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Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain)

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Abstract

This paper intends to analyse seasonal variations of the quality of the water of the Odiel River. This river, together with the Tinto River, drains the Iberian Pyrite Belt (IPB), a region containing an abundance of massive sulphide deposits. Because of mining activity dating back to prehistoric times, these two rivers are heavily contaminated. The Odiel and Tinto Rivers drain into a shared estuary known as the Ría of Huelva. This work studies dissolved contaminant data in water of the Odiel River collected by various organisations, between October 1980 and October 2002, close to the rivers entry into the estuary. Flow data for this location were also obtained. The most abundant metals in the water, in order of abundance, are zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu). Arsenic (As), cadmium (Cd) and lead (Pb) are also present but in much lower quantities. The quality of the river water is linked to precipitation; the maximum sulphate, Fe, Zn, Mn, Cd and Pb concentrations occur during the autumn rains, which dissolve the Fe hydroxysulphates that were precipitated during the summer months. In winter, the intense rains cause an increase in the river flow, producing a dilution of the contaminants and a slight increase in the pH. During spring and summer, the sulphate and metal concentration (except Fe) recover and once again increase. The Fe concentration pattern displays a low value during summer due to increased precipitation of ferric oxyhydroxides. The arsenic concentration displays a different evolution, with maximum values in winter, and minimum in spring and summer as they are strongly adsorbed and/or coprecipitated by the ferric oxyhydroxides. Mn and sulphates are the most conservative species in the water. Relative to sulphate, Mn, Zn and Cd, Copper displays greater values in winter and lower ones in summer, probably due to its coprecipitation with hydroxysulphates during the spring and summer months. Cd and Zn also appear to be affected by the same process, although to a lower degree than Cu, experiencing a slight reduction in summer with respect to Mn and sulphates.

Keywords: Odiel River; Acid mine drainage; Water pollution; Heavy metal; Ría of Huelva

1. Introduction

Both the Tinto River and the Odiel River are located in the south west of Spain and drain one of the most famous sulphide-mining regions in the world: The Iberian Pyrite Belt (IPB) which contained original reserves of the order of 1700 Mt divided up in more than 50 massive sulphide deposits; one of these being the Rio Tinto mining district described as the largest massive sulphide deposit in the world (Sáez et al., 1999).

The mineralogical composition of these deposits is dominated by pyrite (FeS_2), with lesser amounts of

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sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS) and other sulphides containing accessory amounts of Cd, Sn, Ag, Au, Co, Ni, etc.

Sulphides are stable and very insoluble in reducing conditions. Naturally, the pyrite and associated sulphides remain buried in anoxic conditions and only very minor parts of the ore bodies outcrop. Sulphide oxidation takes place once the minerals are exposed to atmospheric conditions generating acidity and sulphates and liberating Fe and accessory metals.

Mining activity in the IPB dates back to prehistoric times, and there is evidence to indicate that the Tinto and Odiel Rivers have transported appreciable quantities of metals for over 4.500 years (Leblanc et al., 2000; Nieto et al., 2004). Mining activity in the IPB became a very important industry during Roman times and contributed heavily to the contamination of these two rivers. After the Roman period, mining activity diminished until the commencement of the industrial revolution in the second half of the 19th century when numerous deposits were intensely exploited, leaving enormous amounts of mining waste in the Odiel and Tinto basins. Today, there is no active sulphide mining in the IPB; however, the contaminating power of the enormous amounts of mining waste generated over the centuries of exploitation remain active and will continue to generate contaminant products and acidity for a long time to come (Younger, 1997).

The Odiel basin has a surface area of 2.333 km^2 and a river 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 too has abundant rains although during the summer months, rainfall is practically nonexistent.

The Tinto and the Odiel flow into a coastal wetland known as the Ría of Huelva Estuary which forms part of a very important Natural Reserve (Marismas del Odiel) famous for its high ornithological diversity and for the presence of halophytic vegetation. This area receives not only contaminants transported by the Tinto and Odiel Rivers but also waste from a large industrial zone located close to the town of Huelva (Fig. 1).

