A study of heavy metal pollution in the Tinto-Odiel estuary in southwestern Spain using factor analysis

J.A. Grande · J. Borrego · J.A. Morales

Abstract The estuary of Odiel and Tinto rivers, located on the southwestern coast of the Iberian Peninsula, receives acidic fluvial water discharges with high concentrations of sulphates and heavy metals from these rivers. In addition, a big industrial complex which efflues directly on the system is located in the same estuary. The effluents induce the presence in the estuary of high concentrations of heavy metals and phospates (nutrients). The application of factorial analysis techniques on the nutrients and heavy metal concentrations in 46 water samples taken from 32 different sampling stations located along the estuary, allows three groups of elements and compounds with a distinct origin to be determinated. So, Cu and Zn have a clear fluvial provenance, whereas PO_4 and As are clearly industrial wastes and Cl, K, Ca, Li, Rb and Sr come from the sea. From the factorial analyses we can deduce the existence of two agents controlling the behavior of the analyzed elements, which are: the tidal exchange with the open sea and the fluvial supply.

Key words Factorial analysis · Heavy metals · Estuarine waters · Huelva coast

Introduction

The space-time distribution and variations of the nutrients and heavy metals dissolved in estuary water have been extensively studied in the last two decades to find out more about the environment and to learn about biomass exchanges between continental zones and the ocean (Apte and others 1990; Zwolsman and others 1997). The biogeochemical cycles of nutrients and metals in these environments are of particular interest as are all the chemical, physical and biological processes that control the distribution and exchange of these elements within estuaries and their flow to and from oceans and rivers.

The estuary of the Tinto and Odiel Rivers, which is in the southwest of the Iberian Peninsula (Figure 1), is one of the estuarine systems on the northwest coast of the Gulf of Cádiz at the confluence of the Atlantic Ocean and the Mediterranean Sea. These recesses in the shore were invaded by seawater about 6000 years ago (Borrego and others 1995) during the final pulse of the Flandrian transgression, which was caused by the last interglacial period. This estuary is fed by the Tinto and Odiel Rivers. The watersheds of these rivers lie to a great extent over Paleozoic materials and especially on formations of what is known as the volcano-sedimentary complex, where there are important mineralized masses that make up one of the largest sulfur deposits in Europe. These ore deposits have been mined since at least 4500 B.P.

In the last hundred years, these mineralizations have been intensively exploited to obtain pyrite concentrates and other commercially valuable metals (gold, silver, etc.). The natural alteration of these sulfide-ore masses, together with the mining activity, have long been a source of pollution to the waters of the Tinto and Odiel Rivers. The waters of these rivers have high concentrations of heavy metals and extremely low pH values, less than 3 (Borrego 1992; Braungardt and others 1998). Because of this sulfide-mining activity near the headwaters of the Tinto and Odiel Rivers, an important industrial complex has developed along the banks of the estuary; since 1966, fertilizer factories, copper foundries, paper mills and other factories have been established. This industrial activity produces a large volume of effluents that find their way into the waters of the estuary, contributing substantial quantities of heavy metals and nutrients, making this one of the most polluted estuarine systems in Western Europe (Ruiz and others 1998). The estuarine waters have a high concentration of nutrients, chlorophyll (Cruzado and others 1998), and heavy metals (Braungardt and others 1998).

