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Sediment and pollutant transport in the Northern Gulf of Cadiz: A multi-proxy approach

R. Gonzalez [a,*], M.F. Araújo [b], D. Burdloff [b], M. Cachão [c], J. Cascalho [d], C. Corredeira [b], J.M.A. Dias [a], C. Fradique [d], J. Ferreira [e], C. Gomes [f], A. Machado [f], I. Mendes [a], F. Rocha [f]

[a] CIACOMAR/CIMA-Universidade do Algarve, Avenida 16 de Junho s/n, 8700-311 Olhão, Portugal
[b] Departamento de Química, Instituto Tecnológico e Nuclear, E.N. 10, 2686-953 Sacavém, Portugal
[c] Centre and Dep. Geology Fac. Scienc. Univ. Lisbon, Rua Escola Politécnica, 58, 1250-102 Lisboa, Portugal
[d] Museu Nacional de História Natural (Univ. de Lisboa), Rua da Escola Politécnica n.° 58 1250-102 Lisboa, Portugal
[e] Geology Centre. Rua da Escola Politécnica, n° 58, 1250-102 Lisboa, Portugal
[f] Departamento de Geociências, Universidade de Aveiro, 3810 Aveiro, Portugal

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Abstract

This paper presents a multi-proxy study of sediment samples from the area of the northern Gulf of Cadiz Shelf (SW Iberia) influenced by the Guadiana River. 471 surface sediment samples from the northern gulf of Cadiz Shelf from January 1999 to November 2003 are analysed for grain size variations and composition, including a series of samples retrieved from the same key locations before, during, and after an important flood event in February 2001. Samples from the shelf and coast around the Guadiana estuarine mouth and the inside of the estuary are analysed for heavy mineral composition. Additionally, 26 samples recovered in November 2001 along three transects are analysed for mineralogy, elemental composition, heavy metals, OC, TN, and nannoplankton. The datasets cover mostly fair weather, low precipitation periods, with the exception of the February 2001 survey, which followed an unusually rainy winter and occurred during large-scale flooding in the Guadiana basin with water discharge levels of up to 3000 m^3/s.

The results show, based on calculations from variations in sedimentary components that the bulk of bedload stemming from the Guadiana Estuary is deposited within the 15 m bathymetric line. An estimated $2–2.5 \times 10^6$ tons (or $7.5–9.5 \times 10^5$ m^3) of sand were exported during the winter 2000/2001 from the Guadiana Estuary onto the inner shelf. Simultaneously, fines were resuspended on the inner shelf, and re-deposited at the upper margin of the middle shelf. Sediments are predominantly transported eastwards by the littoral drift, although results also show a weaker westward component. This is true for the coastline, as well as the upper inner shelf, as shown by the distribution of heavy mineral associations, as the Guadiana has a very characteristic translucent heavy mineral signature, composed mainly by amphiboles and pyroxenes.

Samples retrieved half a year after the February 2001 flood indicate a pollutant export from the Guadiana River basin onto the inner and the middle shelf. The signature of these pollutants diminishes in an offshore and eastwards direction on the middle shelf. Although other studies have shown that the Guadiana is less contaminated than the neighbouring Piedras and Tinto–Odiel Systems, our results show that the influence of contaminants from the Guadiana River on middle shelf sediments is much larger than from the heavier polluted Piedras and Tinto–Odiel systems. Pollutants from these two systems probably remain over longer periods of time within the inner shelf.

* Corresponding author.
E-mail addresses: rmn_gonzalez@bluewin.ch (R. Gonzalez), imendes@ualg.pt (I. Mendes).

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Nannoplankton assemblages show considerable amounts fossil Cretaceous to Pliocene specimen probably originating from the shelf slope, documenting the influence of upwelling bottom currents on the lower shelf sedimentation.
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1. Introduction

During the course of the 20th century anthropogenic influence in river systems has become an increasing limiting factor of river discharge. Consequently, sediment supply to estuaries, adjacent coastal areas and continental shelves has been reduced, as river basins are increasingly dammed and water used for electric power generation, irrigation, and a source of drinking water. The problem of flow regulation and consequent reduction in sediment supply is particularly accentuated in rivers of arid and semi-arid zones. Here, water supplies show large seasonal variations, with low run-off levels during summer months and flooding during the winter. Prominent examples are the Nile River in Egypt (e.g. Summerhayes et al., 1978; Frihy, 1988; Stanley et al., 1998), the Colorado River in the USA (e.g. Bowen and Inman, 1966; Carriquiry and Sánchez, 1999), or the Yangtze River in China (e.g. Chen et al., 2001; Chen et al., 2001).

Before mankind began the systematic exploitation of water resources, river discharges, and sedimentary successions formed by sediment carried by rivers to the continental shelves were mainly the result from the interaction between local and large-scale factors: Climatic variations on an inter-annual to multi-decadal scale have a particularly important geomorphological impact (e.g. Maas and Macklin, 2002; Goy et al., 2003; Viles and Goudie, 2003). Furthermore, the vast influence of the NAO and the Arctic Oscillation/Northern Hemisphere annular mode (AO/NAM) — the most prominent modes of winter climate variation in the northern hemisphere (Wanner et al., 2001) — on European river discharge patterns is well documented (e.g. Goodess and Jones, 2002; Rimbu et al., 2002).

The focus of the present study lies on the shelf off the Guadiana River in the northern Gulf of Cadiz (SW Iberia). The southwest of the Iberian Peninsula has been populated since prehistoric times, exploited 'industrially' for its ores at least since Roman times (Leblanc et al., 2000). Regional rivers contain large amounts of metals from erosion and mining (Nelson and Lamothe, 1993), with some impact on the inner shelf, in particular the Tinto and Odiel system (Van Geen et al., 1997; Morillo et al., 2004).

Similar to other rivers in this area, the Guadiana has experienced an increase in anthropogenic influence during the second half of the 20th century (e.g. Brandão and Rodrigues, 2000; Gonzalez et al., 2001), leading to the reduction of average river discharge levels, with a direct impact on extreme flooding events, altering quantity and type of sediments exported to the adjacent shelf, affecting coastal erosion rates, estuarine infilling, and biotopes.

While many studies have investigated the impact of anthropogenic impact on the estuaries (e.g. Nelson and Lamothe, 1993; Gonzalez et al., 2001; Ruiz, 2001; Ligero et al., 2002; Grande et al., 2003) and nearshore areas of the northern Gulf of Cadiz shelf (e.g. Morillo et al., 2004), fewer studies deal with sediment and pollutant fluxes from nearshore areas to the middle and outer shelf, with notable exceptions focusing mainly on the Guadalquivir (eastern) portion of the shelf (e.g. Nelson et al., 1999).

This paper aims to analyse short (annual) and longer term (decadal to centennial) sediment transfer mechanisms on the shelf in the vicinity of the Guadiana River mouth using a multi-proxy approach, with particular focus on the deposition of pollutants and anthropogenic material on the northern Gulf of Cadiz continental shelf. For this purpose, surface sediment grab samples collected between the Guadiana and Tinto–Odiel rivers between January 1999 and November 2001 were analysed, using selected data from sedimentological and component analyses, heavy mineral assemblages, mineralogical and chemical composition, elemental and isotopic ratios of fine-sized particulate organic matter, and nannoplankton assemblages.

2. Materials and methods

A total of 471 surface sediment samples were collected in the northern Gulf of Cadiz shelf in January and September 1999, January and November 2000, and February and November 2001 on board of the Portuguese Navy vessels, *NRP Almeida Carvalho*, *NRP Andrómeda and NRP Auriga* using a Smith McIntyre grab sampler (Fig. 1).

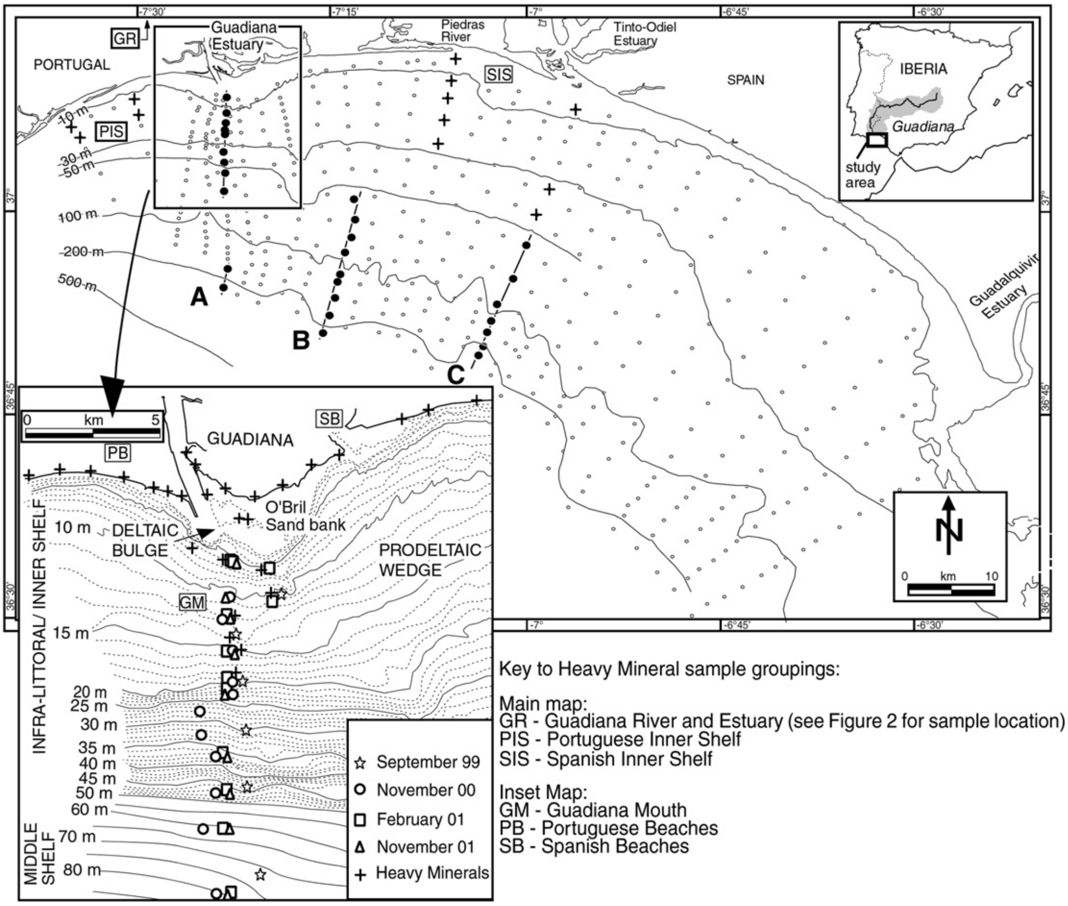

Fig. 1. Study area and sample locations. All samples were used for the maps of sedimentary cover, mean grain size and component types. Transects A, B, and C refer to samples discussed in the geochemical, mineralogical and nannoplankton sections of this study. The inset box shows samples used for the sedimentology. Heavy mineral sample group sites are shown on both maps as +.

The original purpose of the samples used in this study was purely sedimentological. Tight ship schedules and the weather only allowed the area in the vicinity of the Guadiana River mouth to be surveyed in greater detail.

