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Control factors on the composition of superficial sediments in estuaries of the coast of Huelva (SW Spain): a statistical approach

Factores de control sobre la composición de sedimentos superficiales de los estuarios de la costa de Huelva (SO de España): un acercamiento estadístico

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Abstract

The geochemical composition of surface sediments has been analyzed for the following three river estuaries located in the Huelva coast (SW Spain): Guadiana, Piedras and Tinto-Odiel (Ría de Huelva), which represent an area strongly affected by mining activity, mainly for Cu exploitation in the Iberian Pyrite Belt. The main goal of the present study was to evaluate the water and sediment quality of the three estuary systems, which have been subject to different types of anthropogenic activity. Enrichment factors (EF) for several elements were determined for each system, using as reference the composition of the sediments from the Huelva Ría, prior to the intensive mining and industrial activity. Statistical treatment based on factorial analysis allowed establishing the origin of the elements and the main control factors of their geochemical behaviour in the estuarine systems. The estuary of Tinto-Odiel rivers (Ría de Huelva) presents high metal concentrations and strong EF for metals related to acid mine drainage, namely Cu (EF of 75,6), Zn (EF of 36,9), and Pb (EF of 58), indicating severe environmental quality problems. On the contrary, the sediments of the Guadiana and Piedras rivers show no significant EF. Here, the obtained results indicate the absence of antropic metallic contributions, which permits the maintenance of the environmental quality of both systems. Thus, the present study revealed the environmental quality problems of the sediments from Tinto-Odiel estuary, while in Guadiana and Piedras there are no significant metallic contributions, ensuring the maintenance of the their environmental quality.

Keywords: Metal pollution, Sediments, Iberian Peninsula, Estuary, Tinto-Odiel, Piedras, Guadiana.

Resumen

Se ha analizado la composición geoquímica de los sedimentos superficiales en tres estuarios localizados en la costa de Huelva (SO de España), un área fuertemente afectada por la actividad industrial y por la extracción minera de cobre en la Faja Pirítica. Estos estuarios corresponden a los ríos Guadiana, Piedras y Tinto y Odiel (Ría de Huelva). La finalidad de este estudio es comprobar la calidad de las aguas y de los sedimentos en tres sistemas estuarinos que han estado sometidos a diferente actividad antrópica, destacando factores de enriquecimiento (EF) para varios elementos en los tres sistemas, usando como referencia la composición de los sedimentos de la Ria de Huelva, antes de la intensa actividad minera e industrial. Se llevó a cabo un tratamiento estadístico basado en análisis factorial con el fin de establecer el origen de los elementos y los factores de control principales de su comportamiento geoquímico en los sistemas estuarinos. El estuario del Tinto-Odiel (Ría de Huelva) presenta altas concentraciones metálicas y factores de enriquecimiento (EF) fuertes para metales relacionados con el drenaje ácido, a saber Cu (EF de 75,6), Zn (EF de 36,9) y Pb (EF de 58), lo que indica problemas severos sobre la calidad ambiental. Al contrario, los sedimentos del Guadiana y río Piedras no muestran ningún EF significativo. Respecto a estos dos sistemas, los resultados obtenidos indican la ausencia de contribuciones metálicas antrópicas, lo que permite al mantenimiento de la calidad ambiental de ambos sistemas. Este estudio permite asegurar que los sedimentos del estuario Tinto-Odiel presentan una mala calidad ambiental, mientras que el caso de los estuarios del Guadiana y Piedras no se observan contribuciones antrópicas significativas de metales y se pueden considerar que mantienen una buena calidad ambiental.

Palabras clave: Contaminación por metales, sedimentos, Península Ibérica, estuario, Tinto-Odiel, Piedras, Guadiana

1. Introduction

Estuaries are by definition aquatic systems submitted to fluvio-marine interactions. As a consequence, hydrochemistry as well as the properties of suspended matter and of sediments are equally controlled by the nature of fluvial inputs, by marine contributions and by the mixture processes in the estuarine system. In addition, these systems suffer strong antropic pressures caused by the multiple anthropogenic activities that typically take place in estuarine areas. Such activities impose modifications on the biogeochemical conditions inside the estuary as well as on the nature of the fluvial inputs.

Industrial activities and agriculture often contribute to the introduction of chemical substances, resulting in anomalous concentrations in water and sediments. As a consequence, degradation of the ecosystem may occur, leading to severe conditions of pollution.

The estuarine system known as "Ría de Huelva" is located in the Huelva province (SW Spain) and is composed by the estuaries of the Tinto and Odiel Rivers. It contains one of the most important marsh ecosystems in Europe. In fact, the salt marshes associated with the right margin of the Odiel River were declared Biosphere Reserve by UNESCO in 1983, famous for its high ornithological diversity and for the presence of halophytic vegetation (Pérez-López *et al*., 2010). However, the combination of acid water from mines, industrial effluents, and fluvial and sea waters plays a determining role in the evolutionary process of the chemical characteristics of the Tinto and Odiel estuary. Consequently, this is a unique and paradigmatic site in the world by the interest that its study raise (Achterberg *et al*., 2003, Ackerman, 1980; Braungardt *et al*., 2003; Carro *et al*., 2011; Elbaz-Poulichet *et al*., 1999-2000; Grande *et al*., 2000-2003a; Nieto *et al*., 2007; López-González *et al*., 2006; Periañez *et al*., 2012; Sánchez-Rodas *et al*., 2005; Sánchez España *et al*., 2005; Vicente-Martorell *et al*., 2009).