Receoved: 20 November 1998 · Accepted: 11 August 1999

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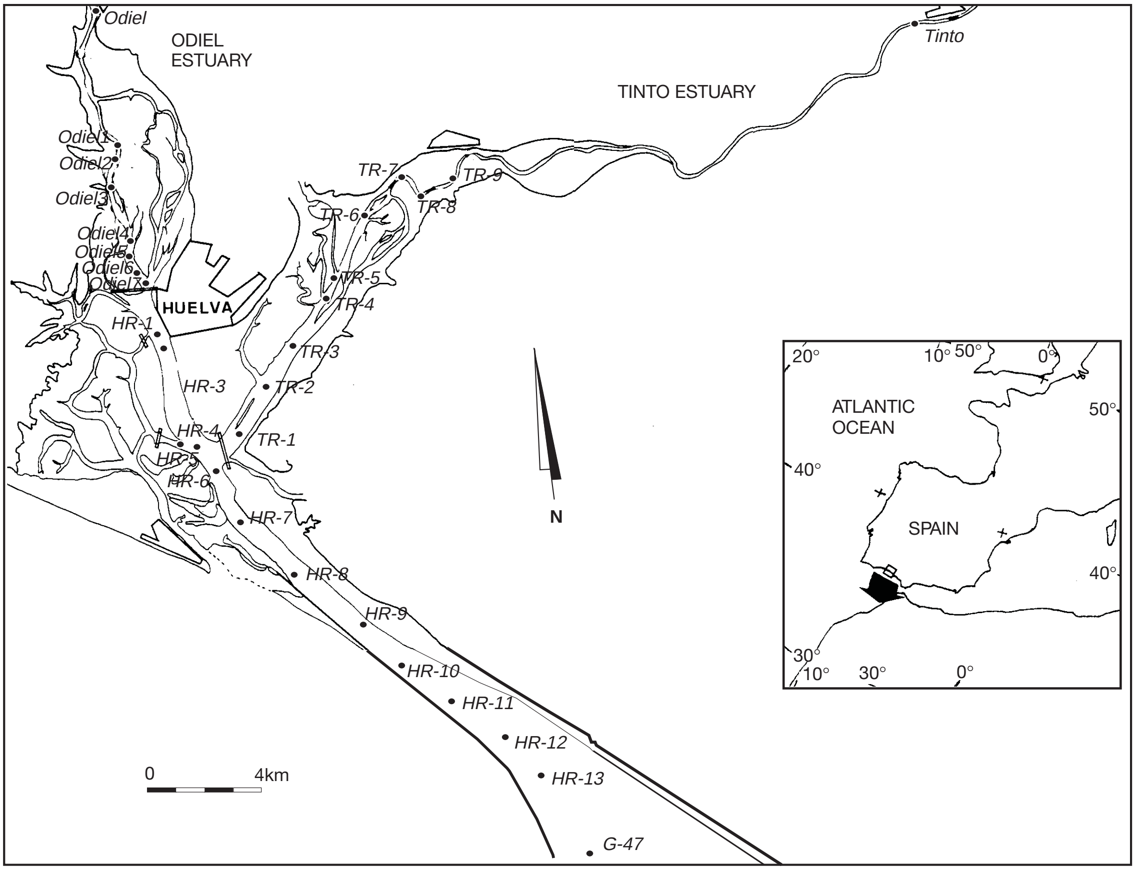

Fig. 1
Location of the estudy area and the studied sampling stations on the estuary

The pollutants in the waters of the estuary come from two different sources: from the rivers (from acidic waters with a high heavy-metal content originating in the mining area) and from metal- and nutrient-rich waters from the chemical industry. The mixture of these industrial wastes, the river water, and water from the open sea that enters the estuary during tidal flood produces a complex system of internal circulation and insufficiently-studied patterns of biochemical behavior. This biochemical behavior is the origin of a continuous dissolution/precipitation processes controlled by the inflow of tidal water, river water and industrial wastes. The introduction of control measures and corrective measures to improve the environmental quality of this natural system calls for a detailed study of the behavior of pollutants throughout the estuary. It is of vital importance to know about the factors that determine the distribution of these pollutants in the estuary and in the marine areas influenced by it. The aim of this paper is to use chemical-analysis data on the waters from the sector being studied to deduce the environmental factors implicated in their evolution, and to employ statistical factorial-analysis methods to establish connections and reasons for interdependence among the different elements dissolved in the estuary water as well as establishing a possible means of controlling their concentrations. This paper also determinates the origin of some of these elements.

General setting

The estuary of the Tinto and Odiel Rivers is on a mesotidal mixed-energy coast (Borrego 1992). The tidal wave moves along the Odiel estuary following a hypersynchronic model (Borrego and others 1993), and along the Tinto estuary according to a hyposynchronic model (ranging within the estuary from 4 m during spring tides to 0.5 m during extreme neap tides. The volumes of water that come in and out of the estuary from the open sea (tidal prism) during a tidal half-cycle (6 h) range from 37.34 Hm^3 during a mean neap tide (1 m of tidal range) to 81.75 Hm^3 in a mean spring tide (3 m of tidal range).

