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A description of how metal pollution occurs in the Tinto–Odiel rias (Huelva-Spain) through the application of cluster analysis

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Abstract

In the last few decades, the study of space–time distribution and variations of heavy metals in estuaries has been extensively studied as an environmental indicator. In the case described here, the combination of acid water from mines, industrial effluents and sea water plays a determining role in the evolutionary process of the chemical makeup of the water in the estuary of the Tinto and Odiel Rivers, located in the southwest of the Iberian Peninsula.

Based on the statistical treatment of the data from the analysis of the water samples from this system, which has been affected by processes of industrial and mining pollution, the 16 variables analyzed can be grouped into two large families. Each family presents high, positive Pearson *r* values that suggest common origins (fluvial or sea) for the pollutants present in the water analyzed and allow their subsequent contrast through cluster analysis.

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1. Introduction

The processes of generation and contribution of pollutants in estuaries are a subject of environmental interest extensively studied in the last decade (Apte et al., 1990; Zwolsman et al., 1997; Grande et al., 2000; Borrego, 1992; Borrego et al., 2001; Sáinz et al., 2002).

The aim of this paper is to use the chemical analysis data on the waters from the area being studied and, by means of cluster analysis, to establish the possible connections and reasons for interdependence among the different elements dissolved in the estuary water as well as to establish a possible means of controlling their concentrations. We would also like to determine the origin of some of them.

In the case described here, the combination of acid water from mines, industrial effluents, and seawater plays a determining role in the evolutionary process of the chemical makeup of the water in the estuary of the Tinto and Odiel Rivers. This estuary is located in the

southwest of the Iberian Peninsula (Fig. 1) and is one of the estuary 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 filled with seawater about 6000 years ago (Borrego et al., 1995) during the last pulse of the Flandrian transgression as a consequence of 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 more specifically on formations of the so-called 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 4000 B.P.

In the last 120 years, these mineralizations have been extensively mined to obtain pyrite concentrations and other commercially valuable metals (gold, silver, etc.). The natural alteration of these sulfide masses, together with the mining activity, has been the cause of a secular pollution of 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 et al., 1998; Grande et al., 2000; Sáinz et al., 2002).

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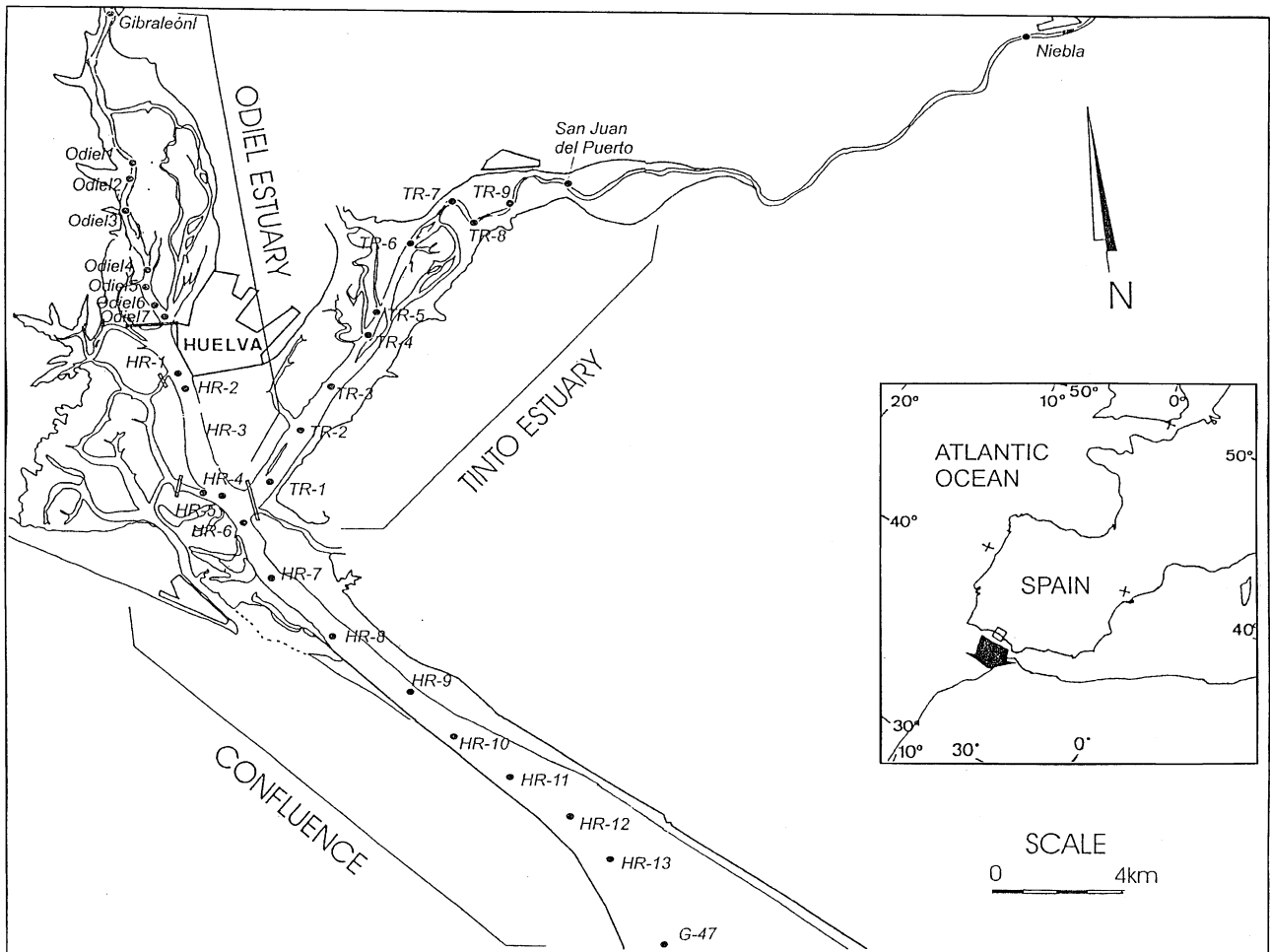


