



# Geochemical signature in off-shore sediments from the Gulf of Cádiz inner shelf Sources and spatial variability of major and trace elements

Laura Sánchez-García<sup>\*</sup>, J.-Ramón de Andrés, J.-Antonio Martín-Rubí

Instituto Geológico y Minero de España, IGME, Ríos Rosas 23, 28003-Madrid, Spain

## ARTICLE INFO

### Article history:

Received 28 January 2009

Received in revised form 1 June 2009

Accepted 20 September 2009

Available online 20 October 2009

### Keywords:

Continental shelf

Enrichment factor

Geochemical composition

Gulf of Cádiz

Heavy metals

Pyritic Belt

## ABSTRACT

The geochemical characterization of 15 surficial sediments from the Gulf of Cádiz (GoC) inner shelf was assessed by examining their granulometric, mineralogic and major–minor elemental composition, in order to evaluate the sources of contaminants and describe environmental conditions. The study involved the comparison of the geochemical signature of the shelf sediments with that of surficial sediments from the main fluvial systems of the region: Guadiana, Piedras, Tinto and Odiel. Although the major supply of sedimentary material in this area is discharged by the Guadiana River, the high absolute concentration of elements associated to sulphide deposits (P, As, Cu, Hg, Pb and Zn) observed in some sediments indicated the important influence of the historically polluted Tinto–Odiel fluvial system in certain locations.

The significant levels (>99%) of positive correlation observed between Al, Fe, K, Ni, V and, in a lesser extent, Na and Ba, suggested the association of these elements in the form of aluminous clay minerals. No correlation was observed between Al and Si (0.20), in contrast to the strong positive correlation found for the latter and Ti (0.91). On the other hand, an inverse relationship occurred between terrigenous–detrital sources and carbonate fractions, presumably related to biogenic origins, according to the significant negative correlations (>99%) observed for Si, respect to Ca (−0.82), Mg (−0.96) and total inorganic carbon (−0.81).

The general enrichment of As, Cu, Hg, Pb and Zn detected in the shelf sediments, together with strong and moderate positive correlations observed among these metals and P, suggested a common origin for all these elements, potentially related to pollutant–anthropogenic activities developed in the industrial area of Huelva city. Those sediments situated closer to the Tinto–Odiel mouth displayed enrichment factors (EF) equal or higher than 2 for As, Cu, Hg, Pb and Zn, particularly evident in one sample (S7), which showed EF of 2.7, 18.7, 8.7, 4.0 and 5.7, respectively. Cluster and Principal Components Analyses allowed us to differentiate four groups of shelf sediments governed by similar geochemical patterns: (i) a first group including the sediments under the Guadiana river influence, formed by coarser siliclastic sediments, with dominant terrigenous–detrital signatures and enrichment of Co and Mn; (ii) a second group of off-shore muddy sediments, Ni-associated, showing moderate enrichment of Cu, Hg, Pb and Zn, as well as important contribution of carbonate forms, which represent the transition towards a dominant marine source; (iii) sample S7, formed by muddy materials and enriched in sulphide associated-heavy metals and phosphorous, according to its proximity to the Tinto–Odiel fluvial system; and (iv) the coarsest sample S13, with high concentration of carbonates and moderate enrichment of heavy metals, which reflects a mixed signature between the detrital influence from Guadiana and Piedras rivers and marine–biogenic sources.

© 2009 Elsevier B.V. All rights reserved.

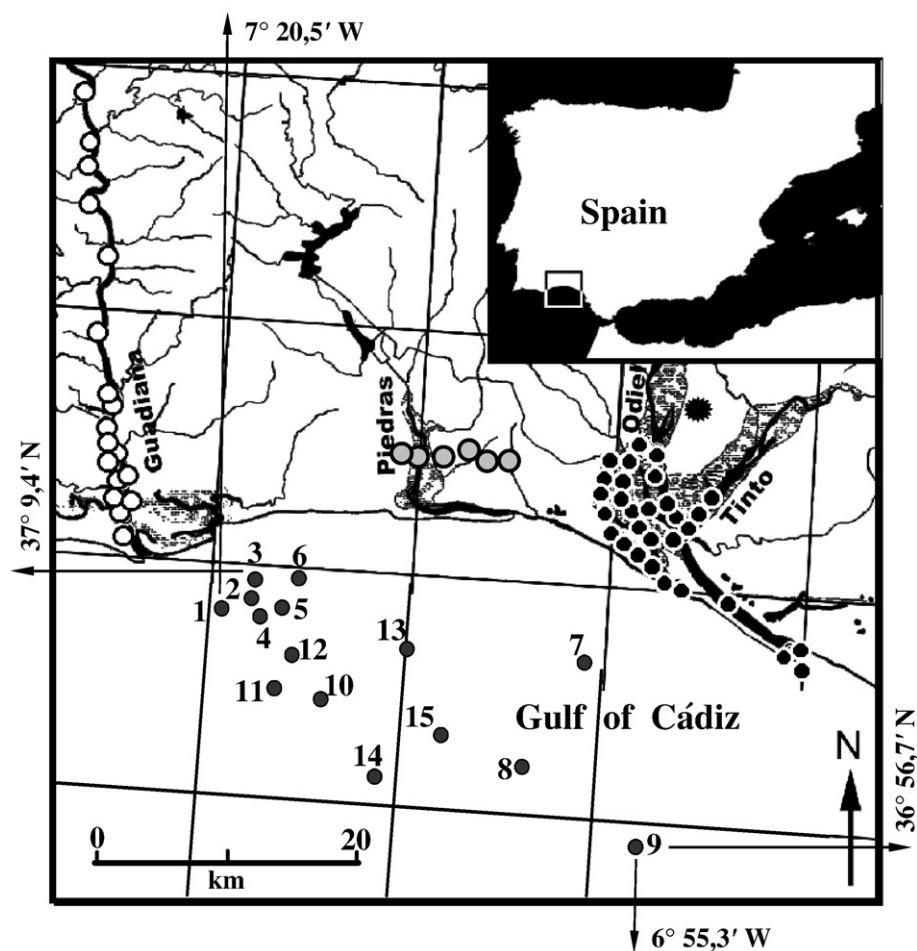
## 1. Introduction

The geochemical composition of recent sediments deposits, dependent on geological, biological and climatic factors, can be very useful as a tracer of origin and environmental changes induced by natural and an-

thropogenic causes (Leblanc et al., 2000; Borrego et al., 2004; García et al., 2004). The major portion of metals of natural or anthropogenic origin introduced into estuarine environments usually arrives in the dissolved phase (Borrego et al., 2004) and is immediately incorporated into organo-metallic compounds or other mineral phases of the suspended particulate matter at the beginning of the saline mixing processes. These complexes are then transported in the water column and finally incorporated into the sediments (Stecko and Bendell-Young, 2000). The concentrations of major and trace elements are used to classify sediments and to build up variation charts between elements and compounds, establishing relationships between the different elements and the geochemical processes that influence their distributions (e.g. Vital et al., 1999). In this context,

<sup>\*</sup> Corresponding author. Present address: Department of Applied Environmental Sciences (ITM), Stockholm University, SE-10691 Stockholm, Sweden. Tel.: +46 736 415 938; fax: +46 8 674 7638.

E-mail addresses: [laura.sanchez@itm.su.se](mailto:laura.sanchez@itm.su.se), [laurix58@hotmail.com](mailto:laurix58@hotmail.com) (L. Sánchez-García).



**Fig. 1.** Map showing the location of the sediments collected from the inner continental shelf (numbers), from the fluvial systems of the Guadiana, Piedras and Tinto–Odiel rivers (white, grey and black circles, respectively) and from the metropolitan area of Huelva at 15 m depth (black asterisk).

estuarine and continental shelf zones constitute interesting scenarios for developing geochemical studies of sources and behaviour of geochemical pollutants, due to the rapid accumulation of sediments of heterogeneous origin.

The northern margin of the inner continental shelf of the Gulf of Cádiz (GoC, SW Spain) receives the drainage of the rivers Guadiana, Piedras, Tinto and Odiel, from W to E (Fig. 1). The last two rivers join and drain together, forming the Huelva Estuary. This coastal stretch

**Table 1**

Location and bulk geochemistry of the shelf sediments.

|     | Longitude<br>(W) | Latitude<br>(N) | Depth <sup>a</sup><br>(m) | Distance <sup>b</sup><br>(km) | Mineral<br>components <sup>c</sup> | Granulometric fractions (%) |    |    |    | TOC<br>(%) | TIC<br>(%) | TS<br>(%) | C/S  |
|-----|------------------|-----------------|---------------------------|-------------------------------|------------------------------------|-----------------------------|----|----|----|------------|------------|-----------|------|
|     |                  |                 |                           |                               |                                    | GR                          | Sa | Si | Cl |            |            |           |      |
| S1  | 07° 20.489'      | 37° 08.458'     | 13                        | 3.61                          | Q (M.A)                            | 2                           | 50 | 33 | 15 | 1.01       | 0.81       | 0.16      | 17.1 |
| S2  | 07° 19.302'      | 37° 08.267'     | 16                        | 3.89                          | Q (M.A)                            | 0                           | 17 | 54 | 29 | 0.77       | 0.38       | 0.32      | 6.5  |
| S3  | 07° 19.237'      | 37° 09.393'     | 12                        | 3.06                          | Q (M.A)                            | 0                           | 24 | 42 | 34 | 0.84       | 0.56       | 0.20      | 11.0 |
| S4  | 07° 19.233'      | 37° 08.160'     | 16                        | 5.28                          | Q (M.A)                            | 0                           | 12 | 54 | 34 | 0.75       | 0.37       | 0.20      | 10.2 |
| S5  | 07° 17.342'      | 37° 08.356'     | 17                        | 5.83                          | Q (M.A)                            | 0                           | 6  | 56 | 37 | 0.82       | 0.54       | 0.26      | 8.3  |
| S6  | 07° 16.058'      | 37° 09.815'     | 15                        | 4.17                          | Q (M.A.C)                          | 0                           | 37 | 43 | 20 | 0.50       | 0.47       | 0.18      | 7.4  |
| S7  | 06° 58.388'      | 37° 05.546'     | 20                        | 8.89                          | Q (C)                              | 0                           | 14 | 50 | 36 | 0.64       | 2.21       | 0.15      | 11.5 |
| S8  | 07° 02.587'      | 37° 00.616'     | 46                        | 19.72                         | Q.C (D.M)                          | 0                           | 4  | 54 | 42 | 0.89       | 2.37       | 0.16      | 14.8 |
| S9  | 06° 55.293'      | 36° 56.698'     | 53                        | 22.22                         | Q.C (A.m.M)                        | 0                           | 6  | 51 | 43 | 0.64       | 2.91       | 0.09      | 19.5 |
| S10 | 07° 15.447'      | 37° 04.010'     | 42                        | 14.44                         | Q (C)                              | 0                           | 3  | 52 | 46 | 0.98       | 1.50       | 0.17      | 15.4 |
| S11 | 07° 18.457'      | 37° 04.349'     | 36                        | 11.94                         | Q (C)                              | 0                           | 9  | 52 | 39 | 1.40       | 1.33       | 0.32      | 11.7 |
| S12 | 07° 17.021'      | 37° 06.079'     | 27                        | 10.00                         | Q                                  | 0                           | 4  | 53 | 44 | 1.38       | 0.55       | 0.21      | 17.5 |
| S13 | 07° 09.639'      | 37° 06.240'     | 22                        | 11.39                         | Q (C.P)                            | 15                          | 43 | 24 | 18 | 0.72       | 2.61       | 0.12      | 16.0 |
| S14 | 07° 12.007'      | 37° 00.316'     | 66                        | 21.94                         | Q.C (D)                            | 0                           | 1  | 55 | 44 | 1.12       | 2.29       | 0.13      | 23.0 |
| S15 | 07° 08.027'      | 37° 02.131'     | 42                        | 18.89                         | Q.C (F.D)                          | 0                           | 1  | 54 | 45 | 0.69       | 2.62       | 0.13      | 14.2 |

A: albite, C: calcite, D: dolomite, F: feldspars, M: muscovite, m: microcline, P: plagioclases, Q: quartz. Gr: gravel (> 2 mm), Sa: sand (2–0.063 mm), Si: Silt (0.063–0.002 mm), Cl: clays (< 0.002 mm); TOC: total organic carbon; TIC: total inorganic carbon; TS: total sulphur; C/S: atomic ration carbon/sulphur.