The volume of fresh water inflow from the Tinto and Odiel Rivers to the inner zone of the estuary reflects a significant seasonal and year-to-year variation. Therefore, from 1960 to 1996, the average monthly inflow of river water was 49.8 Hm^3, and the average yearly inflow was 598 Hm^3. The marked seasonality of this inflow is due to a rainy season from October to March when the inflow may reach 100 Hm^3 per month and a dry period (from

Table 1
Heavy metals mean contributions (ton yr^{-1}) from fluvial discharges of Odiel and Tinto Rivers (Source: Confederación Hidrogràfica del Guadiana)

	As	Cd	Cu	Fe	Mn	Pb	Zn
Tinto	53.4	21.7	955.6	8927.7	1041	*	44.03
Odiel	4.56	6.19	771.6	1390	869.5	339.7	1660

May to September) with average volumes of less than 5 Hm^3 (Borrego 1992).

The variation of the volumes of water from the regime of river-water inflow and from the tidal prism gives rise to different types of mixing models within the estuary.

During the rainy season (with an average volume of flow of 21 $m^3\ s^{-1}$), the mixing conditions within the estuary can be defined as "partial stratification" (following the criteria of Simmons 1955) for any tidal situation. However, during the dry months (volume of flow less than 6 $m^3\ s^{-1}$), the situation can be described as a "good mixing" (Borrego 1992).

The waters that the two rivers contribute to the estuary have an average $SO_4^=$ content of 1200 mg/l, pH values of less than 3.5, and high concentrations of heavy metals (Table 1). The water inside the estuary has an average $SO_4^=$ content of 2950 mg l^{-1} (Cortés and Varela 1992) with negligible variations in the water column; pH values may range from a pH of 4.5 in the upper sections of the estuary with an important fluvial influence to 8.2 at the mouth of the estuary where sea water completely dilutes the pH of the river inflow (Borrego 1992).

Methods

Sampling and analytical methodology

The sampling campaign was carried out in June 1997. Thirty-three sampling stations or points were established (Fig. 1) where a sample of surface water (5 l per station) was taken using a Niskin sampling bottle. The pH was measured with a TURO 130 sampling probe.

Water samples were filtered immediately after collection, stored at 4 °C in the dark, and analyzed with standard methods within one or two days. Nutrients were determined colorimetrically, and major ions and metal concentrations were determined by atomic absorption spectroscopy (Perkin-Elmer 3110) after total digestion in a mixture of $HF\text{-}HCL_4\text{-}HNO_3$ (details are given in Zwolsman and others 1993). Table 1 shows the results obtained for each sample for the different variables.

Statistical analysis

Quantitative analysis of the possible relationships is carried out by applying factorial analysis to a sample of 16 variables (pH, SO_4, SiO_2, PO_4, Na, K, Mg, Ca, Cl, NO_3, Li, As, Rb, Sr, Zn and Cu). This allows us to ascertain the origin of each element based on its level of association with the rest and to determine the factors that control its hydrochemical behavior in the estuarine system.

Factor analysis is a technique that summarizes the information contained in a matrix of data with *n* number of variables. Therefore, a reduced number of *f* factors is identified in such a way that *f* is smaller than *n*. This reduced number of factors represents the original variables with a minimal loss of information.

The mathematical basis of factor analysis is attributed mainly to Spearman (1904), Hotelling (1933), Thurstone (1947), Kaiser (1958), and Harman (1980). A thorough review of these principles can be found in Cuadras (1981). Some examples of applications of factor analysis to geology and hydrogeology are described in Davis (1986) and McCuen and Snyder (1986).

The calculations were performed by multivariate statgraphic methods (STSC 1991). The method can be summarized as follows:

a. Calculation of the correlation matrix of the variables, based on the matrix of original data. Examination of this matrix.
b. Calculation of the factor matrix, based on Pearson's *r* values for the previous matrix.
c. Extraction of the two main factors in order to represent the data.
d. Rotation of the factors to facilitate their interpretation.