Fig. 1. Location map.

Because of this sulfide-mining activity near the headwaters of the Tinto and Odiel Rivers, an important industrial complex has been developed along the banks of the estuary. This industrial activity produces a large volume of heavy metals and nutrients. (Ruiz et al., 1998; Cruzado et al., 1998; Braungardt et al., 1998; Grande et al., 2000; Borrego et al., 2001).

In this context, it is worth mentioning the existence of phosphogypsum deposits located in the area of the Tinto estuary, with a total surface of 12,000,000 m². These deposits collect the wastes from the manufacture of fertilizers at the neighboring factories and are an important source of phosphates, sulfates and arsenic (among others) to the estuary water because, being in contact with the river banks, the tidal action causes the continuous washing up of these deposits.

The mixture of these industrial wastes, the river water, and the 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 continuous dissolution/precipitation processes

controlled by the volumes of tidal water, the inflow of river water and the 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.

2. General setting

The estuary of the Tinto and Odiel Rivers is on a mesotidal (mean tidal range of 2.10 m) mixed-energy coast (Borrego, 1992). The tidal wave moves along the Odiel estuary following a hypersynchronous model (Borrego et al., 1993) 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 Hm³ during a mean

neap tide (1 m of tidal range) to 81.76 H m^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 H m^3 , and the average yearly inflow was 598 H m^3 . The marked seasonality of this inflow is due to a rainy season from October to March when the inflow may reach 100 H m^3 per month and a dry period (from May to September) with average monthly volumes of less than 5 H m^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 $21 \text{ m}^3 \text{ s}^{-1}$), 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 $6 \text{ m}^3 \text{ s}^{-1}$), the situation can be described as a “good mixing” (Borrego, 1992).

3. Materials and methods

3.1. Sampling and analytical methodology

The sampling campaign was carried out in June 1997. Thirty-three sampling stations or points were established 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.

Samples of the water were filtered immediately after collection, stored at $4 \text{ }^\circ\text{C}$ in the dark, and analyzed within one or two days according to standard seawater methods. 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 $\text{HF–HCl}_4\text{–HNO}_3$ (details are given in Zwolsman et al., 1993).

