Environmental impact of mining activities in the Odiel river basin (SW Spain)

Sarmiento Aguasanta[(1)], Nieto José Miguel[(1)], Olías Manuel[(2)] & Cánovas Carlos[(2)]

[(1)]Department of Geology, University of Huelva, Campus “El Carmen”, E-21071, Huelva, Spain.
E-mail address: aguasanta.miguel@dgeo.uhu.es
[(2)]Department of Geodynamics and Palaeontology, University of Huelva, Campus “El Carmen”, E-21071, Huelva, Spain
Keywords: Acid mine drainage, Odiel river, metal pollution.

ABSTRACT

Acid mine drainage (AMD) from abandoned mines degrades close to 1000 km of streams in the Odiel river basin (SW Spain). The Odiel river drains the central part of the Iberian Pyrite Belt, one of the oldest and most important massive sulphide districts in the world. When pyrite and other associated sulphide minerals associated are exposed to water and oxygen, a series of chemical and biochemical reactions produce a leachate characterized by elevated acidity and high concentration of metals such as Fe, Cu, Zn, Co, Cr, Mn, As, etc. These leachates drain into the Odiel drainage network, and their final destination is the Atlantic Ocean. In this work, the results of a study along the whole Odiel basin are showed. During the year 2002, water samples were collected in the Odiel river in 69 different points. Samples were analysed by ICP-OES in order to characterize and quantify the pollutants that the Odiel river receives as a consequence of AMD processes. Due to the great quantity of samples and analytic determinations, the use of statistical multivariate techniques (Principal Component Analysis) was used to study the results.

INTRODUCTION

Acid drainage is one of the biggest environmental problems caused by sulphide deposits mining. Acid mine drainage (AMD) is responsible for the pollution and degradation of groundwater, streams, rivers and complete river basins, such as the Odiel and Tinto rivers basins in Huelva (SW Spain). The Iberian Pyrite Belt (IPB) is one of the most famous sulphide mining regions in the world; it contains original reserves in the order of 1700 Mt (Saez *et al.*, 1999). Mining activity in the IPB dates back to prehistoric times (Davis *et al.*, 2000), and though today there is no active mining, the pollution continues to generate. This is due to mining wastes such as those generated in the mines of Tharsis, Riotinto, Cueva de la Mora, San Miguel, Conceción, San Telmo, etc (Figure 1).

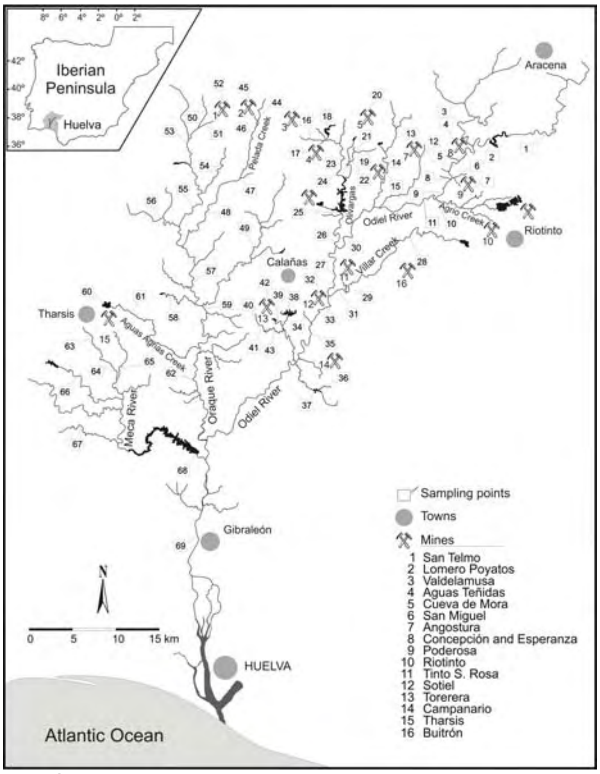

Figure 1. Location map of the Odiel River, showing the sampling points and some of the most important mines

A series of chemical and biochemical reactions take place when pyrite and other sulphide minerals associated are exposed to water and oxygen. These reactions can be generalized by the following equations (Singer & Stumm, 1970):
Oxidation of pyrite by oxygen in the presence of water:

$$FeS_{2(s)} + 7/2\ O_{2(aq)} + H_2O \rightarrow Fe^{2+}, Fe^{3+} + 2SO_4^{=} + 2H^+ \qquad (1)$$