The values of the factor matrix can be improved by rotating the axes using the Varimax Rotation Method (Kaiser 1985), 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 simpler interpretation.

Factor rotation attempts to select the simplest and most easily interpreted solution. In short, it consists in rotating the coordinate axes that represent the factors in order to approach as nearly as possible the variables for which the coordinate axes are saturated.

The rotated factor matrix is a linear combination of the first matrix and explains the same quantity of initial variance (Bisquerra 1989). As a result, we obtain the grouping of variables around certain factors that must be defined. Finally, the variables are shown on relation graphs for the factors being studied. On the graph, the coordinates of the variables show the "weight" that each exerts on the factors considered.

Results

Tables 2 and 3 show the values of the 16 entry variables subjected to factorial analysis at each of the sampling points. The correlation matrix (Table 4) shows high levels of positive or negative correlation (>0.59) among different elements and compounds analyzed. Therefore, arsenic shows high levels of correlation with PO_4 and SiO_2 (0.84 and 0.63 respectively) and all three show a negative correlation with the pH. This negative correlation is high in the case of SiO_2 (-0.76), but less significant for PO_4 and As (-0.43 and -0.40 respectively). Another similar case is that of the pair of elements made up of Cu and Zn, which have a high correlation between them (0.98) and a negative correlation with the pH (-0.75 for Cu and -0.77 for Zn). The opposite case is represented by the elements Cl, K, Ca, Li, Rb, and Sr, which have a high positive correlation with each other and with the pH. Table 5 shows the results obtained from the factorial analysis of the variables studied and shows how the first two factors account for up to 62.27% of the total variance. We chose these first two factors for the case at hand and its factorial matrix is shown in Table 6. The values that appear in table 6 can be improved by rotating the axes using the Varimax Rotation Method. (Kaiser 1958); these rotated values are shown in Table 7 and are plotted on a graph in Figure 2, where the variables are grouped according to the following four fields:

Field 1: This field is well defined in the sector on the right side of the graph that contains variables Rb, Sr, Li,