An interest in other types of analyses only arose within the context of a follow-up project, and by this time some of the older samples were no longer viable for geochemical and other types of analysis. Consequently, only the most recent samples (from November 2001) were selected along three shelf transects, positioned off the main river mouths (Guadiana, Piedras, Tinto–Odiel). As the geochemistry of the nearshore areas has been studied in greater detail elsewhere (e.g. Ruiz, 2001; Morillo et al., 2004), it was decided that the transects off the Piedras and the Tinto–Odiel would only cover the middle and outer shelf.

Grain size analyses were performed on all samples. Where the grain size analysis yielded enough sand a component analysis was carried out. The transects of the November 2001 survey were studied for clay minerals (X-ray diffraction), chemical composition including trace elements (X-ray fluorescence), elemental and stable isotopes, carbonate content, and nannoplankton (Fig. 1). The transects as well as additional samples from the Portuguese and Spanish coastline on both sides of the Guadiana River mouth (collected in July and December 2003), and samples from inside the Guadiana River and Estuary were subject of a heavy mineral analysis (Fig. 1).

2.1. Bathymetry

Bathymetric information used in this study was compiled from Fernández Salas et al. (1999), Instituto Hidrográfico (1998), and Instituto Hidrográfico de la Marina (1990). A bathymetric survey was carried out in October 2002 to map the location of submerged terraces using a JMC Model F-840 Recording Echo Sounder, by making a series of crosshore transects between the 10 and 50 m bathymetric lines between Cacela Peninsula on the Portuguese coast and the eastern limit of the Guadiana delta on the Spanish coast. The data was analyzed using the SURFER software.

2.2. Grain size analysis

Sediment samples were washed several times using increasing concentrations of hydrogen peroxide (10, 30, 80, and 130 volumes/l) to eliminate all organic matter. Coarse sediments (i.e. sands and gravels) were separated from the fine-grained fraction (silt and clay) by wet sieving using a 4 ϕ (63 μm) sieve. Grain size analyses of all samples were carried out using the pipette method for fines and by dry sieving in ϕ intervals for coarse-grained fractions.

2.3. Sediment component analysis

The sediment type in terms of its dominant grain size components (gravel, sand, mud) was determined using the classification of Folk (1954). Descriptive grain size parameters were calculated using the method of moments (e.g. Krumbein and Pettijohn, 1938). All grain sizes in this paper will be given in the ϕ scale of Krumbein (1934).

Sand fraction components (−1 to 4 ϕ) were quantified by counting 100 grains in each fraction using a binocular microscope. Several samples of diagnostic importance were additionally re-counted. Grains were classified visually as quartz, feldspar (where possible), mica, terrigenous carbonates (where possible), other terrigenous grains, aggregates, grains containing glauconite, foraminifera, molluscs, and other bioclasts. Additionally, grains from Paleozoic metaschists and greywacke, widespread within the lower Guadiana River basin (e.g. Oliveira et al., 1979; Oliveira, 1983), were counted as a separate component. These grains are easily identified under the binocular, usually as compact (sometimes laminated) aggregates of silt — to very fine sand-sized particles, and fine-grained mica, giving them a rough surface and 'peppery' appearance.

In samples with a quartz content of over 2%, 100 grains in the 1–2 ϕ as well as the 2–3 ϕ fractions were analysed for morphoscopic groups (*sensu* Cailleux, 1942). Grains were divided into three classes: not used ('non usés'), blunt-shining ('emoussés-luisants', usually associated with transport in water), and round-matt ('ronds-mats' associated with eolian transport).

2.4. Heavy minerals

Samples used for the heavy mineral analysis were distributed in four groups according to their origin (Fig. 1): Guadiana River and Estuary (GR; 6 samples: 3 at Vila Real de Santo Antonio, 2 at Mértola, 1 at Serpa; see Fig. 2 for location), Guadiana mouth (GM; 12 samples), Portuguese inner shelf (PIS; 6 samples), and the Spanish inner shelf (SIS; 12 samples).

Heavy minerals were obtained from the medium (1–2 ϕ; 500–250 μm), fine (2–3 ϕ; 250–125 μm), and very fine sand (3–4 ϕ; 125–63 μm) fractions using bromoform (d=2.89 g cm^{-3}), and were then mounted on Canada balsam slides. The necessary amount of grains to produce each slide was obtained via micro-splitter reduction. About three hundred heavy minerals per slide were counted under the petrographic microscope and converted into numeric percentages.

2.5. Mineral analysis and quantification

Samples were washed with distilled water and wet sieved using the ASTM 230 mesh sieve 4 ϕ (63 μm). Sediment fractions smaller than 4 ϕ were dried at 60 °C in an oven and gently disaggregated in a porcelain mortar. The yielded material was submitted, in non-oriented powder preparations, to X-ray diffraction (XRD) analysis using a Philips powder diffractometer equipped with an automatic slit, using nickel-filtered CuKα-radiation emitted at 20 mA and 40 kV, in a range from 2° to 40° 2θ, at 1° 2θ/min. The XRD reflections were evaluated with the Phillips X′Pert 1.2 and commercial software.

For the semi-quantitative determination of clay and non-clay minerals, the relative content of each identified mineral was estimated on the basis of its characteristic peak area corrected by the corresponding reflective power as recommended by Barahona (1974), Schultz (1964), Thorez (1976), Mellinger (1979) and Pevear and Mumpton (1989). The quantification accuracy was estimated at 5–10%.

2.6. Chemical composition

Samples were wet sieved to separate the silt/clay size fraction (commonly considered to be the most useful fraction for the tracing of anthropogenic inputs), followed by freeze-drying. Pellets of about 2 g of the separated fine fractions were prepared and analysed by Energy-Dispersive X-Ray Fluorescence Spectrometry (EDXRF) using a Kevex Delta XRF Analyst Spectrometer for the elements Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr and Pb. Elemental concentrations were determined using the EXACT computer program, based upon a fundamental parameter method, that uses calibration

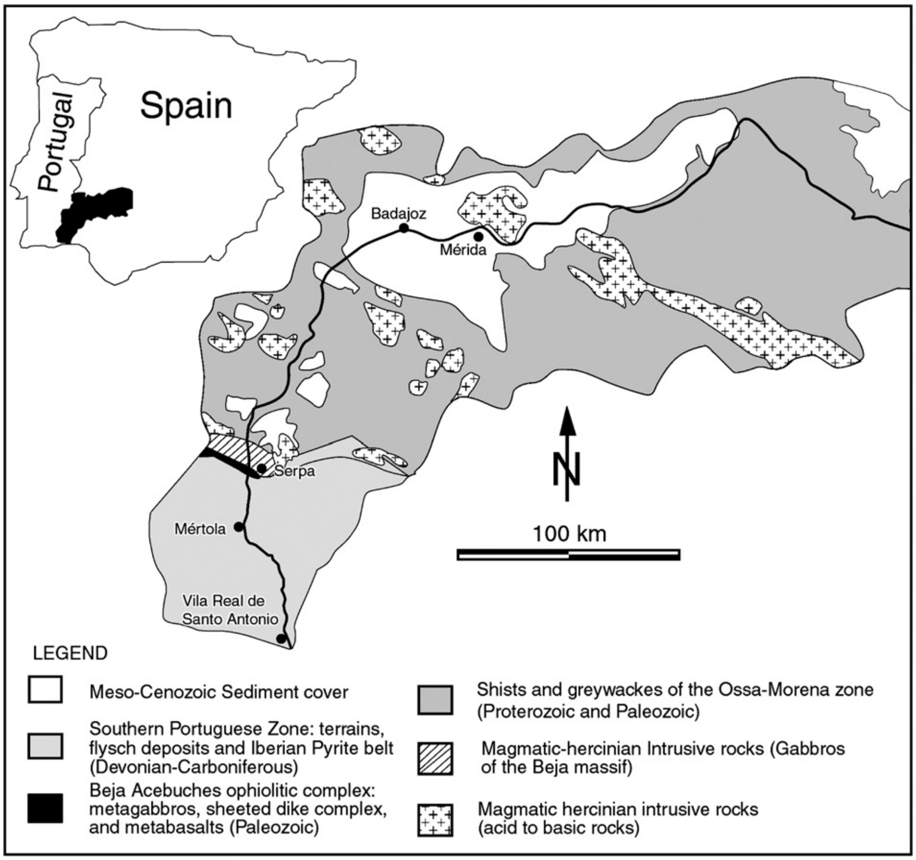

Fig. 2. Rough geological sketch of the western part of the Guadiana basin (adapted from Oliveira et al., 1992; Liñán et al., 1994).

coefficients and accounts for matrix effects. A geological standard reference, the Buffalo Lake Sediment (SRM 2704) from the National Institute for Standard Technology (NIST) was used to correlate the X-rays emitted by the elements ($Z > 12$) constituents of the sample with their correspondent concentrations. A detailed description of the sample preparation, quantitative analysis as well as the accuracy and precision of the overall procedure has been previously published in Araújo et al. (1998, 2002).

2.7. Elemental and stable isotope measurements

Bulk sediment samples were sieved at 4 ϕ (63 μm), and the finer fractions used for these analyses, as residual soil organic matter is more concentrated in fine size fractions (Balesdent and Mariotti, 1996), and a better characterisation of continental sources of organic matter can be expected.

To remove carbonates, the fine size fraction of sediment was carefully treated with 1 N HCl at 70 °C in a way that pH was always maintained at 3, to reduce possible leaching effects on organic matter. All samples were rinsed in deionised water to remove dissolved salts. The solid residue was recovered by high velocity centrifugation (20,000 rpm for 1 h), dried at 35 °C and hand-ground with a mortar.

Organic carbon (OC), total nitrogen (TN) and $\delta^{13}C$ isotope ratios were measured, after carbonate removal, on the same sample aliquot by EA-IRMS (EuroVector 3028-HT Elemental Analyser on line with a SIRA 10 Isotope Ratio Mass Spectrometer) at the Instituto Tecnológico e Nuclear in Sacavém. Results for isotope abundance are reported in per mil (‰) relative to the Pee Dee Belemnite (PDB) standard for $\delta^{13}C$. OC and TN are reported in mg/g of dry sample. The analytical precision ($\pm 1\sigma$) was of ±0.2‰ for $\delta^{13}C$, 0.2 mg/g for OC and 0.02 mg/g for TN. The uncertainty on OC/TN ratios averages 0.2. Data reproducibility was checked by replicate analysis of samples (50%).

2.8. Nannoplankton

Sediment samples were dried in the laboratory. Part of the dried sediment was weighted and then filtered through 0.45 μm Millipore cellulose nitrate membrane filters. A sector of approximately 25° of each filter was permanently mounted on a slide and cover slide with synthetic cement (Entellan). For each sample a radius of the membrane filter was randomly selected and scanned. Species counts were then converted to estimate the total number of coccoliths or nannoliths per gram of dry sample, relating first the overall observed area to the total area of the filter, and then the weighted dry sample filtered. The number of coccoliths counted in each sample ranged from 177 to 418.

Identification and quantification of specimen were performed using a polarizing optical microscope Ortholux II Pol-BK under 1250× magnification. The taxonomy follows Perch-Nielsen (1989) and Bown (1999).

2.9. Factorial analysis of fines

A factorial analysis using STATISTICA (StatSoft) (vers. 7, Module: Multivariate Exploratory Techniques) was carried out on the fine-grained sediment fraction of the sediments occurring along the three studied transects, comprising a total of 26 samples. The following parameters were analysed: water depth (m), organic carbon (mg/g), total nitrogen (mg/g), δ^{13}C (per mil), Al (%), Si (%), Fe (%), Ca (%), Sr (mg/kg), Cu (mg/kg), Zn (mg/kg), Pb (mg/kg), nannoplankton extant ($\times 10^6$), nannoplankton fossil ($\times 10^6$), grain size mean, standard deviation (grain size analysis), filossilicates, quartz, feldspar, carbonates.