Oxidation of pyrite by ferric iron:

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{=} + 16H^+ \qquad (2)$$

Oxidation of ferrous iron by oxygen:

$$Fe^{2+} + 1/4\ O_{2(aq)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad (3)$$

Precipitation of ferric iron:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \qquad (4)$$

The metal sulphides oxidation is accelerated by the presence of bacteria (Gónzalez-Toril *et al.*, 2003) such as Thiobacillus ferrooxidans. Equation 3 determines the rate of the overall acidification process, and bacteria can accelerate the overall process six fold by catalyzing reactions 1 and 3 above (Singer & Stumm, 1970). Thus, the oxidation of mine tailings by biologically catalyzed processes is quite rapid and leads to an overall decrease in pH. With decreasing pH, the mobility of trace elements tends to increase. This produce a mine water discharge characterized by elevated acidity and high concentration of sulphates and metals such as Fe, Cu, Zn, Co, Cr, Mn, As, etc.
Studies at the Odiel river next to the estuary show concentrations averages of 1200 mg/L of sulphates, 23.5 mg/L of Fe, 7.6 mg/L of Cu, etc., (Olias *et al.*, 2004), so the calculated mean contaminant load transported by the Odiel river to the Huelva estuary and Gulf of Cádiz is 820.4 tons/day of sulphate and 45 tons/day of metals (Fe+Zn+Mn+Cu+Pb+Cd) (Sarmiento & Nieto, 2003; Sarmiento *et al.*, 2004a).
The high mining-related contamination existing in the area for years has generated numerous publications (Borrego *et al.*, 2002; Grande *et al.*, 1999; Elbaz-Poulichet *et al.*, 2001; Sainz *et al.*, 2002) but these deal with contaminants within the Tinto and Odiel estuaries. In this work, a study along the whole Odiel basin has been realized. For this, surface water samples have been taken at different points to characterize and quantify the pollutants by AMD in the Odiel river basin.

SITE DESCRIPTION
The Odiel river is located in the southwest of the Iberian Peninsula (Figure 1). It starts in the Sierra de Aracena (Huelva) and, together with the Tinto river, flows into a coastal wetland known as the Ría of Huelva estuary, which forms part of a very important Natural Reserve (Marismas del Odiel). The Odiel river has a catchment area of 2.333 km^2 and a length of 140 km. The average rainfall varies between 600 mm in the lower part of the basin and 1000 mm in the upper northern hills. Almost 50% of the annual rainfall occurs between November and January; April has abundant rains too, and during the summer months, rainfall is practically absent.
The most important tributaries in the Odiel river are the Olivargas, Oraque and Meca for its west margin, and Agrio and Villar for its east margin. Three small watersheds can be differentiated in the Odiel river basin: Oraque, Meca and Odiel watersheds. The biggest reservoirs in the Odiel river basin are the Olivargas and the Sancho, with a capacity of 8, 29 and 58 Hm^3, respectively.

METHODS
During the year 2002, surface water samples were collected in the Odiel river in 69 different points (Figure 1). In all of them, the main physicochemical parameters were measured *in situ*. Temperature, pH and electrical conductivity were measured using a portable MX 300 measurer (Mettler Toledo). The redox potential was also measured in the field using HANNA measurer with Pt and Ag/AgCl electrodes (Crison).
Water samples were filtered immediately through 0.45µm Millipore filters on Sartorius polycarbonate filter holders and were acidified in the field to pH<2 with HNO_3 (2%) suprapur and stored at 4ºC in polyethylene bottles until analysis. Samples collected for alkalinity and anion determinations were filtered but not acidified. Dissolved concentration of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, and Zn were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a protocol especially designed for AMD samples (Ruiz *et al.*, 2003a; Ruiz *et al.*, 2003b). Anions were determined by Ion Chromatography and alkalinity was determined by the titration method.
Statistical multivariate technique (Davis, 1986) was carried out by Principal Component Analysis by means of Spearman correlation matrix to 22 variables analysed (Electrical conductivity, pH, sulphate, As, Ca, Sr, Mg, Mn, Li, Cu, Co, Ni, Al, Fe, Si, Pb, Sn, Cd, Cr, Zn Na and K).

