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Contribution of black carbon in recent sediments of the Gulf of Cadiz: Applicability of different quantification methodologies

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ABSTRACT

In the Southwestern Iberian Peninsula, vegetation fires are rather common, and produce a considerable amount of charred material that, due to erosion, is fluviially transported to the continental margins. The present study constitutes the first comparative assessment of the contribution of this charred material (generally black carbon, BC) to marine sediments of the inner continental shelf of the Gulf of Cádiz (GoC). Given the ambiguity of BC definition and the heterogeneity of quantification techniques, four of the most common and well established methodologies were applied to obtain a representative range of the BC content on four surface sediments: chemical-thermal oxidation (GBC), molecular markers (benzenopolycarboxylic acids, BPCA), thermogravimetry coupled to mass spectrometry (TG-DSC-QMS), and chemical oxidation with sodium chlorite. The BC results obtained for the GoC sediments are compared, and the applicability of each technique on marine sediments is discussed.

The mean BC values of the four methods (4.4–14.4% total organic carbon) were within ranges previously reported for marine sediments from diverse origins. However, a large variability was observed within individual samples when comparing the BC results obtained with the four methods (relative standard deviation from 31% to 75%). The BPCA approach produced the highest BC values, whereas the GBC method the lowest. This reflects the analytical variability derived from the different windows composing the BC continuum. The results derived from the TG-DSC-QMS application generated certain uncertainties, despite the correction factor introduced to reduce the BC overestimation previously reported for this method.

Considerable differences in the BC content of spatially close samples evidenced the complexity of coastal currents and sediment fluxes in the area, suggesting the existence of other factors affecting the BC distribution. The lack of correlation between the BC and TOC, as well as between the BC and lignin contents in all samples, ruled out the occurrence of charring artifacts. Preferential degradation and/or erosion of BC could explain the BC distribution in the area. The use of ancillary terrigenous biomarkers (lignin and inorganic silica) pointed to a preferential fluvial transport of the terrestrial organic matter and indicated that the longer distance from the source, the greater degradation of the OM. In addition, the northern dominant winds in the region may have favored the additional introduction of airborne transported BC in the marine system.

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1. Introduction

Estuarine and coastal areas are sensitive ecosystems of great environmental and socio-economic concern in terms of preservation and sustainable management. Research on the transport and storage of materials in these areas has been recognized as critical

for the understanding of the global carbon cycle. It is estimated that over 90% of the organic matter (OM) buried in ocean sediments remains within the worldwide coastal and shelf regions, which cover only 10% of the entire seafloor (Bernier, 1982). However, the transport pathways and diagenetic processes affecting the OM in shelf sediments are not well understood, due to the great variability of physical and biogeochemical conditions existing in those areas. The fate of terrigenous OM in the ocean was historically described by rapid loss of homogenous plant-derived material seaward of

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river mouths and its subsequent dilution with marine carbon (e.g., Hedges and Parker, 1976). However more recent evidences suggest that delivery and quantification of terrigenous OM in margin sediments is complicated by the heterogeneous nature of the riverine endmember (e.g., Hedges et al., 1986; Prahl et al., 1994; Goñi et al., 1998).

The amount of organic carbon (OC) stored globally in ocean sediments is estimated to be ~160 Tg/year (Hedges and Keil, 1999) and around 6% of this carbon is in form of the so-called “Black Carbon” (BC) (Masiello and Druffel, 1998). This term was used for the first time by Novakov (1984) to describe the carbon fraction in combustion aerosols and particles of black colour. In general, BC is considered an ubiquitous form of refractory organic matter (ROM) derived from incomplete combustion processes, which comprises a wide spectrum of heterogeneous, aromatic and carbon-rich compounds (e.g., Goldberg, 1985; Masiello, 2004). It may be transported by wind, surface run-off or fluvial currents, being ultimately deposited in marine waters and sediments (Lim and Cachier, 1996). This is the reason why sedimentary BC has been used as an indicator of the occurrence of forest fires and fossil fuel emissions in the past (Bird and Cali, 1998). There is a deficit of understanding of the ultimate fate of BC once it enters the ocean though, since both recent and geologic history of BC, as well as its inventories and properties, remain fairly unknown. In this context, estuarine and continental shelves are important ecosystems for the study of BC dynamics, since they play a key role in the accumulation of terrestrially derived OM, including BC.

There are several procedures to quantify BC in soils and sediments that, in turn, are based on different extraction techniques (e.g., Masiello, 2004; Hammes et al., 2007) and cover a certain range of the BC continuum. They can be divided into four main categories: thermal, chemical, optical and molecular markers (Schmidt and Noack, 2000). Most of those techniques are optimized for certain types of samples and are not easily transferable to other matrices without analytical modification. The isolation of BC from natural matrices, such as soils and sediments, is particularly complex, due to the presence of minerals, ROM other than BC, and potential interfering materials (Simpson and Hatcher, 2004). The quantification of BC in this type of matrices is commonly addressed by chemical, thermal or chemical/thermal procedures (e.g., Gustafsson et al., 2001; Nguyen et al., 2004), although its complete achievement is still a challenge, since all the existing methodologies encounter some inconveniences. For example, the use of strong chemical oxidation procedures to remove the interfering material has been reported to attack BC (Knicker et al., 2007) and cause its underestimation, whereas hydrophobic material may still survive the harsh method and cause overestimation. Some thermal oxidation procedures have also a certain risk of artifact formation derived from charring of labile organic compounds during the heating, which causes overestimation of BC (Lim and Cachier, 1996). The heterogeneity of results, techniques and terms of expression leads to BC estimations that are difficult to compare and cause significant problems with respect to interpretation (Forbes et al., 2006).