Due to the intense mining activity, these rivers display a high degree of contamination with pH values typically below 3, and high contents of sulphates and metals, mainly Fe, Zn, Mn and Cu. These

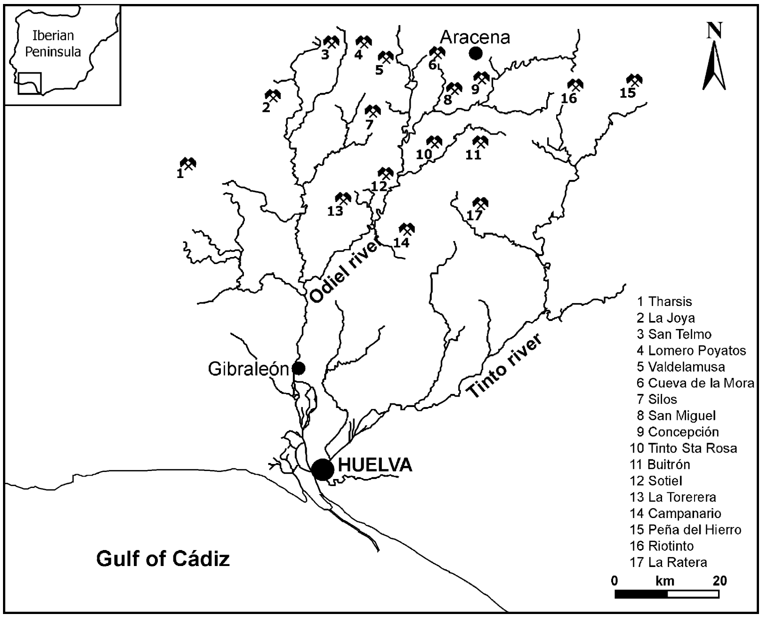

Fig. 1. Location of the Tinto and Odiel rivers, the main mines located within their basins and the Gibraleón control station.

extreme conditions are optimal for the development of ferro- and sulpho-oxidising acidophilic bacteria, together with a great diversity of eukaryotes (Amaral Zettler et al., 2002). The metabolism of these organisms, especially of the chemolithotrophic prokaryotes, is responsible for the maintenance of this extreme environment throughout the continuous production of Fe^{3+} by aerobic oxidation of the ferrous iron in solution (Fernández-Remolar et al., 2004).

Publications covering the subject of contamination of the Tinto and Odiel Rivers are numerous but mostly deal with contaminants within the estuary (e.g., Nelson and Lamothe, 1993; Elbaz-Poulichet and Dupuy, 1999; Achterberg et al., 2003; Braungardt et al., 2003) and the Gulf of Cádiz (e.g., van Geen et al., 1997; Elbaz-Poulichet et al., 2001). Other studies focus on characterising the form in which the metals are found in the river and estuarine sediments (Hudson-Edwards et al., 1999; Morillo et al., 2002; Galán et al., 2003). The composition and generation of the leaching acidic waters in the Odiel basin have been the subject of recent works (Sáinz et al., 2002, 2003). Sáinz et al. (2004) used quality data of the Tinto and Odiel Rivers between 1988 and 2001 (with an average of three analyses every year) to calculate the metal discharge to the estuary. However, there is no study that specifically focuses on the physical–chemical parameters of the water in the Tinto and Odiel Rivers and their seasonal variations, although some earlier papers presenting analytical data from occasional nonsystematic water quality samples exist.

It is in this context that this study is presented; the main objective being the characterisation of the physical–chemical properties of the Odiel River and the variations experienced throughout the year, in response to river flow oscillation, and also the understanding of the processes controlling the concentration of the dissolved contaminants in the river water.

2. Methodology

2.1. Existing data

The principal sources of data for this study have been the analyses undertaken between October 1980 and October 2002 by the Guadiana Hydrographic Confederation at the Gibraleón study station located close to where the Odiel River enters the estuary (Fig. 1). These data have a monthly periodicity until the year 1986/87, and twice monthly since then, although there are frequent breaks in the series (data are missing from 23 months of the 22 years studied). The parameters analysed have also changed over time. The most consistent variables are temperature, electric conductivity, pH, dissolved oxygen, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, NH_4^{+}, SiO_2, As and heavy metals including Cd, Cu, Fe, Mn, Pb and Zn.