3.2. Statistical analysis

Both cluster and discriminatory analysis are used to classify individuals into categories (Bisquerra, 1989). The quantitative analysis of the possible relationships is carried out by applying correlative and cluster 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 observe the characteristics shared by the different communalities.

The program used for this analysis (Statgraphics) applies the single linkage method, also known as the nearest neighbor method. It is a hierarchical method that consists in grouping the items according to their similarities. In any step of the analysis, the distance between two clusters is the distance between their nearest points (Bisquerra, 1989). In short, by applying this technique the variables studied can be classified into different “categories” or proximity ratios.

In this case, the use of the cluster analysis has allowed us to determine the associations among different elements and compounds and their input sources.

4. Results

4.1. Correlation matrix

The correlation matrix (Table 1) shows high levels of correlation (near 6) with both positive and negative values among different pairs of variables. Thus, arsenic

Table 1
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	0.5	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

presents 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 (-0.043 and -0.40 , respectively). Another similar case is that of the pair of elements made up of Cu and Zn, which have a high positive 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. Mg shows low rates with the rest of variables.

4.2. Cluster

The dendrogram in Fig. 2 shows the results of applying a nearest neighbor aggregation strategy. In this strategy, the two elements presenting the nearest distance in the matrix will form the first group or class. The distance from a new element to a group already formed will be taken as the nearest distance between that element and its closest element in the group.

The first level of aggregation is established with the pair Cu–Zn which, at the same time, forms a cluster with the pair PO_4 –As. These two pairs are associated with each other in the next stage and later with SiO_2 . Finally, NO_3 is added, forming a cluster with the previous ones on the right side of the dendrogram.

A second cluster, on the left side of the dendrogram, shows a first level of association with the pair Rb–Sr, as the nearest variables. Then, Li, very close to the previous elements, is added, and later on, K, pH, Ca and Cl, Na and SO_4 . Finally, Mg is associated to the cluster.

Thus, with the exception of Mg, which presents a small affinity with any other group, the variables are grouped in two main clusters:

- Cluster 1: Zn–Cu– PO_4 –As– SiO_2 ;
- Cluster 2: Sr–Rb–Li–K–pH–Ca–Cl–Na– SO_4 .

5. Discussion/conclusions

A study of the correlation matrix of all the variables analyzed, as a step previous to the cluster analysis, is a good indicator of the degree of interrelationship, i.e. of the level of linear association among variables. It allows us to eliminate from the analysis those variables that show a low multiple correlation coefficient.

Grande et al. (2000) demonstrate, by applying factorial analysis techniques, the existence of high correlation levels between two groups of variables for samples from this estuary

- Group 1. SO_4 , Na, K, pH, Ca, Cl, Li, Rb, Sr,
- Group 2. PO_4 , As, Zn, Cu, Mg, SiO_2 , NO_3 ,