This work constitutes the first BC-comparative study exclusively devoted to marine sediments. Here, four of the most common methodologies for isolation and quantification of BC are applied to marine sediments from the inner continental shelf of the Gulf of Cádiz (SW Iberian Peninsula). This coastal region is particularly interesting for the study of BC, given the abundant forest fires taking place in the continent during the dry summer season. The rapid accumulation of sediments occurring in the inner shelf nearby the Guadiana River estuary converts the coastal area in the perfect scenario for the characterization study of fire-derived BC. The main purposes of this study were: i) to test the applicability and

consistency of the different methods to quantify BC in marine sediments, and to discuss the advantages and disadvantages of each technique, ii) to assess the contribution of BC to marine sediments in the SW coasts of the Iberian Peninsula, and iii) to discern the sources and transport ways affecting the accumulation of terrestrial OM and BC in the studied area. In order to achieve the last objective, two complementary geochemical markers (lignin and inorganic silica) were studied together with the BC fraction, because of their terrigenous signature. Lignin is one of the main biopolymers composing the vascular tissues of higher plants (De Leeuw and Largeau, 1993) and, because the latter are essentially confined to land, lignin can serve as an unambiguous marker of land-derived material in aquatic systems (Louchouart et al., 1999). Silica, on the other hand, is one of the major elements of the sediments and, though it can derive from both lithogenic and biogenic sources, its only presence as inorganic silica indicates detrital origin (i.e. terrestrial).

2. Regional Setting

2.1. Area of study

The study area is located in the inner shelf of the SW Iberian Peninsula, in the northern part of the Gulf of Cadiz (Fig. 1). This site is highly influenced by water run-off and sediment load derived from the Guadiana River. A large part of the river water, nutrients and sediments remain on the estuary, on their way towards the continental shelf. The Guadiana River is one of the major rivers in the Iberian Peninsula (742 km in length), having a drainage basin of about 67,000 km². Before reaching the estuary, the Guadiana crosses approximately 130 km of rural terrain, a natural border between the Algarve region (Portugal) and the province of Huelva (Spain), where forest fires are frequent during summer. An average of 205 forest fires per year is reported by the Huelva fire department statistics, burning approximately 4985 ha of forest area (Zamora et al., 2010). Thus, biomass-derived BC, dominantly composed by char and charcoal particles more prone to sedimentation and transport by means of rivers or water run-off, is likely to occur in the study area.

2.2. Climate and fluvial regime

The climate of the Guadiana basin is typical Mediterranean, with mean annual temperatures varying from 14 °C to 18 °C, and a highly irregular precipitation pattern. The fluvial regime, with a mean flow of 83 m³/s (González et al., 2007), is characterized by low flows in summer and episodic run-off periods in autumn and winter. According to its intensity and duration, the Guadiana flow may easily erode soil particles from the drainage basin of the river (Ferreira et al., 2005). The flow of the Guadiana River has been extensively modified during the last century due to a range of anthropogenic activities, including damming, mining, urbanization, deforestation and dredging. Although there are no published data on the Guadiana sediment supply, there are estimations of the mean suspended load (57.90×10^4 m³/y) and bedload (43.96×10^4 m³/y) over the last 44 years (Morales, 1997).

2.3. Geology and surface sediment distribution

The geology of the Guadiana estuary has been extensively studied in previous works (e.g. Borrego et al., 1993; Lobo et al., 2004; González et al., 2007). They describe the Guadiana Estuary as a mesotidal fluvio-marine system, where the mouth of the river was formed as a narrow channel excavated by fluvial incision during the Pleistocene and was then flooded 6500 years ago.

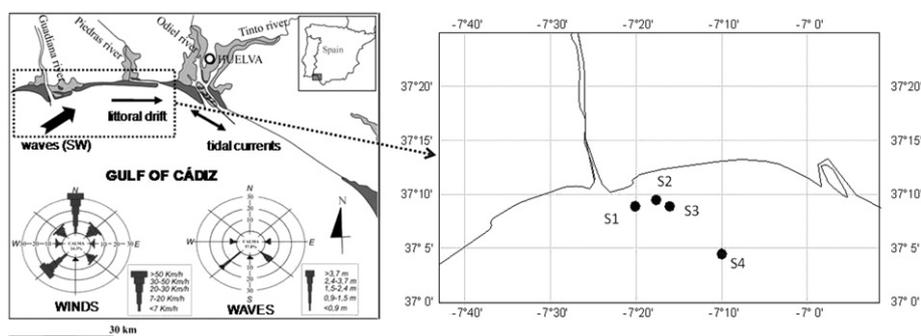


Fig. 1. Samples location and coastal dynamics in the study area. Map showing the location of the sampling sites, together with the coastal dynamics and winds dominating in the study area.

An intense SE-ward littoral drift dominates the region (Morales, 1997), resulting in a Guadiana River input dominantly from the southeast.

The surficial distribution of sediments in the shelf off the Guadiana Estuary is dominated by sandy and silty deposits to a depth of approximately 25 m. The outer infra-littoral spanning between 25 and 30 m mainly contains deposits of sand and sandy mud, whereas the middle shelf is characterized by an extensive mud belt, consisting of very fine-sized clayey material (González et al., 2004). On the outer shelf beyond the 100 m depth, the sediments are generally dominated by sands and silty clays.

3. Materials and methods

3.1. Materials and sediment sampling

Four samples of surface sediment (0–25 cm) were collected in 2001 from the northern part of the Gulf of Cadiz, on a section of the inner continental shelf nearby the Guadiana estuary (Fig. 1). The samples were frozen and stored in glass containers to avoid microbial growth, and then freeze-dried and homogenized before analysis. The location of the sediments was selected with the aim of covering the transition between the fluvial and marine regimes. The sampling sites were chosen taking into account the influence of the North Atlantic Surface water current, which causes most of the sediment supply from the Guadiana River to be deflected to the southeast (Lobo et al., 2004) (Fig. 1). Thus, three of the samples were retrieved from the sediments from the proximity of the river mouth, and the fourth from about 14 km southwest (Fig. 1).

