicate a higher terrigenous organic matter fraction in these samples, which is interpreted as the trace of the Tagus River plume (Fig. 4).

Low correlation coefficients between $\delta^{13}C_{org}$ and fine sediment fraction indicate no major effect of grain size on $\delta^{13}C_{org}$ values in any of the sampling regions (Table 2). This applies also to the relation between fine fraction and C_{org}/N_{total} ratio, except inside the Tagus Estuary, where fine material has lower C_{org}/N_{total} ratios ($R^2=0.84$) (Table 2). This correlation is caused by a higher N content of fine material ($R^2=0.79$), whereas the C_{org} content is indepentent of grain size (R^2 of C_{org} versus fine fraction=0.25). In agriculturally influenced regions, such as the Tagus hinterland, the substitution of NH_4^+ for K^+ is particularly important, as NH_4^+ is a common constituent of fertilisers. As the total N content in estuarine sediments consists of 10–20% inorganic N, obtained from the N_{total} intercept on a C_{org} versus N_{total} plot (Goñi et al., 1998), the C_{org}/N_{total} ratios particularly in fine sediments are probably lowered by the adsorption of inorganic N to clay minerals and thus reflect the input from agricultural sources.

In the other regions the amount of inorganic N is insignificantly low, implying, that the nitrogen content in the sediments is associated to the organic matter.

5.2. Stable nitrogen isotopes

No evidences for N_2-fixation are found in any of the sampling regions, since C_{org}/N_{total} ratios around 6 and higher indicate no influence of nitrogen rich, bacterial biomass. Further, high O_2 concentrations and saturation in the water column along the coast as well as inside the Tagus Estuary (Moita, 2001; Ferreira et al., 2001) indicate, that water column denitrification plays no major role. Additionally there is no effect of grain size on sedimentary $\delta^{15}N$ observed. Therefore marine sedimentary $\delta^{15}N$ values are interpreted as results of isotopic fractionation during NO_3^- uptake.

Close to the Douro and Tagus river mouths and inside the Tagus Estuary sedimentary $\delta^{15}N$ values are relatively high (6–7‰) (Fig. 2 and 5). Particularly the Tagus River drains a watershed, that is dominated by agricultural land. This is observed by high DIN concentrations in the upper estuary (Ferreira et al., 2001) as well as by the strong relation between N_{total} content and grain size ($R^2=0.79$), which can be interpreted as an effect of the substitution of NH_4^+ for K^+ in clays (Müller, 1977). $\delta^{15}N$ values of estuarine sediments may hence be increased by contributions of agriculturally derived DIN, which is particularly evident by two slightly heavier $\delta^{15}N$ values in the uppermost estuary (samples TV29 and TV65), where also DIN concentrations are highest (Ferreira et al., 2001). Alternative explanations for enhanced $\delta^{15}N$ values inside the estuary are contaminations with sewage from the Lisbon urban area or water column denitrification.

Sewage is mainly discharged outside the Tagus Estuary (Silva et al., 2002), close to samples Plutur14 and Po287-27, which show no increased $\delta^{15}N$ (Fig. 4) and give no evidence for contamination. Water column denitrification can be excluded, as oxygen concentrations are with between 6 and 9.5 mg/l high (oxygen saturation between 60 and 130%: Ferreira et al., 2001).

Heavy $\delta^{15}N$ values in sediments directly off the Tagus Estuary and Douro River mouths are interpreted as the traces of estuarine and riverine discharge, transporting agriculturally influenced $\delta^{15}N$ signal to the shelf.

Intermediate $\delta^{15}N$ values between 5 and 6‰ are found in the marine dominated sediments of the Nazaré region and of the northwestern and southeastern parts of the Tagus Prodelta. These $\delta^{15}N$ values are within the range of marine $\delta^{15}NO_3^-$ (5–6‰, Liu and Kaplan, 1989), which is the dominant NO_3^- source during coastal upwelling (Figs. 3 and 5). A gradient towards heavier $\delta^{15}N$ values offshore ($R^2=0.41$) justifies the interpretation of sedimentary $\delta^{15}N$ values in terms of NO_3^- utilisation. However, the fact that the surface sediment $\delta^{15}N$ is most likely an integrated signal of several upwelling seasons, combined with the spatial variability of upwelling in the Nazaré region blurs the gradient from proximal light $\delta^{15}N$ to distal heavier $\delta^{15}N$. Instead, $\delta^{15}N$ values in the range of marine $\delta^{15}NO_3^-$ imply spatially averaged complete NO_3^- assimilation. The consequent NO_3^- limitation of productivity is supported by water column NO_3^- concentrations close to zero during summer and autumn, but coevally higher concentrations of other nutrients (phosphate, silica) (Moita, 2001).

