POLLUTION OF A RIVER BASIN IMPACTED BY ACID MINE DRAINAGE IN THE IBERIAN PYRITE BELT (SW SPAIN)[1]

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Abstract. The Iberian Pyrite Belt (IPB) is one of the most famous sulfide mining regions in the world. Mining activity in the IPB dates back to prehistoric times, and though today there is no active mining, the pollution continues to generate. The result is acidic drainage containing elevated concentration of sulfate and heavy metals. This is responsible for the pollution and degradation of the Odiel River basin in south-western Spain. In this work we have conducted a study along the entire Odiel basin. During the years 2002 and 2003 we have collected water samples at 69 points in order to characterize and quantify the pollutants that the Odiel River receives as a consequence of the AMD inputs within its watershed. The contaminant load transported by the Odiel River into the Huelva Estuary has also been calculated. Due to the great quantity of samples and analyses, the use of statistical multivariate techniques (Principal Component Analysis) was used to interpret the results. PCA of the samples showed strong interrelationships between the generation of acid by sulfide mineral weathering and metal loads. In downstream reaches, the rock forming elements (K, Ca, Na, Mg, etc.) dominate as the acidic waters dissolve the rocks in the stream bed. The contaminant load transported by the Odiel River to the Huelva Stuary is dominated by SO_4^{2-}, Al and Fe, with lesser quantities of Zn, Cu, Cd, etc.

Additional Key words: Odiel River, acid drainage, metal pollution.

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Introduction

Acidic drainage is one of the biggest environmental problems caused by mining sulfide-rich mineral deposit. Acid mine drainage (AMD) is responsible for the pollution and degraded water quality in groundwater, streams, rivers and complete river basins, such as the Odiel and Tinto River basins in Huelva (SW Spain). The Iberian Pyrite Belt (IPB) is one of the most famous sulfide mining regions in the world; it contains original reserves on the order of 1,700 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 located at the mines of Tharsis, Riotinto, Cueva de la Mora, San Miguel, Concepción, San Telmo, etc (e.g., Fig. 1).

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

Oxidation of pyrite by oxygen in the presence of water:

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

Oxidation of pyrite by ferric iron:

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

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:

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

Metal sulfide 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 and 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 concentrations of SO_4^{-2} and metals such as Fe, Cu, Zn, Co, Cr, Mn, As, etc.

Studies at the Odiel River next to the estuary show concentration 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 tons/day of SO_4^{-2} and 45 tons/day of metals (Fe, Zn, Mn, Cu, Pb, Cd) (Sarmiento and Nieto, 2003; Sarmiento et al., 2004a).

Investigations of the high mining-related contamination existing in the area 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 conducted. For this study, surface water samples were taken at different points to characterize and quantify the pollutants by AMD in the Odiel River basin.

