Diagenetic state and source characterization of marine sediments from the inner continental shelf of the Gulf of Cádiz (SW Spain), constrained by terrigenous biomarkers

Laura Sánchez-García\textsuperscript{a,}\textsuperscript{*}, J. Ramón de Andrés\textsuperscript{a}, J. Antonio Martín-Rubi\textsuperscript{a}, Patrick Louchouarn\textsuperscript{b,c}

\textsuperscript{a} Instituto Geológico y Minero de España, IGME, Ríos Rosas 23, 28003 Madrid, Spain
\textsuperscript{b} Department of Marine Science, Texas A&M University at Galveston, Galveston, TX 77553, USA
\textsuperscript{c} Department of Oceanography, Texas A&M University, College Station, TX 77843-3146, USA

\textbf{A R T I C L E   I N F O}

Article history:
Received 11 January 2008
Received in revised form 28 October 2008
Accepted 1 November 2008
Available online 8 November 2008

\textbf{A B S T R A C T}

Surface sediments from the Gulf of Cádiz (GoC) were analyzed by alkaline CuO oxidation, in order to estimate the contribution of terrigenous organic matter (TOM) to the inner continental shelf of the southwest Iberian Peninsula. The parallel analysis of sediment samples from the two most important rivers draining to this coastal area (i.e. Guadiana River and Tinto–Odiel fluvial system) provided fundamental information regarding local terrestrial sources. Relatively constant intensive lignin parameters (\(S:V = 1.0 \pm 0.1\) and \(C:V = 0.22 \pm 0.04\)) and high values of the lignin phenol vegetation index (LPVI = 155 ± 43) indicated that non-woody angiosperm tissues constitute the dominant component of vascular plant material reaching the shelf sediments. The NW to SE decreasing isotopic (\(^{13}C\)) and molecular (\(A_s\)) signatures found among the sediments, coinciding with the Guadiana delivery plume, suggest that this river is the main terrestrial source in the inner GoC shelf. Slightly elevated values of degradation indicative ratios ([Ad:Al]_v = 0.41 ± 0.10; [Ad:Al]_f = 0.34 ± 0.07; [3,5-Bd:V] = 0.14 ± 0.05; \(P:[V + S] = 0.24 \pm 0.09\)) suggested the alteration state of the shelf sediments. The two fold higher ratios of the river sediments (Guadiana: [Ad:Al]_v = 0.82 ± 0.08; [Ad:Al]_f = 0.84 ± 0.03; Tinto–Odiel: [Ad:Al]_v = 0.86 ± 0.12; [Ad:Al]_f = 0.83 ± 0.013) and the increasing degradation trend observed outward in the shelf, lead us to consider preferential sorption processes, instead of in situ diagenesis, to affect the degradation signature of the shelf sediments. Preferentially solubilized degraded OM is more likely to be sorbed and stabilized prior to transport to the marine system, showing an apparently more advanced degradation state. The use of the 3,5-Bd:V ratio in conjunction with [Ad:Al]_f revealed a composition continuum of the sedimentary OM ranging from fresh plant materials to highly altered soil humic constituents. Elemental and molecular analyses show a land to sea gradient by a NW to SE decrease of the terrestrial influence, accounting for larger terrestrial inputs (TOM: 71–98\%) in those sediments near the Guadiana mouth, and predominantly autochthonous composition (TOM: 42–50\%) in those located offshore. This work utilizes lignin derived biomarkers to determine the contribution of terrigenous OM delivered to this poorly described coastal area from regional rivers. Within a context of increasing international efforts to better understand the global C cycling, this study illustrates the relevance of using the alkaline CuO oxidation approach to evaluate C budgets and continental influence in river dominated ocean margins.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Coastal environments are sensitive areas of great environmental and socio-economic concern in terms of ecosystem preservation and sustainable management. Research on transport and storage of materials in these areas has been recognized as critical for the understanding of the global carbon cycle. The significant continental input occurring in these areas is the main source for a broad spectrum of both natural and anthropogenically derived organic materials introduced into the marine environment. Continental margins (deltas and shelves) are the ocean’s major sites of organic matter (OM) preservation, accounting for over 80\% of the global carbon burial (Hedges and Keil, 1995, and references therein). Burial on the shelves is enhanced by high sedimentation rates, stabilization of OM due to sorption onto mineral surfaces, delivery of continental derived OM and high productivity rates that characterize much of the coastal ocean (Gohi et al., 2000). One of the most important yet poorly understood issues of OM...
preservation in oceans is the role played by the OM composition in coastal margins (Goñi et al., 2000). Although numerous studies have investigated a variety of mechanisms that influence carbon preservation in the ocean (e.g. Emerson and Hedges, 1988; Keil et al., 1994; Hartnett et al., 1998), there is a need to gain a better understanding of the basic processes that control the organic carbon (OC) cycle in river dominated ocean margins to predict how climate change will impact its two main components – terrigenous and marine OC (Goñi et al., 2000).

In this context, organic compounds with high relative residence times and resistance to degradation, such as lignin, are particularly useful to monitor the organic carbon cycle in oceans. Lignin is the second most abundant biomacromolecule on earth after cellulose, belonging to a suite of relatively recalcitrant molecular organic compounds, which compose vascular or ‘higher’ plants (de Leeuw and Largeau, 1993). Since vascular plants are essentially confined to land and constitute the major source of TOM to the ocean, lignin can serve as an unambiguous marker of land derived material inputs to aquatic systems (Louchouarn et al., 1999; Houel et al., 2006). The alkaline CuO oxidation of lignin macromolecules yields phenol compounds that have been used extensively in the literature to trace the source and composition of TOM inputs to lacustrine (Ishiwatari and Uzaki, 1987), estuarine (Readman et al., 1986; Louchouarn et al., 1997, 1999), coastal shelf (Hedges et al., 1988a; Goñi et al., 1998; Keil et al., 1998; Dickens et al., 2007) and pelagic marine (Prahl et al., 1994) sediments. Additionally, several studies have employed some specific lignin ratios to identify humified soil OM associated with fine clay minerals, proposing them as robust tracers of terrestrial OC in aquatic systems (Houel et al., 2006; Dickens et al., 2007).