Table 2

General water quality in the Tinto-Odiel Estuary

Samples	$SO_4^=$ (ppm)	SiO_2 (ppm)	PO_4^{3-} (ppm)	Na^+ (ppm)	NO_3^- (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	Cl^- (ppm)	pH
G47	1660	N.D.	0.01	8280	11.28	406	1380	421	16000	7.6
G47tris	2690	N.D.	0.01	8250	N.D.	388	1360	341	19300	8
HR1bis	2700	N.D.	0.13	8610	1.75	370	1320	390	16800	8
HR2	1580	1.14	0.06	7990	0.42	338	911	485	23000	8.21
HR2bis	1220	3.77	0.05	7990	0.42	338	911	485	2300	8.08
HR3	1860	0.16	0.04	N.D.	N.D.	493	1770	273	15900	8
HR3bis	3160	1.89	0.04	10500	1.26	162	600	166	18600	8
HR4	1970	N.D.	N.D.	8300	N.D.	377	1350	251	16500	7.98
HR4bis	1730	0.54	0.07	9290	N.D.	343	1200	368	19700	7.9
HR5	1530	N.D.	0.02	7690	N.D.	405	1390	428	15100	7.77
HR5bis	4230	0.31	0.05	7690	10.46	371	1610	366	18300	7.85
HR6	1880	3.82	N.D.	10300	0.52	366	1370	314	14200	7.8
HR6bis	1300	0.98	0.04	6520	N.D.	359	1300	523	19300	7.81
HR7	1640	2.07	N.D.	9120	N.D.	414	1450	150	14400	7.6
HR7bis	2150	N.D.	0.03	8300	0.52	355	1270	267	19300	7.6
HR8	1100	N.D.	0.03	7340	N.D.	384	1520	404	15200	7.45
HR8bis	1930	N.D.	0.04	10600	1.53	406	1380	421	17700	7.5
HR9	2280	0.33	0.03	6420	N.D.	N.D.	1610	366	19500	7.53
HR9bis	1370	1.84	N.D.	6420	N.D.	371	1610	366	19500	7.2
HR10	1180	N.D.	N.D.	9150	N.D.	136	507	198	14700	7.6
HR10bis	2570	2.24	N.D.	9510	N.D.	410	1870	425	20200	7.32
HR11	1550	N.D.	0.01	9270	N.D.	422	1460	459	17200	7.2
HR11bis	2870	0.57	0.04	8610	0.87	410	1410	401	21700	7.32
HR12	1000	N.D.	N.D.	8540	N.D.	334	1530	342	17200	7.2
HR12bis	2900	0.86	0.04	6790	11.16	405	1480	485	18600	7.5
HR13	2560	N.D.	0.03	7820	0.59	394	1130	263	19500	7.35
HR13bis	1080	N.D.	N.D.	7820	0.59	394	1130	263	19500	7.4
HR65	681	1.97	0.01	5660	N.D.	387	1820	463	19800	6.8
Odiel	898	2.46	N.D.	11400	1.2	116	189	94.6	5320	5.8
Odiel1	586	4.4	N.D.	2610	1.65	126	851	60.2	2660	6.5
Odiel3	942	6.51	N.D.	3690	1.98	126	424	156	5240	3.66
Odiel4	1570	5.41	N.D.	N.D.	2.44	193	967	218	8510	5
Odiel5	1640	12.4	N.D.	10100	3.83	177	828	208	9340	4.2
Odiel6	2510	3.88	N.D.	6750	6.76	214	647	284	12200	3.1
Odiel7	1830	7.21	N.D.	7630	10.81	260	842	228	9600	4
Tinto	992	8.92	N.D.	N.D.	1.36	84	122	87.7	1990	2.65
TR1	3920	4.39	0.11	4100	7.39	247	1116	273	19300	2.73
TR2	1230	9.95	0.17	8750	8.56	208	740	434	17200	3.6
TR3	2590	13.2	0.32	7860	0.66	340	1534	432	18300	2.8
TR4	1350	21.95	0.33	8590	N.D.	317	1440	428	12900	2.87
TR5	1430	17.91	0.07	1020	N.D.	182	842	256	12800	3.21
TR6	2280	20.72	0.1	6730	8.34	253	1140	401	12600	2
TR7	2310	8.32	0.02	4050	7.66	126	526	239	9420	3.35
TR8	1140	19.34	0.04	3410	6.38	137	364	246	15200	2.51
TR9	2310	5.8	0.01	7720	6.6	184	1390	301	620	2.4