3.2. Experimental methods

3.2.1. Elemental, isotopic and granulometric analyses

The sediment samples were finely ground and homogenized in an agate mill. A subsample of sediment was used for the particle size analysis, which was carried out using a Sedigraph 5100 (Micrometrics). The other subsamples were employed for chemical analysis consisting in the determination of total carbon (TC), total nitrogen (TN) and total sulfur (TS) contents. They were determined in triplicate by using a Carlo-Erba NA 1500 Series 2 Elemental Analyzer (CE Elantech, Inc., Lakewood, NJ, USA). The total organic carbon (TOC) was measured on decarbonated samples (3 M HCl) and the total inorganic carbon (TIC) was calculated from the difference between TC and TOC (Nieuwenhuize et al., 1994). The instrumental readings were checked using samples of standard sulphanimide. The ^{13}C composition was measured on the decarbonated sediment samples using an EA Eurovector coupled to an isotope ratio mass spectrometer (Finnigan Isoprime). The $\delta^{13}\text{C}$

results are reported relative to the Pee Dee Belemnite limestone standard (PDB) in the usual parts per thousand (‰) notation. The standard deviation was $\leq 0.05\%$.

3.2.2. BC quantification methodologies

3.2.2.1. Chemical-thermal method (GBC). This method is described in detail in Gélinas et al. (2001). Briefly, a few grams of sediment are subjected to a chemical (wet) pre-treatment with different acids (trifluoroacetic, TFA; HCl and HF), prior to a thermal combustion (Gustafsson et al., 2001). The aim of the pre-treatment is to minimize mineral-catalyzed condensation reactions and avoid the overestimation of the BC content by formation of artifacts (Gélinas et al., 2001). Then, the OC remaining after the thermal oxidation of the non-hydrolyzable OM is quantified as BC (the so-called GBC-BC) with an elemental analyzer (Carlo-Erba model 2400).

3.2.2.2. Molecular marker method (BPCA). This method applies an acid oxidation to convert the BC present in the sample into benzenepolycarboxylic acids (BPCA), which are considered as molecular markers of BC (Glaser et al., 1998). This approach relies on the breakdown of the highly aromatic core of the samples to convert polycyclic or substituted aromatic centres to BPCA during oxidative degradation (Hayatsu et al., 1982). The BPCA method has been employed to study BC in soils (Glaser et al., 1998; Brodowsky et al., 2005) and marine dissolved OM (Dittmar, 2008), and it is described in detail in Glaser et al. (1998) and Brodowsky et al. (2005). Considering the association between the BPCA generated and the BC, the extrapolation of its concentration in the samples is made by applying a conversion factor of 2.27, according to Glaser et al. (1998).

3.2.2.3. Thermogravimetric-mass spectrometry method (TG-DSC-QMS). This method was originally developed by Lopez-Capel et al. (2006) and recently utilized for the detection of BC in reference materials (Hammes et al., 2007) and soils (De la Rosa et al., 2008a). Briefly, an aliquot of sediment (30 mg) was heated at $20\text{ }^{\circ}\text{C min}^{-1}$ in an Al_2O_3 crucible, from ambient temperature to $650\text{ }^{\circ}\text{C}$, under a flow of 20% O_2 in He ($50\text{ cm}^3\text{ min}^{-1}$), and from 650 to $1000\text{ }^{\circ}\text{C}$, under a flow of He in a Thermogravimetric-Differential scanning calorimetry (TG-DSC) system. The conditions of the Quadrupole Mass Spectrometer (QMS) and the ion intensities of interest scanned were the same than reported previously by Lopez-Capel et al. (2006).

In the original method, the BC contribution was calculated as the amount of material lost at the range of temperatures $475\text{--}650\text{ }^{\circ}\text{C}$, which corresponds to the thermal decomposition of BC-like material (Lopez-Capel et al., 2006; De la Rosa et al., 2008a). Nevertheless, overestimation problems were reported when applying this method

to soils and sediments (Hammes et al., 2007), and thus a correction factor was introduced for each sample, proportional to the amount of CO₂ evolved at the range 475–650 °C. The amount of material loss measured at the range 475–650 °C was thus multiplied by the correction factor calculated for each sample by the following formula:

$$\left[\text{Area of the } m/z \text{ 44 signal (}_{475-650 \text{ °C})} / \sum \text{Area } m/z \text{ 30} \right. \\ \left. - 300 \text{ (}_{475-650 \text{ °C})} \right]$$

The area of the *m/z* 44 signal evolved at the range 475–650 °C is assumed as proportional to the amount of BC, while the total area *m/z* 30–300 summarizes all the compounds evolved at that range of temperatures, including BC and non-BC materials.

3.2.2.4. Chemical oxidation with sodium chlorite. The last method was selected because it was specifically developed to be applied on sediments (Simpson and Hatcher, 2004). It consists of a pre-treatment of the samples with HF to remove the mineral matrix, followed by a chemical oxidation with sodium chlorite to remove lignin and other aromatic structures. The removal of these non-BC components facilitates the measurement of BC in the residue, by cross polarization magic angle spinning (CP MAS) ¹³C Nuclear Magnetic Resonance (NMR) spectroscopy. The BC content was determined from the relative amount of aromatic carbon (aromatic signal between 110 and 160 ppm) and the amount of OC left in the sample after sodium chlorite oxidation. The removal efficiency of lignin was tested by examination of the residue by tetramethylammonium hydroxide (TMAH) thermochemolysis Gas Chromatography–Mass Spectrometry (GC–MS), a sensitive method to detect lignin biomarkers (Simpson and Hatcher, 2004).