As an active coastal system, located at the confluence of the Atlantic Ocean and the Mediterranean Sea (SW Spain), the Gulf of Cádiz (GoC) is expected to play an important role in OM burial, given the important input of terrigenous materials (both organic and inorganic) that it receives. Since little is known about OM dynamics in this part of the Iberian continental shelf (Sánchez-García et al., 2008), this study provides the first background information to further understand the factors that control the sources and fate of TOM in this coastal system. We address this issue by examining the organic composition of surface sediments from the GoC inner shelf at the elemental, isotopic and molecular level. The analytical approach includes the characterization of land derived OM in the sediments using a large number of lignin oxidation by-products (LOP), as terrigenous biomarkers to estimate the continental influence on the marine system. To constrain the origin and characteristics of the terrestrial OM accumulating in the GoC shelf, we compare the LOP in the shelf with those from sediments collected from the main rivers draining the region.

2. Materials and methods

2.1. Environmental setting and sampling

The present study was carried out on the northern margin of the GoC (SW Spain), on a section of the inner continental shelf located between the mouths of the Guadiana and Tinto–Odiel rivers (6°55.29′–7°20.49′W/36°56.7–37°9.4′N; Fig. 1). The out flows of the Guadiana, Piedras, and Tinto–Odiel rivers disperse from west to east, forming a medium energy mesotidal system along the eastward coastal stretch of the GoC (Lobo et al., 2001). Sediments in this area are supplied from two major sources: sediment contribution of the Guadiana River, estimated over the last 44 yr between 44.0 and 57.9 \times 10^{6} m^3/yr (Morales, 1997), and the intense south-eastward littoral drift (González et al., 2004), which carries, together with the advection of the North Atlantic Surficial Current, a potential sediment transport estimated between 18 and 30 \times 10^{6} m^3/yr (Cuenca, 1991). Despite the large sediment retention in the Tinto–Odiel Estuary, which leads to wide tidal alluvial basins, this dual river system contributes important sediment discharge to the shelf. In contrast, the inputs from the Piedras River are much less important (Van Geen et al., 1997).

A suite of 15 surficial sediments (upper 20 cm) were sampled in 2001 from the GoC inner shelf by means of a Shipeck dredge along the eastward dispersion plume of the Guadiana River. In a similar way, riverine sediments were obtained between 2000 and 2001 from the most representative rivers discharging in this coastal region (Guadiana, n = 3; Tinto and Odiel, n = 5). All the samples were frozen and stored from the time of collection until processed, when they were either freeze dried or oven dried (40 °C), crushed and homogenized at <0.25 mm prior to analysis. According to Shephard (1954) clastic textural classification, most of the collected sediments consisted mainly of silt–clay clastic minerals, with minor sand contributions, typical of sediment mixtures found on continental–marine transition margins. The contribution of sand became more substantial in sites closer to the Guadiana mouth. Despite the absence of accurate data of the accumulation rate for the particular studied area, a sedimentation rate of ~4 mm/yr can be approximated from the empirical relationship between $\omega$ (sediment accumulation rate, cm/yr) and the ocean depth established by Middelburg and co-workers (1997) which is based on a large global database of $^{210}$Pb profiles (n = 220). Thus, according to the overall grab depth of 20 cm employed in the present study, we may estimate a rough time scale of 45–50 yr for the GoC shelf sediments.

2.2. Elemental analyses

Total carbon (TC) and total nitrogen (TN) were determined on freeze dried sediments by combustion using a Eurovector elemental analyzer. Another set of samples previously decarburnated with concentrated HCl were analyzed to determine the OC content.

Stable isotopic analyses of OC were performed on previously acidified bulk samples. Accurately weighed aliquots of the decarbonated samples were combusted using a Eurovector elemental analyzer (EuroEA-3000) coupled to an IsoPrime isotope ratio mass spectrometer (GV Instruments). The OC was combusted to CO$_2$ at 1050 °C and compared to pre-calibrated reference CO$_2$ gas. The results are reported as $\delta^{13}$C values relative to the Pee Dee Belemnite limestone standard (PDB) in the usual parts per thousand (‰) notation. The standard deviation for this procedure is better than 0.05‰.

2.3. CuO oxidation

Molecular analyses were performed according to the CuO oxidation method initially developed by Hedges and Ertel (1982) and Goñi and Hedges (1992), with slight modifications (Louchouarn et al., 2006). Briefly, a sediment amount providing 2–4 mg OC (Louchouarn et al., 2000) was oxidized under alkaline conditions with CuO at 155 °C for 2–4 hr. The CuO oxidation by-products were performed by gas chromatography-
mass spectrometry on a Varian Ion Trap GC/MS system (3800/4000) fitted with a fused capillary column (VF 5MS, 60 m x 0.25 mm ID; Varian Inc.). Each sample was injected, under splitless injection mode, into a straight glass liner inserted into the GC injection port and He was used as the carrier gas (~1.3 ml/min). The GC oven was temperature programmed from 100 °C at 4 °C/min and held constant at the upper temperature for 10 min. The GC injector and GC-MS interface were both maintained at 300 °C. The mass spectrometer was operated in the electron impact mode (EI, 70 eV), in full scan mode. Compound identification was performed using column retention times and by comparing the full spectra of each sample to those produced by commercially available standards. Quantification was performed using relative response factors adjusted to trans-cinnamic acid as the internal standard. Replicate analyses of standard estuarine sediments (i.e. NIST SRM 1944; n = 12) showed that the analytical precision of the major CuO oxidation products and related parameters averaged ~5%. The average standard deviation obtained from replicate analyses of the GoC samples was in the same range (5–10%).