<sup>a</sup> Water column depth.

<sup>b</sup> Distance to coast.

<sup>c</sup> Principal and secondary minerals (in brackets), according to X-ray diffraction.

**Table 2a**

Analytical data for the 15 shelf sediments.

|                                | S1    | S2    | S3    | S4    | S5    | S6    | S7    | S8    | S9    | S10   | S11   | S12   | S13   | S14   | S15   |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>               | 67.78 | 61.18 | 60.72 | 62.18 | 59.20 | 67.02 | 51.86 | 42.41 | 42.04 | 48.64 | 49.68 | 52.32 | 49.43 | 43.09 | 48.77 |
| Al <sub>2</sub> O <sub>3</sub> | 12.28 | 14.64 | 14.83 | 13.84 | 15.49 | 11.98 | 9.81  | 12.07 | 11.05 | 14.44 | 14.54 | 16.13 | 9.25  | 13.18 | 14.44 |
| CaO                            | 2.04  | 1.89  | 1.93  | 2.35  | 1.73  | 3.00  | 10.33 | 12.44 | 14.38 | 6.36  | 6.34  | 3.13  | 13.08 | 10.40 | 6.33  |
| Fe <sub>2</sub> O <sub>3</sub> | 5.05  | 5.96  | 6.05  | 5.62  | 6.13  | 4.89  | 5.08  | 5.64  | 5.04  | 6.56  | 6.56  | 6.86  | 4.91  | 6.08  | 6.59  |
| TiO <sub>2</sub>               | 1.20  | 1.07  | 1.09  | 1.20  | 1.13  | 1.22  | 0.74  | 0.66  | 0.60  | 0.88  | 0.87  | 1.01  | 0.65  | 0.72  | 0.88  |
| Na <sub>2</sub> O              | 2.39  | 2.87  | 2.59  | 2.88  | 2.69  | 2.41  | 2.42  | 2.11  | 1.78  | 2.60  | 2.37  | 2.83  | 1.90  | 2.70  | 2.45  |
| K <sub>2</sub> O               | 1.80  | 2.27  | 2.22  | 2.05  | 2.42  | 1.78  | 1.79  | 2.44  | 2.32  | 2.48  | 2.53  | 2.53  | 1.70  | 2.55  | 2.51  |
| MgO                            | 1.28  | 1.48  | 1.57  | 1.53  | 1.55  | 1.33  | 1.91  | 2.42  | 2.53  | 2.05  | 2.05  | 1.90  | 1.72  | 2.36  | 2.06  |
| MnO                            | 0.07  | 0.10  | 0.08  | 0.08  | 0.08  | 0.06  | 0.05  | 0.05  | 0.05  | 0.06  | 0.06  | 0.06  | 0.05  | 0.05  | 0.06  |
| P <sub>2</sub> O <sub>5</sub>  | 0.09  | 0.09  | 0.12  | 0.12  | 0.10  | 0.09  | 0.16  | 0.13  | 0.12  | 0.14  | 0.13  | 0.13  | 0.13  | 0.14  | 0.14  |
| As                             | 16    | 29    | 22    | 21    | 26    | 20    | 50    | 28    | 20    | 42    | 32    | 42    | 35    | 36    | 38    |
| Ba                             | 247   | 329   | 309   | 302   | 338   | 279   | 310   | 263   | 238   | 311   | 330   | 351   | 191   | 294   | 279   |
| Co                             | 17    | 21    | 20    | 20    | 21    | 18    | 16    | 16    | 14    | 15    | 16    | 18    | 9     | 13    | 12    |
| Cr                             | 51    | 69    | 70    | 63    | 69    | 52    | 58    | 63    | 62    | 85    | 87    | 94    | 105   | 78    | 75    |
| Cu                             | 26    | 43    | 49    | 47    | 50    | 55    | 224   | 61    | 36    | 90    | 91    | 83    | 70    | 62    | 84    |
| Hg                             | 0.20  | 0.5   | 0.3   | 0.4   | 0.4   | 0.6   | 0.7   | 0.3   | 0.2   | 0.6   | 0.6   | 0.5   | 0.6   | 0.5   | 0.6   |
| Ni                             | 21    | 30    | 30    | 27    | 32    | 21    | 21    | 25    | 25    | 38    | 38    | 44    | 20    | 36    | 35    |
| Pb                             | 18    | 29    | 28    | 29    | 31    | 37    | 113   | 61    | 44    | 101   | 83    | 63    | 80    | 73    | 88    |
| V                              | 80    | 104   | 106   | 100   | 109   | 86    | 87    | 100   | 95    | 116   | 118   | 131   | 71    | 113   | 106   |
| Zn                             | 120   | 211   | 163   | 156   | 157   | 192   | 379   | 237   | 169   | 224   | 214   | 187   | 184   | 204   | 229   |

Concentration of major (%) and trace elements (ppm) in the shelf sediments.

comprises a mesotidal medium energy system (Lobo et al., 2001), where the general southeast circulation over the continental shelf configures its arcuate coast, characterized by the presence of spit bars and lagoons in the river mouths. The dominant winds in this area are south-westerly and they generate a current parallel to the coastline (from left to right) known as a long shore drift with high capacity for carrying matter (Morillo et al., 2004). This littoral drift and the advection of the North Atlantic Surficial Current (Ochoa and Bray, 1991) induce a potential sediment transport that has been estimated to range from 180 to  $300 \times 10^3 \text{ m}^3/\text{yr}$  (CEEPYC, 1979; Cuenca, 1991).

The sources of pollution of this coast are mainly derived from the rivers and the nearby urban centres. Sewage from Huelva City and wastes from the intense industrial activity developed in the area (chemical plants, fertiliser factory, paper mill, petroleum refineries, copper foundries, etc.) are discharged into the Huelva estuary (Grande et al., 2000; Leblanc et al., 2000; Borrego et al., 2002; López-González

et al., 2006). In addition, the Tinto and Odiel rivers pass through one of the most important sulphur deposits in the world (Iberian Pyrite Belt), a region long known for its mining activities to obtain pyrite and other mineral concentrates for at least 4500 years (Davis et al., 2000; Leblanc et al., 2000). This fluvial system is one of the most polluted in Western Europe (Ruiz et al., 1998; Elbaz-Poulichet et al., 1999), with its water and sediments containing high concentrations of nutrients, suspended substances and heavy metals from erosion and mining (Nelson and Lamothe, 1993). Similar to other rivers in the region, the Guadiana has experienced an increase of anthropogenic influence during the second half of the 20th century (e.g. Brandão and Rodrigues, 2000; González et al., 2001), with a direct impact on quantity and type of sediments exported to the adjacent shelf (González et al., 2006). Nevertheless, the overall amount of metal pollution derived from other rivers than Tinto and Odiel draining into the coastal area is considerably less (Nelson and Lamothe, 1993; Van Geen et al., 1997).

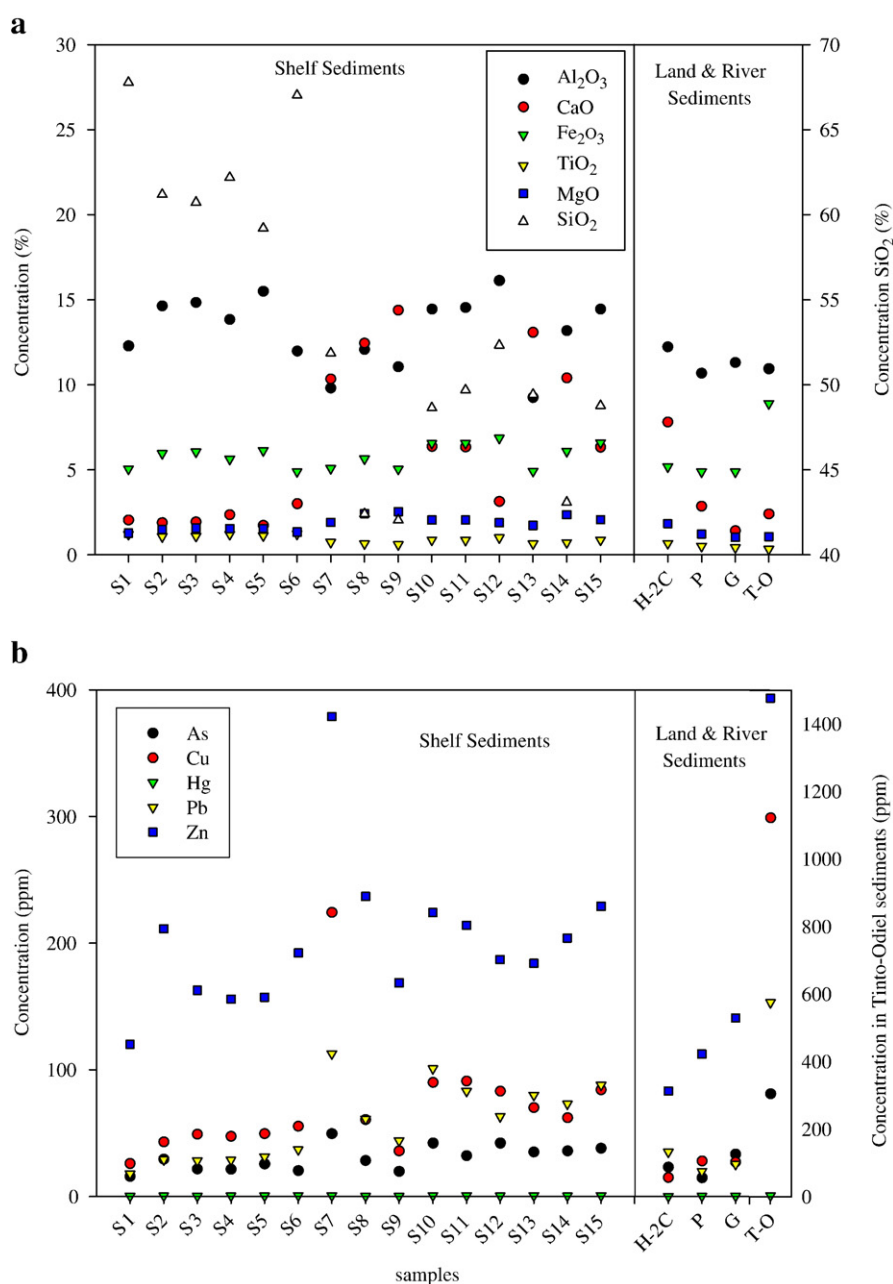
**Table 2b**

Analytical data for the river sediments and regional background.