3.2.3. Lignin content and terrestrial markers

The concentration of inorganic silica (as SiO₂) was determined by X-ray 162 fluorescence, in a Panalytical MagiX (Sánchez-García et al., 2009a). The vascular plants-produced lignin was estimated by means of the oxidation products derived from reaction upon CuO oxidation according to well established methods (Goñi and Hedges, 1992; Louchouart et al., 2006). Briefly, the sediments were oxidized under alkaline conditions with CuO (155 °C; 3 h) and pressurized conditions. The aqueous solution was then acidified with 6 N HCl and extracted three times with ethyl acetate. The CuO reaction products were derivatized with bis-trimethylsilyl trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS), for chromatographic analysis. The separation and quantification of derivatized CuO oxidation by-products were performed by GC–MS on a Varian Ion Trap GC/MS system (3800/4000), fitted with a fused capillary column (VF 5MS, 60 m × 0.25 mm ID; Varian Inc.), according to the conditions detailed in Sánchez-García et al. (2009b). 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 studied samples was in the same range (5–10%).

3.2.3.1. Lignin parameters. Lignin oxidation products (LOP) are useful tools in the characterization of the sources and diagenetic state of vascular plant material found in aquatic systems. For example, the ratios syringyl to vanillyl and cinnamyl to vanillyl phenols (S:V and C:V, respectively) have been used in taxonomic source reconstructions. Acid to aldehyde ratios from vanillyl phenols ([Ad:Al]_v) provide information on the oxidative degradation of the

terrestrial OM prior to sediment burial (Prah et al., 1994; Louchouart et al., 1999). The ratio p-hydroxyphenols to the sum of syringyl and vanillyl phenols (P:[V + S]) inform about specific lignin degradation pathway. All these parameters have been used in the present study to characterize the sources and alteration state of the terrestrial OM and its possible relationship with the BC contents measured in marine sediments by the different methodologies.

4. Results and discussion

4.1. Elemental, isotopic and granulometric analysis

Table 1 reveals the TC, TOC, C/N (atomic TOC/TN ratio), δ¹³C and granulometry values measured in the samples. The TOC levels ranged from 0.84 to 0.69%, which are typical values for coastal and marine sediments (Nieuwenhuize et al., 1994). The C/N ratio (6.2–8.2) provided dominant marine signatures, and the δ¹³C ratio (–25.7‰ to –22.8‰) indicates mixed terrestrial and marine sources. Typical δ¹³C values for marine biomass are in the range of –18‰ to –22‰ (Holtvoeth et al., 2005), whereas those for terrestrial C₃ plants range from –23‰ to –34‰, with an average of ca. –27‰ (Meyers, 1997). The sample S4, located at more than 27 km of distance from the Guadiana River mouth, is the ¹³C-richest sediment (–22.8‰) and presents also the lowest C/N ratio (6.2), reflecting a typical marine signature (Meyers, 1997). In contrast, the ¹³C-depleted values of the samples more close to the coast (S1: –25.5‰, S2: –25.3‰ and S3: –25.7‰) illustrate the influence of terrestrial sources related to C₃ vascular plants (Prah et al., 1994) and/or fossil carbon (Drenzek et al., 2007).

The four sediments studied here are representative of the granulometric distribution described for the continental shelf of the Guadiana Estuary (González et al., 2004). Briefly, as shown in Table 1, the relative amount of fine materials (silt and clay) increases with the distance to the Guadiana River mouth and depth, being S1 the most sand-enriched sample (24% dw) of the four samples, and S4 the one containing the largest amount of fines (~99% silt and clay).

4.2. BC measurements

The four quantification methods produced BC results that are summarized in Table 2 and Fig. 2. In total, the BC concentrations ranged between 0.02% dw (sample S3, method TG–DSC–QMS) and 0.15% dw (sample S2, method GBC) (Table 2). These values compare to BC concentrations reported in coastal sediments in North America (~0.01–0.69% dw; Gustafsson and Gschwend, 1998), North Europe (0.04–1.77% dw; Persson et al., 2002; Sánchez-García et al., 2010), South Atlantic (0.04–0.17% dw; Lohmann et al., 2009), Atlantic–Iberian margin (~0.05–0.16% dw; Middelburg et al., 1999) or Pan–Arctic (~0.02–0.15% dw; Elmquist et al., 2008). In the GoC, the corresponding BC contents normalized to the TOC varied between 2 and 24% TOC, which are within ranges previously

Table 1
Sample location, description and geochemical characterization (elemental, isotopic and granulometric analysis).

| Code | Depth (m) | Distance to ^a (km) | TC (%) | TOC (%) | C/N ^b | δ ¹³ C (‰) | Sand (%) | Silt (%) | Clay (%) |
|------|-----------|-------------------------------|--------|---------|------------------|-----------------------|----------|----------|----------|
| S1 | 12 | 6.6 | 1.40 | 0.84 | 7.0 | –25.5 | 24.0 | 41.8 | 34.2 |
| S2 | 16 | 7.3 | 1.15 | 0.77 | 8.2 | –25.3 | 17.1 | 54.4 | 28.5 |
| S3 | 17 | 9.8 | 1.36 | 0.82 | 8.0 | –25.7 | 6.3 | 56.4 | 37.3 |
| S4 | 42 | 27.4 | 3.31 | 0.69 | 6.2 | –22.8 | 0.9 | 54.2 | 44.9 |

^a Distances were measured to the Guadiana River mouth.