2.4. Description of the lignin parameters used

Over the past 2–3 decades lignin oxidation products (LOP) have been used extensively in geochemistry to characterize the sources and diagenetic state of vascular plant materials found in aquatic systems. For example, internal LOP ratios such as syringyl to vanillyl and cinnamyl to vanillyl phenols (\( S:\bar{V} \) and \( C:\bar{V} \), respectively), have been used for tissue type and taxonomic source reconstructions (i.e. angiosperm versus gymnosperm, soft versus hard tissues). Acid to aldehyde ratios from vanillyl phenols (\([\text{Ad}:\text{Al}]_\bar{V}\)) have provided information on the oxidative degradation of TOM prior to sediment burial. Other specific biomarker ratios, such as 3,5-dihydroxybenzoic acid to vanillyl phenols (3,5-Bd:V) has been applied in terrestrial and marine systems, in conjunction with the (Ad:Al) ratio, to characterize the degradation state of complex terrestrial organic mixtures (Pralh et al., 1994; Louchouarn et al., 1999) and trace inputs of soil OM to sediments (Louchouarn et al., 1999; Farella et al, 2001; Houel et al., 2006; Dickens et al., 2007).

Some other ratios, such as p-hydroxyphenols to the sum of syringyl and vanillyl phenols (\( P:\bar{V} + \bar{S} \)), afford information about specific lignin degradation pathway (brown-rot; Dittmar and Lara, 2001). All these ratios have been used in the present study to characterize the sources and alteration state of sedimentary OM in the GoC inner shelf. Of particular interest is the comparison of compositional signatures between the marine and river samples which permit a finer analysis of the OM degradation state and an improved source reconstruction of the TOM inputs.

2.5. Statistical analysis

In order to identify the specificity of individual variables in tracing OM input and similarity among the samples collected, two different statistical analyses were applied in this study: cluster and principal component analysis (PCA). The statistical calculations were conducted using the statistics software package Statgraphics Plus (version 2.0). PCA and cluster analyses were performed on the elemental, stable carbon isotopic and biomarker data (lignin oxidation products, normalized to the OC content), to determine the factors controlling the OM composition of the GoC sediments.

3. Results and discussion

3.1. Elemental and molecular composition of marine sediments and humic substances

Elemental, molecular and stable carbon isotopic compositions of the studied sediments are presented in Table 1 (shelf) and Table 2 (rivers). The OC concentrations of shelf sediments range from 0.5

---

**Fig. 1.** Map of the Gulf of Cádiz inner continental shelf, showing the location of the marine (n = 15) and river (Guadiana: n = 3, Tinto–Odiel: n = 5) sediment samples.
stations show a factor of four decrease in S:O ratios for T–O 4 (1.1) and T–O 3 (0.7) compared to their Guadiana counterparts (1.3 ± 0.5) (Table 2). Among the shelf sediments, S-11, S-12 and S-14 display the highest OC contents, being enriched by 1.57 ± 0.82 mg/100 mg OC), with two stations (S-7 and S-10) containing almost two fold with respect to the marine sediment average (1.57 ± 0.82 mg/100 mg OC). In contrast, S-10, S-11 and S-12 display significantly lower OC contents (5.3 ± 0.8) mg/100 mg OC respectively; Table 1). In contrast, all the other shelf stations have lower OC contents, with the S-7 station showing the lowest value of 3.6 mg/100 mg OC.

The elemental composition of the shelf sediments from the inner Gulf of Cádiz shows a clear dominance of carbon (C) over nitrogen (N) as the major elements, with C:N ratios ranging from 10:1 to 40:1. The OC content of the sediments is relatively low, with values ranging from 1.0 to 4.5 mg/100 mg OC. The TOM content is also low, with values ranging from 0.01 to 0.18 mg/100 mg OC.

The lignin yields (Table 1), in agreement with the depleted isotopic d13C, stable carbon isotopic composition of organic carbon (% PDB; S4 mass normalized yields of the eight lignin derived phenolic oxidation products (mg/g dw); A4, carbon normalized yields of the eight lignin derived phenolic oxidation products (mg/100mg OC); (S/V), ratio of vanillic acid to vanillin; (Ad:Al), ratio of vanillyl acid to vanillin; (Ad:Al), ratio of vanillic acid to vanillin; (Ad:Al), ratio of syringic acid to syringyl; 3.5-Bd/V, ratio of dihydroxybenzoic acid to vanillic acid; P(V+S), ratio of p-hydroxyacetophenones to the sum of vanillic and syringyl phenols; PON:P, ratio of p-hydroxyacetophenones to total p-hydroxyphenols; Aver, average; SD, standard deviation.

Table 2
Elemental and molecular composition, and molecular intensive ratios of the sediment samples from the rivers discharging to the inner continental shelf of the Gulf of Cádiz, OC, total organic carbon (mg/100 mg dw); (CN), total carbon organic to total nitrogen atomic ratio; d13C, stable carbon isotopic composition of organic carbon (% PDB); S4, mass normalized yields of the eight lignin derived phenolic oxidation products (mg/g dw); A4, carbon normalized yields of the eight lignin derived phenolic oxidation products (mg/100mg OC); (S/V), ratio of syringyl to vanillic phenols; (CV), ratio of cinnamyl to vanillic phenols; (Ad:Al), ratio of vanillic acid to vanillin; (Ad:Al), ratio of syringic acid to syringyl; 3.5-Bd/V, ratio of dihydroxybenzoic acid to vanillic acid; P(V+S), ratio of p-hydroxyacetophenones to the sum of vanillic and syringyl phenols; PON:P, ratio of p-hydroxyacetophenones to total p-hydroxyphenols.