Table 3
Trace metal content of the water sample

Samples	Li (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Rb (ppm)	Sr (ppm)
G47	0.13	0.33	N.D.	N.D.	0.11	7.37
G47tris	0.12	0.33	N.D.	N.D.	0.1	7.22
HR1bis	0.1	0.32	N.D.	N.D.	0.08	5.38
HR2	0.1	0.32	N.D.	N.D.	0.09	5.36
HR2bis	0.1	0.33	0.21	0.02	0.08	5.48
HR3	0.09	0.26	0.17	0.01	0.07	4.41
HR3bis	0.1	0.29	0.05	0.01	0.08	4.71
HR4	0.1	0.32	0.49	0.02	0.08	5.16
HR4bis	0.1	0.3	0.03	0.01	0.08	5.22
HR5	0.1	0.35	0.25	0.03	0.08	5.48
HR5bis	0.1	0.31	0.05	0.01	0.08	5.06
HR6	0.1	0.31	0.25	0.03	0.08	5.22
HR6bis	0.09	0.28	0.08	0.02	0.07	4.6
HR7	0.09	0.28	0.08	0.02	0.08	4.91
HR7bis	0.09	0.31	0.19	0.03	0.07	4.81
HR8	0.1	0.32	0.26	0.03	0.08	4.78
HR8bis	0.09	0.24	0.2	0.02	0.06	3.39
HR9	0.1	0.33	0.36	0.03	0.08	4.79
HR9bis	0.11	0.33	0.39	0.03	0.08	5.11
HR10	0.11	0.32	0.08	0.02	0.08	5.48
HR10bis	0.12	0.34	0.37	0.03	0.09	5.58
HR11	0.12	0.34	0.32	0.03	0.08	5.56
HR11bis	0.12	0.35	0.55	0.04	0.08	5.52
HR12	0.05	0.3	0.14	0.02	0.04	2.39
HR12bis	0.12	0.32	0.39	0.02	0.09	5.33
HR13	0.13	0.38	0.61	0.04	0.09	6.01
HR13bis	0.15	0.46	0.66	0.04	0.13	7.41
HR65	0.1	0.31	0.43	0.03	0.09	5.33
Odiel	0.11	0.66	1.59	0.07	0.09	6.31
Odiel1	0.11	0.31	0.35	0.03	0.1	6.04
Odiel3	0.09	1.43	2.62	0.1	0.08	5.21
Odiel4	0.09	0.98	2.51	N.D.	0.06	4.37
Odiel5	0.07	1.38	3.49	N.D.	0.05	0.53
Odiel6	0.09	1.97	4.02	0.21	0.08	5.48
Odiel7	0.07	1.69	4.09	N.D.	0.06	3.19
Tinto	0.1	3.19	6.98	0.26	0.08	5.28
TR1	0.1	4.7	10.7	0.15	0.07	4.9
TR2	0.06	2.31	5.93	N.D.	0.03	2.21
TR3	0.1	4.51	10.4	0.14	0.08	5.08
TR4	0.08	8.36	20.7	N.D.	0.05	2.47
TR5	0.04	2.84	7.85	N.D.	0.01	0.95
TR6	0.04	2.05	10.2	N.D.	0.04	1.7
TR7	0.02	2.04	5.73	N.D.	N.D.	0.04
TR8	0.09	6.63	16.8	0.02	0.05	3.54
TR9	0.07	10.9	31.4	0.06	0.01	0.18

Ca, Cl, Na, K and SO_4, all of which have high, positive values with respect to factor 1 (x coordinates) and low positive and negative values for factor 2 (y coordinates).
Field 2: Made up exclusively of the Zn and Cu variables, it occupies the sector opposite the previous one; in other words, taking high negative values for factor 1 and negligible positive values for factor 2.
Field 3: The SiO_2, PO_4 and As variables form a group in the upper part of the graph after the factorial rotation and thus obtain high positive values for factor 2 and negligible values for factor 1.
Field 4: Made up of the pH that occupies the sector across from that of the variables of the previous field, it shows high, negative values for factor 2 and low, positive values for factor 1.

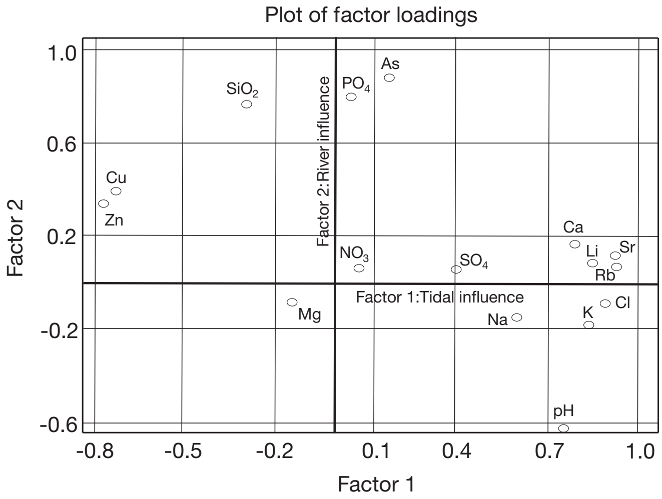

Fig. 2
Plot of correlation between factors 1 and 2

The two remaining variables (NO_3 and Mg) do not show relevant levels of association with any of the groups mentioned above.