$\delta^{15}N$ values below 5‰ are observed in the offshore Douro samples and in the northern Sines region (Fig. 2 and 6). In both regions, relatively high C_{org}/N_{total} ratios indicate no bacterial inputs (Bordovskiy, 1965) and thus no influence of N_2-fixation. Hence, the $\delta^{15}N$ values imply a close proximity to the upwelling centre and a high NO_3^- utilisation of 80–95% (Altabet and Francois, 1994; Montoya, 1994). In the Douro region, satellite chlorophyll images show a regularly large offshore extend of high chlorophyll concentrations and thus upwelling (Fig. 1). Hence, the Douro surface sediments are located within the relatively static upwelling centre.

In the Sines upwelling is largely restricted to the coast (Fig. 1), generating low $\delta^{15}N$ values. Particularly in southern samples $\delta^{15}N$ values are below 4‰ (Fig. 5). These match with high chlorophyll and NO_3^- concentrations between C. San Vicente and south of C. Sines (Fig. 1, Moita, 2001), extending over the southern part of the Sines sampling area. Accordingly low $\delta^{15}N$ values in the southern Sines samples reflect stronger upwelling southward. N_2-fixation, which could lead to low $\delta^{15}N$ during oligotrophic, non-upwelling phases is contradicted by C_{org}/N_{total} ratios, which are in a reasonable marine range (Mil-Homens, 2006 and references therein).

6. Summary

Organic matter along the Portuguese margin appears to be primarily of marine origin, except where large rivers contribute significant amounts of terrigenous sediment to the shelf. Here marine and terrigenous organic matter mixes, resulting in intermediate C_{org}/N_{total} and $\delta^{13}C_{org}$ values. This is the case in the coastal Douro and Tagus samples, where heavy $\delta^{15}N$ values in coastal and estuarine sediments indicate an input of agriculturally affected DIN. Particularly inside the uppermost part of the Tagus Estuary, thorough mixing of marine and terrigenous organic matter is reflected by the geochemical signature. Estuarine $\delta^{15}N$ values appear to be affected by the influx of agriculturally affected DIN. Sediment discharge through the Tagus Estuary mouth occurs mainly westwards to the Tagus mud belt, reflected by a stronger terrigenous source signature and relatively heavy $\delta^{15}N$ values in samples west of the estuary mouth, compared to sediments of the southern and northern Tagus prodelta. In the Douro region, more offshore samples show also a considerable terrestrial organic matter fraction, but $\delta^{15}N$ values indicate a close proximity to the upwelling centre, which regularly extends considerably offshore.

Sediments in the Nazaré region show mainly marine provenance of organic matter, with small contributions of terrigenous material close to the canyon top. $\delta^{15}N$ values in the range of marine $\delta^{15}NO_3^-$ indicate complete NO_3^- assimilation, which is supported by the almost complete depletion of surface water NO_3^- during upwelling. Spatial and temporal variability of upwelling and the time-averaged $\delta^{15}N$ signal in surface sediments results in an only slight gradient towards heavier $\delta^{15}N$ values offshore.

Surface sediments from the Sines region show a clear marine provenance. Stronger upwelling in the southern part of the Sines region, extending southward towards C. San Vicente, is evidenced by light $\delta^{15}N$ values.

The interpretation of sedimentary $\delta^{15}N$ values as a result of fractional NO_3^- utilisation is justified by the absence of processes like N_2-fixation or water column denitrification, which would be reflected by low C_{org}/N_{total} ratios or oxygen deficiency. However, a higher spatial coverage along the Portuguese margin, particularly offshore, is required to substantiate the interpretation in terms of NO_3^- utilisation and the effect of the supply of upwelled marine NO_3^-.