| OC | C:N | d13C | S4 | A4 | CV | S/V | LPVI | (Ad:Al)s | (Ad:Al)i | 3.5-Bd/V | P(V+S) | PON:P |
|----|-----|------|----|----|----|-----|------|-------|---------|---------|---------|-------|------|
| Guadiana | 1.9 | 10.3 | −26.6 | 0.73 | 1.78 | 0.43 | 1.00 | 369.2 | 0.74 | 0.80 | 0.07 | 0.15 | 0.12 |
| G1 | 1.6 | 12.4 | −26.8 | 0.46 | 2.90 | 0.25 | 0.84 | 145.4 | 0.84 | 0.86 | 0.13 | 0.17 | 0.13 |
| G2 | 0.5 | 11.0 | −24.8 | 0.13 | 2.76 | 0.20 | 0.93 | 122.8 | 0.90 | 0.87 | 0.09 | 0.14 | 0.11 |
| G3 | 1.3 | 11.2 | −26.0 | 0.44 | 3.15 | 0.29 | 0.92 | 212.5 | 0.82 | 0.84 | 0.10 | 0.16 | 0.12 |
| Aver | 0.8 | 1.1 | 1.1 | 0.30 | 0.56 | 0.12 | 0.08 | 136.2 | 0.08 | 0.03 | 0.03 | 0.01 | 0.01 |
| SD | | | | | | | | | | | | | |
| Tinto–Odiel | 1.5 | 11.7 | −23.2 | 0.24 | 1.59 | 0.17 | 0.94 | 109.9 | 0.79 | 0.83 | 0.17 | 0.19 | 0.11 |
| T–O 1 | 1.0 | 11.7 | −23.1 | 0.43 | 4.28 | 0.19 | 0.92 | 119.6 | 0.76 | 0.74 | 0.07 | 0.12 | 0.11 |
| T–O 2 | 0.7 | 9.8 | −24.5 | 0.12 | 1.80 | 0.21 | 1.41 | 212.4 | 0.86 | 0.76 | 0.17 | 0.20 | 0.11 |
| T–O 3 | 1.1 | 11.9 | −24.0 | 0.18 | 1.62 | 0.14 | 1.34 | 153.4 | 1.07 | 1.05 | 0.20 | 0.17 | 0.10 |
| T–O 4 | 2.0 | 10.9 | −23.9 | 0.31 | 1.60 | 0.25 | 1.00 | 183.3 | 0.80 | 0.70 | 0.15 | 0.22 | 0.09 |
| Aver | 1.3 | 11.2 | −23.7 | 0.26 | 2.18 | 0.19 | 1.12 | 152.1 | 0.86 | 0.83 | 0.15 | 0.18 | 0.10 |
| SD | 0.5 | 0.9 | 0.3 | 0.12 | 1.18 | 0.04 | 0.23 | 43.9 | 0.12 | 0.13 | 0.05 | 0.04 | 0.01 |

The variability observed in the isotopic composition of the shelf sediments (d13C = −24.3 ± 2.8‰) is consistent with that of the lignin yields. Overall, lighter d13C values (−25.1% to −25.9‰) are found in these sediments presenting higher carbon normalized lignin yields (Table 1), in agreement with the depleted isotopic signatures showed by the nearby Guadiana River (d13C = −26.0‰). In contrast, lower A4 and heavier isotopic signatures (−22.6‰ to −23.1‰) characterize the outermost marine sediments, with the
exception of station S-7, which contains the richest lignin content ($A_8 = 2.92 \text{ mg/100 mg OC}$) and one of the heaviest isotopic signatures ($\delta^{13}C = -23.0\%$) (Table 1). This heterogeneous composition indicates diverse source contributions, whether terrigenous or marine derived (Sánchez-García et al., 2008), and may be reflective of dilution effects from phytoplankton derived OM, as well as particle size sorting causing varying proportions of lignin rich TOM, given that large grain sizes typically retain more lignin than smaller sizes (e.g. Louchouarn et al., 1999; Goni et al., 2000; Kendall et al., 2001). This process (discussed later in more detail) would explain the enhanced lignin yields observed in the sediments closer to the mouths of both the Guadiana and Tinto–Odiel rivers, where higher sand proportions (3–52%) were observed.

Recently, Sánchez-García et al. (2008) employed lipid biomarker patterns to describe the influence of continental inputs on sedimentary OM of the GoC. This study reported that land derived long chain hydrocarbon assemblages were observed almost exclusively in sediments closer to the Guadiana River mouth, whereas most of the remaining samples displayed instead predominant marine signatures. Consistent with these observations, lignin enriched $A_8$ values (1.35–2.45 mg/100 mg OC, Table 1) are observed in the samples located near the Guadiana mouth, whereas $A_8$ values decrease below 0.83 mg/100 mg OC along the river dispersion plume, except for S-7, which shows a notably different composition. This latter sample displays the highest lignin yield in the shelf (2.92 mg/100 mg OC; Table 1), despite the largely marine hydrocarbon signature described for this sediment (Sánchez-García et al., 2008). Considering its location, the land derived OC supply in this sample may be responding to contributions of the Tinto–Odiel system, rather than being affected by the Guadiana (see discussion in Section 3.4). In fact, very similar isotopic signatures are measured in both S-7 ($\delta^{13}C = -23.0\%$) and the Tinto–Odiel fluvial system ($\delta^{13}C = -23.7\%$) (Tables 1 and 2, respectively). Considering the abundance of grassland and brush vegetation described around the Tinto–Odiel watershed (e.g. Cytisus, Cistus, Halimium, Artemisia, Ceratonia, Limoniastrum, Arthrocnemum; Ruiz de la Torre, 1990), inputs from C4 plants could constitute one of the most important terrestrial sources to these sediments. In contrast, the lighter $\delta^{13}C$ signals ($-24.4\%$ to $-25.9\%$) observed in the northwest-most sediments (S-1, S-2, S-3, S-4, S-5, S-6, S-10, S-11 and S-12) are closer to the Guadiana mean value ($-26.0\%$), presumably reflecting the typical signature of the predominance of C3 plants in the nearby area (Cytisus grandiflorus, Cistus sp., Halimium halimifolium; Ruiz de la Torre, 1990).

In conjunction with the lignin and isotopic signatures, the elemental composition of the OM can provide relevant qualitative information of the sources and compositional patterns of the organic materials reaching the sedimentary record (Hedges et al., 1988a). The OM composition of the GoC sediment is graphically presented in Fig. 3, where C:N (OC to TN atomic ratio) and $A_8$ are plotted, including three general possible OC sources (marine algae, C3- and C4-vascular plant detritus, as well as surface and deep soils). Overall the GoC sediments exhibit a large range of C:N values (6.2–23.3, mean of 9.3 ± 4.5; Table 1), which indicates

Fig. 2. Organic matter distribution, lignin yield and biomarker ratios in the 15 shelf sediments of the Gulf of Cádiz.