|                                | Piedras (n = 6) |         |        |       | Guadiana (n = 23) |         |        |        | Tinto–Odiel (n = 24) |         |         |        | H-2C  |
|--------------------------------|-----------------|---------|--------|-------|-------------------|---------|--------|--------|----------------------|---------|---------|--------|-------|
|                                | Mean            | St.dev. | Max    | Min   | Mean              | St.dev. | Max    | Min    | Mean                 | St.dev. | Max     | Min    |       |
| SiO <sub>2</sub>               | n.m.            | n.m.    | n.m.   | n.m.  | n.m.              | n.m.    | n.m.   | n.m.   | n.m.                 | n.m.    | n.m.    | n.m.   | n.m.  |
| Al <sub>2</sub> O <sub>3</sub> | 10.68           | 5.61    | 18.06  | 2.53  | 11.31             | 2.94    | 18.02  | 6.54   | 10.93                | 4.96    | 18.61   | 2.06   | 12.23 |
| CaO                            | 2.85            | 1.81    | 4.72   | 0.59  | 1.41              | 1.94    | 9.20   | 0.14   | 2.40                 | 2.15    | 8.02    | 0.35   | 7.81  |
| Fe <sub>2</sub> O <sub>3</sub> | 4.88            | 2.22    | 7.13   | 1.20  | 4.88              | 1.05    | 7.27   | 3.54   | 8.90                 | 5.12    | 17.11   | 0.51   | 5.18  |
| TiO <sub>2</sub>               | 0.51            | 0.24    | 0.73   | 0.08  | 0.43              | 0.18    | 0.80   | 0.17   | 0.33                 | 0.18    | 0.63    | 0.02   | 0.67  |
| Na <sub>2</sub> O              | 1.08            | 0.36    | 1.35   | 0.36  | 1.28              | 0.23    | 1.74   | 0.80   | 0.81                 | 0.26    | 1.25    | 0.27   | 2.16  |
| K <sub>2</sub> O               | 1.55            | 0.47    | 2.01   | 0.67  | 1.80              | 0.31    | 2.54   | 1.31   | 1.70                 | 0.43    | 2.62    | 0.82   | 2.29  |
| MgO                            | 1.22            | 0.59    | 1.84   | 0.22  | 1.04              | 0.34    | 1.96   | 0.66   | 1.06                 | 0.59    | 1.81    | 0.02   | 1.82  |
| MnO                            | 0.40            | 0.20    | 0.79   | 0.26  | 0.56              | 0.23    | 1.19   | 0.23   | 0.37                 | 0.13    | 0.59    | 0.11   | 0.04  |
| P <sub>2</sub> O <sub>5</sub>  | 0.09            | 0.03    | 0.13   | 0.04  | 0.09              | 0.03    | 0.18   | 0.06   | 1.10                 | 1.10    | 3.97    | 0.05   | 0.10  |
| As                             | 15              | 3.48    | 21.04  | 10.62 | 33                | 19.49   | 78.00  | 10.00  | 304                  | 277.53  | 1156.00 | 20.00  | 23    |
| Ba                             | 208             | 74.44   | 286.33 | 73.76 | 313               | 68.33   | 447.00 | 176.59 | 439                  | 198.40  | 812.00  | 116.00 | 248   |
| Co                             | 12              | 4.87    | 18.27  | 4.66  | 13                | 2.51    | 17.00  | 8.54   | 19                   | 10.61   | 46.00   | 4.00   | 9     |
| Cr                             | 46              | 27.72   | 83.99  | 6.67  | 48                | 17.11   | 104.00 | 25.51  | 66                   | 34.91   | 119.00  | 8.00   | 65    |
| Cu                             | 28              | 13.63   | 47.55  | 8.00  | 27                | 15.97   | 67.00  | 11.00  | 1122                 | 953.78  | 3304.00 | 20.00  | 15    |
| Hg                             | 0.1             | 0.05    | 0.20   | 0.10  | 0.2               | 0.07    | 0.30   | 0.20   | 3.5                  | 4.23    | 11.70   | 0.40   | <0.1  |
| Ni                             | 19              | 8.44    | 31.19  | 10.00 | 24                | 8.43    | 49.00  | 10.88  | 30                   | 14.23   | 47.00   | 10.00  | 27    |
| Pb                             | 20              | 6.65    | 28.96  | 10.00 | 25                | 6.28    | 39.00  | 13.16  | 575                  | 702.50  | 2873.00 | 19.00  | 35    |
| V                              | 68              | 37.26   | 116.12 | 11.82 | 78                | 21.69   | 127.00 | 40.45  | 87                   | 42.93   | 147.00  | 13.00  | 89    |
| Zn                             | 112             | 42.67   | 168.59 | 49.90 | 141               | 43.65   | 303.00 | 61.16  | 1476                 | 1033.18 | 3300.00 | 61.00  | 83    |

Concentration of major (%) and trace elements (ppm) of the sediments collected from the Piedras, Guadiana and Tinto–Odiel rivers, as well as a 15 m depth sample (H-2C) collected from a deep core at SW Huelva (Fig. 1), and considered as a regional reference sample.

max: maximum; min: minimum; st. dev: standard deviation; n.m.: nonmeasured.



**Fig. 2.** Plot of the most important major (a) and minor (b) elements measured in the 15 shelf sediments, river samples and regional background (H-2C). The river samples are displayed as mean values. The error bars have been omitted for the sake of clarity, given the symbol density (standard deviation values can be consulted in Table 2a). Note that the Si concentrations are displayed separately in a right axis (a), as well as the Tinto-Odiel system (b) due to the much higher values observed in both cases.

The geochemical pollution of the GoC coastal area has attracted the interest of many researchers (Nelson and Lamothe, 1993; Van Geen et al., 1999; Davis et al., 2000; Leblanc et al., 2000; Borrego et al., 1990, 2002; González et al., 2004, 2006; and references therein). However, in most cases, these works have targeted estuarine zones and near-shore areas of the northern GoC, particularly the Huelva estuary, but fewer studies have focused on pollution in sediments from the continental shelf (González et al., 2006; González-Pérez et al., 2008). In this study, a group of 15 sediment samples distributed along the inner continental shelf between the Guadiana and Odiel rivers were analyzed and compared in terms of their geochemical composition with 53 samples obtained from the four main rivers draining the area (Guadiana, Piedras, Tinto and Odiel). The main purposes are: (i) to describe the geochemical composition of the shelf and fluvial sediments in order to identify the sources involved in the geochemical signature of the shelf sediments,

(ii) to quantify enrichment levels and determine spatial trends of heavy metals and other important pollutants, and (iii) to evaluate the effect of the historically acid mine-drainage contaminated Tinto-Odiel system on the geochemical composition of the shelf sediments. Since little is known about the terrestrial influence to the GoC inner continental shelf (Sánchez-García et al., 2006; Sánchez-García et al., 2008), this study provides a background approach to further understand the contribution and fate of continental-derived pollutants in this coastal system.

## 2. Materials and methods

### 2.1. Location and sampling

The study area is located in the northern margin of the GoC, on the inner continental shelf between the mouths of the rivers Guadiana

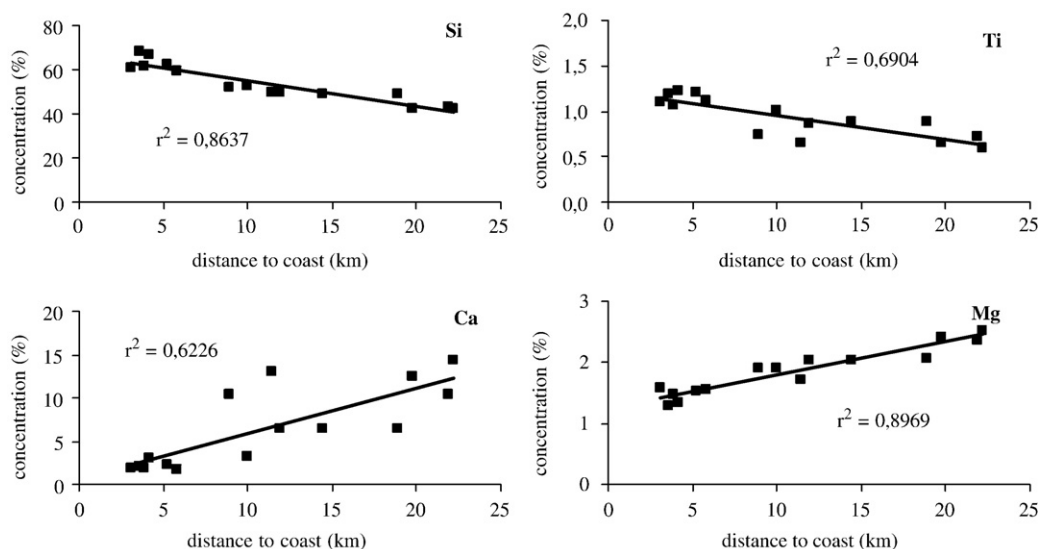


Fig. 3. Plots of well-correlated major elements vs. distance to coast in the shelf sediments.

and Tinto–Odiel, SW Spain ( $6^{\circ}55.29' - 7^{\circ}20.49' \text{ W} / 36^{\circ}56.7' - 37^{\circ}9.82' \text{ N}$ ; Table 1). In an effort to choose a representative area of one of the most important Iberian basin detritus outflow, a suite of 15 surficial (upper 20 cm) samples (Fig. 1) was collected in 2001 from the inner GoC continental shelf by means of a Shipeck dredge. Sediments from the rivers Guadiana ( $n = 23$ ), Piedras ( $n = 6$ ) and Tinto–Odiel ( $n = 24$ ) were also sampled in order to assess the geochemical signature of the main rivers draining the coastal area. An additional sediment sample collected at 15 m depth from an undisturbed metropolitan area of SW Huelva (Fig. 1), was used as geochemical background (see Section 3.2). In order to avoid oxidation and microbial contamination, all the samples were frozen at  $-18^{\circ}\text{C}$  and stored from the time of collection until processing.

## 2.2. Geochemical analysis

The samples were dried at no more than  $40^{\circ}\text{C}$ , to prevent the alteration of the organic fraction, and were then divided in three subsamples. One subsample was used for the particle size analysis, which was carried out using a Sedigraph 5100 (Micromeritics). The subsamples for chemical analyses were crushed and homogenised to  $<0.25 \text{ mm}$  to remove large particles and powdered in an agate mortar. Chemical analyses were performed on the bulk samples by Spanish Geological Survey (IGME).