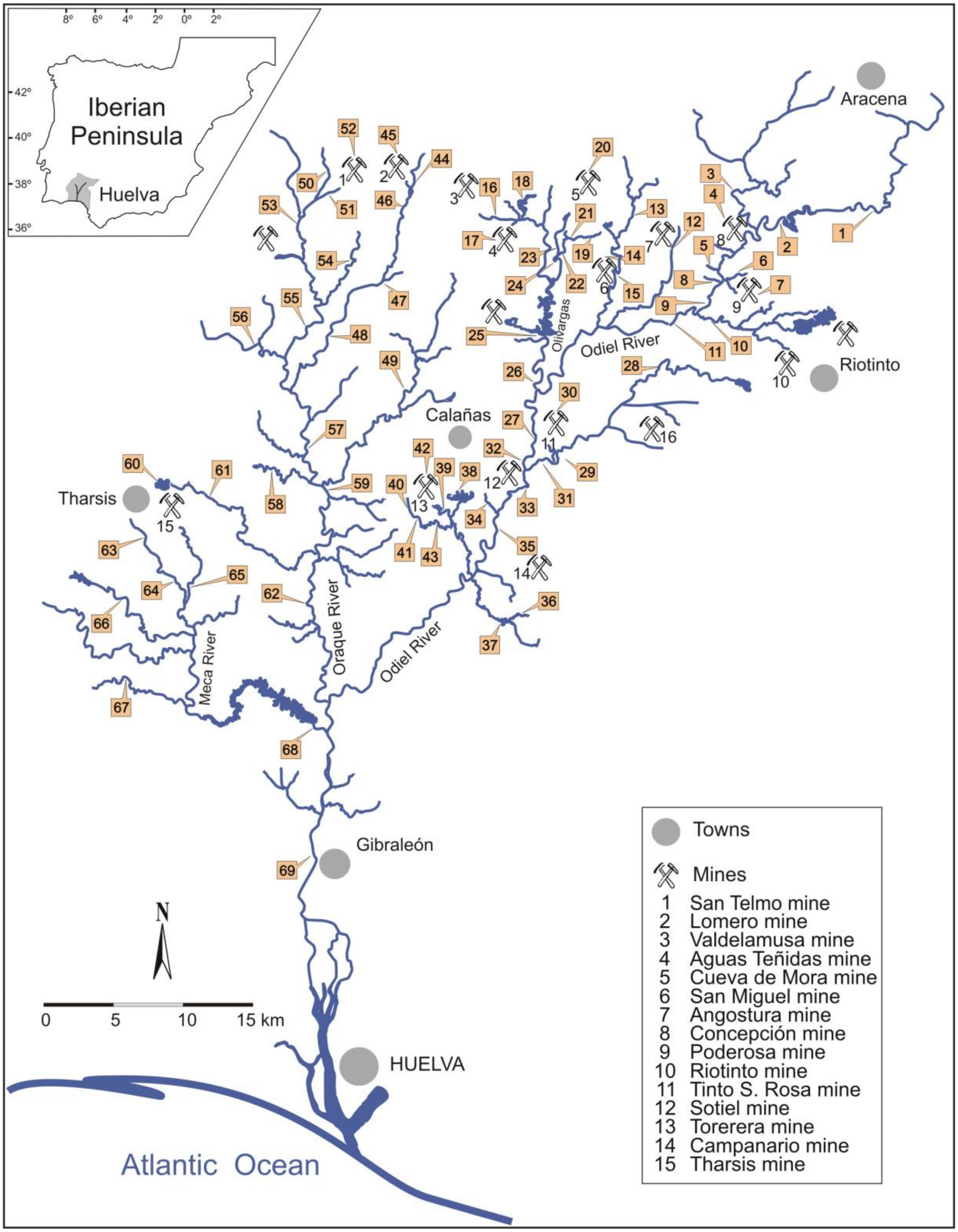

Figure 1. Location map of the Odiel River, showing the sampling points and some of the most important mines.

The Odiel basin

The Odiel River is located in the southwest of the Iberian Peninsula (Fig. 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 1,000 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 29 and 58 cubic hectometres, respectively.

Experimental

During the years 2002 and 2003, surface water samples were collected in the Odiel River at 69 different points (e.g., Fig. 1). In all, 419 water samples have been studied in the last point before the estuary (point 69, Fig. 1). These last samples were collected every week from 1996 to 2001 and analysed by Guadiana Hydrographic Confederation. We have continued this work during the years 2002 and 2003, since then Al and Co were also analysed.

The main physicochemical parameters were measured *in situ*. Temperature, pH and electrical conductivity were measured using a portable MX 300 meter (Mettler Toledo). The redox potential was also measured in the field using Hanna meter with Pt and Ag/AgCl electrodes (Crison). Redox potential and pH were properly calibrated on site against supplied calibration standards Hanna standard solutions (pH 4.01 and pH 7.01) for pH and Hanna standard solution (240 mV and 470 mV) for Eh. The flow data were obtained by the Guadiana Hydrographic Confederation.

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 Yobin-Ybon Ultima2) using a protocol especially designed for AMD samples (Ruiz et al., 2003a; Ruiz et al., 2003b). Single Certified standards from SCP SCIENCE ICP STANDARD SOLUTIONS were employed for the preparation of calibration multielement standards. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material, European Commission Institute for Reference Materials and Measurements, were also carried out. Multielemental Reference Standards, and blanks were employed in the beginning and in the end of each sequence. Detection limits were calculated by average, and standard deviations from ten blanks. Detection limits for major cations were less than 200 µg/L for Al, Fe, Mn, Mg, Na, K, Si and less than 500 µg/L for Ca. For trace elements were 50 µg/L for Zn, 5 µg/L for Cu, 2 µg/L for As and 1 µg/L for Cd, Co, Cr, Ni and P.