Fig. 3. Compositional signature of the sediment OM in the shelf and river samples, as well as in different environmental compartments. Signatures of C3- and C4-vascular plants are taken from Tesi et al. (2007) and Opsahl and Benner (1995), Dalzell et al. (2005), Kuo et al. (2008), Goni and Hedges (1992), respectively; signatures of marine algae are gleaned from Tesi et al. (2007); and those of soils are adapted from Amelung et al. (1999), Farella (1998) and Houel et al. (2006).
diverse OM sources from both terrestrial and marine contributions (Fig. 3). The majority of the shelf sediments, producing A4 yields which vary between 0.5 and 2.9 mg/100 mg OC, show a significant terrestrial signature with substantial contribution from soil derived OM, particularly related to mineral soil horizons (Amelung et al., 1999; Rumpel et al., 2002; Houel et al., 2006). This is consistent with the heterogeneous size distribution of the sediments, which contain sand fractions ranging from 1% to 50% (Sánchez-García et al., unpublished results). Although the river samples show similar compositional signatures, they are characterized by slightly higher C:N ratios, approaching the values observed in surface organic rich soils and suggesting a greater contribution from plant debris. The overall lower values of the C:N ratio may indicate either dilution of TOM by authigenic OM sources or predominance of lignin poor, nitrogen rich OM, associated to fine mineral particles (Hedges and Oades, 1997; Houel et al., 2006).

3.2. Qualitative characterization of lignin sources

The plot of the lignin internal ratios (S:V versus C:V; Fig. 4) shows relatively high S:V values (1.00 ± 0.10; Table 1 and Fig. 2) suggesting that an important fraction of lignin in the shelf sediments originates from angiosperm plants. These signatures are expected to remain high despite potential biochemical alterations presumed to occur during the transport of TOM in coastal systems (Keil et al., 1998; Louchouarn et al., 1999; Benner et al., 2002). However, although the measurable decrease in this ratio is correlated with the distance away from the river mouth ($r^2 = 0.60$), it does not represent a significant change in samples of such a mixed origin, since it constitutes only ~10% of the original signature (1.06 ± 0.08, in in-shore samples, 0.90 ± 0.06, in outmost samples). In fact, similar lignin source signatures are registered in the fluvial systems (Guadiana: 0.92 ± 0.08 and Tinto–Odiel: 1.12 ± 0.23; Table 2), reinforcing the suitability of S:V as source indicator in the studied system. In addition, the shelf sediments show relatively high values of the lignin phenol vegetation index (LPVI, Eq. (1) below) described by Tareq et al. (2004), which ranges here from 100 to 238 (Table 1).

$$\text{LPVI} = \frac{|S(S + 1)/(V + 1) + 1| \times |C(C + 1)/(V + 1) + 1|}{S:V}$$ (1)

On the other hand, the relatively low C:V ratios displayed by the marine sediments (0.22 ± 0.04; Table 1 and Fig. 2), point to the moderate presence of non-woody tissues as input sources to lignin mixtures. Again, selective degradation and/or leaching processes (e.g. ester bound cinnamyl groups related to vanillyl moieties; Hedges and Prahl, 1993; Opsahl and Benner, 1995) could lead to the underestimation of non-woody material inputs to sediments of the shelf. However, this ratio is still expected to retain a good amount of source information (Hedges et al., 2000; Houel et al., 2006), given the similarity of the values measured in the nearby rivers (Guadiana: 0.29 ± 0.12 and Tinto–Odiel: 0.19 ± 0.04; Table 2). The lack of significant variation observed along the shelf transect suggests no significant alteration of the source signature during transport and deposition.

PCA and cluster analyses were performed in order to illustrate the existing relationship between $A_8$ and the p-hydroxyphenol monomers, to better understand the composition of the sediments OM. PCA produced two first principal components (Fig. 5a) explaining together 89% of the variance in the data set. The first component (PC 1) is responsible for the 76% of the variance and explains the terrigenous versus marine character of the samples. While the eight lignin derived phenols (VON, VAL, VAD, SON, SAL, SAD, CAD and FAD), along with p-hydroxyphenols (PAL, PON and PAD) (see Fig. 5 caption for the acronym equivalence), plot...
together in the right side of the PCA diagram in relation to the terrestrial character, both OC and δ13C plot in both the lower and upper parts of the left side, respectively. Given the correlation existing between the lignin derived phenols and 3,5-Bd, which falls also within the right portion of the diagram, it seems likely that this non-lignin oxidation product is derived from terrigenous rather than marine sources in the present study area. This observation is consistent with a similar relationship and conclusion from samples in the shelf region of the Gulf of Lions (Tesi et al., 2007). The second component (PC 2) explaining 12% of the variance is related to the OM content and its signature. The PC shows an inverse relationship between OC depletion and δ13C enrichment across all samples.

The PCA plot thus separates samples by their marine versus terrigenous character and lighter versus heavier isotopic composi-
tion. The samples located in the proximity of both river mouths (S-1, S-3, S-4, S-5, S-6 or S-7) show strong terrigenous character, by plotting on the right portion of the diagram. In contrast, the samples located offshore (S-8, S-9, S-13, S-14 or S-15) plot on the upper left side of the graph, displaying a higher marine influence of heavier isotopic composition and relatively poorer OC content. Additionally, whereas most of the terrigenous samples are grouped on the lower part of the graph and relatively close to each other, indicating a lighter and richer OC composition, sample S-7 is clearly set apart from the rest. Both PCA (Fig. 5a) and cluster analysis (Fig. 5b) indicate the unique character of sample S-7, which is consistent with the geochemical differences aforementioned here (higher lignin content and heavier δ13C) and in previous works (Sánchez-García et al., unpublished results), which suggests an independent source for this sample, most probably related to the Tinto–Odiel fluvial influence. These statistical analyses contribute to illustrate the factors controlling the OM sources and composition of the studied sediments.