^b TOC/TN atomic ratio.

Table 2
BC content of the Gulf of Cádiz sediments determined by four different methods.

| Sample Code | GBC ^a | | BPCA ^b | | | TG-DSC-QMS ^c | | Sodium Chlorite ^d | | Average results | | | | |
|-------------|------------------|-------|-------------------|--------------|-------|-------------------------|-------|------------------------------|-------|-----------------|-------|--------------|-------|--------------|
| | % dw | % TOC | % dw | S.D. (n = 3) | % TOC | S.D. (n = 3) | % dw | % TOC | % dw | % TOC | % dw | S.D. (n = 4) | % TOC | S.D. (n = 4) |
| S1 | 0.030 | 3.6 | 0.038 | 0.035 | 4.5 | 4.1 | 0.022 | 2.6 | 0.047 | 5.6 | 0.034 | 0.011 | 4.1 | 1.3 |
| S2 | 0.112 | 14.6 | 0.148 | 0.103 | 24.0 | 18.9 | 0.075 | 9.7 | 0.072 | 9.4 | 0.102 | 0.036 | 14.4 | 6.8 |
| S3 | 0.027 | 3.3 | 0.102 | 0.070 | 12.4 | 8.5 | 0.016 | 2.0 | 0.059 | 7.2 | 0.051 | 0.039 | 6.2 | 4.7 |
| S4 | 0.026 | 3.8 | 0.033 | 0.013 | 4.7 | 1.9 | 0.109 | 15.8 | 0.064 | 9.3 | 0.058 | 0.038 | 8.4 | 5.5 |

% dw; Percentage referred to the weight of dried sediment.

S.D. values for BPCA method are calculated taking into account the results given by 3 replicates.

^a Graphitic Black Carbon method (GBC).

^b Benzene Polycarboxylic Acid method (BPCA).

^c Thermogravimetry coupled-Differential scanning calorimetry-Quadrupole mass spectrometry method (TG-DSC-QMS).

^d Sodium Chlorite oxidation treatment.

reported for marine sediments elsewhere. For example, [Cornelissen et al. \(2005\)](#) estimated values of BC for ~300 sediments from different locations around the world ranging 5–18% TOC of quartile range (median of 9%). Smaller-scale studies described BC values of 5–38% TOC in surface sediments from the Mediterranean Sea ([Lim and Cachier, 1996](#)), 3–15% TOC in sediments from the Gulf of Maine ([Gustafsson and Gschwend, 1998](#)), 13–56% TOC in marine sediments from different seas in the European Northern hemisphere ([Middelburg et al., 1999](#)), 4–16% TOC in fjord sediments in the south of Norway ([Persson et al., 2002](#)), 3–17% TOC in surface sediments from the GoC ([De la Rosa et al., 2008b](#)) or 2–47% TOC in sediments from the Swedish continental shelf ([Sánchez-García et al., 2010](#)).

The BC values in the GoC sediments show significant differences between the different samples and quantification methodologies. In order to simplify the discussion, hereafter we will only discuss the BC results normalized to the TOC content. The samples S3 and S4 showed larger variations of the BC contents determined with the different methodologies ([Table 2](#)). S3 yielded a BC range of 2% (TG-DSC-QMS method) to 12.4% (BPCA method) (mean of $6.2\% \pm 4.7$), while S4 varied from 3.8% (GBC) to 15.8% (TG-DSC-QMS) (mean of $8.4\% \pm 5.5$). S2 contained the largest amount of BC (9.4%–24%; [Table 2](#)), independently of the quantification method employed (mean of $14.4\% \pm 6.8$). In contrast, S1 registered the lowest and less variable BC values that ranged from 2.6% (TG-DSC-QMS method) to 5.6% (Sod. Chlorite method) (mean value of $4.1\% \pm 1.3$; [Table 2](#)). The low content measured in S1 is unexpected, considering the location ([Fig. 1](#)) and terrestrial signature of this sample inferred by the ancillary markers (see [Fig. 3a, b](#)). However, episodic run-off events characteristic of this site might be responsible for the erosion and washing off of sedimentary OM (including BC) in locations closest to the river mouth.

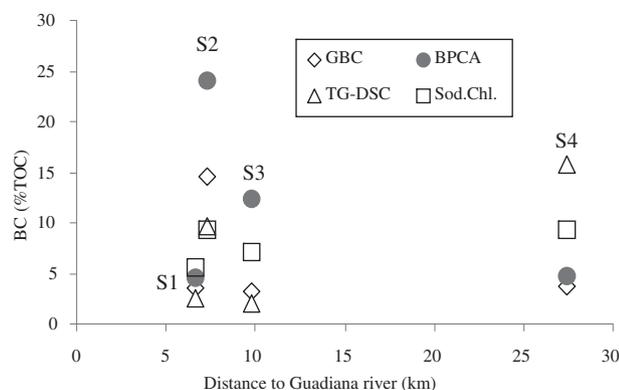


Fig. 2. Plot of the variation of Black Carbon concentrations (%TOC) for each sample quantified by the four methods with respect to the distance to the Guadiana River mouth.

This is supported by the sandy texture of the sediments in S1, which is deposited in the proximity of the river output ([Fig. 4](#)).

The comparison of the values obtained with the four methods ([Fig. 2](#)) allow us to discuss the pros-and-cons and characteristic aspects of each approach. The GBC method produced BC values lower than the mean ([Table 2](#)). The thermal step of this method is considered to only detect the most condensed forms of BC and to exclude the bigger BC particles derived from char and charcoals ([Gustafsson et al., 2001](#)). Considering the frequency of fire episodes in the Mediterranean region and that biomass burning dominantly produce bigger particles of BC (char and charcoal type), the lower BC values measured by the GBC method in the GoC is consistent with certain underestimation of the bigger BC particles. Despite this method is particularly appropriate for BC quantification in marine sediments ([Gélinas et al., 2001](#)), its applicability should be conditioned to the specific type of BC to measure.