3. Regional setting

The study area is located in the eastern part of the northern Gulf of Cadiz shelf (south-western Iberian Peninsula; Fig. 1).

3.1. Geology of the Guadiana River basin

As this study focuses on sediments exported from the Guadiana River basin, it is worth making a short summary of the geological setting of this area.

The area included in the Guadiana River basin is composed of a wide range of geologic formations of Proterozoic to Mesocenozoic age (Fig. 2). The Proterozoic and Paleozoic terrains belong to the Southern Portuguese and Ossa–Morena Iberian paleogeographic and tectonic zones (Ribeiro et al., 1979).

Within the Southern Portuguese zone the most significant outcrops are flysch deposits, volcano-sedimentary formations (Iberian Pyrite Belt) and meta-basalts of Devonian and Carboniferous age. The Ossa–Morena zone is composed of outcrops of Precambrian to Carboniferous age including a very wide variety of lithological types such as schists, greywacke, siltites, gneisses, quartzites, amphibolites, gabbros, diorites and granites (Oliveira et al., 1992; Liñán et al., 1994). The mafic–ultramafic complex of Beja–Acebuches found between the Southern Portuguese and Ossa–Morena zones is composed mostly of amphibolites, serpentinites, and gabbros (Oliveira et al., 1992).

Mesocenozoic terrains occur near the Guadiana estuary mouth as well as in some areas of the inner Guadiana basin interior namely, in the Badajoz–Almendralejo and Moura–Brinches region (Liñán et al., 1994).

3.2. Shelf physiography

The Guadiana shelf lies in a transition zone between the narrow, relatively steep Portuguese shelf, with a width of 5 km between Cape Santa Maria and Tavira and a slope of 0.5°, and the north-eastern corner of the Gulf of Cadiz where the shelf is more than 30 km wide off the Guadalquivir River mouth, with slopes of less than 0.2° (Lobo et al., 2001). The shelf break lies at 140–150 m water depth off the Guadiana River (Baldy, 1977; Vanney and Mougenot, 1981).

The inner (infralittoral) and middle/outer portions of the continental shelf in the northwestern Gulf of Cadiz are separated by a series of well-defined steep terraces between 30 and 50 m water depth (e.g. Fernández Salas et al., 1999; Gonzalez et al., 2004). These become less prominent toward the easternmost part of the shelf, i.e. the mouth of the Guadalquivir River.

3.3. External forcing factors

3.3.1. Meteorology

The climate of the Guadiana basin has typical Mediterranean characteristics with mean annual temperatures ranging from 14 °C to 18 °C, and highly irregular precipitation patterns (e.g. Loureiro et al., 1986; http://snirh.inag.pt).

According to Silva et al. (2000a), based on data collected at the Tavira meteorological station (at the western edge of the study area) between 1999 and 2000, wind forcing in the area was dominated by diurnal variability. At periods longer than 1.5 days ("low-frequency"), there was a tendency for the wind to blow along a direction some 25° to the left of the local direction of the coastline. The strongest low-frequency winds, however, were perpendicular to the coast, the most frequent from NW and the strongest from SE. Most gales were south-easterly, usually lasting for 1–3 days.

3.3.2. Wave regime

The wave regime in the southern coast of Portugal is characterized by significant height monthly averages ranging between 0.6 and 1.5 m, with values always exceeding 1 m during winter (October to March) (Costa et al., 2001; based on wave data collected off the coast of Faro, about 50 km west of the study area). Average periods range between 4 and 6 s and peak periods between 6 and 11 s with maximum values between November and January. During the summer there is an increase in W peak directions, while winter months show a higher incidence of SW directions. In both situations SE directions made up about 23% of the occurrences. In this same study, storm events were defined as periods with significant heights over 3.5 m. These events can be divided into three main groups: events associated with W and SW atmospheric circulation patterns in the Atlantic generating SW wave directions significant heights from 3 to 5 m (sometimes exceeding 6 m); SE events associated with E/SE circulation patterns characterized by short periods and significant heights below 5 m; and events associated by rotating atmospheric conditions linked to moving low pressure zones in SW Portugal with short duration and significant heights of 4 to 5 m.

3.3.3. River flow

River flow values in the Guadiana estuary, measured in the Pulo do Lobo station (about 70 km upstream of the estuary mouth) between the 1940's and 2001 show an average flow of 141 m^3/s, decreasing to 83 m^3/s during the last decade. In the 1950′s, only 47% of the monthly averaged flows were below 20 m^3/s. This proportion has risen to 67% in the 1990's. The interannual variability is very high, reflecting a combined influence of climatic fluctuations and regulation management (Silva et al., 2000b). 1999 and 2000 were characterized by low discharge values. In effect, flow values in the Guadiana basin were near zero since mid-1998 including in the periods that preceded the September 1999 and November 2000 field surveys. The only exceptional flood event in February 2001 in the three-year period 1998–2001 coincided with one of the field surveys. This flood event was characterized by flows of over 3000 m^3/s.

3.3.4. Current regime

The current signals in the south-eastern Portuguese shelf are dominated by the semi-diurnal tide, particularly in the N–S "cross-shore" barotropic component (Silva et al., 2000a). The E–W "long-shore" component shows baroclinicity and long period variability. The "long-shore" component is spatially coherent in horizontal direction and most of its variability does not seem related to meteorological forcing. During an extreme event like the February 2001 flood, current meter series in the inner shelf off the Guadiana mouth showed higher current velocities at mid-water with maxima exceeding 0.4 m/s heading east. Near the bottom, currents were weaker and tended to follow the ENE–WSW axis with maxima of 0.25 m/s due east and mean values of less than 0.1 m/s.

3.4. Sediment supply

Sediment is supplied to the study area from two main sources. The Guadalquivir is the largest source of sediment. However, most sediment is deflected south-eastward, due to the influence of the North Atlantic Surface Water current (e.g. Lobo et al., 2004). The largest regional sediment source is the Guadiana River. The estimated sediment supply from the Guadiana River basin to the shelf between 1946 and 1990 was in the range of 57.90×10^4 m^3/a for the average suspended load and 43.96×10^4 m^3/a for bedload (Morales, 1997).

The second regional sediment source is the littoral drift. Prevailing onshore wave conditions along the coastline produce an eastward net annual littoral drift estimated to be between 10×10^5 and 30×10^5 m^3/a of mostly sandy sediment, carrying sediments from the southern Portuguese coast towards the eastern portion of the Gulf of Cadiz (Gonzalez et al., 2001). While some of these sand- and gravel-sized sediments are trapped in the Guadiana estuarine system as they pass the river mouth, most sediment remains within the inner shelf.

3.5. Sediment cover

Terrigenous sandy deposits dominate the shelf down to a water depth of approximately 25 m, particularly in near-shore zones (Figs. 3 and 4; *cf*. Moita, 1986; Fernández Salas et al., 1999). A prodeltaic wedge off the Guadiana Estuary (see Fig. 1 for location) consists of strips of sandy mud and mud forming an oblong mud patch with an area of about 60 km^2 (Fig. 3; *cf*. Fernández Salas et al., 1999). Within this mud patch mean grain sizes are as fine as 8 ϕ (Fig. 4a) and sand-sized sediments are dominated by bioclasts (Fig. 4b). Terrigenous components other than quartz occur in large quantities off the Guadiana mouth and to the northwest of the Guadalquivir estuary, but are lacking off any of the other estuaries (Fig. 4b).

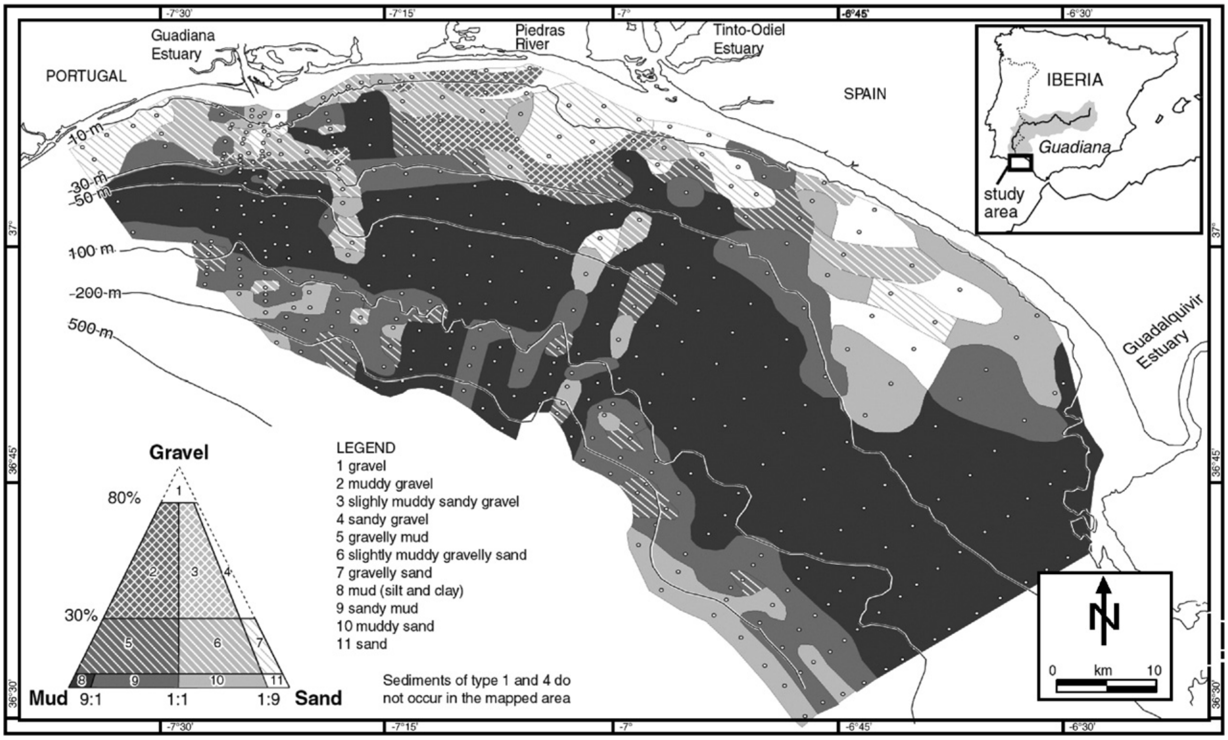

Fig. 3. Sediment cover of the northern gulf of Cadiz Shelf between the Guadiana and Guadalquivir estuaries.

The outer infralittoral between 25 and 30 m consists of sands and sandy mud. Additionally, this area features a series of rocky outcrops of reduced extent, and probably of Holocene age (Rey and Medialdea, 1989; Fernández Salas et al., 1999), containing varying amounts of terrigenous gravel. The area also features patches of densely vegetated bryozoan temperate water reefs. The transition between the inner and middle shelf is characterised by the aforementioned steep terraces which only feature thin sediment covers, characterised by sand and gravels in the upper portion and becoming more mud dominated towards the bottom.