Major elemental concentrations were determined by X-ray fluorescence, in a Panalytical MagiX ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,

$\text{TiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$ ), while minor elements were measured by inductively coupled plasma mass spectrometry, in a Thermo Jarrel Ash ICAP-61 (As, Ba, Co, Cr, Cu, Ni, Pb, V and Zn), with previous nitric aqua regia digestion. Mercury determination (Hg) was performed following the EPA 7471 procedure and detected by atomic absorption spectroscopy in a Varian Spectra 220-FS, whereas Na was measured by atomic absorption spectroscopy and acetylene flame emission in a Varian Spectra 220-FS, after treatment with  $\text{LiBO}_2$  ( $950^{\circ}\text{C}$ ).

The semiquantitative mineralogical analysis of the sediments was performed on carefully grinded samples, arranged on an aluminium sample-carrier. They were measured in a Philips diffractometer (model PW1700), equipped with Cu tube, graphite monochromator and automatic divergence slit. The conditions used for the R-X generator were 40 mA and 40 kV, Cu anode and Ni filter, for the wavelengths  $\alpha_1$  1.54056 and  $\alpha_2$  1.54439, the slip window was 12 mm and the angle range oscillated between  $2^{\circ}$  and  $62^{\circ}$ . The identification of the different phases was made by comparison with crystallographic records in the ADP Philips software database. The diffractograms were taken by Cu K $\alpha$ 1 and K $\alpha$ 2 with resolution of 0.02 and 2 s. The XRD analysis was developed in semiquantitative mode for each phase using the reflective power of Schultz (1964) and Barahona et al. (1985) adapted for our diffractometer.

Total carbon (TC) and sulphur (TS) were determined on freeze-dried samples of the 15 shelf sediments by elemental analysis of combusted aliquots (30-mg) using a Eurovector elemental analyzer. Total organic carbon (TOC) was measured on previously decarbonated samples

Table 3

Enrichment factors (EF) of trace elements and  $\text{P}_2\text{O}_5$  in the shelf sediments (relative to sample H-2C).

|                        | S1         | S2         | S3         | S4         | S5         | S6         | S7          | S8         | S9         | S10        | S11        | S12        | S13        | S14        | S15        | P          | G          | T-O         |
|------------------------|------------|------------|------------|------------|------------|------------|-------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------------|
| $\text{P}_2\text{O}_5$ | 0.9        | 0.8        | 1.0        | 1.0        | 0.8        | 0.9        | <b>2.0</b>  | 1.4        | 1.4        | 1.2        | 1.1        | 1.0        | 1.8        | 1.3        | 1.2        | 1.2        | 1.1        | <b>12.4</b> |
| As                     | 0.7        | 1.1        | 0.8        | 0.8        | 0.9        | 0.9        | <b>2.7</b>  | 1.2        | 1.0        | 1.5        | 1.2        | 1.4        | <b>2.0</b> | 1.5        | 1.4        | 1.0        | <b>1.7</b> | <b>14.6</b> |
| Ba                     | 1.0        | 1.1        | 1.0        | 1.1        | 1.1        | 1.2        | <b>1.6</b>  | 1.1        | 1.1        | 1.1        | 1.1        | 1.1        | 1.0        | 1.1        | 1.0        | 1.1        | 1.4        | 2.2         |
| Co                     | <b>1.9</b> | <b>1.9</b> | <b>1.9</b> | <b>2.0</b> | <b>1.8</b> | <b>2.0</b> | <b>2.2</b>  | <b>1.8</b> | <b>1.8</b> | 1.4        | 1.5        | 1.5        | 1.3        | 1.3        | 1.1        | <b>1.7</b> | 1.6        | 2.3         |
| Cr                     | 0.8        | 0.9        | 0.9        | 0.9        | 0.8        | 0.8        | 1.1         | 1.0        | 1.0        | 1.1        | 1.1        | 1.1        | <b>2.1</b> | 1.1        | 1.0        | 0.8        | 0.8        | 1.1         |
| Cu                     | <b>1.7</b> | <b>2.4</b> | <b>2.7</b> | <b>2.8</b> | <b>2.6</b> | <b>3.8</b> | <b>18.6</b> | <b>4.1</b> | <b>2.6</b> | <b>5.1</b> | <b>5.1</b> | <b>4.2</b> | <b>6.2</b> | <b>3.8</b> | <b>4.7</b> | <b>2.4</b> | <b>1.9</b> | <b>74.7</b> |
| Hg                     | <b>2.0</b> | <b>4.2</b> | <b>2.5</b> | <b>3.5</b> | <b>3.2</b> | <b>6.1</b> | <b>8.7</b>  | <b>3.0</b> | <b>2.2</b> | <b>5.1</b> | <b>5.0</b> | <b>3.8</b> | <b>7.9</b> | <b>4.6</b> | <b>5.1</b> | <b>2.1</b> | 0.7        | <b>8.3</b>  |
| Ni                     | 0.8        | 0.9        | 0.9        | 0.9        | 0.9        | 0.8        | 1.0         | 1.0        | 1.0        | 1.2        | 1.2        | 1.2        | 1.0        | 1.2        | 1.1        | 0.9        | 1.0        | 1.3         |
| Pb                     | 0.5        | 0.7        | 0.7        | 0.7        | 0.7        | 1.1        | <b>4.0</b>  | <b>1.8</b> | 1.4        | <b>2.4</b> | <b>2.0</b> | 1.4        | <b>3.0</b> | <b>1.9</b> | <b>2.1</b> | 0.8        | 0.8        | <b>17.9</b> |
| V                      | 0.9        | 1.0        | 1.0        | 1.0        | 1.0        | 1.0        | 1.2         | 1.1        | 1.2        | 1.1        | 1.1        | 1.1        | 1.1        | 1.2        | 1.0        | 0.8        | 0.9        | 1.0         |
| Zn                     | <b>1.4</b> | <b>2.1</b> | <b>1.6</b> | <b>1.7</b> | 1.5        | <b>2.4</b> | <b>5.7</b>  | <b>2.9</b> | <b>2.2</b> | <b>2.3</b> | <b>2.2</b> | <b>1.7</b> | <b>2.9</b> | <b>2.3</b> | <b>2.3</b> | <b>1.9</b> | 1.9        | <b>18.6</b> |

EF > 1.5 are marked in bold. S: shelf sediments; P, G, T-O: average of sediments from the rivers Piedras, Guadiana and Tinto–Odiel.



**Table 4**  
Pearson's correlation coefficient (*r*).

|                                | SiO <sub>2</sub>    | Al <sub>2</sub> O <sub>3</sub> | CaO            | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub>    | Na <sub>2</sub> O  | K <sub>2</sub> O    | MgO            | MnO            | P <sub>2</sub> O <sub>5</sub> | As            | Ba                  | Co                  |
|--------------------------------|---------------------|--------------------------------|----------------|--------------------------------|---------------------|--------------------|---------------------|----------------|----------------|-------------------------------|---------------|---------------------|---------------------|
| SiO <sub>2</sub>               | 1                   |                                |                |                                |                     |                    |                     |                |                |                               |               |                     |                     |
| Al <sub>2</sub> O <sub>3</sub> | 0.20**              | 1                              |                |                                |                     |                    |                     |                |                |                               |               |                     |                     |
| CaO                            | <b>−0.82**</b>      | <b>−0.72**</b>                 | 1              |                                |                     |                    |                     |                |                |                               |               |                     |                     |
| Fe <sub>2</sub> O <sub>3</sub> | −0.20**             | <b>0.87**</b>                  | −0.39**        | 1                              |                     |                    |                     |                |                |                               |               |                     |                     |
| TiO <sub>2</sub>               | <b>0.91**</b>       | 0.56**                         | <b>−0.96**</b> | 0.16**                         | 1                   |                    |                     |                |                |                               |               |                     |                     |
| Na <sub>2</sub> O              | 0.46**              | <b>0.68**</b>                  | <b>−0.76**</b> | 0.54**                         | 0.65**              | 1                  |                     |                |                |                               |               |                     |                     |
| K <sub>2</sub> O               | −0.48**             | <b>0.75**</b>                  | −0.08**        | <b>0.86**</b>                  | −0.10**             | 0.27**             | 1                   |                |                |                               |               |                     |                     |
| MgO                            | <b>−0.96**</b>      | −0.13**                        | <b>0.76**</b>  | 0.21**                         | <b>−0.83**</b>      | −0.42**            | 0.54**              | 1              |                |                               |               |                     |                     |
| MnO                            | <b>0.68**</b>       | 0.59**                         | <b>−0.80**</b> | 0.25**                         | <b>0.74**</b>       | 0.63**             | 0.09**              | −0.65**        | 1              |                               |               |                     |                     |
| P <sub>2</sub> O <sub>5</sub>  | <b>−0.67**</b>      | −0.33**                        | 0.60**         | 0.11**                         | <b>−0.68**</b>      | −0.16**            | 0.06**              | 0.60**         | <b>−0.67**</b> | 1                             |               |                     |                     |
| As                             | −0.43**             | −0.18**                        | 0.32**         | 0.22**                         | −0.47**             | 0.13**             | 0.02 <sup>ns</sup>  | 0.31**         | −0.42**        | <b>0.82**</b>                 | 1             |                     |                     |
| Ba                             | 0.23**              | <b>0.67**</b>                  | −0.59**        | 0.62**                         | 0.43**              | <b>0.80**</b>      | 0.42**              | −0.16**        | 0.43**         | 0.03 <sup>ns</sup>            | 0.28**        | 1                   |                     |
| Co                             | 0.66**              | 0.49**                         | <b>−0.74**</b> | 0.12**                         | <b>0.73**</b>       | 0.61**             | 0.04**              | −0.53**        | <b>0.74**</b>  | −0.53**                       | −0.38**       | <b>0.66**</b>       | 1                   |
| Cr                             | −0.37**             | 0.27**                         | 0.11**         | 0.52**                         | −0.25**             | 0.00 <sup>ns</sup> | 0.36**              | 0.19**         | −0.12**        | 0.23**                        | 0.32**        | −0.02 <sup>ns</sup> | −0.44**             |
| Cu                             | −0.19**             | −0.48**                        | 0.33**         | −0.19**                        | −0.37**             | −0.03              | −0.36**             | 0.13**         | −0.43**        | <b>0.76**</b>                 | <b>0.82**</b> | 0.23**              | −0.18**             |
| Hg                             | −0.03 <sup>ns</sup> | −0.18**                        | 0.06**         | 0.08**                         | −0.12**             | 0.18**             | −0.22**             | −0.09**        | −0.23**        | 0.48**                        | <b>0.77**</b> | 0.25**              | −0.30**             |
| Ni                             | −0.24**             | <b>0.84**</b>                  | −0.33**        | <b>0.96**</b>                  | 0.13**              | 0.52**             | <b>0.86**</b>       | 0.26**         | 0.15**         | 0.10**                        | 0.21**        | 0.60**              | 0.08**              |
| Pb                             | −0.58**             | −0.36**                        | 0.54**         | 0.10**                         | −0.64**             | −0.19**            | −0.01 <sup>ns</sup> | 0.48**         | −0.66**        | <b>0.89**</b>                 | <b>0.90**</b> | 0.03 <sup>ns</sup>  | −0.61**             |
| V                              | −0.23**             | <b>0.85**</b>                  | −0.34**        | <b>0.92**</b>                  | 0.15**              | 0.56**             | <b>0.88**</b>       | 0.30**         | 0.19**         | 0.08**                        | 0.16**        | <b>0.72**</b>       | 0.28**              |
| Zn                             | −0.29**             | −0.50**                        | 0.42**         | −0.21**                        | −0.46**             | −0.07**            | −0.28**             | 0.25**         | −0.41**        | <b>0.72**</b>                 | <b>0.79**</b> | 0.19**              | −0.18**             |
| TIC                            | <b>−0.81**</b>      | −0.61**                        | <b>0.91**</b>  | −0.25**                        | <b>−0.91**</b>      | <b>−0.71**</b>     | −0.00 <sup>ns</sup> | <b>0.75**</b>  | <b>−0.76**</b> | 0.65**                        | 0.38**        | −0.60**             | <b>−0.84**</b>      |
| TOC                            | −0.24**             | 0.54**                         | −0.15**        | <b>0.68**</b>                  | −0.00 <sup>ns</sup> | 0.28**             | 0.60**              | 0.25**         | −0.04**        | 0.10**                        | 0.13**        | 0.43**              | 0.03 <sup>ns</sup>  |
| TS                             | 0.42**              | 0.59**                         | −0.63**        | 0.43**                         | 0.52**              | 0.53**             | 0.26**              | −0.41**        | 0.70**         | −0.44**                       | −0.15**       | <b>0.67**</b>       | 0.65**              |
| Sand                           | 0.62**              | −0.43**                        | −0.17**        | −0.65**                        | 0.32**              | −0.23**            | <b>−0.80**</b>      | <b>−0.69**</b> | 0.13**         | −0.46**                       | −0.38**       | −0.49**             | −0.01 <sup>ns</sup> |
| Slip                           | −0.27**             | 0.51**                         | −0.12**        | 0.55**                         | 0.00 <sup>ns</sup>  | 0.47**             | <b>0.68**</b>       | 0.41**         | 0.14**         | 0.17**                        | 0.20**        | <b>0.68**</b>       | 0.36**              |
| Clay                           | <b>−0.69**</b>      | 0.40**                         | 0.23**         | <b>0.66**</b>                  | −0.39**             | 0.15**             | <b>0.79**</b>       | <b>0.76**</b>  | −0.25**        | 0.56**                        | 0.41**        | 0.42**              | −0.10**             |