3.3. Diagenetic state signatures

If the lignin derived inputs in the GoC shelf were comprised of a mixture of land organic materials, the internal (Ad/Al) ratios of lignin phenols should be indicative of different degradation states, since the vanillic acid is known to become more abundant during microbial or photochemical degradation (Aufdenkampe et al., 2001; Hernes et al., 2007). Thus, the increase observed in the (Ad:Al) ratios from NW to SW shelf sediments, could be explained by a higher degradation extent toward the SW, albeit not necessarily occurring within the sediments. Instead, the alteration could have taken place prior to the sorption process, and then solubility preferences, hydrodynamic sorting and selective transport would have resulted in increasing degradation along the land to sea terrestrial delivery path. In fact, the twofold higher (Ad:Al) ratios registered in both the Guadiana ([Ad:Al]v: 0.82 ± 0.08) and Tinto–Odiel ([Ad:Al]v: 0.86 ± 0.12) sediments, indicate the more advanced degradation state of the terrestrial fluvial sources, and lead to the consideration of mechanisms other than in situ degradation to explain the lower alteration signature of the offshore sediments. Instead, the rather altered lignin derived OM delivered by the fluvial systems may have undergone selective sorption and transport processes in relation to the size sorting observed in the shelf, as introduced in Section 3.1. Accordingly, coarser particles typically retaining more lignin would have been deposited close to the delivery site, whereas smaller sizes, presumably enriched in acidic compounds, would have been easily carried to remote locations. It seems that solubility effects and sorption partitioning of the lignin moieties prior to the entrance in the marine system, instead of diagenetic processes, explain better the apparent degradation gradient observed in the shelf sediments. In addition, the significant positive correlation (r2 = 0.94) calculated for (Ad/Al)v and (Ad/Al)2 indicates parallel behaviours of both ratios and supports the idea of more acid rich signatures in outermost sediments, due to alteration processes likely occurring prior to the inputs of the lignin components into the marine system.

The compound 3,5-Bd is thought to be a common product of soil degradation processes (Prahl et al., 1994) and its normalization to total vanillyl produces a ratio (3,5-Bd:V) that has been used effectively to trace soil OM inputs to aquatic systems (Prahl et al., 1994; Louchouarn et al., 1999; Farella et al., 2001; Houel et al., 2006; Dickens et al., 2007). Here, this ratio oscillates in the shelf between 0.07 and 0.22 (Table 1 and Fig. 2), consistently displaying enhanced values in the sediments showing higher (Ad/Al)v ratios. It has been inferred that the likely precursors of the phenolic product 3,5-Bd are not altered lignin macropolymers but tannins and other flavonoids with hydroxyl groups present in alternate positions on the aromatic rings (Goñi and Hedges, 1995). Because tannin-like materials tend to accumulate within decaying cells (de Leeuw and Largeau, 1993), the relative increase of this compound in deep soil minerals may be related to the extent of degradation and humification of fresh vascular plant
tissues (Houel et al., 2006), which is supported by extremely low 3,5-Bd content and 3,5-Bd:V ratios produced by fresh plant materials upon CuO oxidation (Louchouarn, 1997). In this study, the (Ad:Al)\(_S\) and 3,5-Bd:V signatures of the shelf sediments vary from those observed in leaf tissues to those from soil sources (Fig. 6), appearing to represent a mixture of fresh and more degraded TOM, and the positive correlation existing between both ratios (\(r^2 = 0.81\)) suggests association between both degradation indicators. On the other hand, the values measured in the Guadiana sediments are similar to those from humus materials, whereas most of the Tinto–Odiel sediments better match typical soil signatures (Farella, 1998), in both cases indicating degradation extent.

In the same way that elevated 3,5-Bd:V has been used to indicate humification processes of soil OM, increases in the \(P:(V+S)\) ratio are considered to indicate a specific lignin degradation side chain pathway (brown-rot), leading to demethylation of methoxylated vanillyl and syringyl constitutents (Dittmar and Lara, 2001). Although vascular plant tissues are not exclusive sources of p-hydroxyphenol (Goñi and Hedges, 1995), in the present study \(P\) compound inputs from autochthonous sources are probably negligible, since p-hydroxyacetophenone to total p-hydroxyphenols ratios (PON: \(P\)) remain relatively constant (0.23 ± 0.03) throughout all samples (Table 1). Since PON is derived mainly from lignin poor degraded materials upon CuO oxidation (Louchouarn, 1997). In this study, the (Ad:Al)\(_S\) and 3,5-Bd:V (Table 1) and highlights the apparent lower extent of degradation of sediments closer to the Guadiana mouth (\(P:(V+S) = 0.18 ± 0.03\) and 3,5-Bd:V = 0.11 ± 0.04) compared to those located offshore (\(P:(V+S) = 0.34 ± 0.07\) and 3,5-Bd:V = 0.17 ± 0.03). It appears that fresher lignin rich materials are preferentially retained close to land, according to the size sorting aforementioned, whereas lignin poor degraded materials are transported and deposited away from the river mouth, agreeing with the preferential transport along the land to sea continuum reported by different groups (Prahl et al., 1994; Louchouarn et al., 1999; Goñi et al., 2000). In the present case, the transport occurs almost parallel to the GoC coast, as the plume of the Guadiana River is diverted in the NW to SE direction by southeast-ward coastal dynamics and dominant winds (Morales, 1997; Lobo et al., 2001).