The TG-DSC method returned values generally lower than the average in the estuarine samples (S1–S3), except for S4 that registered the highest BC content ([Table 2](#) and [Fig. 2](#)). These results indicate that there are uncertainties which need to be solved in order to improve the reliability of this new method, such as the range of temperatures corresponding to the thermal decomposition of BC-like materials. In this study, it was determined the range 475–650 °C was used, according to [Lopez-Capel et al. \(2006\)](#), although other ranges have been also reported for BC and ROM determinations ([Plante et al., 2009](#)) depending on the thermal stability of different OM nature. In addition, the correction factor introduced here to reduce the possible BC overestimation is proportional to the area of the m/z 44 ion detected by QMS, which corresponds to CO₂ and N₂O gases. However, other gases may actually be released during the thermal decomposition of BC. This would mean the underestimation of BC and could explain the relatively low values obtained for S1, S2 and S3, in comparison to the other methods. On the other hand, the presence of mineral impurities in the sediments may cause BC overestimation when applying this method to natural matrices ([Hammes et al., 2007](#)). The higher content of clays and carbonates of the more marine S4 ([Table 1](#)) may have affected the determination of BC by this method, therefore causing BC overestimation.

The Sodium Chlorite oxidation method presents the smallest variability of BC results ([Fig. 2](#)). This method was specifically developed for marine sediments ([Simpson and Hatcher, 2004](#)), applying several chemical treatments in order to remove interference materials, such as lignin, and minimize BC overestimation. However, although artifact formation derived from the “charring” effect can be virtually excluded with this method, there are other alteration factors that may interfere the actual measurement of BC. Potential problems are over-oxidation of target compound derived from kinetic limitations or failure to detect certain portions of the combustion spectrum. As for thermal methods, chemical oxidation

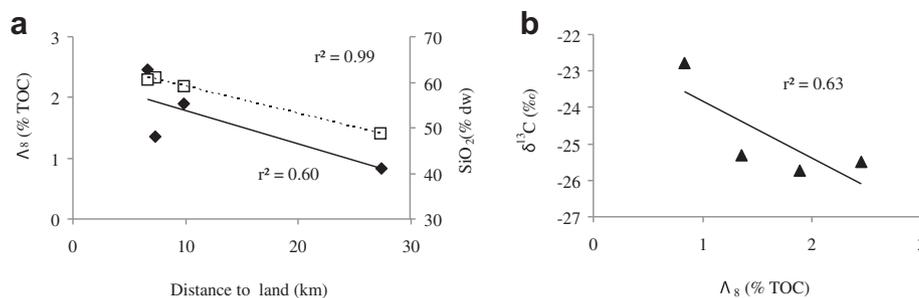


Fig. 3. a, b. Plot of the variation of the complementary terrestrial markers, lignin (black diamonds) and inorganic silica (white squares) with respect to the distance to the Guadiana River mouth (a) and correlation between the lignin content and isotopic composition ($\delta^{13}\text{C}$) of the four marine sediments (b).

is more prone to detect small and highly condensed particles although it covers a slightly wider range of sizes (Masiello, 2004). Hence, larger particles produced during forest fires are susceptible to be at least partially neglected by the sodium chlorite oxidation method.

The use of BPCA as molecular markers of the presence of BC provided the wider BC range in the GoC sediments (4.5–24% TOC; Table 2 and Fig. 2). This method is by definition able to detect the entire BC continuum with exception of the highly condensed combusted material (Hammes et al., 2007) and therefore, it is in principle expectable that it produces greater BC values compared to the other methods. The BC values determined from BPCA concentration in the GoC sediments are overall higher than the average values (Table 2 and Fig. 2). Considering the dominant type of BC produced in the area, this method provides the most comprehensive amount of BC in the GoC sediments, including slightly charred biomass to charcoal-BC. However, the intrinsic basis of the method indirectly estimating BC from BPCA concentrations should be carefully interpreted.

The range of results presented here illustrates the complexity of measuring BC in marine sediments. The chemical heterogeneity of BC, particularly in this sort of natural matrices, makes it hard for one method to measure all regions of the combustion continuum. Still and despite need of further refinement, a few conclusions can be extracted from the presented results. Apparently, S2 is the sample containing the larger amount of BC, according to three of the four methods applied. This result is consistent to the proximity of this sample to the Guadiana River mouth. The lower content observed in the neighboring S1 may be explained by the frequency of run-off episodes affecting this closer site. The differences observed from applying the four methodological approaches on the GoC sediments manifest the need of further investigation and the convenience of using complementary proxies for interpretation. In

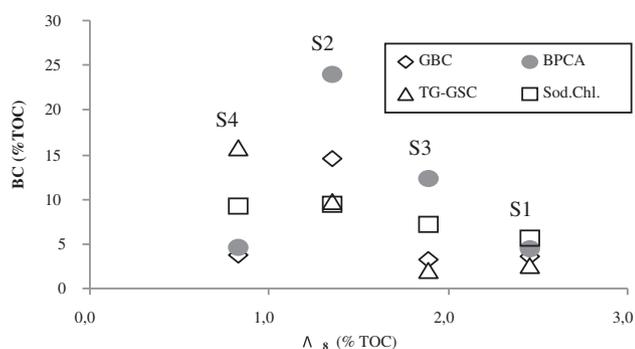


Fig. 4. Plot of the variation of Black Carbon concentrations (%TOC) for each sample quantified by the four methods with respect to the amount of lignin (expressed as the lamda-8 ratio: Λ_8 , % TOC).

this study, ancillary molecular markers were used to assist in the interpretation of BC distribution, and are discussed in combination with the BC results in the next sections.