The middle shelf is characterised by an extensive mud belt, consisting of very fine-grained clayey material (Figs. 3 and 4a; *cf*. Nelson et al., 1999). Rare sand grains are commonly of bioclastic nature, mostly molluscs and Foraminifera (Fig. 4b). Crossing from north to south through the surface of the outer infralittoral ridge and the upper middle shelf mud deposits lie a series of transgressive deposits composed of muddy gravely sands and muddy sands (Figs. 3 and 4a) (*cf*. Gonzalez et al., 2004).

Outer shelf sediments below 100 m are dominated by mixtures of sand and silty clay, interrupted locally by large patches of sand and gravely sand in the vicinity of the shelf edge (Figs. 3 and 4a). Some of these deposits are relictic in nature (Gonzalez et al., 2004), as documented by occasional occurrences of terrigenous material (Fig. 4b). Mostly however, the sand grain fraction is dominated by Foraminifera, both recent as well as tests covered with glauconite.

4. Results

4.1. Sedimentary dynamics

4.1.1. Grain size composition off the Guadiana in function of river discharge

Fig. 5 shows the grain size composition (gravel, sand, silt, and clay) of samples taken at equivalent locations during several surveys (see Fig. 1 for sample locations). The nearshore portion is sand-dominated, with fines making up about 20% of sediments. Prominent accumulations of gravel occur at the edge of the infralittoral, peaking at around 40% at water depths of about 20 to 25 m. Part of these gravels are relictic in nature, containing mostly well-rounded terrigenous components with iron oxide patinas, while the other part is composed of shells and bryozoan fragments (Gonzalez et al., 2004). The amount of fines increases below about 25 m water depth, and makes up 95 to 100% of sediments below 35 m (see also Fig. 3).

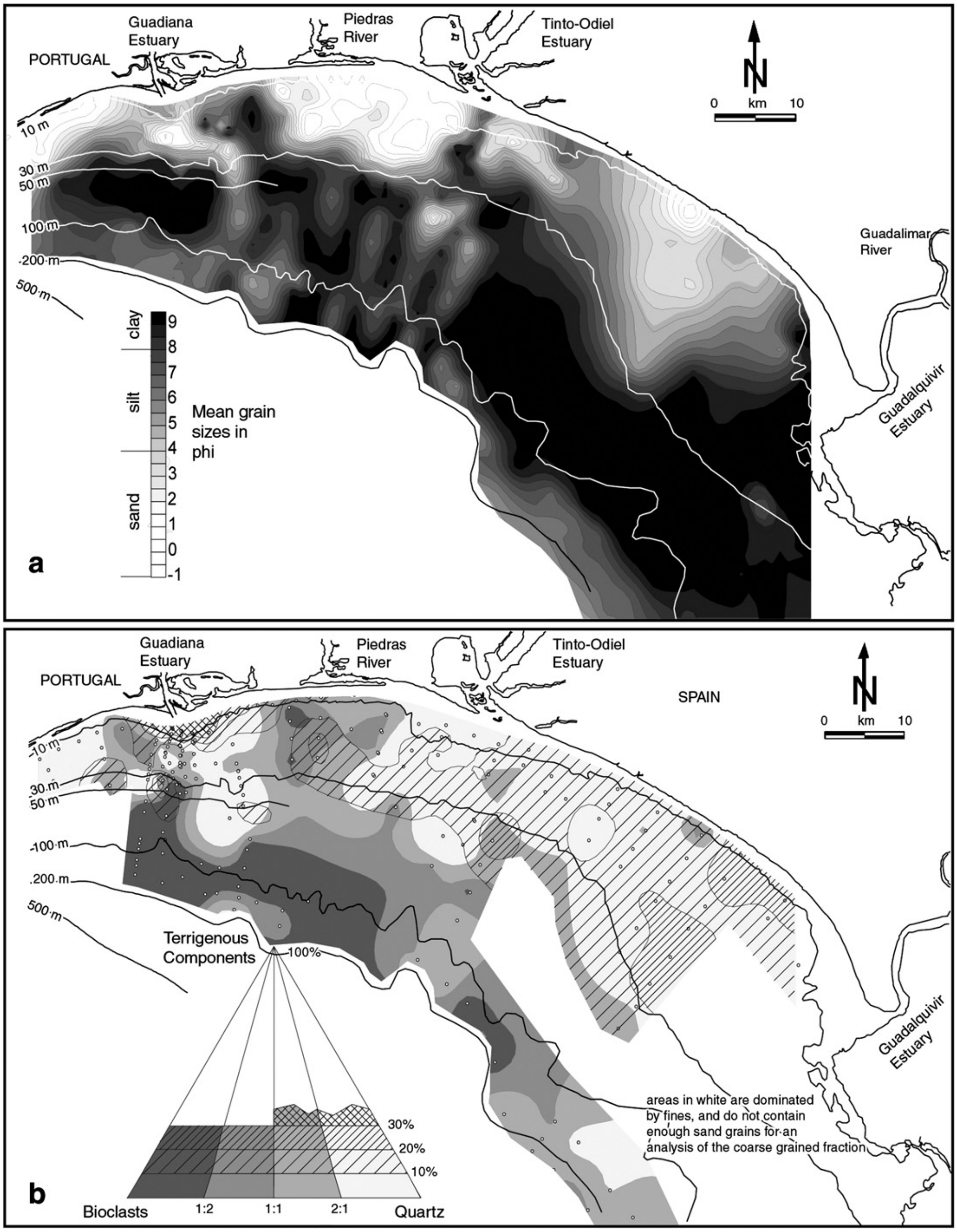

Fig. 4. Sedimentological characterisation of northern gulf of Cadiz Shelf between the Guadiana and Guadalquivir estuaries: a) Mean grain size distribution; b) main sand-sized components.

Between November 2000 and February 2001 sample values show a reduction in fines near the river mouth (Fig. 5a,b), with clays becoming nearly non-existent within the infralittoral — probably due to remobilization of fines during storm events occurring during this period — and silt occurring in proximity of the river mouth down to a water dept of about 10 m (or a distance from the mouth of 3500 m), possibly associated with high discharge levels during the flood.

Fig. 5c shows the situation in November 2001, 9 months after the flood. Percentages of silt have increased down to water depths of about 13 m (or a

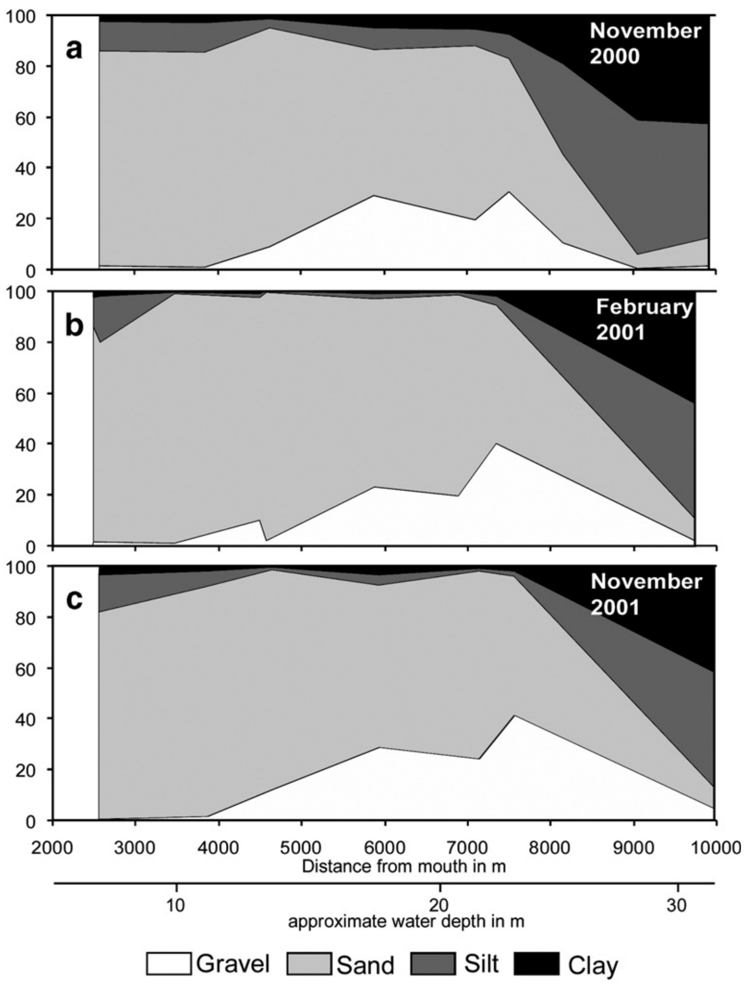

Fig. 5. Comparison of sediment composition off the Guadiana mouth as sampled on equivalent locations in November 2000, February 2001, and November 2001. For location of sampling stations see inset box on Fig. 1.

distance from the mouth of about 5000 m), and also have increased in the lower infralittoral. Amounts of clay have increased everywhere on the inner shelf.

4.1.2. Short-term sediment export signature

Fig. 6 shows the distribution of metashist and greywacke particles (MSGR) on the inner shelf. As these grains are rapidly abraded under the influence of currents and waves, they can be used as a proxy reflecting short-term (in the range of years) export mechanisms from the Guadiana River mouth to the shelf. MSGR are exported to the northern Gulf of Cadiz inner shelf almost exclusively by the Guadiana River, and do not occur elsewhere in significant (>2%) quantities, although these sediments occur in the Piedras, or Tinto–Odiel river basins.

Fig. 6 shows that the percentage of MSGR is slightly skewed to the east. They peak at about 18–20% immediately off the Guadiana estuary mouth, with most grains occurring within 2 km to the west and about 6 km to the east of the river mouth, and still amounting to 5% 5 km west —, and 10 km eastwards, respectively. This indicates a strong influence of the eastward littoral drift in their longshore distribution. MSGR make up to 10% of grains down to a water depth of about 10 m, but disappear almost completely below 15 m. Exceptions are probably related to submarine outcrops of relic sediments (Gonzalez et al., 2004).

Differences in MSGR in the top 0.15 m of sediment from around the Guadiana estuary mouth between November 2000 and February 2001 were used to roughly estimate sand export from the Guadiana estuary to the inner shelf. The estimates of exported sediments is based on the additional amounts of estuarine sand necessary on already existing shelf sand in order to account for variations in MSGR. The February 2001

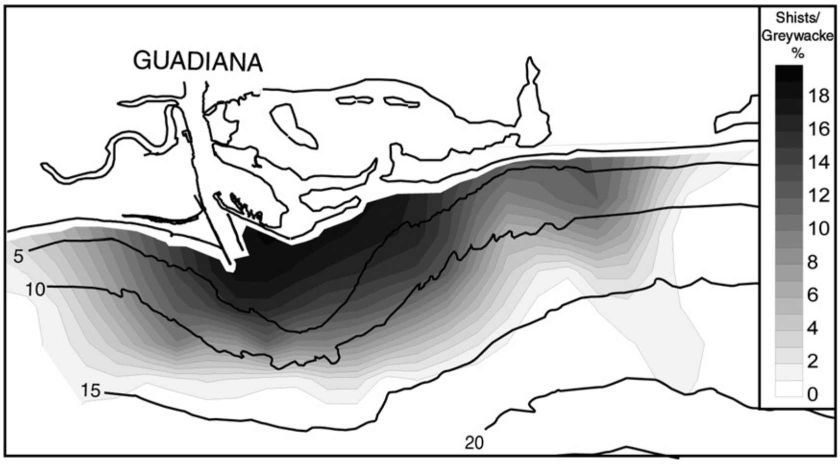

Fig. 6. Distribution of shist/greywacke fragments in the vicinity of the Guadiana River mouth.

survey followed a winter with above average rainfall and river discharge levels. Any evaluation of sediment export is a value for the total sand exported during the winter 2000/2001 (see also Figs. 5 and 7), but it is likely that most sand export occurred during the February 2001 flood.