Discussion and conclusion

A study of the matrix shows the existence of high Pearson's *r* values in pairs of variables, which can be interpreted as the result of a common origin – sampling was carried out in a sector subjected periodically to tidal influence and river inflow. Therefore, the As/PO_4 pair reaches a correlation coefficient of 0.84, which suggests a common origin due to the leaching of phosphogypsum deposits on the banks of the estuarine system and from direct discharge at fertilizer factories.
The chlorides show high, positive Pearson indices with a pH of 0.72, as do Rb and Sr with a pH greater than 0.73. This phenomenon is the consequence of the decrease in pH induced by the inflow of acid river water with low chloride contents, while the chlorinity increases with the tidal influence that brings sea water with a high salts concentration. The Rb-Sr pair is a well known indicator of marine origin and has a correlation coefficient of 0.95. The same justification is valid for the Li/Rb and Li/Sr pairs, which take values of 0.90 and 0.89 respectively.
At the other extreme, a coefficient of 0.98 for the Cu/Zn pair is evidence of a common origin in the leaching of mines and dumps near the headwaters.
There is a notable association of potash with the rest of the marine indicators, registering indices greater than 0.7 with chlorides, pH, lithium, rubidium and strontium.
With other elements, we can often observe high, negative values that prove inverse correlation because when one correlated pair increases, the other decreases. Because it is highly acidic, the river water is able to bring large amounts of dissolved metals to the estuary. The lower

Table 4
Correlation matrix

	SO_4	SiO_2	PO_4	Na	NO_3	K	Mg	Ca	Cl	pH	Li	Cu	Zn	As	Rb	Sr
SO_4	1															
SiO_2	−0.12	1														
PO_4	0.07	0.49	1													
Na	0.26	−0.34	−0.01	1												
NO_3	0.24	0.11	−0.14	−0.14	1											
K	0.26	−0.45	−0.07	0.53	−0.09	1										
Mg	−0.04	0.03	−0.10	−0.27	−0.08	−0.14	1									
Ca	0.23	−0.07	0.16	0.40	0.12	0.67	−0.12	1								
Cl	0.41	−0.29	−0.02	0.50	−0.02	0.72	−0.16	0.75	1							
pH	0.25	−0.76	−0.43	0.60	−0.05	0.78	−0.14	0.44	0.72	1						
Li	0.35	−0.27	−0.01	0.44	0.14	0.70	−0.14	0.62	0.63	0.60	1					
Cu	−0.20	0.42	0.22	−0.48	0.02	−0.63	0.01	−0.51	−0.71	−0.75	−0.41	1				
Zn	−0.21	0.41	0.19	−0.50	0.03	−0.66	0.01	−0.53	−0.72	−0.77	−0.45	0.98	1			
As	0.06	0.63	0.84	0.01	−0.03	−0.01	−0.10	0.23	0.05	−0.40	0.16	0.17	0.14	1		
Rb	0.37	−0.18	0.01	0.50	0.16	0.72	−0.05	0.70	0.75	0.62	0.91	−0.62	−0.65	0.18	1	
Sr	0.37	−0.23	0.04	0.43	0.19	0.71	−0.10	0.67	0.73	0.61	0.90	−0.60	−0.63	0.22	0.95	1

Table 5
Factors analysis

Factor	Eigenvalue	Percent of variance	Cumulative percentage
1	7.208	45.053	45.053
2	2.755	17.223	62.277
3	1.354	8.464	70.741
4	1.123	7.024	77.765
5	0.831	5.175	82.960
6	0.791	4.944	87.904
7	0.504	3.151	91.055
8	0.441	2.757	93.812
9	0.389	2.432	96.244
10	0.223	1.399	97.643
11	0.150	0.941	98.585
12	0.095	0.595	99.180
13	0.054	0.341	99.520
14	0.041	0.254	99.775
15	0.027	0.171	99.945
16	0.008	0.055	100.000

acidity of the estuary water causes the metals to precipitate, producing high concentrations of these metals in estuary sediments (Borrego 1992). This same phenomenon has been observed by other authors (Braungardt and others 1998) who found that the concentrations of labile Cu and Zn present in estuary water vary considerably depending on the volume of river inflow. This explains why river-borne Cu and Zn from industrial and mining activity show high negative values with the marine indicators (K, Ca, Cl and pH).