Anions were determined by Ion Chromatography using a Dionex DX-120 machine fitted with an AS 9-HC of 4 x 250 mm column and a 4 mm ASRS-ULTRA suppressing membrane. Detection limits were 0.1 mg/L for F^- and Cl^-, and 0.5 mg/L for SO_4^{-2}. Alkalinity was determined by the titration method (Standard Methods 2320 for the Examination of Water and Wastewater) with standardized HCl and bromcresol green indicator.

Principal Component Analysis (Davis, 1986) was carried out by means of a Spearman correlation matrix to 22 variables (Electrical conductivity, pH, SO_4^{-2}, As, Ca, Sr, Mg, Mn, Li, Cu, Co, Ni, Al, Fe, Si, Pb, Sn, Cd, Cr, Zn Na and K) and 52 contaminated samples were analysed in this manner.

Results and discussion

Sulfide 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 concentrations of HCO_3^- and SO_4^{-2} are 212 mg/L and 63 mg/L respectively. The composition of the samples is shown in Fig. 2 (square symbols). In general, the uncontaminated waters in the Odiel basin are bicarbonate-sulfate waters, depending on the location of the streams: Ossa-Morena Zone (samples 1, 2 and 3; Fig. 1) (limestone materials) or Sud-Portuguese Zone (polymetallic sulfide ores).

AMD contaminated streams

The mean pH is around 4 in the contaminated streams and the electrical conductivity is around 2.2 mS/cm (e.g., 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 Fig. 2 (blue circle symbols). All the samples are more or less sulphate waters (mean concentration of 1,590 mg/L) and SO_4^{-2} concentration varies depending on the level of contamination of the AMD effluent, distance from the contaminant effluent, and seasonal variations (Olias *et al.*, 2004).

The maximum levels of Fe (1740 mg/L), Al (765 mg/L), Zn (466 mg/L), Cu (122 mg/L), As (4.7 mg/L), Co (7.3 mg/L), SO_4^{-2} (12,400 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 SO_4^{-2}. 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 (1,330 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. Meanwhile, 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 and 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, 1,230 mg/L of Mg and 119 m/L of Mn (e.g., Table 1).

Table 1. Mean chemical and physicochemical parameters and range for the two types of streams.

	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	1590	31.6	12400	2310	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.	4690	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	7330	1430	--	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.	1740	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	1230	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	4430	708	--	n.a.	--	--	--
P (µg/L)	52	106	n.d.	1210	239	17	64.8	n.d.	330	122
Pb (µg/L)	52	135	n.d.	1990	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.	--	--	--

(S.D.: Standard deviation; n.d.: Not detected; n.a.: Not analysed)