Metashist and greywacke (MSGR) percentages within the final 10 km of the estuary consistently reach about 30%. This percentage was used as the base value for MSGR content in sediment exported from the estuary. It was assumed that sediments were distributed over the shelf mimicking patterns shown on Fig. 6, excluding the easternmost area. Based on Fig. 7 it was assumed that most sand is deposited within 5–10 m water depth off the estuary mouth, with levels of deposited sediments decreasing west — and eastwards.

Using these assumptions it is estimated that sand was deposited over a total area of 85 km^2 during the winter 2000/2001, 25 km^2 of which fall into the area where most sand was accumulated. Percentages of MSGR within sand are significantly increased by an average of about 5% in most nearshore samples down to 20 m water depth (Fig. 7a) during the Winter 2000/2001. We estimate that about $2–2.5\times10^6$ tons (or $7.5–9.5\times10^5$ m^3) of exported sand were deposited onto the inner shelf during this period in order to account for this increase (note that these numbers are only rough estimates, as almost nothing is known about mixing depth levels within the area; we based our calculations purely on the sediment composition of samples, which were taken within the top 10 cm of the sea bed). Interestingly, levels of MSGR drop back to previous values for the November 2001 survey, documenting fast coarse-grained sediment turnover in the area.

4.1.3. Longterm sediment export trends to the shelf

Quartz has been used to determine sediment sources and sinks on continental shelves (e.g. Prusak and Mazzullo, 1987) although quartzitic particles have a

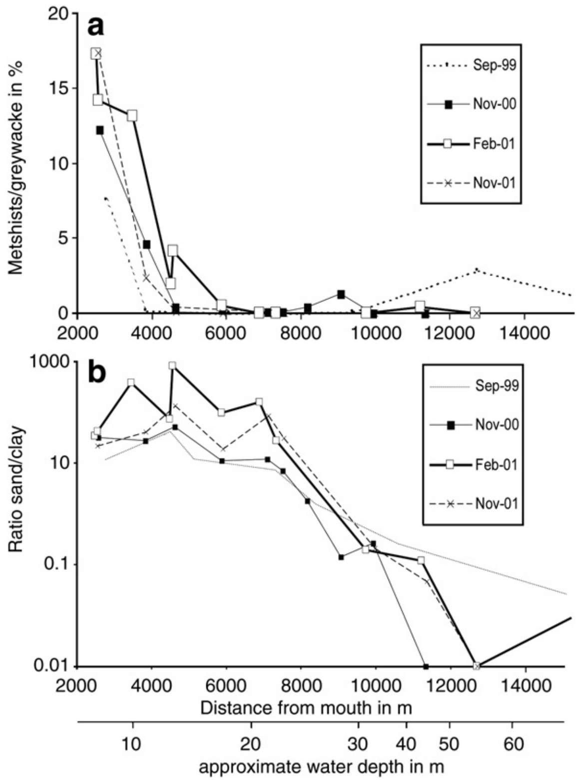

Fig. 7. Comparison of sediments sampled at equivalent locations during four surveys. a) amount of Metashists/greywacke in %; b) ratio sand/clay (Note logarithmic scale). For location of sampling stations see inset box on Fig. 1.

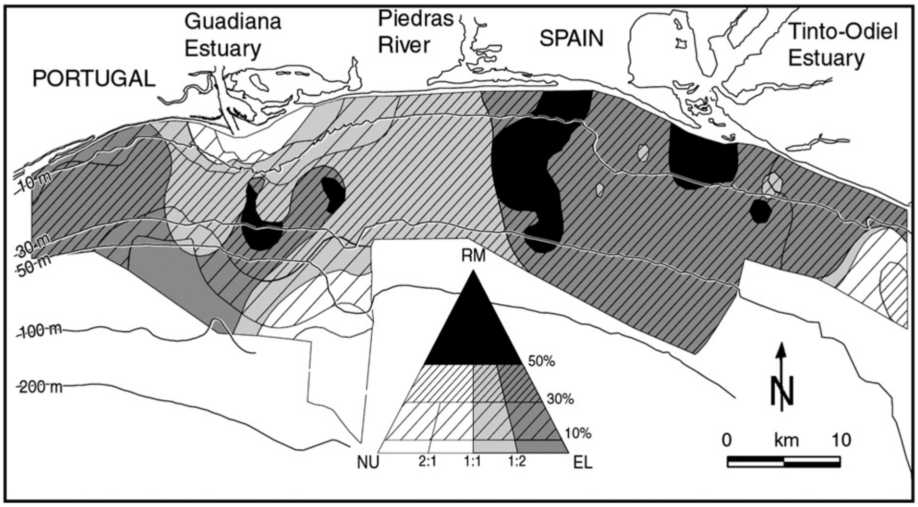

Fig. 8. Quartz type distribution in the northern Gulf of Cadiz inner shelf classified according to the nomenclature of Cailleux (1942).

long lifespan and can return during various sea-level cycles into a sedimentary system, making a distinction of past and present hydrodynamic regimes difficult (e.g. Gutiérrez-Mas et al., 2003). In spite of this, an attempt was made using quartz to determine longterm export patterns from the Guadiana, with the simple method for the identification of quartz grains proposed originally by Cailleux (1942) (Fig. 8).

A high concentration of NU (not-used) quartz with mostly fresh, unused broken surfaces and edges occurs in the vicinity of the Guadiana estuary mouth indicating a possible direct association with this river basin (Fig. 8). Additionally, fresh quartz grains (of NU, but also EL type) are distributed across the shelf to a water depth of up to 50 m (with decreasing influence below 20 m water depth) both in a SSW and a broad SE direction. Both areas are separated by strip of seafloor at the outer boundary of inner shelf off the Guadiana River mouth where older (Pleistocene) sediments crop out (Lobo et al., 2001; Gonzalez et al., 2004).

East of the Piedras River, grains of EL type (associated with transport in water), with shiny, polished surfaces and round edges dominate. No significant amount of fresh quartz (NU) from either the Piedras or Tinto–Odiel river systems occur, indicating that coarse-grained sediment export from these rivers is much less efficient than from the Guadiana River. Areas off the main river mouths show large accumulations of RM grains (usually associated with eolian transport), with well-rounded surfaces and covered by a matt, ferruginous patina. It is likely that these grains are linked with fluvial contributions to the area during the Pleistocene (e.g. Moreno et al., 2002).

4.2. Heavy minerals

Of the analysed samples, the Guadiana River assemblage (GR) is the richest in heavy minerals

Table 1
Heavy mineral average weight percentage and range values according to the different sample groups

Sample group	# Samples	Heavy mineral %	Range (%)
GR	6	13.6	0.7–43.7
GIS	12	3.2	1.1–6.1
PIS	6	0.4	0.1–0.6
SIS	12	1.3	0.01–5.9

The values represent the sum of the results obtained in the three analysed grain-sizes classes (0.5–0.063 mm).

Table 2
Average percentage of the main heavy mineral species (average values from 60 analysed samples)

Heavy minerals	Average %	Minimum %	Maximum %
Tourmaline — TO	8.82	0.0	33.76
Andalusite — AND	5.93	1.96	12.45
Staurolite — ST	2.38	0.0	11.05
Epidote — EP	0.50	0.0	1.61
Clinopyroxene — CPX	0.95	0.0	2.86
Orthopyroxene — OPX	0.94	0.0	5.17
Green amphibole — GAM	11.42	0.0	29.15
Brown amphibole — BAM	3.55	0.0	10.99
Garnet — GA	1.06	0.0	4.66
Zircon — ZI	0.58	0.0	2.12
Biotite — BI	0.95	0.0	15.78
Others — OTH	0.58	0.0	1.31
Opaque — OP	53.59	29.94	75.16
Alterites — ALT	10.59	4.02	19.89

Table 3
Main translucent heavy mineral species in the different sample groups (average values in %)

Main translucent heavy minerals	GR	GIS	PIS	SIS
TO	2	19	58	23
AND	14	14	21	30
ST	0	6	18	3
CPX	8	4	0	2
OPX	11	3	0	2
GAM	42	41	3	29
BAM	25	13	0	11

(13.6%), while the inner shelf has the lowest values (1.3% in the eastern SIS group and 0.4% in the western PIS group; Table 1). The fundamental translucent heavy mineral spectrum is composed of the following main minerals (>1% of sample): tourmaline (TO), andalusite (AND), staurolite (ST), epidote (EP), clinopyroxene (CPX), orthopyroxene (OPX), green amphibole (GAM), and brown amphibole (BAM), garnet (GA), zircone (ZI), and biotite (BI). Furthermore, considerable amounts alterites and opaque minerals were identified. The mean values and correspondent maxima and minima are shown on Table 2.

An analysis of the occurrence of the principal translucent species within the four sample groups shows that there is a specific Guadiana heavy mineralogical association (GR association), dominantly composed of amphiboles and pyroxenes (representing more than 80% of the fundamental translucent heavy mineral spectrum). This association is very well represented in the groups GM and SIS, but almost absent in the PIS group (Table 3, Fig. 9). In fact, the Portuguese inner shelf (PIS) is composed of a very peculiar heavy mineral spectrum compared to the other sample groups, and only contains tourmaline, andalusite and staurolite (Table 3, Fig. 9).

4.3. Fine fraction mineralogy

Results discussed here relate to the three transects (A, B, C) shown on Fig. 1.

The dominant minerals within the silt and clay grain size fractions are mica/illite (average 33%; max 42%;

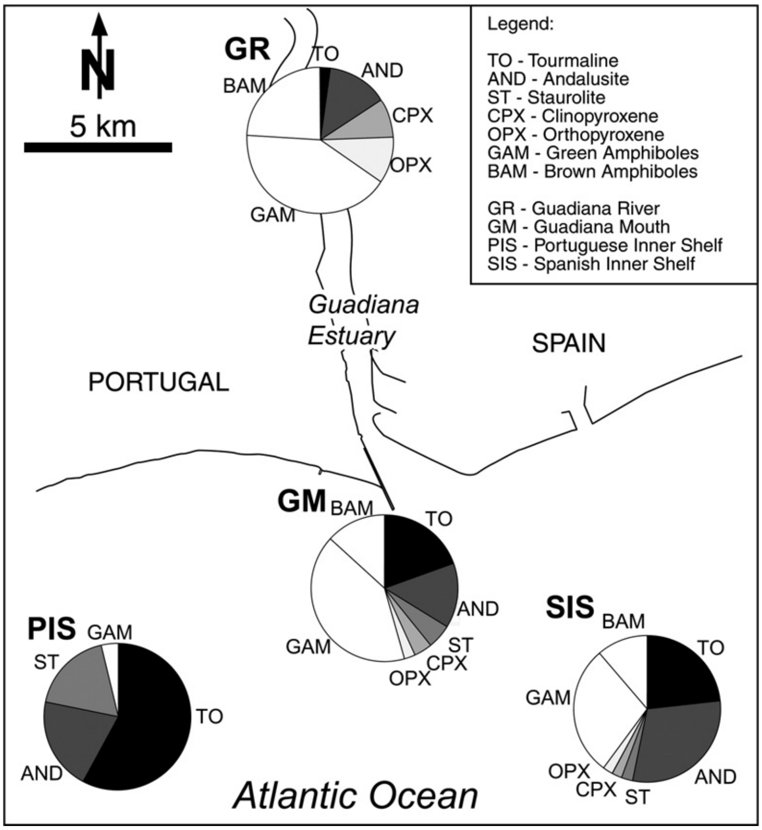

Fig. 9. Heavy mineral spectrum present in the different groups.