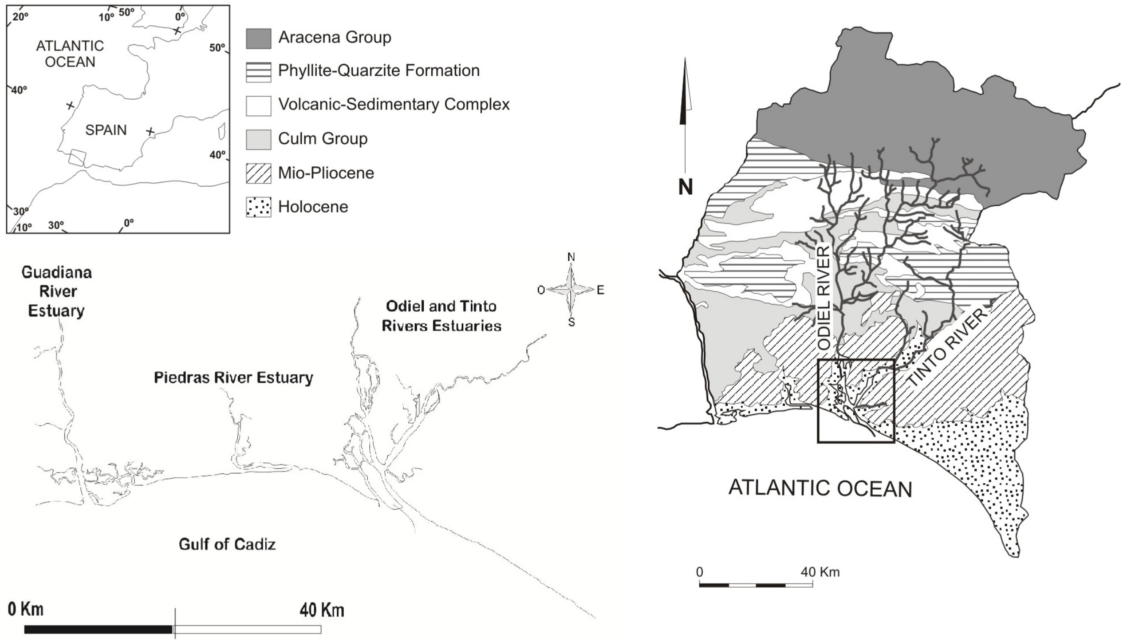
The fluvial basin of these rivers lies, to a great extent, over Paleozoic materials and, more specifically, on formations of the so-called volcano-sedimentary complex, where there is one of the most important mineralized sulfide areas in the Europe. The ore deposits have been mined since at least 4500 B.P. (Leblanc *et al.,* 2000). The weathering of sulfide masses, together with the mining activity, has been the cause of a secular pollution in the Tinto and Odiel Rivers. Such pollution is expressed by the acidification of their waters, which are characterized by high concentrations of heavy metals and extremely low (less than 3) pH values (Grande *et al*., 2000). Water acidification results from natural processes known as ARD (Acid Rock Drainage), and from AMD (Acid Mine Drainage), which is related with mining effluents. The AMD and ARD processes that affect the regional drainage network have been broadly described by several authors: Aroba *et al.,* 2007; Carro *et al*., 2011; de la Torre *et al*., 2011; Grande *et al.,* 2003a-b.

The water acidification results in strong modifications on the biosociology of the media, in such a way that increasing acidity produces reduction in the number of species. Therefore, at $pH<4$ all the vertebrates and the majority of invertebrates and many species of microorganisms disappear. The same happens with most of the superior plants, being the ecosystem reduced to some acidophilic algae (Valente and Leal Gomes, 2007) and bacteria. Thus, the mining effluents are recognized as a primary cause of fish mortality, as pointed out in the United States by Usero (1991)

Since 1966, fertilizer factories, copper foundries, paper mills, as well as phosphogypsum deposits and facilities for cleaning aggregate have been established along the margins of the Tinto and Odiel estuaries (Fig. 1). This industrial activity produces a large volume of effluents that find their way into the waters of the estuary and contribute with large quantities of heavy metals and nutrients. These inputs make this estuarine system one of the most

Fig. 1.-Local setting of the Guadiana, Piedras, Tinto and Odiel estuaries

Fig. 1.- Mapa de localización de los estuarios Guadiana, Piedras Tinto y Odiel.



polluted in the Western Europe (Ruiz *et al.*, 1998; Grande *et al.*, 2000; Borrego *et al.,* 2002).