Bivariate regression analysis of the granulometric and geochemical components for the shelf sediments. \*\*Significant correlation at the 0.01 level; \* Significant correlation at the 0.05 level; (ns) non significant correlation. The correlation coefficients higher than 0.6, showing significant correlation at the 0.05 level are highlighted as bold.

(3 M HCl) and total inorganic carbon (TIC) was calculated from the difference between the TC and TOC readings (Nieuwenhuize et al., 1994).

### 2.3. Statistical analysis

Statistical analyses were conducted using the statistics software package Minitab (version 15). The relationship between major elements, heavy metals, granulometry fractions and other geochemical parameters (TS, TOC and TIC) was determined by bivariate analysis, measuring the linear association between all pairs of variables with a 2-tailed Pearson's coefficient. Principal components and cluster analyses were performed on the enrichment coefficients (see explanation later on) of MnO, P<sub>2</sub>O<sub>5</sub>, As, Co, Cr, Cu, Hg, Ni, Pb and Zn for the shelf sediments and on all the studied major and minor elements for the entire set of shelf and fluvial samples (Guadiana, Piedras and Tinto–Odiel) in order to find homogeneous groups of samples on the basis of their geochemical characteristics.

## 3. Results

### 3.1. Granulometry and bulk geochemistry

The location and bulk geochemical description of the 15 shelf sediments are presented in Table 1. According to their bulk mineralogy and grain size, the sediments are distributed between quartz-dominated coarser fractions (S1, S2, S3, S4, S5 and S6) mainly composed of quartz, albite and muscovite and combined quartz-carbonate and silt-clayish fractions (S7, S8, S9, S10, S11, S12, S14 and S15), which include carbonates, feldspars and plagioclasas (apart from quartz). Note that the sediments offshore are mainly composed of silt and clay fractions (86–99% of fines), whereas those sediments located nearby the Guadiana mouth contain coarser components (12–43% of sand), particularly evident in the case of S13 (15% gravel and 43% sand; Table 1).

The shelf sediments show TC concentrations varying between 0.97% and 3.55%, whereas the content of TOC and TIC ranged from 0.50% to

1.40% and from 0.37% to 2.91% respectively (Table 1). The TIC fraction, mainly composed of carbonates, shows some enrichment in the remotest sediments relative to the Guadiana mouth (S-7, S-8, S-9, S-13, S-14 and S-15). Despite the low TS concentrations (0.09–0.32%), heterogeneous C/S atomic ratios (C/S = 6–23) were measured in the sediments.

### 3.2. Major elements

Tables 2a and 2b present the results of the major and minor elements analyzed in the samples of both continental shelf (Table 2a), rivers and land (H-2C, Fig. 1) (Table 2b). The values of the latter may be considered preantropic, being comparable to those reported to have been deposited at the beginning of mining activities and the construction of the industrial complex at the riverbanks of the Tinto–Odiel estuary (Ruiz et al., 1998). Thus, the geochemical composition of H-2C may be used to compare the concentrations of major and minor elements analyzed under natural conditions without human intervention, and therefore assumed as regional background here.

The most abundant major element in the shelf sediments is SiO<sub>2</sub> (53.75 ± 8.65%), followed by Al<sub>2</sub>O<sub>3</sub> (13.20 ± 20.6%), CaO (6.38 ± 4.60%) and Fe<sub>2</sub>O<sub>3</sub> (5.80 ± 0.68%) (Fig. 2a). The remaining oxides have significantly lower values. By order of abundance we find: Na<sub>2</sub>O (2.47 ± 0.33%), K<sub>2</sub>O (2.22 ± 0.32%), MgO (1.85 ± 0.40%), TiO<sub>2</sub> (0.93 ± 0.22%), P<sub>2</sub>O<sub>5</sub> (0.12 ± 0.02%) and MnO (0.06 ± 0.01%) (Table 2a). These results are very similar to those obtained from the fluvial sediments (Table 2b), which solely differ in 2–3 times lower values of CaO (1.41%–2.85%), Na<sub>2</sub>O (0.81%–1.28%) K<sub>2</sub>O (1.55%–1.8%) and MgO (1.04%–1.22%) (Table 2b, Fig. 2a). Overall, the major elements content ranges in the same magnitude order for both the shelf and river sediments (Fig. 2a). The relevant difference observed is that concerning the concentration of Fe<sub>2</sub>O<sub>3</sub> (Fig. 2a) and P<sub>2</sub>O<sub>5</sub> (Table 2b), which registers higher values in the Tinto–Odiel sediments (8.90 ± 5.10% and 1.10 ± 1.10%), compared with those from the shelf (5.80 ± 0.68% and 0.12 ± 0.02%; Table 2a), Piedras (4.88 ± 2.22% and 0.09 ± 0.03%) and Guadiana (4.88 ± 1.05% and 0.09 ± 0.03%) (Table 2b). On the other hand, the shelf samples which are closest to Guadiana (S1, S2, S3, S4, S5 and S6) display higher

| Cr      | Cu            | Hg                  | Ni            | Pb                 | V              | Zn      | TIC            | TOC     | TS      | Sand           | Silt          | Clay |
|---------|---------------|---------------------|---------------|--------------------|----------------|---------|----------------|---------|---------|----------------|---------------|------|
| 1       |               |                     |               |                    |                |         |                |         |         |                |               |      |
| −0.13** | 1             |                     |               |                    |                |         |                |         |         |                |               |      |
| 0.26**  | <b>0.69**</b> | 1                   |               |                    |                |         |                |         |         |                |               |      |
| 0.57**  | −0.22**       | 0.07**              | 1             |                    |                |         |                |         |         |                |               |      |
| 0.29**  | <b>0.80**</b> | <b>0.74**</b>       | 0.09**        | 1                  |                |         |                |         |         |                |               |      |
| 0.38**  | −0.19**       | −0.03 <sup>ns</sup> | <b>0.96**</b> | 0.02 <sup>ns</sup> | 1              |         |                |         |         |                |               |      |
| −0.23** | <b>0.95**</b> | 0.65**              | −0.26**       | <b>0.78**</b>      | −0.19**        | 1       |                |         |         |                |               |      |
| 0.09**  | 0.33**        | 0.12**              | −0.25**       | 0.61**             | −0.32**        | 0.42**  | 1              |         |         |                |               |      |
| 0.56**  | −0.15**       | −0.04*              | <b>0.76**</b> | 0.08**             | <b>0.73**</b>  | −0.24** | −0.24**        | 1       |         |                |               |      |
| 0.11**  | −0.17**       | 0.08**              | 0.37**        | −0.31**            | 0.43**         | −0.16** | <b>−0.72**</b> | 0.43**  | 1       |                |               |      |
| −0.13** | −0.13**       | −0.04*              | −0.63**       | −0.34**            | <b>−0.73**</b> | −0.22** | −0.23**        | −0.32** | −0.04** | 1              |               |      |
| −0.20** | 0.09**        | 0.01 <sup>ns</sup>  | 0.52**        | 0.09**             | 0.69**         | 0.21**  | −0.07**        | 0.22**  | 0.28**  | <b>−0.89**</b> | 1             |      |
| 0.18**  | 0.16**        | 0.01 <sup>ns</sup>  | <b>0.66**</b> | 0.41**             | <b>0.73**</b>  | 0.22**  | 0.31**         | 0.36**  | −0.09** | <b>−0.97**</b> | <b>0.78**</b> | 1    |

concentrations of SiO<sub>2</sub> (63.01 ± 3.54%) or TiO<sub>2</sub> (1.15 ± 0.07%), together with much lower MgO (1.46 ± 0.12%) and CaO (2.16 ± 0.46%) compared to the outermost sediments (S7, S8, S9, S13, S14 and S15) (Table 2a, Fig. 2a). In fact, these elements show significant (>95%) negative (Si and Ti) and positive (Mg and Ca) correlations with distance to coast (Fig. 3).

### 3.3. Minor elements

Among the minor elements, the highest concentrations in the inner shelf are Ba (291 ± 43 ppm), Zn (202 ± 59 ppm) and V (101 ± 16 ppm), followed by Cr (72 ± 15 ppm), Cu (71 ± 47 ppm), Pb (59 ± 30 ppm), Ni (30 ± 7 ppm), As (30 ± 10 ppm), Co (13 ± 3 ppm) and Hg (0.5 ± 0.2 ppm) (Table 2a). These results are comparable to those observed in the rivers Guadiana and Piedras (Table 2b), except for some elements (Cu, Hg or Zn), which are slightly higher in the shelf (Fig. 2b). However, a clear difference is detected with respect to the Tinto–Odiel samples, whose concentrations of As, Cu, Hg, Pb or Zn are approximately 10, 15, 7, 10 and 7 times the values of the shelf and even higher in comparison to the Piedras and Guadiana samples (Fig. 2b). In this way, an evident enrichment of these elements (Zn: 379 ppm, Cu: 224 ppm, Pb: 113 ppm, As: 50 ppm and Hg: 0.7 ppm) is observed in S7 (Fig. 2b) with respect to the rest of shelf sediments. Relative to H-2C (Table 2b), the shelf samples are enriched in some of these metals, presenting values ~4.8 times (Cu), 4.7 times (Hg), 2.4 times (Zn), 1.8 times (Co) and 1.7 times (Pb) higher than those of the geochemical background.