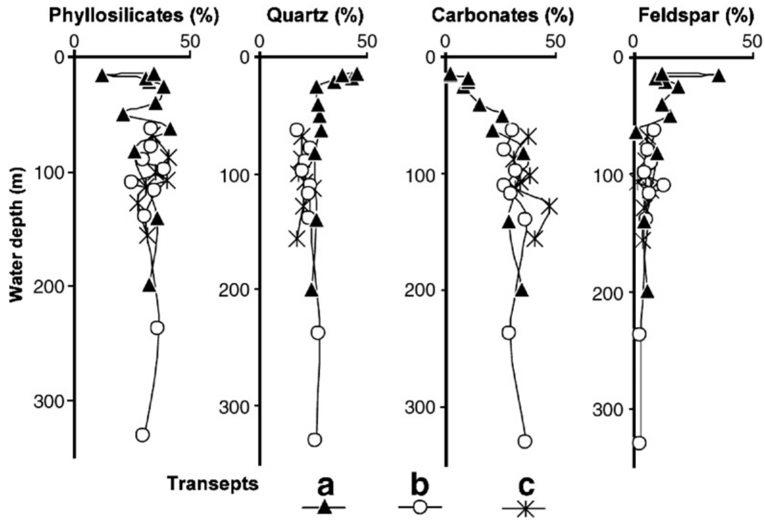

Fig. 10. Main mineral components within the three transects versus water depth.

min 12%; SD 6%), quartz (average 26%; max 45%; min 18%; SD 7%) and about equal amounts of calcite and dolomite (average 27%; max 47%; min 2%; SD 12%). Feldspars (K feldspars — FK and Na–Ca feldspars — P) show an average content of 8% (max 36%; min 1%; SD 7%). Other accessory minerals, such as opal C/CT, anhydrite, hematite, pyrite, anatase, goethite and amphiboles, are present in smaller proportions.

The water depth variations of phyllosilicates, quartz, carbonates and feldspars are shown on Fig. 10. Amounts of phyllosilicates are lowest close to the Guadiana mouth, increasing to a water depth of 25 m, followed by a decrease down to 50 m and a successive increase, with the highest values on the middle shelf (50–90 m) for all studied samples.

Quartz and feldspar exhibit an opposite behaviour (Fig. 10). Quartz is most common close to the Guadiana River mouth with percentages decreasing towards the outer shelf. Below 25 m, the amount of quartz remains constant in all three transects. Feldspars are most common off the Guadiana mouth.

Carbonates, either of biogenic or chemical origin (calcite, dolomite and siderite), show a significant increase with water depth (Fig. 10). Values are rather low off the Guadiana mouth and peak at the mid-shelf locations on the easternmost transect (C). This tendency reflects the increase of the biogenic contribution with a subsequent decrease of terrigenous sediments towards east on the middle and outer shelf.

The analysis of mineralogical data was used to estimate key mineral ratios (Machado, 1999) (Fig. 11):

The Feldspar/Quartz (Felds/Qz) ratio is used as an indicator of mineralogical maturity of sediments. This parameter shows high values close to Guadiana River mouth extending down to 50 m water depth, indicating a low mineralogical maturity for this zone. On the mid-shelf, the maturity index shows low values in samples collected along transects B and C, or high maturity, suggesting a reduction of continental sedimentary sources.

The ratio of fine detritic minerals/coarse detrital minerals [Phyl/(Qz+FK+P)] is used to assess the hydrodynamic conditions. This ratio allows the definition of two major areas, one close to the Guadiana River mouth distinguished by a high energy environment and low ratios, and another one down to about 100 m

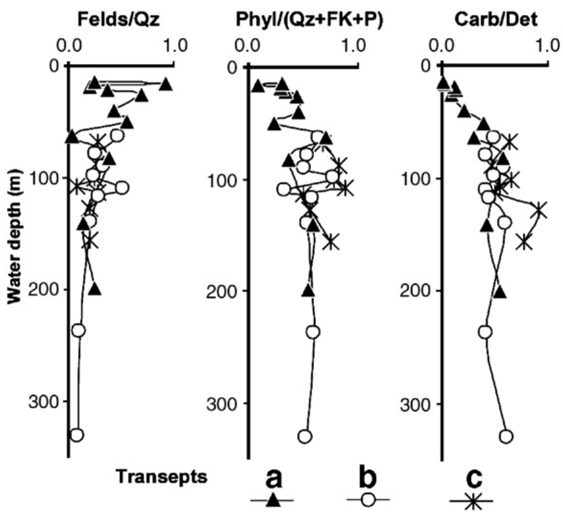

Fig. 11. Plots of depth variation of Felds/Qz; Phyl/(Qz+FK+P); Carb/Det.

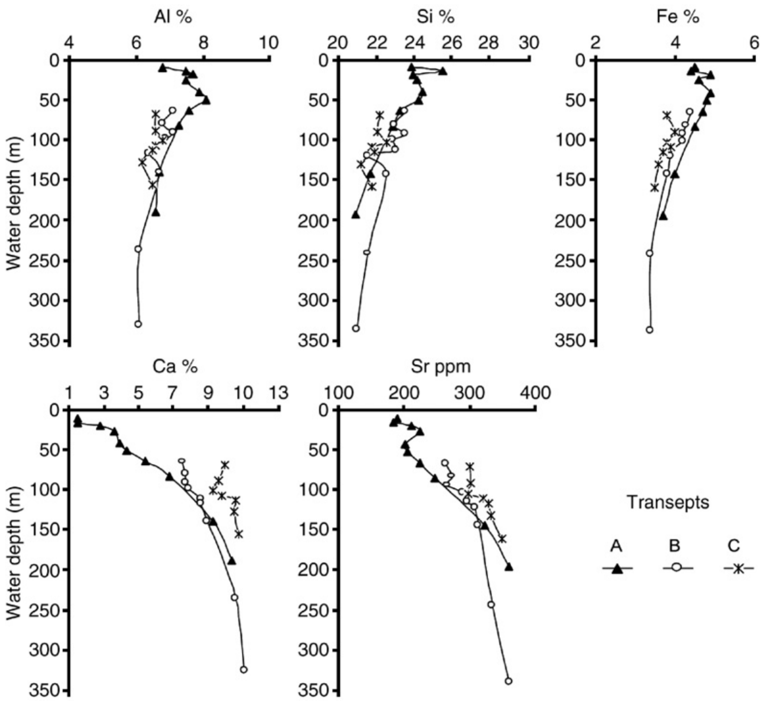

Fig. 12. Variation of Si, Al, Fe, Ca and Sr concentrations within the <4 ϕ (64 μm) fraction in function of water depth.

characterised by a low energy environment and high ratios.

The ratio of carbonate/detritic minerals (Carb/Det) expresses the dichotomy between the detritic transport and the biogenic component, allowing the definition of two distinct zones, one, essentially detritic, positioned close to the Guadiana River mouth, and another in which the carbonate component dominates, dominating the eastern part of the middle shelf.

4.4. Elemental composition

The most significant variations in the chemical composition of the fine grain size fraction of the

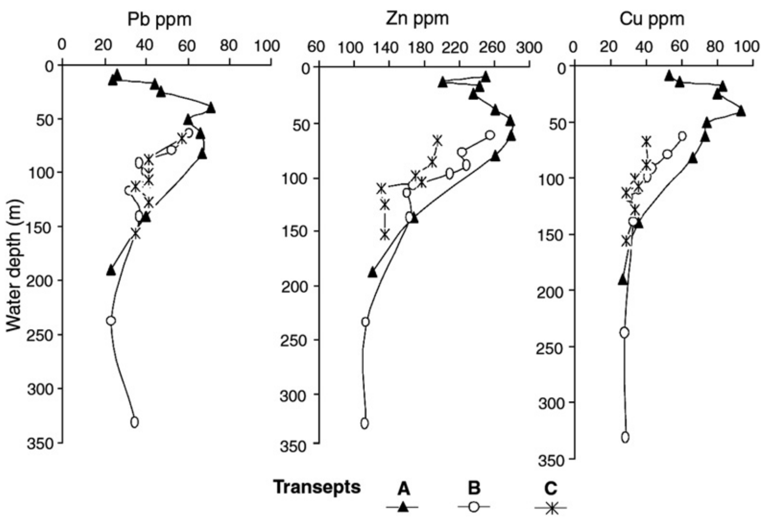

Fig. 13. Concentration of heavy metals Cu, Zn and Pb in ppm within the <4 ϕ (64 μm) fraction in function of depth.

sediments collected along the transects A, B and C are plotted versus water depth; Fig. 12 shows examples for lithogenic/biogenic (Al, Si, Fe, Ca and Sr) elemental distribution while anthropogenic elements (Cu, Zn and Pb) are shown on Fig. 13.

Al, Si and Fe concentrations show a general tendency to decrease with water depth, after an increase for nearshore samples (down to ~ 20 m) collected off the Guadiana (Fig. 12). In contrast Ca and Sr concentrations significantly increase with water depth (~ 1–11% Ca; ~ 180–350 mg/kg Sr), peaking in mid-shelf sediments collected along transect C.

The "anthropogenic" heavy metal (Cu, Zn and Pb) distribution patterns along the shelf (Fig. 13) are similar to those of Al and Si although presenting high concentrations values down to about 100 m. The highest heavy metal concentrations are observed in transect A (Cu = 93 ppm, Zn = 279 ppm and Pb = 71 ppm) decreasing eastwards (to C), being opposite to the Ca and Sr peak. These high Cu, Zn and Pb values in shelf sediments can be associated to sulphide minerals, related to the discharge of mineral wastes from mines and factories in the so called Pyrite belt located within the main regional river basins, particularly the Tinto–Odiel and Piedras Rivers (Elbaz-Poulichet et al., 2001).

4.5. Organic carbon and total nitrogen

Organic carbon (OC) and total nitrogen (TN) concentrations, OC/TN ratio and the stable isotopic composition, $\delta^{13}C$, are displayed for fine (<63 μm) size fractions of sediments carried, in Fig. 16.

OC concentrations of 5.7 mg/g to 13.1 mg/g and TN concentrations of 0.8 mg/g to 1.6 mg/g are obtained. Lower values of OC (<10 mg/g) and TN (<1.4 mg/g) were restricted to surficial sediments down to a water depth of about 20 m. The lowest contents of OC (<6 mg/g) and TN (<0.8 mg/g) coincided with the lowest water depths located at the Guadiana River mouth. Surficial sediments below about 20 m display roughly constant concentrations with water depth (average ± 1σ: OC = 10.9 ± 0.6 mg/g, TN = 1.4 ± 0.1 mg/g), and cannot be distinguished from various shelf transects.

The OC/TN ratios expressed as molar ratio (mol mol^{-1} as in the Redfield ratio) ranged from 8.5 to 10.3 (Fig. 14). Most of the ratios for deeper sediments (of the order of 8.5) are in the range of the mean ratio for marine phytoplankton (7.4 ± 1.3; Anderson and Sarmiento, 1994). High OC/TN (> 10) were obtained for the sediments in the vicinity of the Guadiana River mouth, although a slight decreasing trend is displayed by the shallowness sample.