In this context, the fertilizer factories have particular relevance. The phosphoric acid is obtained through the treatment of the phosphate rock with sulfuric acid. The rock is mainly phosphorite mineral, which contains high levels of radionuclides from the uranium series. Additionally, a by-product called phosphogypsum is formed in the chemical process. Phosphogypsum is composed mainly of gypsum ($CaSO_4\ 2H_2O$). However, it also contains minor quantities of trace elements, rare earth elements, and fluorine (Arocena *et al.*, 1995), which may be toxic for human health and biota. Moreover, only about 15% of the world phosphogypsum is recycled. The remnant 85% forms great accumulation surfaces, causing environmental problems (IFA, 1998).

In the present case, the phosphogypsum dumps, with an average height of 5 m and covering 1200 ha (compared to 1100 ha of urban area of Huelva), contain about 100 Mt of phosphogypsum and are located in the tidal prism of the estuary. Therefore, acid effluents from their leaching may even affect some remote zones of the rivers as a result of tidal action (Bolivar *et al*., 2002).

Taken in account this geological and industrial context, the main objective of this work is to analyze the geochemical characteristics of the superficial sediments and water from the Huelva coast, and to evaluate their environmental quality. For that, enrichment factors (EF) for several elements will be compared in three distinctive systems, using as reference the composition of the sediments from Tinto-Odiel estuary prior to the intensive mining and industrial activity.

The study provides a statistical method that can be valid for testing any estuary in the world with similar geoenvironmental conditions, since there is affection by human activity.

2. Geological Setting

The Guadiana, Piedras, Odiel and Tinto Rivers drainage network crosses rocks belonging to the southernmost units of the Hesperian Massif of the Iberian Peninsula (Fig. 1), which occupies a large part of the so called 'Central Domain' or 'Iberian Pyrite Belt' (IPB) of the South Portuguese Zone. This Central domain has a large number of giant ore deposits. It is considered one of most important pyrite provinces in the world, due to the amount of reserves as well as to the amount of sulfides in relation with the total surface of the mining province (Leistel *et al*., 1998). Ore estimations are of around 750 Mt in accordance with IGME (1982) and more than 1.700Mt as proposed by Barriga and Carvalho (1997). According to the terminology used by Julivert *et al.* (1974), Schermerhorn (1971) divides the IPB into three big groups, based on their stratigraphic features: a) Phyllite-Quartzite Formation (PQ); b) Volcanic Sedimentary Complex (VSC); and c) Culm Group.

The PQ (Devonian) is regionally present at the base of the belt. It consists of alternating shales and quartzites with local lenses of conglomerate and carbonates. The VSC is represented by subaerial to marine felsic and mafic volcanic (Routhier *et al.*, 1980), and epiclastic volcanic sediments; the Culm Group, constituting the stratigraphic top of the Pyrite Belt, comprises a succession of shales and greywackes; turbidite and flysch Unit (Moreno, 1993).

Thus, the economic interest of the IPB is focused on the VSC, where there are a large number of stratiform