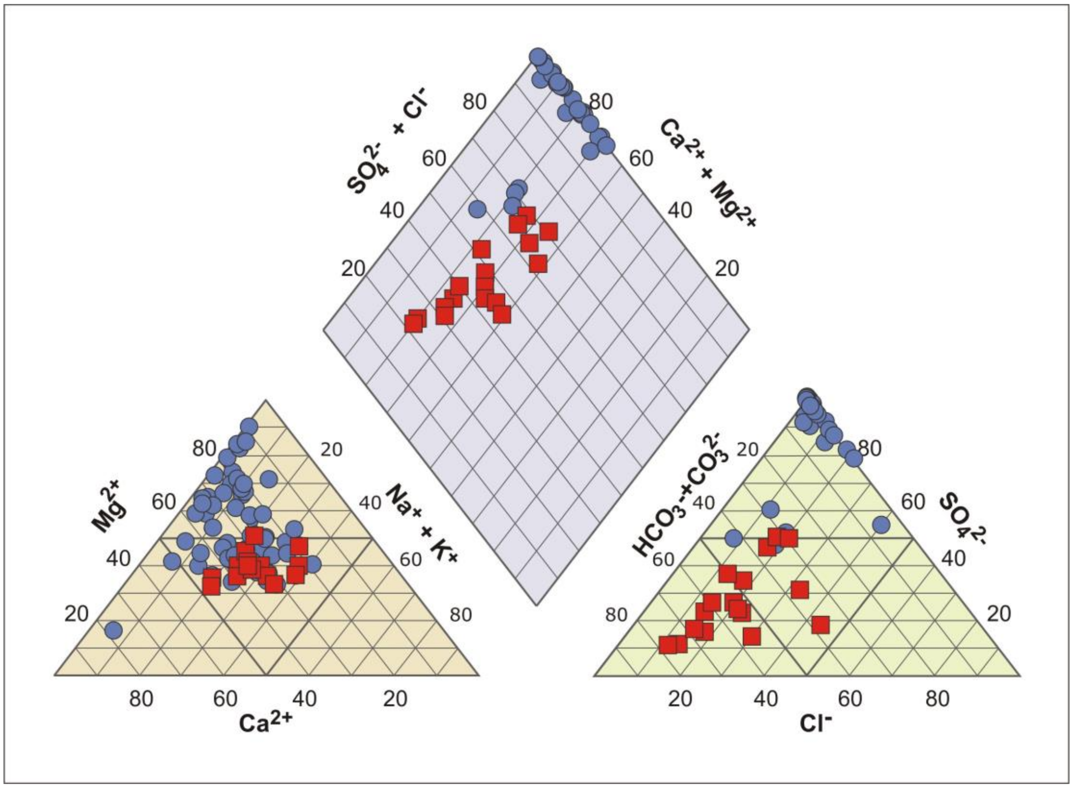

Figure 2. Piper diagram of the samples analysed (square symbols are AMD-uncontaminated samples and circle symbols are AMD-contaminated samples)

Statistical multivariate techniques were used for the analysis of 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 77% 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 sulfide 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 sulfide 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 environments, which are different from other metals (Sarmiento et al., 2004b).