The $\delta^{13}C$ values increased from the mouth of the Guadiana River towards the outer shelf of the northern Gulf of Cadiz, ranging from −23.3‰ to −26.4‰. The isotope values coming from two other transects of the northern Gulf of Cadiz shelf in front of Piedras and Tinto/Odiel rivers display roughly constant $\delta^{13}C$ values with water depth (average ± 1σ:$\delta^{13}C$ = −24 ± 0.3‰). They contrast with those measured for shallowness samples of the Guadiana transect that average −26.2 ± 0.2‰, while, as for OC/TN ratios, the isotopic values measured for deeper samples (below 80 m) do not show significant deviations from Guadiana transect sediment (−23.9 ± 0.6‰).

4.6. Coccolithophore assemblages

Coccolithophore assemblages were generally abundant and well preserved in all shelf surface sediments. Associations were dominated by placoliths of *Gephyrocapsa ericsonii*, *Emiliana huxleyi*, *Gephyrocapsa*

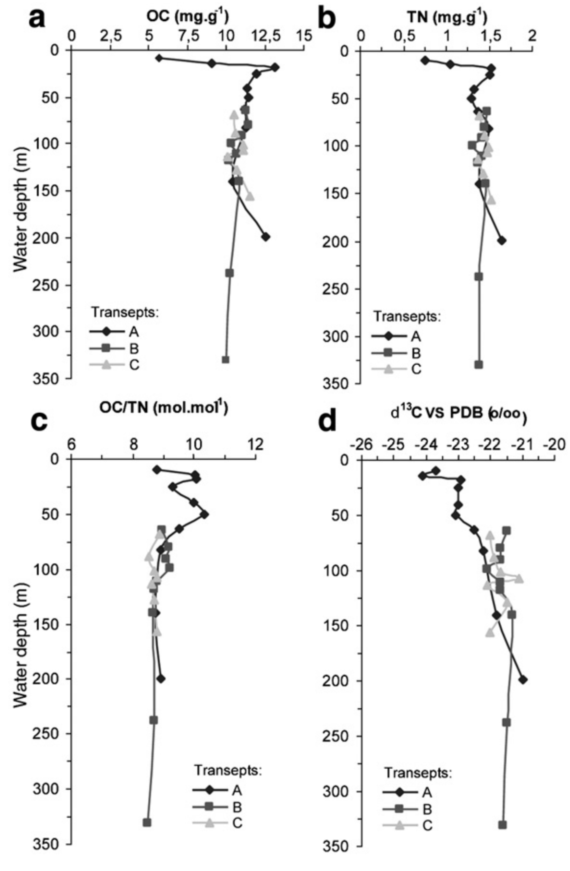

Fig. 14. Plots of depth variation of a) OC, b) TN, c) OC:TN molar ratios, and d) $\delta^{13}C$, for fine (<63 μm) size fractions of carbonate-free samples.

oceanica, and *G. muellerae* (for details referring to the assemblages, and distribution of nannofossil taxa we refer to Ferreira and Cachão, 2005). Reworked nannofossils, Cretaceous to Pliocene in age, were found to be an important component of the association. Dominant species here are *Dictyococcites productus*, *Reticulofenestra minuta*, *Watznaueria barnesea*, *Cyclicargolithus floridanus*, and *Discoaster* spp.

Fig. 15 compares the distribution of fossil and extant nannoplankton assemblages with water depth. The abundance of both assemblages increases with distance to the coast. This is not directly linked to bottom hydrodynamic conditions, as their distribution does not follow the amount of fines found in the sediment, particularly at the outer edge of the shelf (Fig. 15). Note also that while the distribution of fossil assemblages generally increases regularly towards the shelf edge, extant assemblages show greater variations in abundance.

4.7. Results of the factorial analysis

The factorial analysis shows that the first factor contains 39% of variance, the second 22.5%, and the third 15.7%. In total they explain 77.4% of the total variance found in the analysed sediments. The first factor was found to be directly related to the opposition between Al, Fe, Si, Cu, Zn, Pb on one side, and water depth (which can be considered as a proxy to the distance of the source), Ca, and Sr on the other side. The second factor translates the opposition between the amount of nannoplankton (extant and fossil) and the percentage of quartz and feldspar. The third factor is influenced by the amount of organic

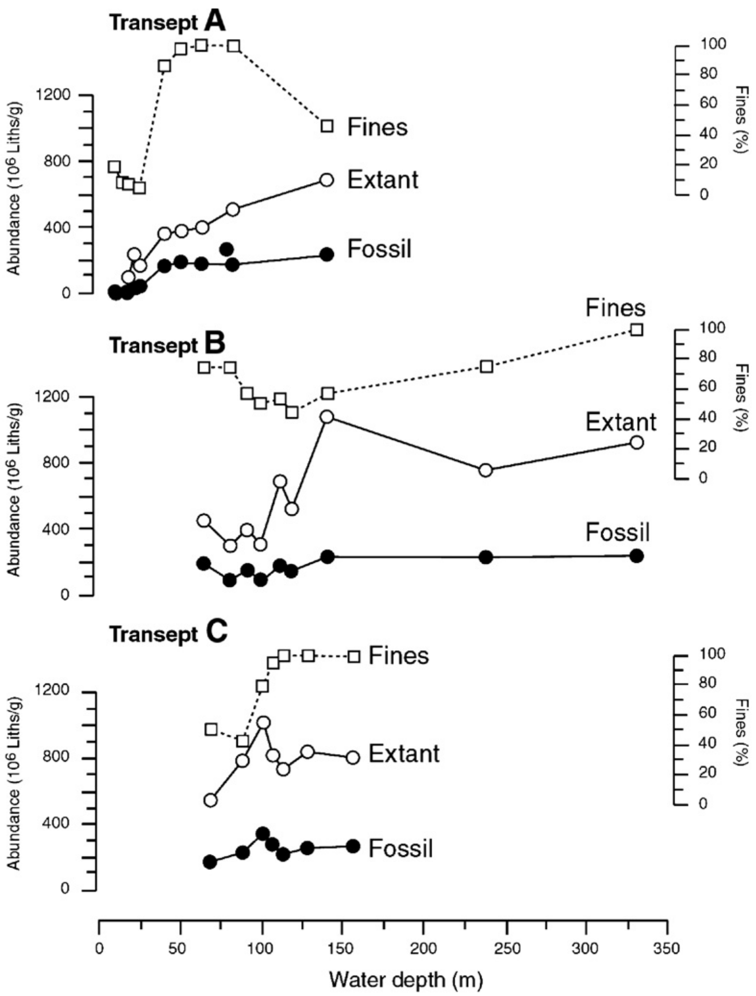

Fig. 15. Difference between living and fossil nannoliths in surface sediments.

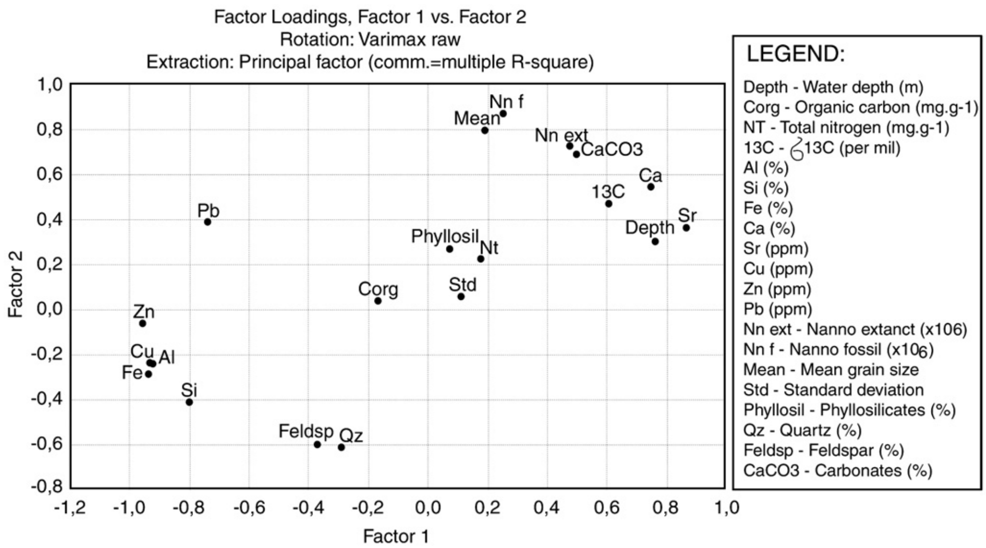

Fig. 16. Results of factorial analysis. Plot of Factor 1 versus Factor 2.

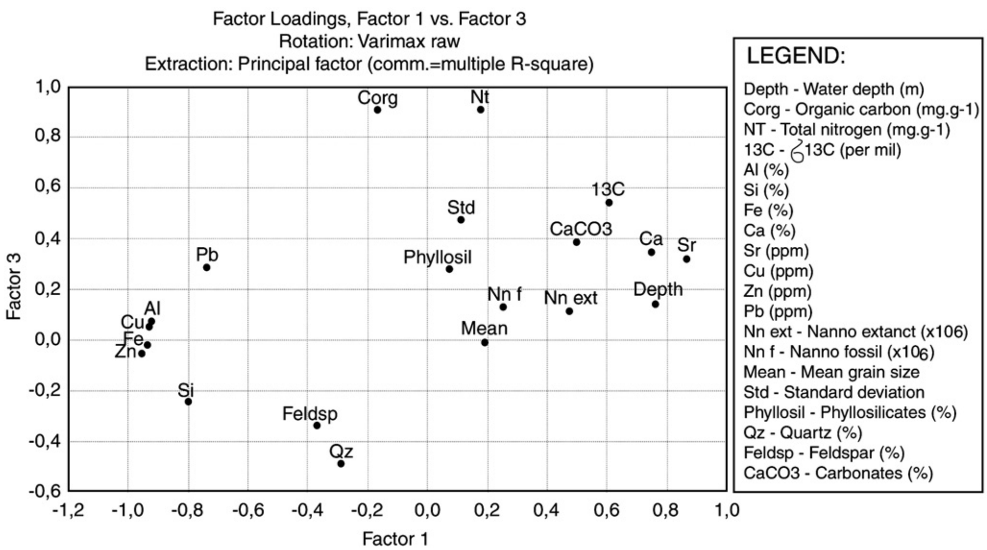

Fig. 17. Results of factorial analysis. Plot of Factor 2 versus Factor 3.

carbon and total Nitrogen. This data is summarised on the plots on Figs. 16 and 17.

5. Discussion

Our estimates show that about $2–2.5\times10^6$ tons (or $7.5–9.5\times10^5$ m^3) of sand were exported onto the inner shelf during the winter 2000/2001. These numbers are about twice the 1.17×10^6 tons (4.4×10^5 m^3) estimated by Morales (1997) for the average yearly bedload exported from the estuary between 1946 and 1990 (or about five times the yearly littoral drift of $1.5–1.8\times10^5$ m^3; e.g. Gonzalez et al., 2001; Boski et al., 2002).

The winter 2000/2001 was exceptionally rainy compared to winters in the previous 10 years. Additionally, in February 2001, a few weeks after said flood event, the Alqueva dam was inaugurated, increasing the dammed area within the Guadiana River basin by 12% to a total of 89% (estimates based on areas of the Guadiana River basin and its tributaries). It seems unlikely that similar amounts of sediment export will be reached in future years.