Acknowledgements

The work was conducted as a part of the SEDPORT project (Sedimentation Processes on the Portuguese Margin: The Role of Continental Climate, Ocean Circulation, Sea Level, and Neotectonics) and funded by the German Science Foundation (DFG) as part of the EUROMARGINS/EUROCORES program. Samples were provided by the Marine Geology department of the Instituto Nacional de Engenharia, Tecnologia e Inovação (INETI, former IGM), Lisbon, Portugal.

Thanks are also due to the crew of *RV Poseidon* during the cruise PO304, to A. Völker, S. Lebreiro, E. Salgueiro, I. Gil, J. Köster and C. Wienberg for their discussions and additional information as well as to H. Buschhoff, M. Segl and B. Meyer-Schack for their technical support.

References

Abrantes, F., Moita, M.T., 1999. Water column and recent sediment data on diatoms and coccolithophorids, off Portugal, confirm sediment record of upwelling events. Oceanol. Acta 22 (3), 319–336.

Altabet, M.A., Francois, R., 1994. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. Glob. Biogeochem. Cycles 8 (1), 103–116.

Bordovskiy, O.K., 1965. Sources of organic matter in marine basins. Mar. Geol. 3, 5–31.

Craig, H., 1953. The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acta 3, 53–92.

Dias, J.M.A., Nittrouer, C.A., 1984. Continental shelf sediments of northern Portugal. Cont. Shelf Res. 3 (2), 147–165.

Dias, J.M.A., Jouanneau, J.M., Gonzalez, R., Araujo, M.F., Drago, T., Garcia, C., Oliveira, A., Rodrigues, A., Vitorino, J., Weber, O., 2002. Present day sedimentary processes on the northern Iberian shelf. Prog. Oceanogr. 52, 249–259.

Drago, T., Araujo, F., Valerio, P., Weber, O., Jouanneau, J.M., 1999. Geomorphological control of fine sedimentation on the northern Portuguese shelf. Bol. Inst. Esp. Oceanogr. 15 (1–4), 111–122.

Ferreira, J.G., Simas, T., Nunes, J.P., 2001. Production and fate of organic matter: Organic matter cycling models in estuaries. European Salt Marsh Modelling — EUROSSAM Final Report. DGXII—Environment Programme: Part 2, Task 4. Project ENV4-CT97-0436. 63 pp.

Fiúza, A.F.G., 1983. Upwelling patterns off Portugal. In: Suess, E., Thiede, J. (Eds.), Coastal Upwelling: Its Sediment Record. Plenum, New York, pp. 85–98.

Fontugne, M.R., Duplessy, J.C., 1981. Organic carbon isotopic fractionation by marine phytoplankton in the temperature range −1 to 31 °C. Oceanol. Acta 4 (1), 85–90.

Fontugne, M.R., Jouanneau, J.M., 1987. Modulation of the particulate organic carbon flux to the ocean by a macrotidal estuary: evidence from measurements of carbon isotopes in organic matter from the Gironde system. Estuar. Coast. Shelf Sci. 24, 377–387.

Freudenthal, T., Neuer, S., Meggers, H., Davenport, R., Wefer, G., 2001. Influence of lateral particle advection and organic matter degradation on sediment accumulation and stable nitrogen isotope ratios along a productivity gradient in the Canary Islands region. Mar. Geol. 177 (1–2), 93–109.

Goñi, M.A., Ruttenberg, K.C., Eglinton, T.I., 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. Geochim. Cosmochim. Acta 62 (18), 3055–3075.

Jouanneau, J.M., OMEX-I Project members, 2004. Grain Size Analysis of Sediment Core Plutur6-BoxT01 to 25. PANGAEA. doi:10.1594/PANGAEA.217915.

Jouanneau, J.M., Garcia, C., Oliveira, A., Rodrigues, A., Dias, J.A., Weber, O., 1998. Dispersal and deposition of suspended sediment on the shelf off the Tagus and Sado estuaries, S.W. Portugal. Prog. Oceanogr. 42, 233–257.

Lima, L., 1971. Distribuição dos Minerais Argilosos na Plataforma Continental entre os Cabos Raso e Espichel. 1° Congresso Hispano–Luso–Americano de Geologia Económica, Madrid.

Liu, K.-K., Kaplan, I.R., 1989. The eastern tropical Pacific as a source of 15 N-enriched nitrate in seawater off southern California. Limnol. Oceanogr. 34 (5), 820–830.