In order to quantify the relative enrichment of these elements to natural concentrations and evaluate the anthropogenic contribution to the sediments, it is necessary to eliminate the influence of other factors, such as the mineralogy or grain size (Borrego et al., 2002). As a means of compensating for these effects and determining the tendencies in the surficial distribution and different source contribution, a normalization of the data is required (Loring, 1991). For this purpose, Al is considered an appropriate element to normalize the metal contents and to quantify the terrigenous–detrital fraction in near-shore environments (Brumsack, 2006). Comparing the element/

Al relationship of the sediments and H-2C, we obtain the anthropogenic enrichment factor (EF) (Brumsack, 2006):

$$EF = (\text{element}/\text{Al})_{\text{sample}} / (\text{element}/\text{Al})_{\text{H-2C}}.$$

Table 3 presents the EF of the minor elements and P<sub>2</sub>O<sub>5</sub> for shelf and fluvial sediments (the latter as mean of each river). Whereas Cu, Hg and Zn show enrichment in the continental shelf (means of 4.7, 4.5 and 2.3, respectively) and Piedras river (2.4, 2.1 and 1.9), Co and Pb seem preferentially enriched only in certain samples (Table 3). The highest enrichment is that observed in the Tinto–Odiel system, reaching EF values of 12.4 (P<sub>2</sub>O<sub>5</sub>), 14.4 (As), 74.7 (Cu), 8.3 (Hg), 17.9 (Pb) and 18.6 (Zn). In this context, the case of S7 is particularly striking, since it displays a notable enrichment of the most metals and P<sub>2</sub>O<sub>5</sub> with respect to the rest of shelf sediments: EF of 18.6 (Cu), 8.7 (Hg), 5.7 (Zn), 4.0 (Pb), 2.7 (As), 2.2 (Co) or 2.0 for P<sub>2</sub>O<sub>5</sub>.

### 3.4. Correlation between the geochemical and granulometric characteristics

The correlation matrix (Table 4) displays the existence of remarkable levels of correlation (significance level >99%) with both positive and negative values among different variable pairs for the shelf sediments. On one hand, SiO<sub>2</sub> presents a high or moderate level of positive correlation with TiO<sub>2</sub> (0.91), MnO (0.68) and sand (0.62), as well as strong or moderate negative correlation with MgO (−0.96), CaO (−0.82), clays (−0.69) and P<sub>2</sub>O<sub>5</sub> (−0.67). On the other hand, Al<sub>2</sub>O<sub>3</sub> is positively correlated with Fe<sub>2</sub>O<sub>3</sub> (0.87), Na<sub>2</sub>O (0.68), K<sub>2</sub>O (0.75), Ba (0.67), Ni (0.84) and V (0.85), although it doesn't correlate well with SiO<sub>2</sub> (0.20). A strong positive correlation is observed for CaO with TIC (0.91), with both components presenting a positive correlation with MgO (0.76 and 0.75, respectively) and a strongly negative correlation with TiO<sub>2</sub> (−0.96 and −0.91), Na<sub>2</sub>O (−0.76 and −0.71) and MnO (−0.80 and −0.76). It is also noteworthy that As, Cu, Hg, Pb and Zn have positive correlations with each other and with P<sub>2</sub>O<sub>5</sub>, showing correlation coefficients of 0.82 (As), 0.76 (Cu), 0.89 (Pb) and 0.72 (Zn).

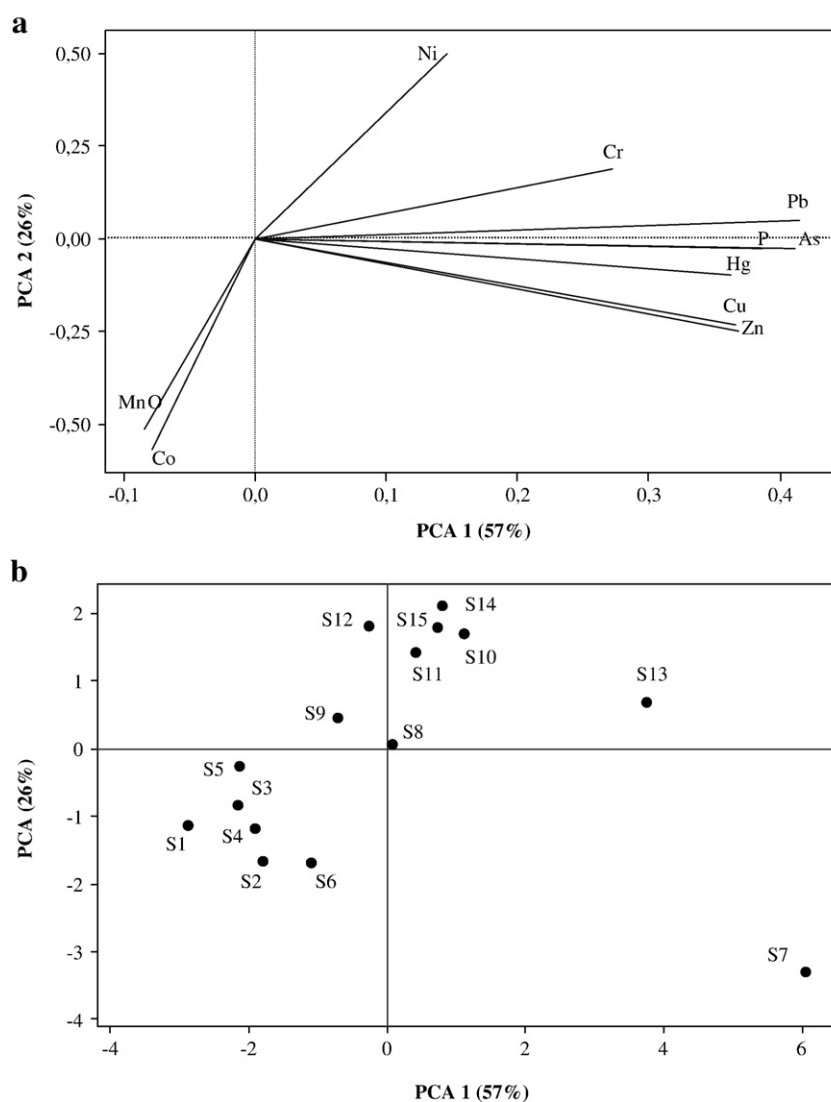


Fig. 4. Plot of the principal components loads (a) and sample scores (b). Principal Component Analysis on EF values of the shelf sediments.

## 4. Discussion

### 4.1. Geochemical signature of the shelf sediments

The bulk mineralogy and grain size (Table 1) indicate that the shelf sediments derive from a combination of terrestrial and marine inputs, consisting mainly of silt–clay clastic materials, according to Shepard's (1954) clastic textural classification, and minor sand contributions. Those sediments located nearby the Guadiana mouth (S1, S2, S3, S4, S5, S6; Fig. 1) are represented by a quartz-dominated mineralogy, rich in lithogenic-derived components (quartz, feldspar and micas; Table 1) (Kastner, 1999). These results indicate the relevance of detrital sources in the mineralogical signature of the innermost marine sediments. Beside quartz components, the remaining samples demonstrate the important contributions of carbonates, including calcite and dolomite forms (Table 1), indicating the influence of marine sources. Accordingly, coarser fractions (predominantly sand) are significant only for near-shore sediments (Table 1), whereas silt–clay type fractions dominate the off-shore sites.

The concentration of TOC (Table 1) is within typical low ranges for coastal sediments (Dickens et al., 2004) and similar to those reported for marine sediments from the Iberian margin of the Atlantic Ocean (0.22–2.60%; Middelburg et al., 1999). Despite the low TS concentration

measured in the shelf (Table 1), the overall high C/S atomic ratios and the observation of occasional authigenic pyritic remains through the chemical treatment, in microcrystal forms, with angular sides and without alteration rests, may be related to the presence of anoxic deposition conditions in which sulphate reduction would have dominated the sulphur incorporation into the early diagenetic products (Hadas et al., 2001). Although further specific techniques such as micro-sensors or electron microscopy, would be desirable to contrast this assumption, the presence of pyrite in the marine sediments suggests anoxic deposition characteristics, since this mineral is widespread in continental margin sediments with medium to high sedimentation rates and is known to occur in excess-Fe or S-deficient anoxic pore waters (Kastner, 1999).

The geochemical composition of the shelf sediments agrees with that reported for the average shale (Wedepohl, 1991) and the Earth's crust (Turekian and Wedepohl, 1961) in terms of major elements, showing slightly enhancement of CaO or Na<sub>2</sub>O as a consequence of the marine environment. In fact, the highest values of Ca and TIC were observed in the off-shore samples (Figs. 2a and 3), suggesting together with the positive correlation (Table 4) of both components to Mg the marine association of the three variables (Ca, TIC and Mg). The study of the correlation matrix (Table 4) proves the existence of a positive relationship of Al with Fe, K, Ni, V and Na, presumably indicating the



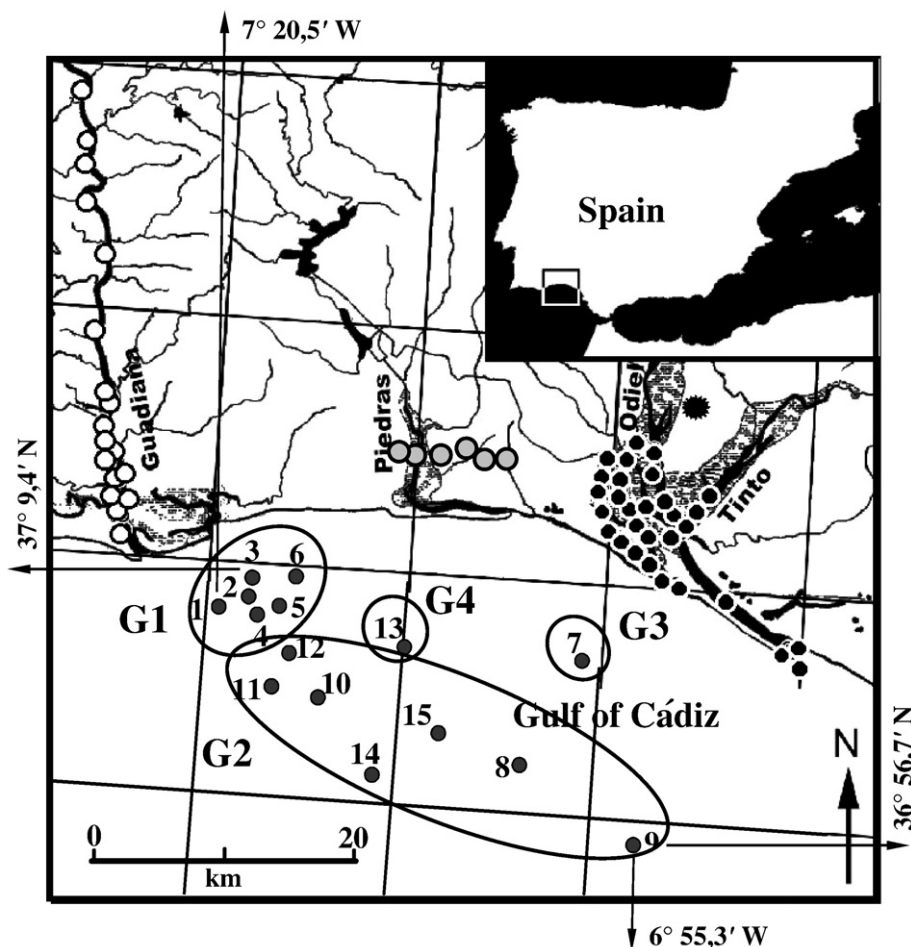


Fig. 5. Map showing the classification (4 groups) of the shelf sediments, according to their geochemical and granulometric composition.