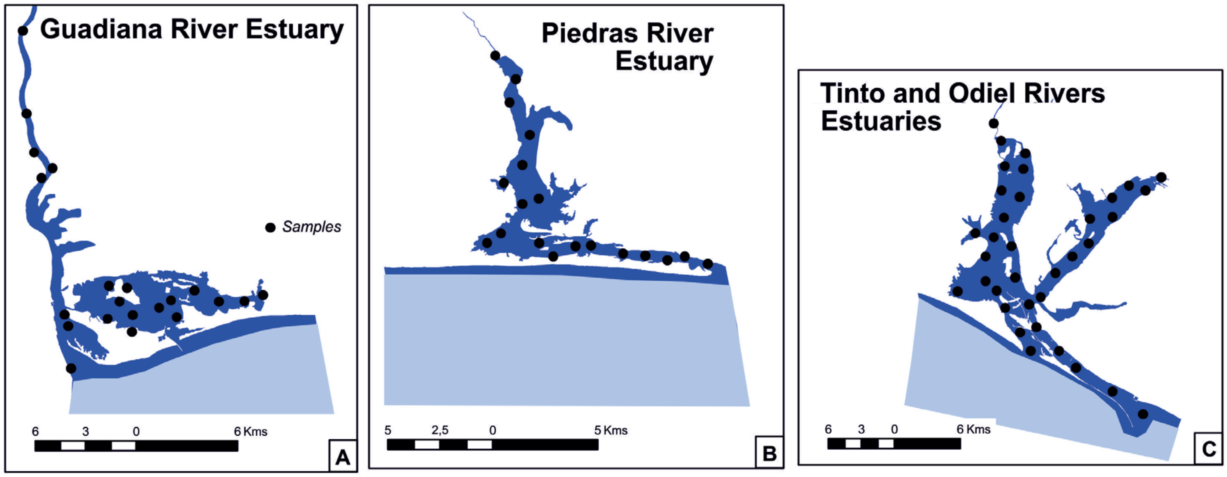


Fig.2. Location maps of sampling sites

Fig.2. Mapa de localización de los lugares de muestreo

and lenticular massive sulfide bodies, subject to mining exploitation (Tornos, 2006). Concerning mineralogy, the ore deposits contain mainly pyrite, although there are also sphalerite, tetrahedrite, arsenopyrite and pyrrhotite. In addition, IPB has also important stratiform Mn deposits (Pinedo, 1963). All these ore deposits have been exploited for more than 2000 years, leaving numerous traces of mining works as well as several millions of tones of ancient wastes with varied composition. Nowadays, most of the mining facilities are abandoned, leading to numerous and dispersed waste accumulations in the Huelva Province, which provide an inexhaustible focus of environmental impact in the water, sediments and landscape (Pinedo, 1963).

The input of acid drainage from these mining areas, most of them without rehabilitation, leads to modifications in the physical-chemical characteristics of the streams. The result is an increase of the water acidity, metals and sulfate contents, followed by extreme contamination of the sediments, which are enriched in metals and metalloids (USEPA, 1994; Lyew and Sheppard, 2001; Grande *et al.,* 2005).

The studied area is located in the estuaries of Guadiana, Piedras and Tinto-Odiel (Fig. 1), all of them receiving waters affected by acidification processes.

3. Methodology

This section presents the sampling and analytical procedures carried out to obtain and analyze the sediment samples. Also, it includes the statistical approach applied to the raw data set.

A total of 75 samples of superficial sediments were collected in the three studied systems, obeying to the following distribution: 20 samples from Guadiana estuary, 20 samples from Piedras estuary and 35 samples from Tinto-Odiel estuary. The sampling sites are presented in Fig. 2 (a,b,c).

3.1. Sampling and analytical methodology

3.1.1. Grain size analysis

The subsamples for grain size (50 g) were sifted through sieves with a screen battery between 2 and 0.063 mm. The mud fraction (Mud) was then run on a Coulter Counter utilizing a 100-mm tube and an analysis range of between 2 and 70 mm.

3.1.2. Metal analysis

Chemical analysis for major elements and trace metals were performed on the bulk samples by X-Ray Assay

	Guadiana	Piedras	Huelva	Bacuta
%SiO_2	61.4	66.0	54.2	73.1
%Al_2O_3	12.8	11.2	12.6	7.7
%CaO	3.5	0.3	1.3	4.4
%MgO	1.4	1.0	1.4	1.0
%Na_2O	1.8	2.0	2.0	1.3
%K_2O	2.0	2.0	2.0	1.6
%Fe_2O_3	5.0	3.9	12.1	3.1
%Mn	0.1	0.0	0.1	0.0
%TiO_2	0.8	0.7	0.7	0.5
%P_2O_5	0.1	0.1	1.0	0.1
Ni(mg L^{-1})	29.3	25.8	27.3	8.0
Cu(mg L^{-1})	44.9	69.2	823.7	11.1
Zn(mg L^{-1})	142.5	113.6	999.9	27.6
Pb(mg L^{-1})	36.7	31.6	788.6	13.7
Cr(mg L^{-1})	80.7	82.4	93.6	14.8
Rb(mg L^{-1})	102.8	98.7	94.3	96.0
Sr(mg L^{-1})	190.1	95.0	156.9	90.2
Ba(mg L^{-1})	403.5	363.6	680.5	20.9
%Mud	35.2	61.1	48.8	

Table 1.- Average values of the concentrations of the elements and compounds studied in the sediments of three estuarine systems and the Bacuta core.

Tabla 1.- Valores medios de las concentraciones de los elementos y compuestos estudiados en los sedimentos de los tres estuarios y el testigo de Bacuta.

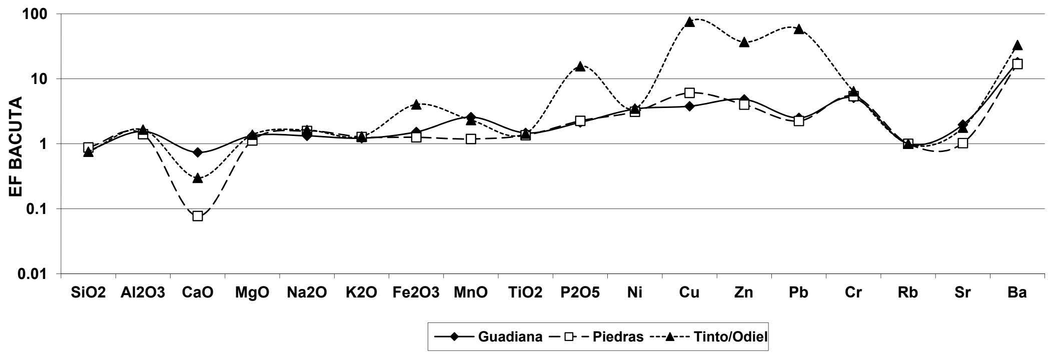


Fig. 3.- Enrichment factors (EF) of elements for studied surface sediments

Fig. 3.- Factores de enriquecimiento de los elementos en los sedimentos superficiales estudiados

Laboratories, Toronto (Canada). Metal concentrations were determined by X-Ray Fluorescence (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, TiO_2, K_2O, Na_2O, P_2O_5) and ICP Mass Spectrometry (Mn, Ni, Cu, Zn, Cr, Sr, Rb, Ba, Pb), with previous *aqua regia* digestion. The calibration is based on the analysis of over 40 international standard reference materials. The LOI (loss in ignition) calculation was made as the difference between the sum total of major and minor elements, and 100%.