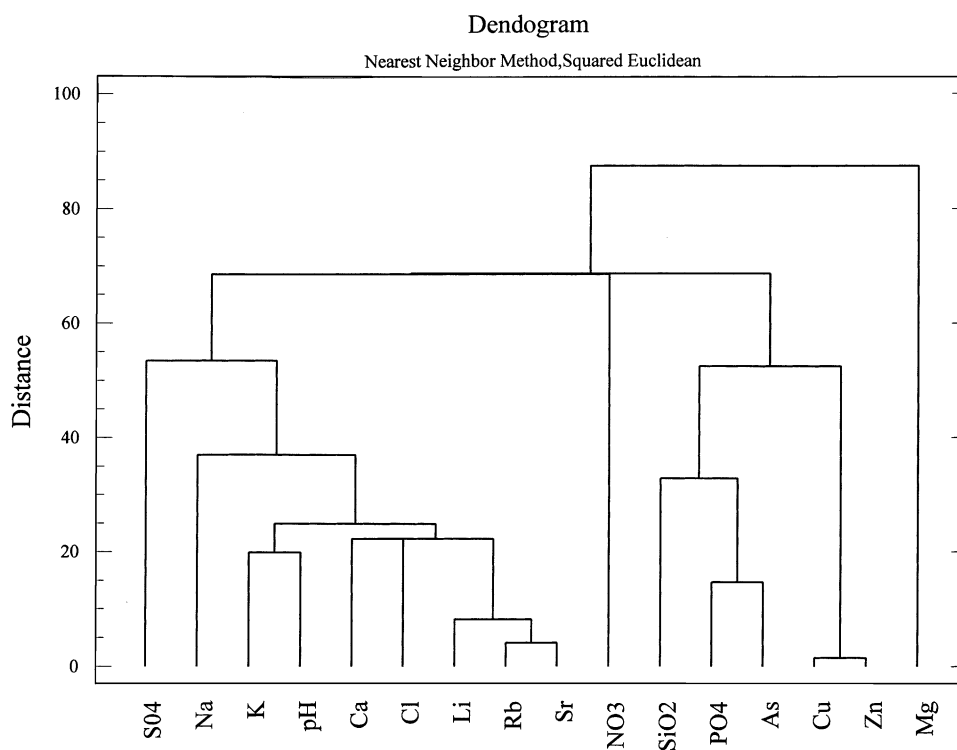


Fig. 2. Dendrogram.

and suggest that group 2 is highly affected by fluvial influence, whereas group 1 is subjected to tidal influence. For these authors, the values of the variables analyzed depend on the intensity of two environmental factors: the influence of acid river water, rich in metals from the leachates of the mines and industries within the watershed of both rivers, and the tidal activity, which chlorinates and increases the pH of the medium twice a day.

The studied area is a sector where the process of “tidal clash” occurs. Acid fluvial waters with dissolved metals undergo a sudden increase of pH when they reach the area of tidal influence. This results in the precipitation of metals that are no longer soluble and concentrate in the sediments, which show high concentrations of these metals (Borrego, 1992; Braungardt et al., 1998; Grande et al., 2000; Sáinz et al., 2002; Borrego et al., 2001).

Under these circumstances, the dendrogram in Fig. 2 shows the association of all analyzed variables in two big families (with the exception of Mg). They represent, in each case, the variables that quantify the concentration of typically marine indicators (Na, K, pH, Ca, Cl, Li, Rb and Sr) on the one hand, and typically fluvial ones (Cu, Zn, As, PO₄ and SiO₂) on the other.

Dissociation in these two big clusters can be interpreted as follows: the pH in estuarine zones is the factor that regulates the concentration of metals dissolved in the water and, at the same time, is subjected to the cyclical character of the tide. As a result, in the presence of fluvial metal-rich contributions, the variables analyzed are grouped according to their fluvial or marine origin.

The closest level of association appears in the pair Cu–Zn. This is easy to interpret if we recognize that they have a common origin with the large amounts of poly-metallic sulfates present in the headwater of these rivers. These metals would have been dissolved by the acid waters (with pH close to 1.5 in the dumping areas) and carried downstream to the area of the estuary, where the new conditions of acidity induced by the tidal clash cause the precipitation of Cu and Zn. For this same reason, Cu and Zn of fluvial origin show high, negative correlation values with the marine indicators (Ca, K, Cl and pH).

With a remarkable level of association and within the cluster comprising the variables of fluvial origin, we find the pair PO₄–As. Their affinity is justified by the presence of phosphogypsum deposits within the area of tidal influence: the continuous “washing” of these deposits by the tidal action causes the entry of PO₄ to the estuary water. As a consequence of the presence of weak acids that are rich in As in the deposits themselves, PO₄ presents a high affinity ratio with As. Thus, both are associated to the variables of fluvial origin.

Sulfates equally brought by these deposits show a different behavior to that of phosphate in the dendrogram, and they do not associate with the previous elements; instead, they enter weakly the cluster that

comprises the variables of fluvial origin. This phenomenon can be interpreted as a consequence of the fact that seawater is also a source of contribution with mean concentrations in the sector of 2.5 mg l⁻¹ (Borrego, 1992). Another argument that supports this interpretation is the transportation mechanism itself and their electrochemical affinity; while phosphates are transported as particulated material, sulfates do it in complete dissolution in the estuary water.

The pair Rb–Sr presents, within the marine indicators, a high affinity as a consequence of their already known common origin (Grande et al., 2000; Borrego et al., 2001). These two variables are associated immediately afterwards to the rest of the marine indicators in correlation decreasing order: Li, Cl, Ca, K, pH and Na.

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