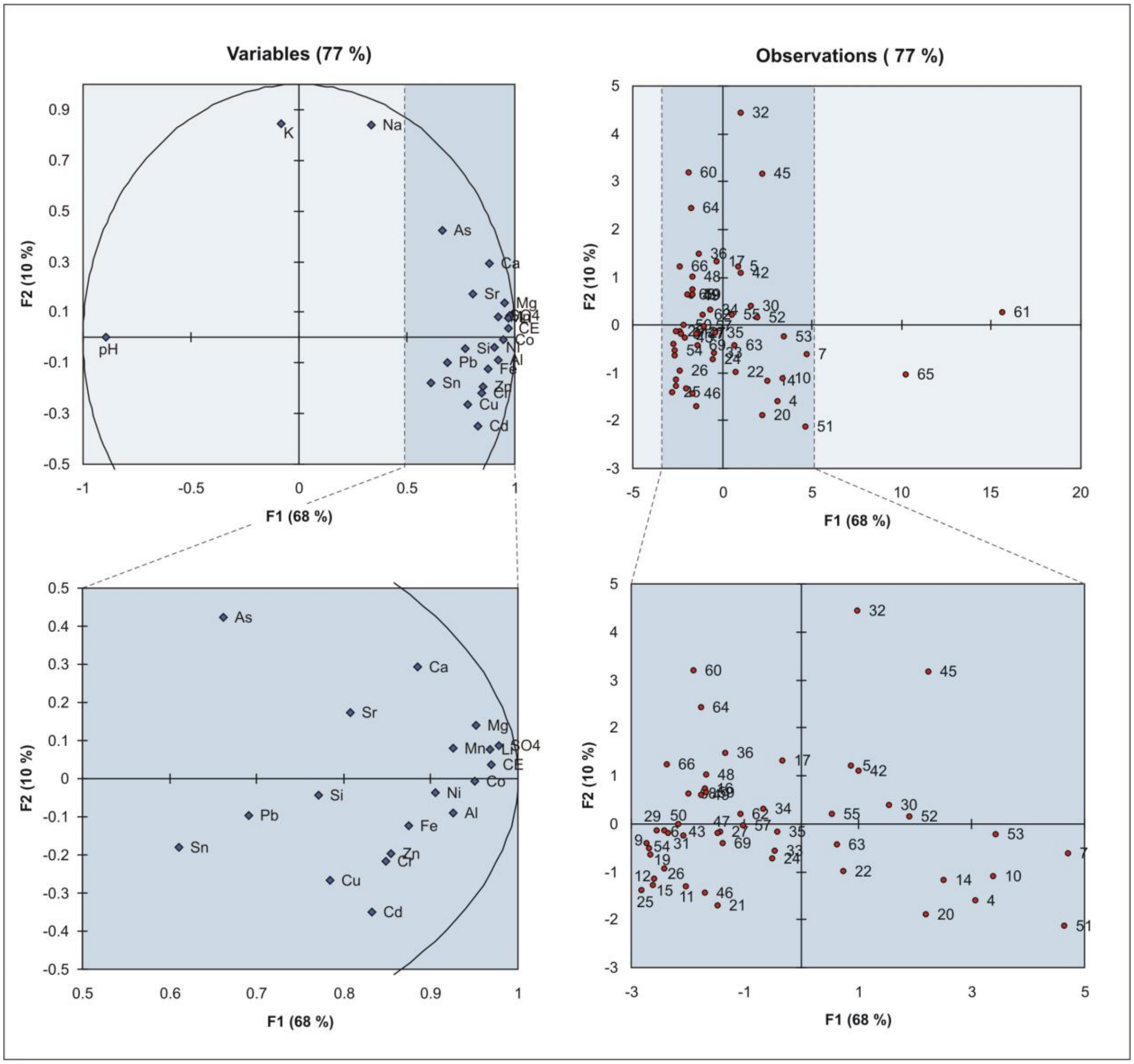

Figure 3. PCA plot between factor 1 and 2 of the variables and observation points analysed.

<u>Spatial distribution of the contamination in the Odiel basin</u>

This section shows the contamination profile in two of the most important streams of the Odiel basin: The Oraque River (e.g., Fig. 4A) and the Odiel River (e.g., Fig. 4B).

<u>Oraque River</u>. The Oraque River is the most important tributary to the Odiel River. The first mine leachate flowing into the Oraque River is from the San Telmo mine (points 51 and 52; e.g., Fig. 1). This outflow has a high level of contamination (pH 2.5, 3,400 mg/L of SO_4^{-2} and Fe and Al each 200 mg/L). Other mines flowing into the Oraque River, such as Lomero Poyatos, Valdelamusa or Tharsis (e.g., Fig. 4A), also represent important contaminant loads to the Oraque.

The Tharsis mine is the most important polluting source in the Odiel River basin, and the leachate flow is constant all year. In this leachate, concentration up to 1.7 g/L of Fe, 765 mg/L of Al, 12.4 g/L of SO_4^{-2}, 4.3 mg/L of As, etc., have been determined. The high dissolved metal 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.