3.1.3. Radiocarbon dating

Carbon-14 dating (C-13 corrected, Geochron Laboratories) was performed on two sediment samples (sample 9: reference GX-21287; sample 15: reference GX-21288) with abundant remains of shells, mainly Ostreidae. The shells (15–20 g) were cleaned thoroughly in an ultrasonic cleaner. They were then leached with dilute HCl to remove additional surficial material, which may have been altered, and to be sure only fresh carbonate material was used. The cleaned shells were then hydrolyzed with HCl, under vacuum, and the carbon dioxide was recovered for analysis.

3.2. Statistical analysis

Quantitative analysis of the relationships was carried out by applying factorial analysis of principal component to samples of 26 variables. This allows ascertaining the origin of each element based on its level of association with the rest and to determine the factors that control its geochemical behavior in the estuarine system. The values of factor matrix can be improved by rotating the axes using the Varimax Rotation Method (Kaiser 1958), which in reality maximizes factor variance. Varimax rotation attempts to simplify the columns of the factor matrix by making all values close to either 0 or 1. This method tends to minimize the number of variables that show high saturations for a factor, resulting in a simple interpretation. All statistical calculations, including Pearson correlation coefficients, were conducted using SYSTAT for Windows Ver. 5.0.

4. Results

The chemical composition of the sediments from the three estuarine systems is presented in table 1.

The enrichment factors (EF) have been calculated, using Rb as a reference element (Ackerman 1980; Salomons and Förstner 1984; Loring 1991; Shumilin et al., 2002; Borrego et al., 2004). EF values were calculated in accordance with the following equation:

$$EF = ([El] / [Rb])_{sed} : ([El] / [Rb])_{Bacuta}$$

Where $[El]_{sed}$ is the content of the chemical element in the sediments; $[Rb]_{sed}$ is the content of Rb in the sediments; $[El]_{Bacuta}$ and $[Rb]_{Bacuta}$ are the average concentration of the element and Rb in sediments of a non-polluted core collected in the central zone (Bacuta core) of the estuary of the Odiel and Tinto rivers (Ruiz *et al.,* 1998). These values represent average concentrations of deposited sediments between 2000 and 5300 B.P. (^{14}C dating) (Ruiz *et al*., 1998) in an estuarine environment of a shallow channel (depth < 10 m) (Borrego *et al.,* 1999). The use of the pre-anthropogenic sediment metal concentration of the same estuary, like the normalization factor, allows a better approach of the enrichment levels originated by the anthropic activity (Ridgway and Shimmield, 2002).

Enrichment factors (EF) for the studied elements in the three estuaries are presented in Figure 3.

4.1. Guadiana estuary.

The highest concentrations of CaO and Sr (3.47 % and 190.1 mg/Kg, respectively) were obtained in the Guadiana estuary.

The statistical analysis displayed three factors (F I-F III), which explain 91.4 % of the total variance and account for 43.2 %, 25.9 % and 22.2 % of the total variance, respectively. Fig. 4 presents the varimax rotated factor loading of these factors graphically. Factor F I is characterized by high positive loadings (> 0.5) for Al, Mg, K, Fe, P, Ni, Cr, Rb, and Ba, and negative loadings for Si. Factor II displays high positive loadings for the associa-