Our study indicates that the Guadiana has an almost unique heavy mineral signature. The high quantities of amphibole and pyroxene grains present in the GR group define a provenance signal most likely belonging to mafic and ultramafic rocks such as gabbros and amphibolites from within the Beja Igneous Complex and Beja–Acebuches Ophiolite Complex described in Oliveira et al. (1992). These minerals are highest within the river sample group (GR = 13.4%), and the river mouth (GM = 3.2%). The eastern Spanish inner shelf (SIS) is much richer in heavy mineral content (1.3% on average) than the western Portuguese inner shelf (PIS = 0.4%), which is mirrored by beaches on the Spanish (SB = 2.3%) and Portuguese side (PB = 1.1%), thus again demonstrating the dominant eastwards sediment transport, prevalent throughout the entire northern Gulf of Cadiz (e.g. Gutiérrez-Mas et al., 1994; Lobo et al., 2004). The results from heavy mineral analysis and MSGR (Fig. 6) show little indication of west-ward directed sediment transport component on the inner shelf as postulated by Lobo et al. (2004) from seismic data.

That sediment transfer mechanisms from the inner to the middle shelf seem to be extremely efficient in the northern Gulf of Cadiz, particularly where fines are concerned. Stevenson (1977) notes that the edge between the inner and the middle shelf forms the boundary between the eastward upwelling anti-cyclonic Tarif Eddy and warm water located in the inner shelf, calling it the 'Huelva Front'. Here, the steep terraced pre-existing morphology clearly exerts a strong influence on current and sedimentation patterns. This area is thus particularly susceptible as a catchment and re-distribution area for pollutants associated with fine-grained sediments exported from the river basins to the inner shelf.

The increase in Al, Si and Fe from the nearshore sediments down to ~ 20 m can be associated with the amount of fines increasing below about 25 m water depth. The following drop in Al, Si, and Fe concentrations with increasing water depth can probably be attributed to an offshore decrease in alumino-silicates (amphibole, pyroxene, clay minerals) and iron oxides with increasing distance to the source, although the most important factor seems to be the dilution of those continental with an increasing bioclastic fraction on the total sediment. This is clearly demonstrated by the Ca (and Sr) concentrations which show an opposite behaviour related to an increasing percentage of biogenic marine materials (Figs. 4b and 14). Ca and Sr have a similar chemical behaviour, as Sr often substitutes Ca in marine carbonates (Libes, 1992). Their profiles are identical to the carbonates, proving the biogenic origin of these elements, and the Ca and Sr enrichment with water depth dilutes the continental (lithogenic and anthropogenic) component of the sediments, which is clearly displayed by the compositional variations of the sediments collected along the transect C.

Fine OC concentrations are low (<15 mg/g) but within the same range as values reported for surface marine sediments on the shelf off the Tagus and Sado estuaries on the western Portuguese coast (Jouanneau et al., 1998). The regular decrease of OC and TN down to a water depth of about 20 m in shorewards sediments suggests either a gradual decrease in fine-sized organic matter supply to the shallow continental shelf, or a resuspension-related degradation trend of sedimentary organic matter. An argument against degradation is that fine-sized organic matter recovered in sediments is mainly composed of "refractory" OC (Huon et al., 2002), less sensitive to postdeposition degradation processes. As revealed from similar environments, the transition between the inner and outer shelf sediments is characterised by a major change in sediment composition (Gordon and Goñi, 2004; Jouanneau et al., 1998). River-dominated sediment (low OC content), typical of estuarine sedimentation, are gradually replaced by marine derived organic matter (high OC content). Thus, biological sediment supply increases toward the open sea. Evidence of a changing source of organic matter is revealed by the obtained values of $\delta^{13}C$ and the OC/TN on the continental shelf. The increase in the trend of OC/TN, from 8.8 at water depths around 80 m to 10 for nearshore samples, corresponds to an increase of fine OC concentration with respect to TN; a first-order estimate of a changing sedimentary organic matter supply along the northern gulf of Cadiz shelf. Although only scarce data exists for fine size fractions of sediments of the south-western Iberian continental shelf, the $\delta^{13}C$ of outer shelf sediments mirror present-day marine surface organic matter values (−20‰ to −22‰). Thus, the concomitant decrease of $\delta^{13}C$, fine OC, and TN concentrations suggests a dilution of marine sedimentary organic matter by organic continental supply. In that sense, the continental organic matter source is characterised by depleted $\delta^{13}C$, low OC and TN concentrations, and high OC/TN ratios. This contribution decreases towards the mid-shelf, and below 70 m water depth is evenly distributed along the entire of the northern gulf of Cadiz shelf.

Phyllosilicate-rich sediments were found to be heavy metal enriched, especially those within the inner shelf off the Guadiana mouth, where the total Zn, Cu and Pb contents can reach 279 ppm, 93 ppm, 71 ppm, respectively. The pollution by these heavy metals decreases significantly to the outer shelf. Thus, the Guadiana sediment load appears to be a major contributor to the contamination of the continental shelf. Similarly, along the transects B and C, down to a water depth of about 99 m, sediments are enriched in fine detrital minerals with low maturity index, also presenting high contents in heavy metals, which decrease to the outer shelf.

Recent studies have shown that the Iberian Pyrite Belt is the main source of Ni, Cu, Cd, Zn and As found in sediments of the western Mediterranean basin (Elbaz-Poulichet et al., 2001). The present study indicates concentrations of heavy metals in the sediments above the regional background values down to 120 m water depth and highest in transect A, decreasing eastwards. Elbaz-Poulichet and Leblanc (1996) have suggested that the trace metal enrichments determined in the south-western Spanish Atlantic waters can be explained by the high metal fluxes proceeding from the Tinto–Odiel system to the ocean. These rivers are extremely rich in heavy metals due to the acid mine tailings that exist near their catchments. Also, Fernández Caliani et al. (1997) and Morillo et al. (2004) have studied sediments from the Tinto–Odiel estuary and adjacent coastal areas and found rather high heavy metals concentrations. However, the heavy metal composition analysis performed within the present study indicates that the contamination of the inner shelf caused by the Tinto/Odiel system does not seem to extend onto the middle shelf. Heavy metal distributions along transect C are comparable to those of transect A (Guadiana) if the local biogenic dilution is taken into account, as evidenced by the increased gradient in Ca, Sr and carbonates.

This makes sense, as the Guadiana River exports sediment much more efficiently than either the Piedras or the Tinto–Odiel, and is the main sediment source for the entire northern Gulf of Cadiz (as the bulk of sediments from the larger Guadalquivir are deflected towards south-east, away from the area discussed here; *cf*. Lobo et al., 2004). Consequently, in spite of being much less contaminated than either the Piedras or the Tinto–Odiel, the Guadiana can be seen as a main contaminant of the middle shelf. Furthermore, the data indicates indirectly that contaminants coming from the Piedras and Tinto–Odiel probably remain in the inner shelf close to their respective sources. This area is much less energetic than the shelf off the Guadiana or Guadalquivir.

The analysis of Nannoplankton communities within transects strongly indicates that, beside the south-easterly offshore transport along the inner shelf, there is a strong oceanic influence in sediments along the upper middle shelf possibly related to upwelling patterns (e.g. Fiúza, 1983). Along all three sampled transects the extant calcareous nannoplankton dominate over the fossil forms. However, considering the surrounding geological units that crop out in the region reworked forms occur in unexpected high abundance. The extant coccolithophore assemblages recovered from all samples follow those found by Sierro et al. (1999) in deep terraces located between 400 and 700 m water depth, just below the upper Gulf of Cadiz continental slope and those found by Kenyon et al. (2001) and Pinheiro et al. (2003) also in the Gulf of Cadiz.

In all three transects densities of calcareous nannoplankton vary according to bottom hydrodynamic conditions. This is shown by the similarity of the distribution pattern of both extant and fossil coccoliths (Fig. 15). This co-variation can only be achieved if factors such as near bottom currents influence sedimentation of present day coccoliths deriving from neritic productivity and the passive transport of reworking forms within the oceanic water masses. This is confirmed by surface samples with less than 10% of fines occurring in the inner shelf where there is a significant decline in nannoplankton abundance (see Fig. 15). Here overall coccolithophore and nannofossil densities drop from 4×10^8 to 2×10^8 liths/g or less as it approaches shoreline.

This plethora of information is summed up by the factorial analysis (carried out on the fine-grained fraction of 26 samples), where the first factor indicates a strong opposition between the terrigenous signal formed by the group of elements Al, Fe, Si, Cu, Zn, and Pb; and the oceanic signal represented by water depth, Ca, and Sr. This makes sense, as the nannoplankton makes up about 80% of calcareous material within the fines of studied samples. Also the second factor shows a strong opposition between quartz and nannoplankton.

6. Conclusions

The northern Gulf of Cadiz shelf between the Guadiana and Guadalquivir rivers (SW Iberia) was analysed by means of a series of grab sample surveys between January 1999 and November 2001. The focus of the study was primarily the Guadiana River sediment export to the shelf. While most of the survey period showed low river flow volumes, the winter 2000/2001 had an unusual amount of rain, and a large-scale flood event with river discharges of up to 3000 m^3/s in February 2001. This flood event coincided with one of the surveys carried out in this project.

The Guadiana River has an almost unique heavy mineral signature, composed mostly of amphiboles and pyroxenes, as well as andalusite. Furthermore, an analysis of sedimentary components in the sand-sized grain fraction shows that the Guadiana River exports particles eroded from Paleozoic metaschist and greywacke (MSGR) to the inner shelf, which are found almost exclusively in the vicinity of the Guadiana River mouth.

Both heavy minerals and MSGR fragments indicate that sediment from bedload is predominantly exported towards east and south-east on the inner shelf; only little material is carried in a west-ward and south-westward direction. Our estimates based on differences in MSGR content between November 2000 and February 2001 show that an estimated $2–2.5\times10^6$ tons (or $7.5–9.5\times10^5$ m^3) of sand were exported from the Guadiana onto the inner shelf over an area of about 85 km^2 during the winter 2000/2001.

A drop in Al, Si, and Fe concentrations within sediments with increasing water depth can be attributed to an offshore decrease in alumino-silicates (amphibole, pyroxene, clay minerals) and iron oxides, while increase in Ca and Sr concentrations are related to an increasing percentage of biogenic materials.

The decrease of $\delta^{13}C$, fine OC, and TN concentrations suggests a dilution of marine sedimentary organic matter by organic continental supply. The continental organic matter source is characterised by depleted $\delta^{13}C$, low OC and TN concentrations, and high OC/TN ratios. This contribution decreases towards the middle shelf, and is evenly distributed below 80 m water depth along the entire of the northern gulf of Cadiz shelf.

Phyllosilicate-rich sediments were found to be heavy metal enriched within the inner shelf. The pollution by these heavy metals decreases significantly to the outer shelf and eastwards. The Guadiana sediment load appears to be a major contributor to the contamination of the continental shelf. In contrast, there was no evidence for heavy metals exported from the Tinto–Odiel system within the analysed transects, and it is concluded that these pollutants probably remain within the inner shelf.

The analysis of nannoplankton communities within transects seems to indicate that, beside the south-easterly offshore transport along the inner shelf, and particularly along the upper middle shelf, there is a strong oceanic influence in sediments possibly related to upwelling patterns, as fossil nannoplankton forms (that crop out on the on the shelf slope) appear in larger than expected numbers.

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