Middelburg, J.J., Nieuwenhuize, J., 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde estuary. Mar. Chem. 60 (3–4), 217–225.

Mil-Homens, M., 2006. Assessment of Heavy Metal Contamination in Three Areas of the Portuguese Shelf. PhD Thesis, Department of Geology, Earth Science Centre, Göteborg University. 128 pages.

Miltner, A., Emeis, K.-C., Struck, U., Leipe, T., Vos, M., 2005. Terrigenous organic matter in Holocene sediments from the Central Baltic Sea, NW Europe. Chem. Geol. 216, 313–328.

Moita, M.T., 2001. Estrutura, variabilidade e dinâmica do fitoplâncton na costa de Portugal continental. Ph.D. thesis, Faculdade de Ciências da Universidade de Lisboa. 272 pages.

Moita, M.T., Oliveira, P.B., Mendes, J.C., Palma, A.S., 2003. Distribution of chlorophyll a and *Gymnodinium catenatum* associated with coastal upwelling plumes off central Portugal. Acta Oecologica. Proceedings of the Plankton Symposium, Espinho, Portugal, vol. 24 (Supplement 1), pp. S125–S132.

Montoya, J.P., 1994. Nitrogen isotope fractionation in the modern ocean: implications for the sedimentary record. In: Zahn, R., Pedersen, T.F., Kaminski, M.A., Labeyrie, L. (Eds.), Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change. NATO ASI Series, vol. 17. Springer, Berlin, pp. 259–279.

Müller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochim. Cosmochim. Acta 41, 765–776.

Müller, P., Schneider, R., Ruhland, G., 1994. Late Quaternary pCO_2 variations the Angola current: evidence from organic carbon $\delta^{13}C$ and alkenone temperatures. In: Zahn, R., et al. (Ed.), Carbon Cycling in the Glacial Ocean: Constraints of the Ocean's Role in Global Change. NATO ASI Series, vol. 1(17). Springer, pp. 343–366.

Oliveira, I., Valle, A., Miranda, F., 1982. Littoral problems in the Portuguese west coast. Proc. Coastal Eng. 82, 1950–1969.

Oliveira, A., Vitorino, J., Rodrigues, A., Jouanneau, J.M., Dias, J.A., Weber, O., 2002. Nepheloid layer dynamics in the northern Portuguese shelf. Prog. Oceanogr. 52, 195–213.

Peters, K.E., Sweeney, R.E., Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23 (4), 598–604.

Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of seawater. In: Hill, M.N. (Ed.), The Sea, vol. 2. Wiley, New York, pp. 26–79.

Sackett, W.M., Thompson, R.R., 1963. Isotopic organic carbon comnposition of recent continental derived clastic sediments of the East Gulf Coast, Gulf of Mexico. AAPG Bull. 47, 525–532.

Sackett, W.M., Eckelmann, W.R., Bender, M.L., Bé, A.W.H., 1965. Temperature dependence of carbon isotope composition in marine plankton and sediments. Science 148, 235–237.

Schubert, C.J., Calvert, S.E., 2001. Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. Deep-Sea Res., Part 1, Oceanogr. Res. Pap. 48, 789–810.

Schubert, C.J., Nielsen, B., 2000. Effects of decarbonation treatments on $\delta^{13}C$ values in marine sediments. Mar. Chem. 72, 55–59.

Silva, J.F.D., Duck, R.W., Hopkins, T.S., Anderson, J.M., 2002. Airborne observations of water circulation in the nearshore zone of the Aveiro Coast, Northern Portugal. Littoral 2002, The Changing Coast, Porto, Portugal.

Smith, B.N., Epstein, S., 1971. Two categories of $^{13}C/^{12}C$ ratio for higher plants. Plant Physiol. 47, 380–384.

van Weering, T.C.E., de Stigter, H.C., Boer, W., de Haas, H., 2002. Recent sediment transport and accumulation on the NW Iberian margin. Prog. Oceanogr. 52 (2–4), 349–371.

Wada, E., Minagura, M., Mizutani, H., Tsuji, T., Imaizumi, R., Karasawa, K., 1987. Biogeochemical studies on the transport of organic matter along the Otsuchi River watershed, Japan. Estuar. Coast. Shelf Sci. 25, 321–336.