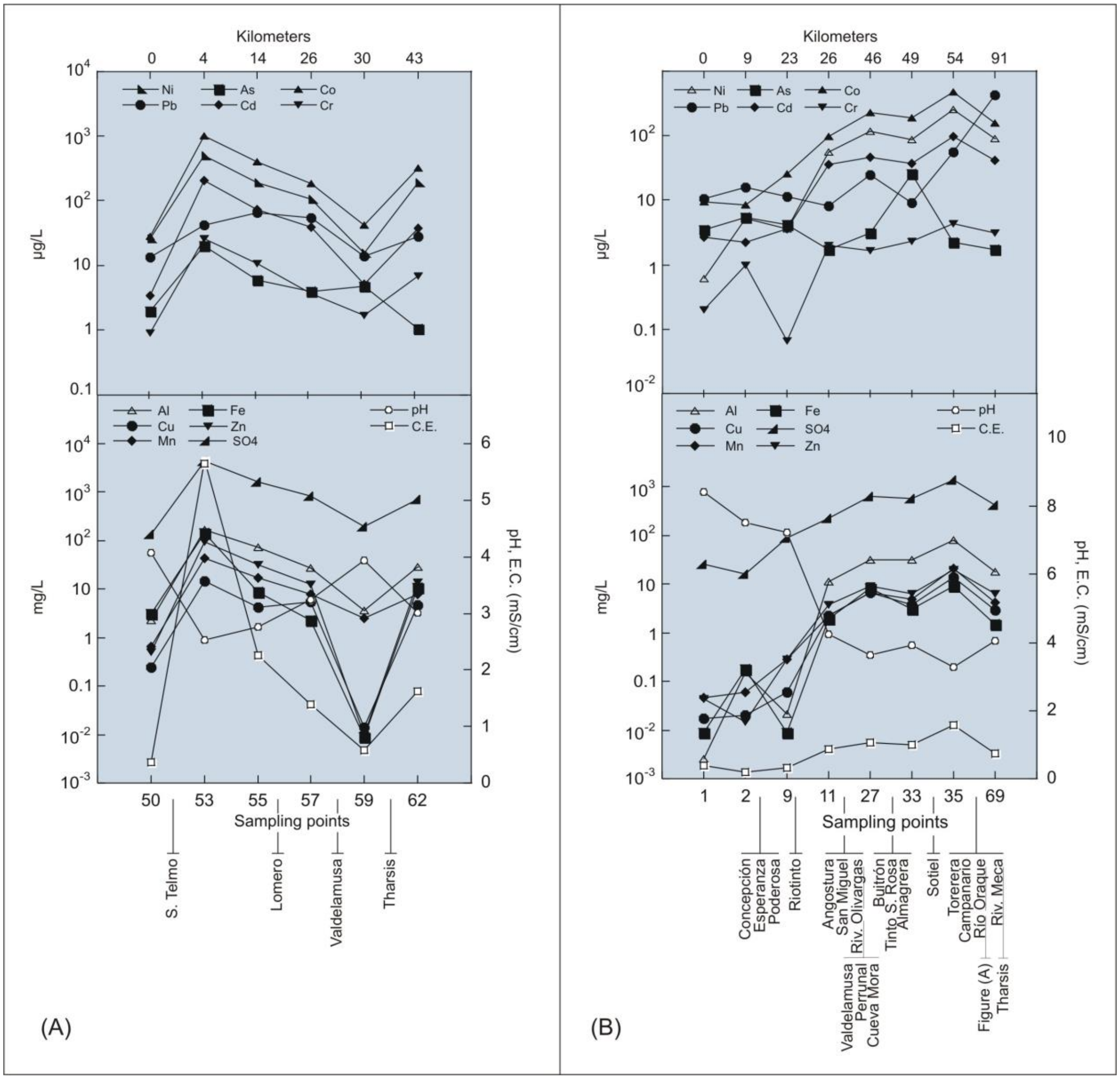

Figure 4. Evolution of some of the parameters in the ways of the Oraque River (Fig. 4A) and Odiel River (Fig. 4B). Distances are in relation to kilometres toward the estuary from the headwaters.

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 SO_4^{-2} have been measured.

Odiel River. The streams located in the northern part of the basin (points 1, 2 and 3; Fig. 1) have a HCO_3^- composition and a pH around 8. In these samples the lower concentration of SO_4^{-2} 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 sulfide 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. (e.g., Fig. 1). After 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 (e.g., Fig. 4B).

After a few kilometres from its source, the quality of the Odiel River is at its best (point 9; Fig. 4B). However, after joining the Agrio creek, that drains part of the Riotinto mining area, the water of the Odiel River is deteriorated (point 11 and following).

Other polluted streams have been monitored in the Odiel River basin, such as the Meca River (e.g., Fig. 1) which is strongly contaminated by the outflows of the Tharsis mining district. In the Meca River, electrical conductivity of 8 mS/cm, 7,500 mg/L of SO_4^{-2}, 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; Fig. 1 and 4B). At this point, the pH is about 3.5, 1.2 mS/cm of electrical conductivity, 800 mg/L of SO_4^{-2}, 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.

The contaminant load transported by the Odiel river to the Huelva Estuary

Table 2 shows the calculated mean contaminant load (in t year^{-1}) transported by the Odiel River to the Huelva Estuary based on yearly mean values for the period between 1996 to 2003.

Among the dissolved metals, the Al load is the largest, although Fe has a higher mean concentration in the river (e.g., Table 1). The Al remains longer than Fe in the water because the pH is less than 4 in these waters (e.g., Fig. 4b), therefore Al does not precipitate. The main contaminants transported by the Odiel River are the SO_4^{-2}, Al, Fe, and Zn, so the total main metals transported to the Huelva Estuary was estimated at 12,900 tons every year. Figure 5 represents the relation between the annual precipitation data and the contaminant load calculated for the different elements. As expected, the SO_4^{-2} and metal loads transported by the Odiel River are correlated with the annual mean rainfall.