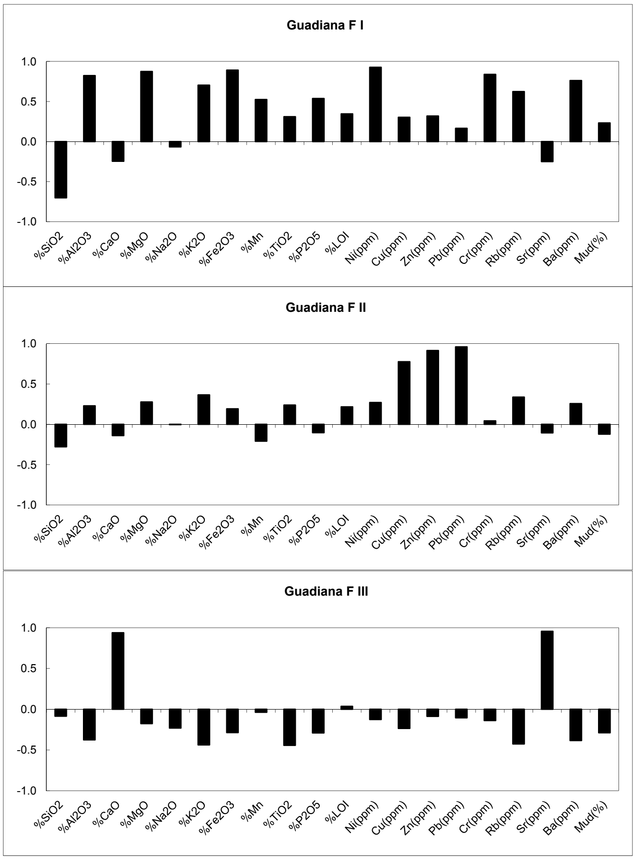


Fig. 4.- Bivariate plots of major and trace elements vs. Al_2O_3 of the surface sediments. Guadiana estuary

Fig. 4.- Gráficos bivariantes de elementos mayores y traza, frente a Al_2O_3 de los sedimentos superficiales. Estuario Guadiana

tion of Cu, Zn, and Pb (Fig. 5). Factor III is characterized by high positive loadings for Ca.

4.2. *Piedras estuary.*

At this system the sediment samples displayed the highest concentrations of SiO_2 (66.0 %) and the lowest levels of Al_2O_3 and CaO (11.2 % and 0.35 %) (Table 1).

Three factors (F I-F III) were obtained, which explained 83.7 % of the total variance and accounted for 62.4 %, 11.8 % and 9.5 % of the total variance, respectively. Fig. 5 presents the varimax rotated factor loading of these factors graphically. Factor F I is characterized by high positive loadings for Al, Mg, Na, K, Fe, Mn, Ti, P, LOI, Ni, Zn, Pb, Cr, Rb, Sr, Ba and Mud, moderate for Zn and Pb and negative loadings for SiO_2. Factor II displays high positive loadings for Ca and Sr. Factor III is characterized by high positive loadings for Cu and moderate for Zn.

4.3. *Tinto and Odiel estuary.*

The samples from Tinto and Odiel estuary are characterized by high concentrations of Fe_2O_3 (12.10%) and P_2O_5 (0.97%). This behavior has correspondence on the high EF, presenting the values of 4 and 15 for Fe_2O_3 and P_2O_5, respectively in opposition to the considerable lower EF (1.5 and 2.5) observed in Guadiana and Piedras estuaries (Fig. 3).

These samples also present very high concentrations of Cu, Zn, and Pb (about 12.7 to 37 times the levels obtained in the other estuaries) (Table 1). In accordance, there are high EF (75.36 and 58), for the reference samples, representing pre-industrial conditions. In respect to Ba, concentration in the sediments of the Ria de Huelva is 680 ppm (Table 1).

Three factors (F I-F III) were obtained, which explained 65.04 % of the total variance and accounted for 24.8 %, 21.4 % and 18.9 % of the total variance, respectively. Fig. 6 presents the varimax rotated factor loading of these factors graphically. Factor F I is characterized by high positive loadings (> 0.5) for Fe, P_2O_5, Cu, Pb, Cr, Ba, and Y, and negative loadings for SiO_2. Factor II displays high positive loadings for the association of Al, Mg, Na, Ti, Mud, Ni, and Rb. Factor III is characterized by high positive loadings for Ca, Na, Sr, Y, and Nb.

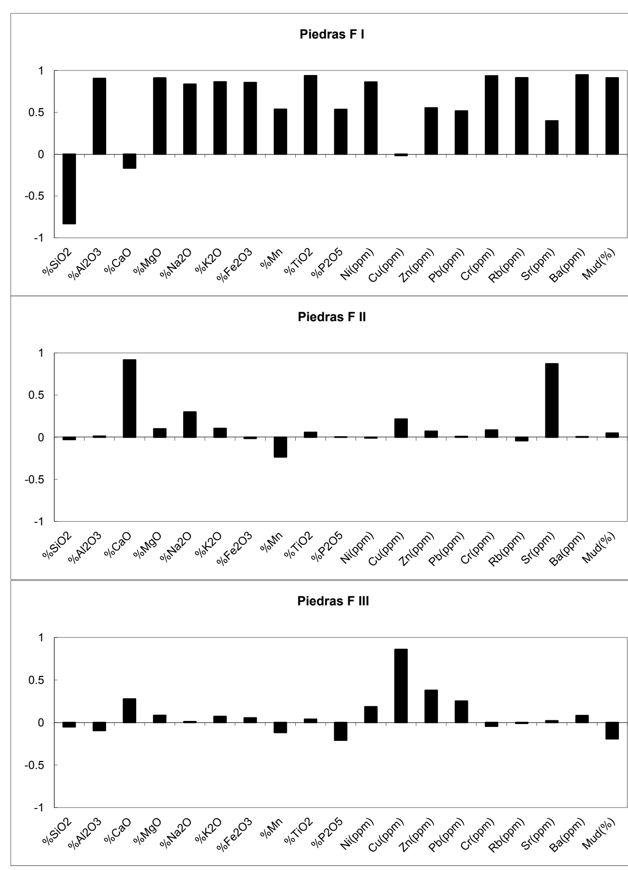


Fig. 5.- Bivariate plots of major and trace elements vs. Al_2O_3 of the surface sediments. Piedras estuary