4.3. Terrestrial markers (including inorganic silica, lignin and LOP ratios)

The distribution of both terrestrial markers in the studied sediments is depicted in Fig. 3 a. The silica content, expressed as SiO_2 , varied from 49 to 61% dw, and the amount of lignin, calculated from the eight major oxidation products derived upon CuO oxidation (expressed as the lamda-8 ratio: Λ_8 , % TOC) ranged from 0.8 to 2.5% TOC.

The terrestrial markers showed a distinct decreasing trend with distance to land (given as km to the Guadiana River mouth). The samples located near the Guadiana mouth (S1, S2 and S3) presented higher lignin concentrations (Λ_8 of 1.4–2.5%) coinciding with the richest values of SiO_2 (~60% dw). In contrast, S4 showed a significant depletion of lignin (~60%) and SiO_2 (~20%) with respect to the other samples. Both markers are strongly correlated with the distance to the Guadiana mouth (Fig. 3a) and with the $\delta^{13}\text{C}$ ratio (Fig. 3b), more evident for SiO_2 ($r^2 \sim 1$ and 0.93, respectively) than for Λ_8 ($r^2 = 0.60$ and 0.63, respectively). The Λ_8 and $\delta^{13}\text{C}$ ratios are well established markers to distinguish marine from terrestrial OM and the trend observed from enriched values close to the Guadiana (S1, S2 and S3) to more depleted values SE-ward (S4) signals the decline of the terrestrial signature along the Guadiana River plume. These results evidence the higher terrigenous character of the samples S1, S2 and S3, which receive a larger fluvial input of land-derived material than the more remote S4, where marine sources become more important.

Values corresponding to different LOP ratios and diagenetic markers are summarized in Table 3. Lignin S:V ratio showed relatively high values (1.04 ± 0.08), indicative of a significant contribution of angiosperm plants. Relatively low C:V ratios (0.23 ± 0.03 ; Table 3) suggest the moderate presence of non-woody tissues as input sources to lignin mixtures. Although selective degradation or

Table 3

Lignin parameters in the Gulf of Cádiz Sediments. Λ_8 , carbon normalized yields of the eight lignin derived phenolic oxidation products (mg/100 mg OC); S:V, ratio of syringyl to vanillyl phenols; C:V, ratio of cinnamyl to vanillyl phenols; (Ad:Al)_V, ratio of vanillic acid to vanillin; (Ad:Al)_S, ratio of syringic acid to syringin; 3,5-Bd:V, ratio of dihydroxybenzoic acid to vanillic acid; P:(V + S), ratio of p-hydroxyphenols to the sum of vanillyl and syringyl phenols.

| Sample | Λ_8 | C:V | S:V | (Ad:Al) _V | (Ad:Al) _S | 3,5-Bd:V | P:(V + S) |
|--------|-------------|------|------|----------------------|----------------------|----------|-----------|
| S1 | 2.45 | 0.26 | 1.15 | 0.32 | 0.26 | 0.09 | 0.18 |
| S2 | 1.35 | 0.21 | 1.07 | 0.34 | 0.28 | 0.15 | 0.19 |
| S3 | 1.89 | 0.23 | 1.02 | 0.35 | 0.30 | 0.12 | 0.19 |
| S4 | 0.83 | 0.20 | 0.95 | 0.54 | 0.42 | 0.17 | 0.35 |

leaching processes could lead to the underestimation of non-woody material inputs to sediments on the shelf, the lack of significant variation along the transect indicates no significant alteration of the source signature during transport and deposition.

Internal ratios of lignin phenols (Ad/Al) are indicative of different degradation states, with the acid moiety (Ad) becoming more abundant as degradation advances (Goñi et al., 1993). In this study, the (Ad/Al) ratios of vanillyl and syringyl ($[Ad:Al]_V = 0.43 \pm 0.11$ and $[Ad:Al]_S = 0.33 \pm 0.07$, Table 3) are within the ranges commonly considered to indicate moderate degradation (Hedges et al., 1988) and oxidative alteration of vascular plant material (Goñi et al., 1993). A slight increase in those values is observed in the sample S4 that could be indicative of further decomposition extent likely occurring prior to the sorption process and entrance in the marine system (Sánchez-García et al., 2009b). In addition, other processes such as leaching or selective sorption must be also taken into account Hydrodynamic sorting and selective transport could have resulted in increasing degradation from the land to the sea.

The 3,5-dihydroxybenzoic acid (3,5-Bd) is a common product of soil degradation processes through the humification of fresh vascular plant tissues (Goñi and Hedges, 1995) as well as a component of macroalgae. In this study, the marine origin of this phenolic compound was considered negligible on the basis of the linear correlation with the terrigenous Δ_8 ($r^2 = 0.99$). The 3,5-Bd:V ratio is the result of its normalization to total vanillyl, which has been effectively used to trace soil OM input to aquatic systems (Louchouart et al., 1999). Here, this ratio ranged 0.09–0.17 (Table 3), with the highest value observed for the sample S4. In general, values greater than 0.1 are commonly observed in geochemical samples containing highly altered lignin, such as soils and highly decayed woods (e.g., Hedges et al., 1988 and Prahl et al., 1994). The same pattern was observed for P(V + S) parameter, with values increasing from ~0.19 in the samples nearby the coast to 0.35 in the most remote sample S4. The spatial distribution of the degradation ratios shows how the most altered materials reach further distance offshore. Taken together, the lignin biomarkers suggest that selective sorption of the most degraded materials, most likely associated with soil-derived fine clay, may be responsible for the offshore transport and deposition of highly altered lignin remains.