Table 2. Contaminant load transported by the Odiel River

	Mean	Minimun	Maximun
Rainfall (mm)	981	376	1366
SO_4^{2-} (t yr-1)	147000	34900	305000
As (t yr-1)	23.1	3.6	41.2
Cd (t yr-1)	7.1	2.1	9.8
Cu (t yr-1)	1252	288	3020
Fe (t yr-1)	2850	611	5690
Mn (t yr-1)	1450	387	3260
Pb (t yr-1)	11.8	4.5	17.9
Zn (t yr-1)	2610	690	6590
Al (t yr-1)	4560	4440	4680
Co (t yr-1)	62.5	60.5	64.4

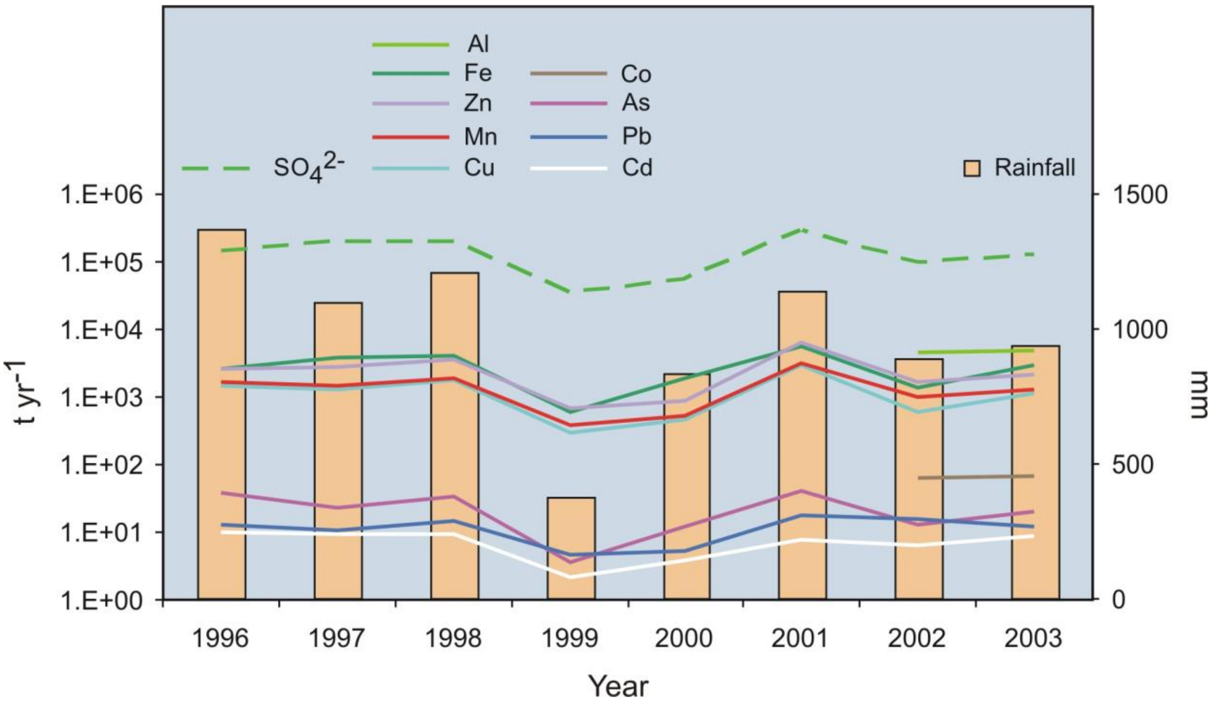

Figure 5. Relation between annual rainfall and the contaminant load transported by the Odiel River into the Huelva Estuary.

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 and Ni are located at the streams draining the Tharsis and Riotinto mining districts. The outflow from the 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. On the other hand, 419 surface water samples have been studied at the last point before the estuary and the contaminant load transported by the Odiel River has been calculated. Aluminium and Fe are the main metals transported (4,600 and 2,800 tons year^{-1} respectively).

Acknowledgements

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