Fig. 5.- Gráficos bivariantes de elementos mayores y traza, frente a Al_2O_3 de los sedimentos superficiales. Estuario Piedras

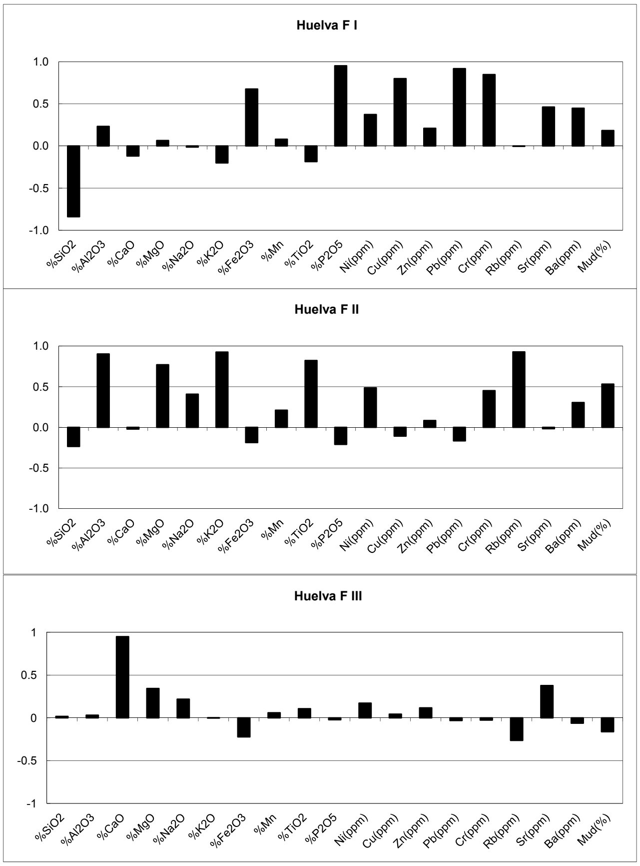


Fig. 6.- Bivariate plots of major and trace elements vs. Al_2O_3 of the surface sediments. Tinto and Odiel estuary (Huelva FIII)

Fig. 6.-Gráficos bivariantes de elementos mayores y traza, frente a Al_2O_3 de los sedimentos superficiales. Estuario Tinto y Odiel (Huelva FIII)

5. Discussion

5.1. Guadiana estuary.

Compared with other estuaries high percentages of CaO and Sr in the sediments indicate the contribution of biogenic carbonates (rests of bivalves) (Morales 1997) to the global composition of the environment. This justifies the obtained EF for CaO, which is near 1 (0.7), while presents considerable lower values for the other two systems (0.07 and 0.3 for Piedras and Huelva Ría, respectively) (Fig. 3)

FI represents the control exerted by the origin over the chemical composition of the sediments. It divides clay minerals from a siliciclastic component (SiO_2), indicating that the main control factor on the geochemical behavior of this estuary appears related with the processes that govern the grain size distribution.

Factor F II is characterized by high loadings of Cu, Zn, and Pb, which may be reflecting some contribution from AMD inputs (EF between 3 and 5) (Fig. 3). These may be related with the weathering processes of sulfides or with the mining activity that occurred in the Guadiana watershed.

In many estuaries, the scavenging processes on iron oxihydroxides have been pointed as the main control factor on the concentration of metals and minor elements such as Cu, Zn, and Pb in the particulate matter and in the sediments (Sholkovitz 1992). In the present case, such influence should be null due to the absence of reactive iron in solution.

Factor III indicates the presence of bioclastic rests, which are very abundant in the outer zone of the estuary (Morales 1997).

5.2. Piedras estuary.

The high concentrations of SiO_2 and low levels of Al_2O_3 and CaO obtained in this estuary may be reflecting the dominance of the quartz fraction over the phyllosilicates and the bioclastes. The concentration of minor elements, are similar to Guadiana estuary, revealing an identic pattern for the EF (Fig. 3).

Factor I represents the separation imposed by the grain size distribution, meaning quartz and phyllosilicate fractions. In addition, inorganic scavengers (clay minerals) should be the dominant factors controlling trace metal distribution in the catchment. Factor II, although explaining a low percentage of the variance (11.8 %), indicates the presence of a biogenic carbonate fraction. Finally, factor III, which explains only 9.5 % of total variance, represents the influence of inputs from Tinto-Odiel estuary that reach the outer zone of this system during the displacement of tidal wave in the half-cycles flow (Borrego and Pendon 1989). This effect could explain the EF obtained for Cu and Zn (6 and 4 respectively). They cannot be provoked by direct AMD contribution since this river does not drains the CVS, where are the massive sulfides. (Fig. 1).