4.4. BC and terrestrial markers

The use of lignin and inorganic silica as ancillary terrestrial markers (Section 4.3) pointed to the Guadiana River as the main source of terrestrial OM in the area. This observation is not so clearly observed for the BC content (Fig. 2) that showed no significant correlation with the distance to the Guadiana mouth ($r^2 = 0.015$). Overall, the samples situated closer to the river contain more BC than the more remote S4 (Fig. 2), but not distinct trend can be extracted. Comparing the BC with the lignin content (expressed as Δ_8), there is no clear relation between the two terrestrial compounds. Apparently, an inverse relationship exists, with lower amounts of lignin as the BC content increases. Although the pattern is not clear for all samples, it could mean that lignin moieties are not interfering in the BC determination. On the other hand, this result is in accordance with the fact that coarser particles typically retain more lignin (Hedges et al., 1988) of less altered nature, which would explain the inverse relationship with the fossil BC fraction. These types of fresh and coarse particles are mainly deposited close to the delivery site (S1), whereas more degraded and smaller particles, presumably enriched in BC and other condensed structures, are easily carried further.

The frequent pyrogenic events taking place in the area during the summer season suggest a dominant biomass burning source of BC in the area. Due to the larger size of the emitted particles

(macro-particles), this type of BC is prone to deposition. Weathering and run-off contribute to the collection of the deposited BC that will be delivered by rivers into the sea. Although fluvial transport constitutes the dominant method of transport, other ways such as aerial may also play some role. Charcoal particles, produced during the several fire events reported upstream along the Guadiana River (Zamora et al., 2010), may be accompanied by minor amounts of soot and graphitic BC which, in contrast to larger particles, are mainly airborne transported. As the winds in this area are dominantly coming from the north (Fig. 1), the contribution of certain amounts of soot and graphitic-like BC from the land cannot be completely ruled out. Taken together, the large uncertainties derived from the methodological heterogeneity prevent a final interpretation of the BC distribution in the GoC. Although there is a certain trend toward decreasing contents of BC with distance to land, a conclusive pattern is lacking.

5. Conclusions

This study accomplished the first methodological comparison of BC in marine sediments from the GoC Continental Shelf. The application of four of the most common and well established BC quantification produced values (2–24% TOC) comparable to those reported in coastal sediments elsewhere. The large variability of results among the different methods hindered definition of a clear spatial distribution of BC in the studied area. The use of ancillary proxies, such as lignin and inorganic silica, assisted in interpretation of the terrestrial influence in the marine system. The analysis of these terrestrial markers indicated that the Guadiana River is the main source of terrestrial OM in the studied region. The spatial distribution of the lignin compounds on the GoC Continental Shelf showed higher amounts of fresh lignin close to the river mouth and further transport offshore of highly altered lignin remains, most likely associated with soil-derived fine clays.

Such a spatial distribution was not so clearly observed for BC, which did not show a distinct relationship with distance to land. However, some conclusions can be inferred from this analysis. Overall, there was a higher presence of BC in the sediments collected closer to the Guadiana River mouth, supporting the hypothesis of dominant river transport of BC. The outstanding difference of BC amount observed in the neighboring S1 and S2 illustrated the complexity of the coastal currents affecting the area, and indicates the incidence of other potential factors. River floods and run-off events might have been responsible for the erosion and winnowing of sedimentary OM (including BC) in locations closest to the river mouth. The coarse granulometry of S1 shows the different hydrodynamic conditions in this site compared to the other three, and may explain the lower BC amount measured in this sediment. The analysis of BC in combination with the ancillary terrestrial markers indicates that the Guadiana River is the major source of terrestrial OM in this region. However, the contribution of other BC sources, such as aerial, cannot be ruled out. The participation of this method of transport (dominantly of highly condensed BC particles) would help to explain the heterogeneous BC distribution in the GoC.

The different methodological approaches applied to quantify BC produced a wide range of results that needs a cautious interpretation. Significant variations are reported among the different methods, with relative standard deviations ranging from 31% for S1, to 65% and 75%, for S4 and S3, respectively. A direct comparison between BC values obtained by the four different methodologies is not possible, as each method is based on different properties (thermal and chemical stability, condensation degree, formation conditions, recalcitrance extent, etc.) and isolates different parts of the BC continuum (char/charcoal versus soot/graphitic BC).

For instance, the high content of carbonates in samples of such a nature is likely to interfere in the isolation of the BC molecular markers by the BPCA method, which was originally developed for soil matrices without salts and carbonates. Similarly, the TG-DSC method is susceptible of BC overestimation in carbonate-enriched samples, despite its advantages as a fast procedure and easy handling. The correction factor introduced here in this regard is still in need of further development and testing before establishing a more reliable parameter. Another potential problem of the GBC method or Sodium Chloride oxidation is the underestimation of the bigger char particles inherent in the chemical or thermal methods.

The differences observed from applying the four methodological approaches on the GoC sediments manifest the need of developing further efforts to define-unify BC quantification routines. The contribution of airborne transported BC, added to the complexity of the marine currents in this coastal area, and to possible BC preferential transport and degradation, may explain the lack of pattern found in the distribution of BC in the studied sediments. Therefore, further research will be essential to achieve a complete understanding of the BC fluxes in the area, with study of the preferential degradation/erosion of BC in certain sedimentological environments. Specifically, the use of sediment cores would be a convenient complement for further study, such as comprehensive geochemical characterization and chronological dating of the BC fraction. In addition, complementary techniques such as Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) would be very valuable to assist interpretation. However, despite the need of further refinements, the results of this study constitute an important contribution to the field as the first methodological comparison of BC quantification on marine sediments.

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