RESULTS Y DISCUSSION
Sulphide oxidation processes control the main features of the Odiel river. Of the 69 sample points studied, 52 are affected by AMD and only 17 are uncontaminated streams. Mean chemical composition and range for the two types of streams are listed in Table 1.

AMD uncontaminated streams
In the uncontaminated streams the mean pH is around 7. The maximum levels (pH 8.5) are located in the north part of the river, due to the presence of limestones in the bedrock. The electrical conductivity does not exceed 420 µS/cm and the maximum level in bicarbonates and sulphates are 212 mg/L and 63 mg/L respectively. The

composition of the samples is shown in the Piper diagram of Figure 2 (square symbols). In general, the uncontaminated waters in the Odiel basin are bicarbonated and sulphated waters depending on the location of the streams: Ossa-Morena Zone (samples 1, 2 and 3) (limestone materials) or Sud-Portuguese Zone (polymetallic sulphide ores).

AMD contaminated streams

The mean pH is around 4 in the contaminated streams and the electrical conductivity is around 2.2 mS/cm (Table 1). These values have large variations throughout the whole basin (pH between 2 and 7 and electrical conductivity between 0.2 and 14 mS/cm). The composition of the samples is shown in the Piper diagram of figure 2 (circle symbols). All the samples are more or less sulphated waters (mean concentration of 1586 mg/L) and sulphate concentration varies depending on the level of contamination of the AMD effluent, distance from the contaminant effluent, and seasonal variations (Olias *et al.*, 2004).

	AMD-contaminated streams					AMD-uncontaminated streams				
	n	Mean	Range		S.D.	n	Mean	Range		S.D.
pH	52	3.92	2.05	7.25	1.36	17	7.07	5.98	8.44	0.65
Eh (mv)	35	392	77.0	582	132	7	184	125	224	34.4
CE (mS/cm)	51	2.23	0.19	14.2	2.71	17	0.24	0.15	0.42	0.09
CO_3^{2-} (mg/L)	44	n.d.	n.d.	n.d.	0.00	17	0.47	n.d.	7.92	1.92
HCO_3^- (mg/L)	44	5.88	n.d.	97.1	18.4	17	83.8	30.0	212	46.1
F^- mg/L	16	0.69	n.d.	4.82	1.57	14	0.03	n.d.	0.12	0.04
Cl^- mg/L	16	17.7	6.58	46.8	10.2	16	19.5	8.71	64.5	14.7
SO_4^{2-} (mg/L)	52	1586	31.55	12416	2311	17	31.1	12.9	62.9	15.4
Al (mg/L)	52	70.7	n.d.	765	142	17	0.03	n.d.	0.16	55.2
As (µg/L)	52	239	n.d.	4686	879	--	n.a.	--	--	--
Ca (mg/L)	52	74.6	2.70	644	101	17	15.6	5.24	38.1	8.32
Cd (µg/L)	52	84.5	n.d.	589	132	--	n.a.	--	--	--
Co (µg/L)	52	617	9.13	7326	1434	--	n.a.	--	--	--
Cr (µg/L)	52	14.5	n.d.	180	35.2	--	n.a.	--	--	--
Cu (mg/L)	52	7.67	n.d.	122	18.8	17	0.05	0.01	0.19	68.2
Fe (mg/L)	52	175	n.d.	1739	375	17	0.19	n.d.	0.91	323
K (mg/L)	52	1.70	n.d.	7.97	1.48	17	1.85	0.58	4.38	0.91
Mg (mg/L)	52	114	3.51	1228	197	17	10.7	4.61	20.7	4.56
Mn (mg/L)	52	14.2	0.07	118	22.2	--	n.a.	--	--	--
Na (mg/L)	52	17.5	3.15	52.3	9.38	17	14.2	5.01	35.5	7.61
Ni (µg/L)	52	293	3.65	4429	708	--	n.a.	--	--	--
P (µg/L)	52	106	n.d.	1207	239	17	64.8	n.d.	330	122
Pb (µg/L)	52	135	n.d.	1985	293	--	n.a.	--	--	--
Si (mg/L)	52	10.5	0.2	41.5	9.74	17	2.16	n.d.	6.64	2.36
Zn (mg/L)	52	38.5	n.d.	466	81.0	--	n.a.	--	--	--

Table 1. Mean chemical and physicochemical parameters and range for the two types of streams. (S.D.: Standard deviation; n.d.: Not detected; n.a.: Not analysed)

The maximum levels of Fe (1739 mg/L), Al (765 mg/L), Zn (466 mg/L), Cu (122 mg/L), As (4.7 mg/L), Co (7.3 mg/L), sulphates (12416 mg/L), etc., are located near the Tharsis mine (samples 61 and 65), Riotinto mine (sample 10), San Telmo mine (sample 52), Cueva de la Mora mine (sample 20) and La Poderosa mine (sample 7).