The non-linear relationship observed between carbon normalized lignin yields (\(A_S\)) and biomarker ratios (\(P:(V+S)\)) and 3,5-Bd:V in the shelf sediments (Fig. 7) is consistent with the signature behaviour predicted for mixtures of two end members having vastly different biomarker concentrations (Hedges and Prahl, 1993; Louchouarn et al. 1999; Houel et al., 2006). Houel et al. (2006) reported that signatures in sediments from a boreal reservoir in Québec (Canada) were controlled by a conservative mixture between two identified pools: lignin rich litter and lignin poor fine particles associated with soil mineral fractions. In this context, the marine sediments of this study distribute according to a good non-linear relationship (\(r^2 = 0.89\)) between their lignin yield and degradation extent (\(P:(V+S)\); Fig. 7a). All the samples but S-7 (see discussion below) respond to a similar mixture between fresher lignin rich matter and more altered lignin poor particles that suggest differential transport of soil size fractions with differing OM quality (Keil et al., 1998; Louchouarn et al., 1999; Goñi et al., 2000). However, the mixing model using \(A_S\) versus the 3,5-Bd:V ratio (Fig. 7b) shows a weaker fit (\(r^2 = 0.51\)), indicating that this ratio may not represent the degraded soil OM end member as well as the \(P:(V+S)\) ratio. The tight relationship of the latter parameter (Fig. 7a) confirms the role of the hydrodynamic sorting in shelf systems towards selective transport/deposition of terrigenous particles with different sizes, densities and lignin loadings along the land to sea gradient (Keil et al., 1998; Louchouarn et al., 1999; Goñi et al., 2000).

3.4. Abundance of terrestrial OM within the GoC sedimentary record

All the shelf sediments studied in this paper contain substantial amounts of terrestrial biomarkers, leading us to assume that at least some fraction of the total OM is provided from land derived sources. Consistently, carbon normalized yields of vascular biomarkers decrease with distance from the Guadiana mouth, pointing to the increasing dilution of the terrestrial signature with marine sources along the land to sea transect. The evaluation of such dilution and the quantification of the terrigenous and marine fractions (%TOM and %MOM, respectively) in the total sedimentary OM pool would provide an added constraint on the development of accurate carbon budgets for shelf systems like the GoC (Macdonald et al., 1998). In this context, a two end member isotopic mass balance approach is applied to estimate the abundance of TOM in the shelf sediments (e.g. Hedges et al., 1996a; Prahl et al., 1994; Louchouarn et al., 1999; Goñi et al., 2000) according to a linear mixing model between a marine and terrestrial end member (Louchouarn et al., 1999; Goñi et al., 2000):
%TOM = 100 × \left( \frac{[\delta^{13}C_{\text{terr}} - \delta^{13}C_{\text{mar}}]}{[\delta^{13}C_{\text{terr}} - \delta^{13}C_{\text{mar}}]} \right)

where \( \delta^{13}C_{\text{terr}} \) and \( \delta^{13}C_{\text{mar}} \) are the isotopic signatures of TOM and MOM end members. The abundance of MOM is then determined as 100 − %TOM.

Alternatively we considered using a three end member mixing model (e.g. Gordon and Goñi, 2003) relying on the double contribution of C3 and C4 derived soil OM to the terrigenous input. However, this model was considered inappropriate given the unsuitability of the C4 signatures to represent the overall set of samples, which are mostly influenced by the C3 dominant Guadiana system. In fact, the alternative Tinto–Odiel influence appears fairly restricted to S-7, which shows distinct OM composition (higher \( A_8 \) yield and enriched \( \delta^{13}C \) signature) and selective enrichment of heavy metals (As, Cu, Hg, Pb, Zn) (Sánchez-García et al., unpublished results), with respect to the rest of sediments. This heavy metal enrichment has been reported to be associated with sulphide deposits and links this sample to the historically metal rich outputs derived from the Tinto–Odiel fluvial system (van Geen et al., 1997). Hence, based on geochemical and statistical evidence (see Fig. 5), we decided to exclude this sample from the mixing model calculations in order to prevent potential biases generated by such an outlier. Thus, we propose a two end member mixing model considering marine and soil derived OM the most adequate to the quantification of terrigenous and marine contribution in this continental margin.

To this end, we consider the mean value of the Guadiana River sediments (\(-26.0 ± 1.1‰; \) Table 2) as a typical \( \delta^{13}C_{\text{terr}} \) signature, according to the dominant land influence that this river exerts on the GoC coastal system. The marine end member value was chosen on the basis of published microphytoplankton \( ^{13}C \) values measured in the Gulf of Lions (Harmelin-Vivien et al., 2008). Since no seasonal differences were observed by the authors in the microphytoplanktonic \( ^{13}C \) values, the average value of both studied seasons (spring and autumn) is considered here (\(-20.1‰\)). First order estimates of %TOM (Table 1) show a decrease of the abundance of terrigenous OC as a function of distance from the Guadiana mouth (\( r^2 = 0.74 \)). While the highest terrigenous contributions (71–98%) occur within the innermost shelf sediments (S-1, S-2, S-3, S-4, S-5, S-6, S-10, S-11 and S-12), the lowest %TOM (42–50%) are revealed in the outermost ones (S-8, S-9, S-13, S-14, S-15), revealing dominant marine inputs (Sánchez-García et al., 2008).

However, we recognize a potential caveat to this simple source reconstruction based on the proposed binary \( ^{13}C \) end member approach. Louchouarn et al. (1999) and Goñi et al. (2000) have shown that differential transport of terrestrial particles with differing size fractions and OM signatures could cause serious underestimation of the terrestrial contribution to the total pool of sedimentary OM in outer shelf environments. The reason lies in the relatively low carbon normalized yields found in fine soil particulates (Keil et al., 1994; Amelung et al., 1999; Houel et al., 2006) that are transported selectively to the outer regions of the shelves (Keil et al., 1998). According to the selective solubility and sorption processes aforementioned, a similar underestimation effect should be considered here. Hence, the low \( A_8 \) values observed in the most distant stations do not preclude high TOM content if such inputs are predominantly comprised of fine soil particulates, since we assume two general sources dominating the OM delivery: (i) a lignin rich and coarse fraction, more representative of riverine signatures, and (ii) a lignin poor source finer fractions, showing apparently more degraded signatures. We thus use a second terrigenous end member more typical of soil fine particles and which average \( A_8 \) value was derived from a series of lignin analyses from deep soils and clay fractions (Amelung et al., 1999; Rumpel et al., 2002; Houel et al., 2006).