Data from a series of analyses undertaken in the same location by the "Delegación Provincial de Huelva de la Consejería de Medio Ambiente de la Junta de Andalucía" (Huelva local delegation of the Environmental Council of the Andalusia Regional Government) between March 1996 and May 2001 were also made available. The periodicity of these data is weekly during 1996 and 1997 and twice weekly for the rest of the time. The parameters measured in these controls were temperature, electrical conductivity, pH, dissolved oxygen, suspended matter, SO_4^{2-}, As, Cd, Cu, Fe, Mn, Pb and Zn. Besides, in the Andalusia Regional Government's littoral coastline waters vigilance scheme, water analysis sampling was also undertaken at this same location and analytical results from 1988 to 1999 were made available to us, with a reading of three samples a year. These are the analyses used by Sáinz et al. (2004). These controls measured the pH, electric conductivity, As, Cd, Cu, Fe, Mn, Pb and Zn as well as others.

Finally, since February 2002, we have been undertaking a weekly control on the quality of the Odiel River. A large number of elements were analysed following the methodology described later, although this study only deals with the variables coincident with the earlier samplings, which are pH, electrical conductivity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, SiO_2, As, Cd, Cu, Fe, Mn, Pb and Zn.

Daily flow data for the period 1980/81 to 2001/02 were also obtained from a monitoring station operated by the Guadiana Hydrographic Confederation, located close to the point used for the previously mentioned water quality sampling. This data set is continuous, although there is a large gap in the data between November 1997 and February 1999 caused by malfunctioning of the monitoring station.

After the recompilation of these data, clearly anomalous results were eliminated based on the relationship between the different variables and by observing their temporal cycles. There were more apparent issues with data pertaining to the early years of the series. In the years where the data from various sources are available, there is a good correlation between the datasets, although some significant differences exist in the concentration of Mg^{2+} and SiO_2 between samples analysed by ourselves and those belonging to the Hydrographic Confederation of the Guadiana's quality control network. Despite this, these differences do not influence the conclusions of this work which focuses on the annual pH evolution, electrical conductivity, sulphates, arsenic and heavy metals.

Once the data had been screened, basic statistics and principle relationships using the Spearman correlation coefficient (given that the majority of the data do not show a normal distribution) were obtained, graphs of the seasonal variation were prepared and studied and finally, a better understanding of the factors that control the behaviour and distributions throughout the year was possible.

2.2. Analytical methodology

This section deals only with the sampling undertaken by us, which followed a protocol similar to that described by Johnson (1986). For cation determination, the samples were collected in 250-ml high-density polythene bottles previously washed in 10% nitric acid and then with mili-Q water (18.2 MΩ), and only prewashed in mili-Q water (18.2 MΩ) were samples used for anion determination. Conductivity and pH were measured in situ and later, the samples were filtered through 0.45-μm pore Teflon filters. The samples destined for cation determination were acidified with suprapure nitric acid and all of the samples remained refrigerated until analysis.

The chemical analysis was undertaken at the Central Research Services of the Huelva University following a custom-designed protocol specific to these types of water (Ruiz et al., 2003a) that was contrasted with international and natural calibrated standards (Ruiz et al., 2003b). The cations were analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Jobin Yvon (JY ULTIMA 2) spectrometer fitted with an ultrasonic nebuliser (CETAC U6000AT+) to improve the sensitivity of the equipment. The anions were determined by ion chromatography using a Dionex DX-120 machine fitted with an AS 9-HC of 4 × 250 mm column and a 4 mm ASRS-ULTRA suppressing membrane.

3. Results and discussion

Due to the main part of the Odiel basin being underlain by impermeable materials and therefore having low natural regulation, river flow displays a very strong inter-and intraannual variation, in response to the rainfall regime. Flow rates are rapidly affected by rainfall and the river can completely dry up in the summer months. The average annual river flow of the Odiel at Gibraleón during the period between 1980/81 and 2001/02 was 14.8 $m^3 s^{-1}$, with a minimum of 0.4 $m^3 s^{-1}$ in 1991/92 and a maximum of 67.8 $m^3 s^{-1}$ in 2000/01.