Usually, all the contaminated streams follow the same pattern. Low pH effluents have high contents in Fe, As, Cu and sulphates. These waters show a greenish colour. It is due to the lack of precipitates because at low pH these metals are in solution. This is the case of La Poderosa mine leach (point 07), which carries high contents of Fe (1330 mg/L), Cu (122 mg/L) and As (4.7 mg/L) in solution and a low pH (2.05). When the pH increases, the waters show a reddish colour due to the formation of Fe-oxyhydroxides and the metal content decreases due to precipitation and adsorption processes. Meantime, the acid water flows and dissolves minerals in the bedrock. For this reason, the acidity is reduced gradually and new elements are incorporate in the water due to mineral hydrolysis, such as Al and Mn (Banwart & Malmstrom, 2001). In fact, these metals are in large amounts in the acid waters of the Odiel river: 765 mg/L of Al, 644 mg/L of Ca, 1228 mg/L of Mg and 119 m/L of Mn (Table 1).

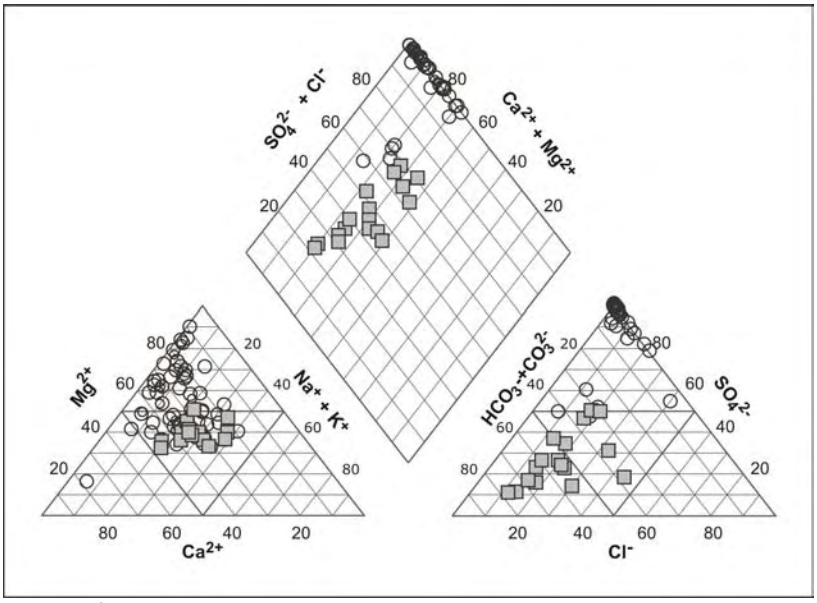

Figure 2. Piper diagram of the samples analysed (square symbols are AMD-uncontaminated samples and circle symbols are AMD-contaminated samples).

Statistical multivariate techniques were used for the analysis of the possible relationships. The analysis was carried out by Principal Component Analysis to 22 variables analysed at each contaminated sample (52 samples). 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 behaviour in the Odiel river basin.

Figure 3 shows the results obtained from the PCA analysis of the variables studied, and shows how the first two factors account for 78% of the total variance. The first factor (F1) account for up to 68% of the total variance and it is associated with the salinity of the samples due to sulphide oxidation. For this reason all the variables show a negative correlation with pH. In the second factor (F2) the variables are classified according to two groups. The metals which form part of the sulphide ores (Cu, Cd, Fe, Zn, Pb, etc.) are located in the negative component of this second factor. In the positive part, the metals which are associated with the hydrolysis of bedrock minerals (Mg, Ca, Sr, Na, Mn, K, etc.) are located. Arsenic is an exception possibly due to the hydrochemical characteristics that this metalloid has in acidic environements, which are different to other metals (Sarmiento *et al.,* 2004b).