Thus, using this lower lignin yield (1.2 ± 0.8 mg/100 mg OC, Fig. 8) we extrapolate the correlation line to the zero biomarker intercept to constrain a marine isotopic end member, which is more typical of marine signatures (−18.7‰). Recalculating the %TOM proportion using this latter marine signature changes very little the prediction of TOM proportions for inner shelf sediments but does increase substantially the estimated TOM proportions in the most distant stations (up from ~46% to ~56%). The varying signatures of 3,5-Bd:v and P/(V+S) in the sediments along the transect support the notion that fine soil particulates are selectively transported to the outer sections of the shelf and suggest that a single terrigenous end member is not appropriate for the reconstruction of TOM proportions in this system (and probably most shelf environments). Using a combination of both surface and deep soil signatures and lignin yields is critical for a better constraint on sources of TOM to aquatic systems along hydrodynamic gradients (Farella et al., 2001; Houel et al., 2006).

4. Conclusions

The lignin contribution to the sedimentary record of the GoC inner shelf was estimated using alkaline CuO oxidation method and averages 1.57 ± 0.82 mg/100 mg OC. A factor of three depletion in the carbon normalized yield was observed from the Guadiana River to the outermost shelf sediments. The examination of specific phenolic products (\( S:V \) and C:V, 1.00 ± 0.10 and 0.17 ± 0.04, respectively) revealed compositional signatures corresponding to temperate angiosperm tissues as major TOM sources. Slightly elevated (\( \text{Ad:Al} \)) and (\( \text{Ad:Al} \)) ratios in some samples suggested that at least part of the lignin present in the sediments had been oxidatively degraded. However, the two fold higher ratios measured in the river samples, together with the size sorting observed in the shelf sediments, suggest that preferential solubility and sorption fractionations as likely factors affecting the degradation signature of the sediments prior to their entrance in the marine system. Thus, the increasing trend in diagenetic ratios ((\( \text{Ad:Al} \)), (\( \text{Ad:Al} \)), 3,5-Bd:v, P/(V+S)) observed with distance away from the Guadiana River, suggests selective transport of more degraded (and lignin poor) materials along the land to sea gradient. The positive relationships observed between degradation ratios among the sediments reveal a mixture of fresh and degraded TOM within the shelf, whereas the river sediments display ratios matching either humus (Guadiana) or soil (Tinto–Odiel) signatures. A combination of molecular and isotopic signatures of
sedi-mentary OM along the land to sea transect show a decreasing gradient in TOM from the mouth of Guadiana river to the GoC shelf, revealing a significant degree of spatial heterogeneity that must be accounted for in the determination of oceanic carbon budgets. Overall, TOM dominates the composition of the innermost shelf sediments, with TOM abundances ranging from 64% to 98% (S-1, S-2, S-3, S-4, S-5, S-6, S-10, S-11, S-12), whereas autochthonous inputs predominate in outermost locations (S-8, S-9, S-13, S-14, S-15), where TOM contributes less than 40% of the sedimentary OC. These results confirm previous observations, based on lipid biomarkers reporting higher terrigenous inputs in the sediments located nearby the Guadiana delta. The relatively low $\delta^{13}$C and C/N values in the sediments suggest, however, that fine particle associ-at-ed OM may also contribute substantially to the TOM inputs to this system. Finally, despite the homogeneous taxonomic origin of the land derived OM observed along the shelf, one particular sediment (S-7) reflects instead a stronger influence of the metal rich, historically contaminated Tinto–Odiel system. The similar high carbon normalized lignin yield and relatively heavy $\delta^{13}$C signature displayed by S-7 ($\delta^{13}$C = -23.0‰) and Tinto–Odiel ($\delta^{13}$C = -23.7‰) suggest that sample S-7 is dominantly influenced by this fluvial system, instead of the Guadiana River.

Acknowledgements

This research project (REN2002-04602-C01-02) was supported by grant from the Spanish Ministry of Education and Science (MEC) and a Ph.D. scholarship to the first author. The lignin extrac-tion and posterior analyses were conducted at the Department of Marine Science of Texas A&M University, Galveston (Texas). The manuscript greatly benefited from valuable discussions and com-ments by three anonymous reviewers.

Associate Editor—Klaas Nierop

References

Aufdenkampe, A.K., Hedges, J.J., Richey, J.E., Krusche, A.V., 2001. Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine particle associ-ated OM may also contribute substantially to the TOM inputs to this system. Finally, despite the homogeneous taxonomic origin of the land derived OM observed along the shelf, one particular sediment (S-7) reflects instead a stronger influence of the metal rich, historically contaminated Tinto–Odiel system. The similar high carbon normalized lignin yield and relatively heavy $\delta^{13}$C signature displayed by S-7 ($\delta^{13}$C = -23.0‰) and Tinto–Odiel ($\delta^{13}$C = -23.7‰) suggest that sample S-7 is dominantly influenced by this fluvial system, instead of the Guadiana River.

Acknowledgements

This research project (REN2002-04602-C01-02) was supported by grant from the Spanish Ministry of Education and Science (MEC) and a Ph.D. scholarship to the first author. The lignin extrac-tion and posterior analyses were conducted at the Department of Marine Science of Texas A&M University, Galveston (Texas). The manuscript greatly benefited from valuable discussions and com-ments by three anonymous reviewers.

Associate Editor—Klaas Nierop

References

Aufdenkampe, A.K., Hedges, J.J., Richey, J.E., Krusche, A.V., 2001. Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine particle associ-ated OM may also contribute substantially to the TOM inputs to this system. Finally, despite the homogeneous taxonomic origin of the land derived OM observed along the shelf, one particular sediment (S-7) reflects instead a stronger influence of the metal rich, historically contaminated Tinto–Odiel system. The similar high carbon normalized lignin yield and relatively heavy $\delta^{13}$C signature displayed by S-7 ($\delta^{13}$C = -23.0‰) and Tinto–Odiel ($\delta^{13}$C = -23.7‰) suggest that sample S-7 is dominantly influenced by this fluvial system, instead of the Guadiana River.

Louchouarn, P., Opsahl, S., Benner, R., 2000. Isolation and quantification of dissolved lignin from natural waters using solid-phase extraction (SPE) and GC/MS selected ion monitoring (SIM). Analytical Chemistry 13, 2780–2787.