association of these elements to aluminosilicate fractions. The strong level of correlation of Si with Ti suggests a common origin of both elements, likely related either to detrital or biogenic sources. However, the absence of opal-A and rutile in the mineralogical composition of the sediments leads us to surmise that the better explanation is terrigenous–detrital sources. In addition, the overall negative correlation between Si–Ti–Mn and Ca–Mg–TIC may be interpreted as indicators of the origins of these groups of components, being associated with terrigenous–detrital and biogenic sources respectively. In this context, the enhanced concentration of detritic components (Si and Ti) and coarser fractions observed in S1, S2, S3, S4, S5 and S6 (Tables 2a), denote a dominant terrigenous Guadiana-derived influence, whereas the higher values of carbonates-associated components (Ca, Mg and TIC) and finer sediments measured in samples from the middle–inner shelf reflect increasing marine characteristics.

The shelf sediments contain a general enrichment of Co, Cu, Hg, Pb and Zn (Table 3), which could indicate an important degree of dispersion of these metals from anthropogenic sources. Particularly obvious is the S7 sample, which displays the highest EF values for the most heavy metals and P (Table 3). The high concentrations of Cu, Pb and Zn in the area have been attributed to the contributions of the mining and industrial-polluted rivers Tinto and Odiel (e.g. Nelson and Lamothe, 1993; Elbaz-Poulitchet et al., 1999; Leblanc et al., 2000). The high proportions of P, in association with other metals such as As or Hg, have been reported to be related to fertiliser industry disposals (Elbaz-Poulitchet et al., 1999). Consistently, the strong positive correlation of P to the most enriched metals (As, Cu, Pb and Zn) suggests a common non-natural origin of all these elements, which given the location of the

highest EF values determined in the shelf (corresponding to S7), appear to be related to the inputs of the historically polluted Tinto–Odiel waters. Even though most of the load of polluting heavy metals supplied from mining and industrial activities are deposited in the vicinity of the estuarine sediments (Borrego et al., 2002), the enrichment observed here in the shelf sediments demonstrates the substantial dispersion of these metals, as previously noted by Borrego et al. (1990), Elbaz-Poulitchet and Leblanc (1996) and Van Geen et al. (1997) for marine sediments located on adjacent estuaries (Piedras) or on the continental shelf.

In order to find similar patterns in the geochemical composition of the shelf sediments, the concentrations of MnO,  $P_2O_5$ , As, Co, Cr, Cu, Hg, Ni, Pb and Zn were subjected to principal component analysis. Only components with eigen values greater than 1 were included. The two principal components (PCA1 + PCA2) accounted for 83% of the total variance. To illustrate the contribution of the different variables and samples to individual principal components, the distribution of the loads and sample scores in the PCA1–PCA2 axis is shown in Fig. 4. The most important component (PCA1), accounting for 57% of the variance among the elements, is characterized by positive loads for Pb, As,  $P_2O_5$ , Zn, Cu and Hg (Fig. 4a). Considering the high enrichment in heavy metals and P observed in the Tinto–Odiel sediment samples, the first principal component may be considered as the influence exerted by this polluted system. On the other hand, 26% of the variance is accounted for the second component (PCA2), which shows a positive contribution for Ni as well as negative ones for MnO and Co. These results suggest that sediments can be classified using the positive or negative values for each component in relation to Ni or

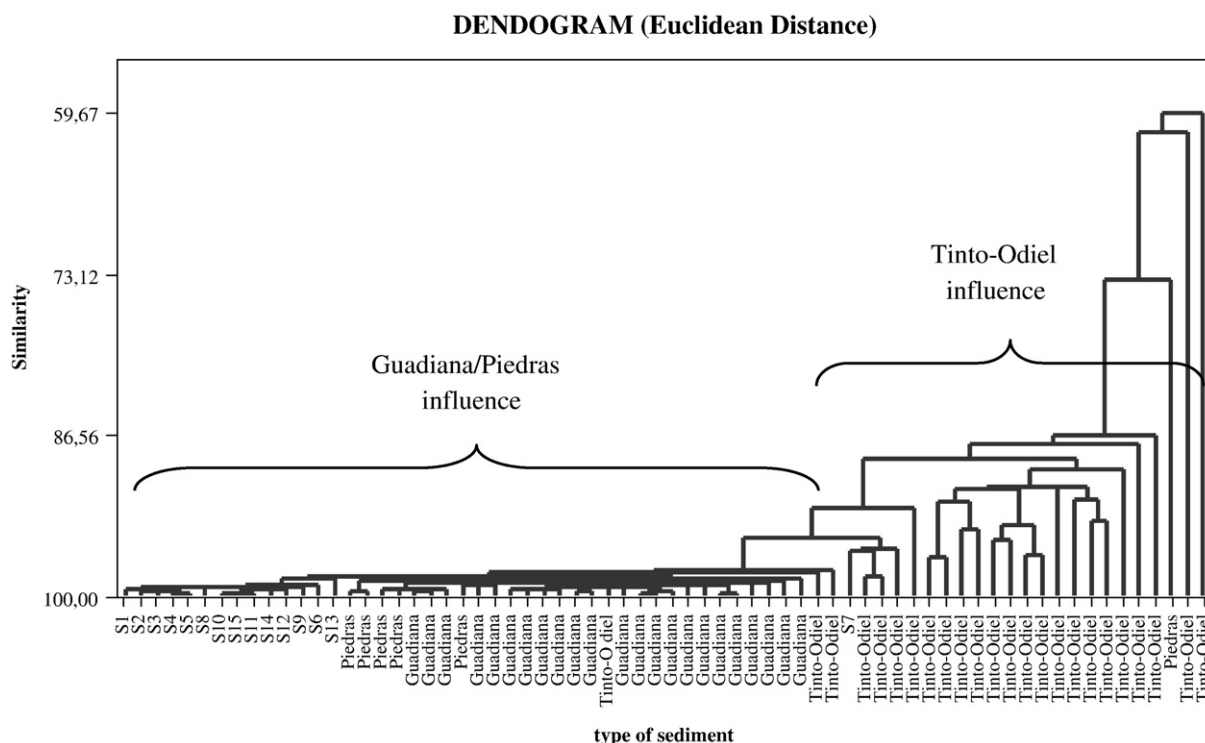


Fig. 6. Dendrogram samples from cluster analysis of the EF values of major and minor elements of the shelf sediments (S) and river samples (Guadiana, Piedras, Tinto–Odiel).

Mn/Co sources respectively. In terms of sediments scores, the samples S7, S10, S11, S13, S14 and S15 display positive values for the first component, particularly evident for S7 and S13 (Fig. 4b), demonstrating the role played by Tinto and Odiel as geochemical sources of the latter sediments. On the other hand, the group of samples S14, S12, S15, S10 and S11 shows higher positive values for the second component, whereas S3, S1, S4, S2 and S6 display negative scores, suggesting Ni-association for the former group and Co and Mn-association for the latter. According to the granulometry and mineralogy, the stronger influence of Co and Mn appears more important for the sediments located closest to the Guadiana mouth, consistent with the higher concentration of Mn registered on the Guadiana fluvial samples (Tables 2a and 2b). The Ni factor, in contrast, seems to mainly affect the middle-inner shelf sediments.

#### 4.2. Geochemical sources and spatial variability

The study of the correlation matrix and the principal component analysis allowed us to classify the shelf sediments, according to their geochemical composition and granulometric characteristics. Four main different sample groups can be established considering the variables studied so far (Fig. 5):

- Group 1: formed by coarser sediments (average sand content: 25%; Table 1), characterized by higher concentrations of Si, Ti and Mn (Table 2a, Fig. 2a), enrichment of Co (Table 3) and clastic quartz-dominated fractions (Table 1). This group, composed of those sediments located nearby the Guadiana mouth (S1, S2, S3, S4, S5 and S6), is related to lithogenic sources.
- Group 2: constituted by muddy sediments (average of silt + clay fractions: 96%; Table 1), has moderate or high enrichment of Cu, Hg, Pb and Zn (Table 3) and shows a mineralogy with an important contribution of biogenic carbonate-associated components (Table 1), consistent with their higher amounts of Ca and Mg (Fig. 2a). This group is composed of samples S8, S9, S10, S11, S12,

S14 and S15, and could be geochemically described as the south-eastward transition from terrestrial-detritic sources to dominant biogenic-marine origins.

- Group 3: sample S7 (silt + clay: 86%; Table 1), which has a carbonate-rich composition (Table 1 and 2). This sediment, collected from the location closest to the Tinto–Odiel estuary, is highly enriched with P, As, Co, Cu, Hg, Hg, Pb and Zn (Table 3, Fig. 2b) and strongly suggests that the main source of these elements is the acid and heavy metal-polluted Tinto–Odiel system.
- Group 4: uniquely composed by the sample S13, contains the coarsest fraction (gravel: 15% and sand: 43%), according to its detritic quartz-dominated mineralogical composition (Table 1), and shows enrichment of As, Cr, Cu, Hg, Pb and Zn (Table 3). This sediment, with the lowest  $\text{Al}_2\text{O}_3$  concentration (9.25%) and one of the highest of TIC (Table 1) and CaO (Table 2b), combines the influence of both the marine-biogenic and the fluvial-detritic inputs, and also reveals some signs of influence from the polluted Tinto–Odiel waters.

Finally, a cluster analysis was carried out on the shelf sediments along with the river samples in order to determine possible associations between shelf and nearby fluvial systems according to their geochemical composition. As Fig. 6 shows, no clearly defined clusters are obtained. Instead, a variable distribution of samples shows higher levels of similarity in both the Guadiana and Piedras rivers, than in the Tinto–Odiel system. Overall, the sediments from the shelf are more similar to those from the Guadiana and Piedras rivers, whereas the sediments from the Tinto–Odiel system have substantial heterogeneity in their geochemical composition. From the distribution displayed by the 15 shelf sediments among the nearby rivers samples, it may be concluded that the geochemical composition of S7 is closer to that of the sediments from Tinto and Odiel rivers, giving further evidence that the main source of heavy metals (As, Cu, Hg, Pb, Zn) and P detected derives from this acid and heavy metal-polluted fluvial system. In contrast, the remaining sediments of the shelf,

displaying a more homogeneous geochemical signature, are closely associated to those from the Guadiana and Piedras rivers. However, varying degrees of influence from the polluted Tinto–Odiel system is observed in some shelf sediments, related to the distance of the sample from this estuary. These results indicate the high level of dispersion of some heavy metals and other pollutants from this source area, as well as revealing the magnitude of anthropogenic pollution effects.