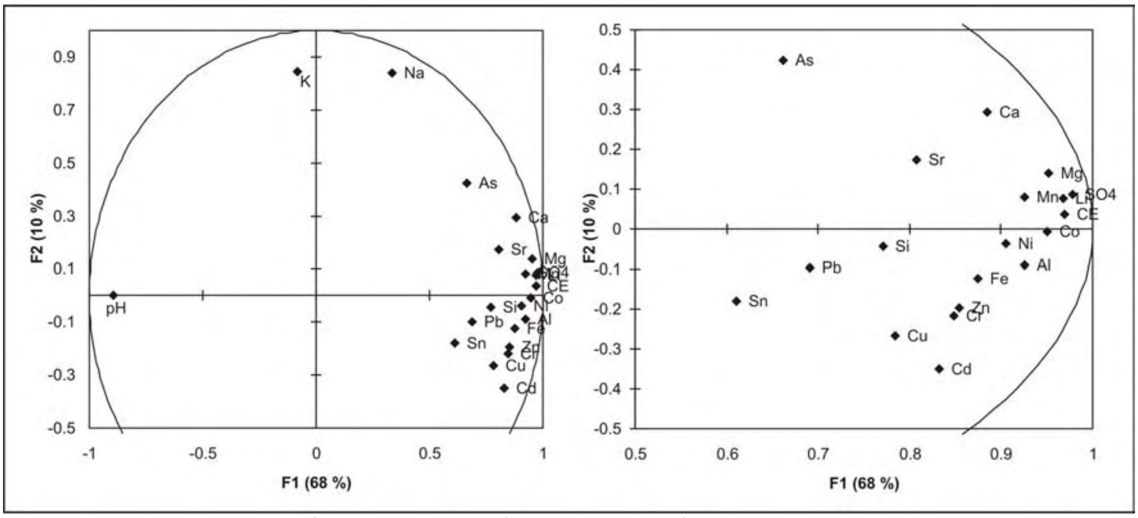

Figure 3. PCA plot between factor 1 and 2 of the variables analysed.

Spatial distribution of the contamination in the Odiel basin

This section shows the contamination profile in two of the most important streams of the Odiel basin: The Oraque river (Figure 4A) and the Odiel river (Figure 4B).

Oraque river

The Oraque river is the most important affluent of the Odiel river. The first mine leachate flowing into the Oraque river is the San Telmo mine (points 51 and 52; Figure 1). This outflow has an important contamination (2.5 of pH, 3400 mg/L of sulphates and Fe and Al above 200 mg/L). Other mines flowing into the Oraque river, such as Lomero Poyatos, Valdelamusa or Tharsis (Figure 4A), also represent an important contaminant load to the Oraque.

The Tharsis mine is the most important polluting source in the Odiel river basin, and the leaching flow is constant all the year. In this leaching, concentration up to 1.7 g/L of Fe, 765 mg/L of Al, 12.4 g/L of sulphates, 4.3 mg/L of As, etc., have been determined. The high dissolved metallic content of the samples is related to the high conductivity measured, 14 mS/cm. These values represent the maximum level of pollution recorded in the Oraque river.

In the last sampling point analysed before flowing into the Odiel river (point 62, figure 4A), pH values of 3.5, and 30 mg/L of Al, 11 mg/L of Fe and 730 mg/L of sulphates have been measured.

Odiel river

The streams located in the northern part of the basin (points 1, 2 and 3; figure 1) have a bicarbonated composition and a pH around 8. In these samples the lower concentration of sulphates has been determined (less than 22 mg/L). This water composition is usual in the streams draining the Ossa-Morena zone due to the presence of limestones in the bedrock and the lack of polymetallic sulphide ores. Therefore, these streams are not contaminated by AMD. However, from that point to the south, the Odiel river is polluted by more than 15 different mines: Concepción, Poderosa, Cueva de la Mora, etc. (Figure 1). Alter receiving the outflows from the first mines, the pH of the Odiel river decreases from 8 to about 3.5, and the contaminant load increases (figure 4B).