5.3. Tinto and Odiel estuary.

The enrichment in Fe_2O_3 (about 4 times the other two estuaries) in the sediments from Tinto-Odiel estuary can be explained by the acidic inputs from the Tinto and Odiel river waters with pH less than 3 (Grande *et al*., 2000) and high levels of Fe and other soluble metals are arriving to both estuaries and, specifically, to the mixture zone.

The mixture with seawater promotes an increasing in pH, which results in the precipitation of iron oxihydroxides and organic complexes that will incorporate the suspended particulate matter and further the sediment load (Elbaz-Poulichet *et al*., 1999; Achterberg *et al.,* 2003; Carro *et al*., 2005). These iron-rich precipitates are some of the most abundant phases in the sediments of this system.

Regarding P_2O_5, the high concentrations detected in the Huelva Ría samples (9 times the observed in the other two estuaries) have an industrial origin, associated to the fertilizer plants that produce phosphogypsum wastes. These wastes, resulted from the processing of phosphate rock, justify the high concentrations of P as well as the positive anomalies in U, Th, and light and medium rare earths that are known to occur in the sediments of the Ría (Elbaz-Poulichet *et al*.,1999; Borrego *et al.,* 2004).

These metals are transported in solution by the Odiel and Tinto rivers. In the medium-high salinity zone of the estuary, that has pH values in the range 2.7 to 6.5, they are adsorbed on suspended matter, mainly iron oxihydroxides and organic matter (Achterberg *et al*., 2003). Further, they are incorporated in the sediment.

In the Guadiana and Piedra rivers, Ba appears clearly associated with Al_2O_3, which is not observed in the Tinto-Odiel estuary. The transport of soluble Ba by the acidic waters of Odiel and Tinto rivers (pH less than 3.3) can be explained by the presence of Paleozoic sediments, which are enriched in Ba (average concentration of 396 mg/k); the mixture of these acidic waters with the seawater, slightly basic (pH 8.2), promotes precipitation in the form of Ba sulfate (Lozano-Soria *et al*., 2005).

Based on the factor analysis (Fig. 6), is possible to assume that inorganic scavengers (Fe oxides followed by clays) are the dominant factors controlling trace metal distribution in the catchments.

FI represents the control exerted by iron oxihydroxides and organic complexes over Ni, Cu and other metals. It is known from other highly contaminated estuaries that the removal of metals from the water column also takes place by scavenging involving Fe on surface active of suspended matter (Kitts *et al.,* 1994). In the case of Tinto-Odiel estuary, this scavenging effect was demonstrated by Elbaz-Poulichet *et al.,* 2000 and Carro *et al*., 2005. The formation of these phases results from the precipitation of soluble iron transported by the acidic fluvial waters, provoking a strong enrichment of the suspended matter in Fe-oxides and Fe-organic complexes (Carro *et al*., 2005). Conditions of low energy, which take place during the last moments of periods of low and high tide, when tidal currents are almost nulls, allowed its subsequent deposition. For this reason, these elements show strong incompatibility with the silicic fraction (SiO_2 with high negative loading for Factor I, -0.88).

Factor F II, characterized by high loadings of Al, Mg, Ti, Rb, and mud, reflects the presence of clay minerals. Contrarily to the other estuaries, the phyllosilicate fraction does not present incompatibility with the quartz fraction. This indicates that the energy gradient, responsible for grain size distribution, is not a relevant control factor in the geochemistry of these sediments (Borrego *et al.*, 2004).

Finally, F III represents the presence of a bioclastic fraction formed by shells, and therefore dominated by the elements Ca and Sr, just like it was detected for Guadiana and Piedras estuaries.

6. Conclusions

The geochemistry of superficial sediments from three estuaries in the Huelva coast was analyzed: Guadiana, Piedras and Tinto-Odiel Rivers. The enrichment factors for major and minor elements were determined using, as reference, ancient estuarine compositions (sediments with 2000 to 5300 years old) from Tinto-Odiel estuary.

Results indicate that the estuaries of Piedras and Tinto-Odiel are impoverished relatively to CaO, which are due to the rarity of biogenic carbonates in the sediments. The major components Fe_2O_3 and P_2O_5 showed the highest concentrations in the sediments from Tinto-Odiel estuary, revealing an anthropogenic origin, related with mining and industrial activity in the Odiel and Tinto catchments. Fe_2O_3 is introduced in the estuary by the AMD inputs from Odiel and Tinto, while P_2O_5 is due to the wastes from fertilizer plants.

The sediments from Guadiana and Piedras rivers do not revealed significant enrichment for the analyzed elements relatively to preindustrial conditions. On the contrary, the samples from Tinto-Odiel estuary show very high EF for metals associated with AMD (Cu, Zn, Pb), This enrichment, associated with average concentrations above 750 mg L^{-1}, indicate the low level of environmental quality of the Tinto-Odiel estuary sediments. On the other side, the results from Guadiana and Piedras estuaries suggest the absence of relevant antropic contributions and indicate the maintenance of their environmental quality.

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