Silica, which has a value of 0.75 when correlated with pH, has higher concentrations in the river water samples and can be used as an indicator of fluvial origin. River waters contribute silica at the same time that they lower the pH due to their acidity.

In Fig. 2, the 16 variables considered are grouped into four fields around the two factors that must be determined. In the graph, the coordinates of the variables represent the “weight” that each one exerts on the factors

Table 6
Variable loadings on first two factors from a principal component analysis of chemical composition data

Variable	Factor 1	Factor 2
SO_4	0.401	0.178
SiO_2	−0.480	0.696
PO_4	−0.142	0.836
Na	0.640	−0.009
NO_3	0.050	0.107
K	0.864	0.006
Mg	−0.146	−0.144
Ca	0.732	0.361
Cl	0.877	0.118
pH	0.868	−0.420
Li	0.804	0.262
Cu	−0.812	0.209
Zn	−0.837	0.180
As	−0.045	0.935
Rb	0.886	0.277
Sr	0.871	0.296

Table 7
Variable loadings on first two factors after Varimax rotation

Variable	Factor 1	Factor 2
SO_4	0.423	0.116
SiO_2	−0.370	0.761
PO_4	−0.015	0.848
Na	0.630	−0.105
NO_3	0.066	0.098
K	0.856	−0.124
Mg	−0.166	−0.121
Ca	0.778	0.247
Cl	0.885	−0.015
pH	0.795	−0.546
Li	0.835	0.138
Cu	−0.771	0.329
Zn	−0.801	0.304
As	0.096	0.931
Rb	0.917	0.141
Sr	0.906	0.162

considered. The influence of the acid river-water rich in metals from the leachates of the mines and from the industries within the watershed together with the tidal activity that, twice a day, chlorinates and increases the water's pH can be represented by two factorial axes. Therefore, if we define factor 1 as tidal influence and factor 2 as fluvial influence, we can see how the variables grouped in field 1 have a significant positive influence on factor 1 (tidal influence). This fact, already seen in the initial correlative analysis in this paper, is supported by factorial analysis where, once again, we can observe how the tidal influence groups variables that quantify the concentration of typically marine indicators. The environment is periodically affected by acid inflow from the river which is counteracted by tidal activity.

Within this field, with high, positive values for factor 1, the variables in field 1 are dissociated into two subfields that take negative values for factor 2 in the case of Na, K, Cl and pH, while SO_4, Ca, Li, Rb and Sr take positive values. This fact can be interpreted as follows: the first group of elements has a negative value for fluvial activity because they are exclusively marine salts, so with a larger river inflow, the medium will have a lower salt content. The entry of larger or smaller amounts of river water has little influence on the elements in the second subfield because the acid river water facilitates the dissolution of carbonates present in the environment associated with Li, Sr and Rb. In the case of sulfate, this behavior can be explained by the high content of dissolved sulfate (from the oxidation of sulfides) that characterizes the waters of these two rivers.

The important influence of the variables from field 2 on the tidal influence factor should be understood as the consequence of the notable influence on the system of these pollutants that are transported by the river water and mixed with sea water. The Cu-Zn variables have a large negative impact on the tidal influence factor and a medium positive impact on fluvial influence. This fact is justified because the acid river water flowing into the estuary carries high concentrations of Cu and Zn. The capacity for dissolution of these metals in water depends mainly on the pH of the environment, so when the pH induced by the mixture of sea water and river water causes the metals to precipitate in the tidal area, the Cu and Zn concentration in the waters falls. The third field, made up of phosphates, silica and arsenic, includes the variables that present a marked fluvial character and occupies the upper sector of the graph, showing a high, positive influence for factor 2 and a low influence for factor 1. Both phosphates and arsenic would have come from the phosphogypsum deposits near the river upstream from the sampling area. Silica, typically a continental indicator, has high values for factor 2 and takes negligible values for 1. As was set forth in the initial correlative analysis, nitrates and magnesium have a low level of association.

Acknowledgements The results exposed in this paper constitutes a contribution from TOROS project (contract ENV4-CT96 – 0217 of the ELOISE E.C. project).

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