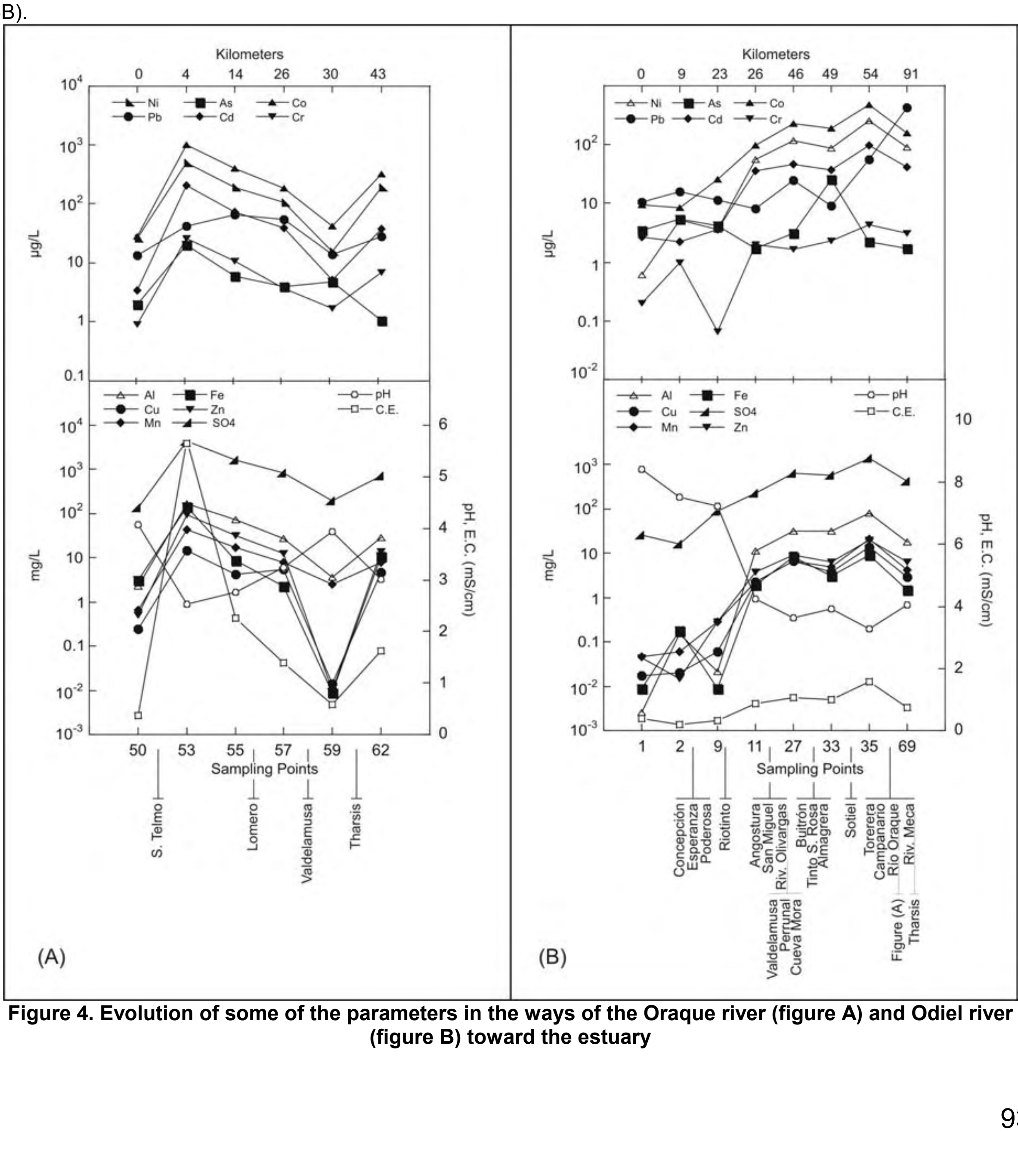

Figure 4. Evolution of some of the parameters in the ways of the Oraque river (figure A) and Odiel river (figure B) toward the estuary

After a few kilometres from it source, the quality of the Odiel river is at best (point 9; figure 4B). However, after joining the Agrio creek, that drains part of the Riotinto mining area, the water of the Odiel river is irreversibly deteriorated (point 11 and the following).
Other polluted streams have been monitored in the Odiel river basin, such as the Meca river (Figure 1) which is strongly contaminated by the outflows of the Tharsis mining district. In the Meca river, electrical conductivity of 8 mS/cm, 7500 mg/L of sulphates, 630 mg/L of Fe, 37 mg/L of Cu, 7 mg/L of Co, or 600 mg/L of Al have been measured.
The last point analysed is located just before the Huelva estuary (point 69; Figures 1 and 4B). At this point, the pH is about 3.5, 1.2 mS/cm of electrical conductivity, 800 mg/L of sulphates, 18 mg/L of Al, 4 mg/L of Mn, 6 mg/L of Zn, 3 mg/L of Cu, etc. These values represent the contamination levels that the Odiel river transport into the Atlantic Ocean.