Further research on the geochemical characteristics of the GoC sediments by combined use of more specific techniques (e.g. quantitative mineral analysis, sequential extraction procedures, scanning electron microscopy or geochemical modelling), would be of enormous interest to contrast and complement the interpretations arrived in this study based on sediment composition.

## 5. Conclusions

The present study gives preliminary but still relevant information about the geochemical composition and dispersion of inorganic pollutants among sediments from the GoC inner continental shelf. The granulometric, mineralogical and geochemical characteristics of the 15 shelf sediments studied here reveal the dominant silt–clay clastic composition of these coastal sediments, which spatial variability shows mixed contribution of terrigenous–detritic and biogenic–marine sources. High values of the C/S ratio suggest anoxic or suboxic depositional conditions. According to the principal components and cluster analyses, the shelf sediments may be classified in four groups, in relation to their geochemical composition and the influence exerted by the different fluvial systems discharging into the coastal area. The first group, including the sediments under the dominant influence of the Guadiana River, is formed by coarser siliclastic sediments with a major terrigenous–detrital signature and enrichment of Co and Mn. The second group is formed by muddy sediments, associated with Ni and with moderate enrichment of Cu, Hg, Pb and Zn, as well as important contribution of carbonate forms. This group is made up of off-shore samples, which represent the transition towards dominant marine sources. The third group is represented by the muddy sediments from S7. This sample has the highest concentration of sulphide associated-heavy metals and phosphorus, not surprising given its close proximity to the polluted Tinto–Odiel estuary. The last group, corresponding to the coarsest fractions and high concentration of carbonates, as well as moderate enrichment of heavy metals, is formed by S13, which reflects a mixed signature of the Guadiana–Piedras detritic influence and marine-biogenic sources. The geochemical enrichment of sulphide-derived heavy metals and P observed in the shelf sediments, particularly evident in S7, reveals the influence of anthropogenic pollution as well as the great capacity for dispersion of these elements.

## Acknowledgements

This research project (REN2002-04602-C01-02) was supported by a grant from the Spanish Ministry of Education and Science (MEC) and a PhD scholarship for the first author.

## References

- Barahona, E., Huertas, F., Pozzuoli, A., Linares, J., 1985. Firing properties of ceramic clays from Granada province, Spain. *Miner. Petrogr. Acta* 29-A, 577–590.
- Borrego, J., Morales, J.A., Pendón, J.G., Romero-Segura, M.J., 1990. Evolución del contenido en algunos metales pesados en la Ría del Piedras (Huelva, España). *Consecuencias ambientales*. *Geol. 4*, 21–29.
- Borrego, J., Morales, J.A., de la Torre, M.L., Grande, J.A., 2002. Geochemical characteristic of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). *Environ. Geol.* 41, 785–796.
- Borrego, J., López-González, N., Carro, B., 2004. Geochemical signature as paleoenvironmental markers in Holocene sediments of the Tinto river estuary (southwestern Spain). *Estuar. Coast. Shelf Sci.* 61, 631–641.
- Brandão, C., Rodrigues, R., 2000. Hydrological simulation of the international catchment of Guadiana River. *Phys. Chem. Earth, Part B Hydrol. Oceans Atmos* 25, 329–339.
- Brumsack, H.J., 2006. The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 232, 344–361.
- CEEPYC, 1979. Plan de estudio de la dinámica litoral de la provincia de Huelva. Informe de la Dirección General de Puertos y Costas, Madrid.
- Cuena, G.J., 1991. Proyecto de regeneración de las playas de Isla Cristina. Servicio de Costas, MOP.
- Davis Jr, R.A., Welty, A.T., Borrego, J., Morales, J.A., Pendón, J.G., Ryan, J.G., 2000. Rio Tinto estuary (Spain): 5000 years of pollution. *Environ. Geol.* 39, 1107–1116.
- Dickens, A.F., Gélinas, Y., Masiello, C.A., Wakeham, S., Hedges, J.L., 2004. Reburial of fossil organic carbon in marine sediments. *Nature* 427, 336–339.
- Elbaz-Poulichet, F., Leblanc, M., 1996. Transfer de métaux d'une province minière à l'océan par des fleuves acides (Rio Tinto, Espagne). *Comptes Rendus de l'Académie des Sciences de Paris* 322, 1047–1052.
- Elbaz-Poulichet, F., Morley, N.H., Cruzado, A., Velásquez, Z., Achterberg, E.P., Braungardt, C.B., 1999. Trace metal and nutrient distribution in an extremely low pH (2.5) river–estuarine system, the Ría of Huelva (south-west Spain). *Sci. Total Environ.* 227, 73–83.
- García, D., Ravenne, C., Maréchal, B., Moutte, J., 2004. Geochemical variability induced by entrainment sorting: quantified signals for provenance analysis. *Sediment. Geol.* 171, 113–128.
- González, R., Dias, J.M.A., Ferreira, Ó., 2001. Recent rapid evolution of the Guadiana Estuary (Southern Portugal/Spain). *J. Coast. Res.* SI 34, 516–527.
- González, R., Dias, J.M.A., Lobo, F., Mendes, I., 2004. Sedimentological and paleoenvironmental characterization of transgressive sediments on the Guadiana Shelf (Northern Gulf of Cádiz, SW Iberia). *Quat. Int.* 120, 133–144.
- González, R., Araújo, M.F., Burdloff, D., Cachão, M., Cháscale, J., Corredera, C., Dias, J.M.A., Fradique, C., Ferreira, J., Gomes, C., Machado, A., Mendes, I., Rocha, F., 2006. Sediment and pollutant transport in the Northern Gulf of Cádiz: a multi-proxy approach. *J. Mar. Syst.* 68, 1–23.
- González-Pérez, J.A., de Andrés, J.R., Clemente, L., Martín, J.A., González-Vila, F.J., 2008. Organic carbon and environmental quality of riverine and off-shore sediments from the Gulf of Cádiz, Spain. *Environ. Chem. Lett.* 6, 41–46. doi:10.1007/s10311-007-0107-0.
- Grande, J.A., Borrego, J., Morales, J.A., 2000. A study of heavy metal pollution in the Tinto–Odiel estuary in southwestern Spain using factor analysis. *Environ. Geol.* 39, 1095–1101.
- Hadas, O., Pinkas, R., Malinsky-Rushansky, N., Markel, D., Lazar, B., 2001. Sulfate-reduction in lake Agmon, Israel. *Sciences of the Total Environment* 266, 202–209.
- Kastner, M., 1999. Oceanic minerals: their origin, nature of their environment, and significance. *Proceedings of the Natural Academy of Sciences of the United States of America* 96, 3380–3387.
- Leblanc, M., Morales, J.A., Borrego, J., Elbaz-Poulichet, E., 2000. 4,500-years-old mining pollution in southwestern Spain: long-term implications for modern mining pollution. *Econ. Geol.* 95, 655–662.
- Lobo, F.J., Hernández-Molina, F.J., Somoza, L., Díaz del Río, V., 2001. The sedimentary record of the post-glacial transgression on the Gulf of Cádiz continental shelf (Southwest Spain). *Mar. Geol.* 178, 171–195.
- López-González, N., Borrego, F., Ruiz, F., Carro, B., Lozano-Soria, O., Abad, M., 2006. Geochemical variations in estuarine sediments: provenance and environmental changes (Southern Spain). *Estuar. Coast. Shelf Sci.* 67, 313–320.
- Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES J. Mar. Sci.* 48, 101–115.
- Middelburg, J.J., Nieuwenhuize, J., van Breugel, P., 1999. Black carbon in marine sediments. *Mar. Chem.* 65, 245–252.
- Morillo, J., Usero, J., Gracia, I., 2004. Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere* 55, 431–442.
- Nelson, C.H., Lamothe, P.J., 1993. Heavy metals anomalies in the Tinto and Odiel River Estuary System, Spain. *Estuaries* 16, 496–511.
- Nieuwenhuize, J., Maas, Y.E.M., Middelburg, J.J., 1994. Rapid analysis of organic carbon and nitrogen in particulate materials. *Mar. Chem.* 45, 217–224.
- Ochoa, J., Bray, N.A., 1991. Water mass exchange in the Gulf of Cadiz. *Deep-Sea Res.* 38, 465–503.
- Ruiz, F., González-Regalado, M.L., Borrego, J., Morales, J.A., Pendón, J.G., Muñoz, J.M., 1998. Stratigraphic sequence, elemental concentrations and heavy metal pollution in Holocene sediments from the Tinto–Odiel estuary, southwestern Spain. *Environ. Geol.* 34, 270–278.
- Sánchez-García, L., de Andrés, J.R., Martín-Rubí, J.A., 2006. Geochemical characterization of sedimentary organic matter by comparative study of molecular markers in the Gulf of Cádiz inner continental shelf (SW Iberia Peninsula). *Bol. Geol. Min.* 117, 571–576.
- Sánchez-García, L., de Andrés, J.R., Martín-Rubí, J.A., González-Vila, F.J., Polvillo, O., 2008. Use of lipid biomarker patterns as proxy of environmental variability in coastal sedimentary record from the Gulf of Cádiz, (SW Spain). *Organic Geochemistry* 39, 958–964.
- Schultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. *U. S. Geol. Surv. Prof. Pap.* 392-B, B1–B19.
- Shepard, F.P., 1954. Nomenclature based on sand–silt–clay ratios. *J. Sediment. Petrol.* 21, 151–158.
- Stecko, J.R.P., Bendell-Young, L.I., 2000. Contrasting the geochemistry of suspended particulated matter and deposited sediments within and estuary. *Appl. Geochem.* 15, 753–775.

- Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the Earth's crust. *Geology Society of American Bulletin* 72, 1751–1791.
- Van Geen, A., Adkins, J.F., Boyle, E.A., Nelson, C.H., Palanques, A., 1997. A 120 yr record of widespread contamination from mining of the Iberian pyrite belt. *Geology* 25, 291–294.
- Van Geen, A., Takesue, Z., Chase, Z., 1999. Acid mine tailings in southern Spain. *Sciences of the Total Environment* 242, 221–229.
- Vital, H., Stattegger, K., Garbe-Schönberg, C.D., 1999. Composition and trace-element geochemistry of detrital clay and heavy mineral suites of the lowermost Amazon river: a provenance study. *J. Sed. Res.* 69, 563–575.
- Wedepohl, K.H., 1991. The composition of the upper Earth's crust and the natural cycles of selected metals. Metals in natural raw materials. *Natural Resources*. In: Merian, E. (Ed.), *Metals and their Compounds in the Environment*. VCH, Weinheim, pp. 3–17.