CONCLUSIONS

Surface water samples were collected in the Odiel river basin at 69 different points in order to quantify the AMD contamination levels of the basin. The maximum levels of Fe, Al, Mn, Co, Cd y Ni are located at the streams draining the Tharsis and Riotinto mining districts. The outflow from La Poderosa mine represent the maximum concentrations of Cu and As, and the maximum levels of Zn and Pb are recorded at the Cueva de la Mora and San Telmo mines respectively. These effluents are the major polluting sources in the Odiel river basin.

ACKNOWLEDGEMENTS

This work has been financed by the Spanish Ministry of Education and Science through project REN2003-09590-C04-03, and by the European Union through project e-EcoRisk (EVG1-CT-2002-00068).

REFERENCES

Banwart, S.A. & Malmstrom, M.E., 2001. Hydrochemical modelling for preliminary assessment of minerwater pollution. *Journal of Geochemical Exploration*, Vol. 74, 73-97.

Borrego, J. *et al.*, 2002. Geochemical characteristics of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). *Enviromental Geology*, Vol. 41, 785-796.

Davis, J.C., 1986. Stadistics and data analysis in Geology. John Wiley and sons, New York.

Davis, R.A. *et al.*, 2000. Rio Tinto estuary (Spain): 5000 years of pollution. *Enviromental Geology*, Vol. 39(10), 1107-1116.

Elbaz-Poulichet, F. *et al.*, 2001. Metal biogeochemistry in the Tinto-Odiel rivers (Southern Spain) and in the Gulf of Cadiz: a synthesis of the results of TOROS project. *Continental Shelf Research*, Vol. 21, 1961-1973.

Gónzalez-Toril, E. *et al.*, 2003. Geomicrobiology of the Tinto River, a model of interest for biohydrometallurgy. *Hydrometallurgy*, Vol. 71, 301-309.

Grande, J.A. *et al.*, 1999. A study of heavy metal pollution in the Tinto-Odiel estuary in southwestern Spain using factor analysis. *Environmental Geology*, Vol. 39(10), 1095-1101.

Olias, M. *et al.*, 2004. Seasonal water quality wariations in a river affected by acid mine drainage: The Odiel river (south west Spain). *Science of the Total Environment*, Vol. 333, 267-281.

Ruiz, M.J. *et al.* 2003a. Calibración de un estándar natural para el análisis de muestras de drenaje ácido de minas (AMD) mediante UN-ICP-OES. *Proceedings IV Iberian Geochemical Meeting*, Coimbra, Portugal, 414-416.

Ruiz, M.J. *et al.* 2003b. Optimizacion del analisis de elementos mayores y traza mediante UN-ICP-OES en muestras de drenaje acido de mina. *Proceedings IV Iberian Geochemical Meeting*, Coimbra, Portugal, 402-404.

Saez, R. *et al.*, 1999. The Iberian type of volcano-sedimentary massive sulphide deposits. Mineralium Deposita, Vol. 34, 549-570.

Sainz, A. et al., 2002. Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers. Journal of Environmental Management, Vol. 64, 345-353.

Sarmiento, A.M. & Nieto, J.M., 2003. Estudio preliminar de la carga de contaminantes transportada por el rio Odiel. Geogaceta, Vol. 34, 207-210.

Sarmiento, A.M. et al. 2005. Características físico-químicas en dos embalses de la cuenca del río Odiel afectados por drenaje ácido de mina (AMD). VI Simposio del Agua en Andalucía, Sevilla, 2, 1343-1351.

Sarmiento, A.M. et al., 2004a. The contaminant load transported by the river Odiel to the Gulf of Cádiz (SW Spain). Applied Earth Science, Vol. 113(2), 117-122.

Sarmiento, A.M. et al., 2004b. Variación estacional en la especiación y movilidad de Fe y As en aguas afectadas por drenaje ácidos de mina en la cuenca del río Odiel (Huelva). *Geogaceta*, Vol. 37, 115-118.

Singer, P.C. & Stumm, W., 1970. Acidic mine drainage: the rate determining step. Science, Vol. 167, 1121-1123.