3.1. Basic statistics of the physical–chemical characteristics

The data in Table 1 show a summary of the basic statistics of the analysed parameters; note that pH values are very constant with a minimum of 2.5, 3.2 at the 75th percentile, and with a mean of 3.1.

Pollution associated with mining contamination shows high sulphate concentrations, with an average value of 1204 mg l^{-1}, followed in order of abundance by Zn (mean 24.2 mg l^{-1}), Fe (23.5 mg l^{-1}), Mn (13.7 mg l^{-1}) and Cu (7.6 mg l^{-1}). Concentrations of lead, cadmium and arsenic are much lower (average values 0.21, 0.08 and 0.07 mg l^{-1}, respectively).

The major ions, calcium, magnesium and silica, are also found in high concentrations (Table 1). However, in contrast, concentrations of chloride and sodium are very low due to the absence of evaporite rocks in the Odiel River basin.

In summary, the composition of the Odiel River at Gibraleón displays a high degree of mining-derived pollution, elevated concentrations of heavy metals, high sulphate content and very low pH values. The only parts of the river free from contamination are restricted to the higher parts of the basin upstream of the mining district.

Table 1
Basic statistics of the variables analysed during the period from 1980/81 to 2001/02

		Data number	Mean	Median	Mode	Standard deviation	Variation coefficient (%)	Minimum	Maximum	Percentile 25	Percentile 75
pH		550	3.07	2.93	2.80	0.47	15	2.50	6.30	2.80	3.20
EC	mS/cm	550	1.94	1.86	2.00	0.97	50	0.16	4.80	1.24	2.53
SO_4^{2-}	mg l^{-1}	393	1204	1058	650	776	64	50.7	3960	627	1576
Cl^-	mg l^{-1}	219	23.6	20.5	22.0	12.3	52	6.5	68.6	15.1	29.6
Ca^{2+}	mg l^{-1}	305	112.6	91.5	121.5	80.2	71	10.8	413.5	54.1	150.3
Mg^{2+}	mg l^{-1}	305	94.0	87.6	51.0	52.7	56	6.4	259.2	56.5	128.1
Na^+	mg l^{-1}	324	26.6	22.8	15.4	14.3	54	5.7	90.0	17.0	32.1
K^+	mg l^{-1}	231	3.2	2.7	2.3	1.9	59	0.1	12.2	2.0	3.9
NH_4^+	mg l^{-1}	135	1.49	0.86	0.90	1.92	129	0.01	13.50	0.52	1.70
SiO_2	mg l^{-1}	286	50.0	40.5	21.1	35.8	72	1.1	157.8	22.1	74.6
NO_3^-	mg l^{-1}	173	5.5	4.4	1.0	4.3	79	0.4	28.8	2.6	7.1
As	mg l^{-1}	196	0.068	0.008	0.001	0.316	466	0.0002	3.300	0.003	0.024
Cd	mg l^{-1}	495	0.081	0.070	0.040	0.058	71	0.001	0.380	0.040	0.109
Cu	mg l^{-1}	525	7.60	6.74	2.92	4.79	63	0.01	37.62	4.59	9.39
Fe	mg l^{-1}	469	23.47	13.07	2.61	28.59	122	0.03	262.71	5.09	32.51
Mn	mg l^{-1}	498	13.70	11.49	6.83	9.91	72	0.49	60.33	6.68	17.94
Pb	mg l^{-1}	294	0.207	0.121	0.090	0.224	109	0.004	1.180	0.070	0.251
Zn	mg l^{-1}	506	24.23	19.26	5.18	18.57	77	0.17	130.23	11.54	31.01

EC: Electrical Conductivity. Variation coefficient is calculated as percentage of standard deviation respect mean.

3.2. Seasonal variation

Fig. 2 displays the seasonal variation of some of the variables analysed as box-and-whisker plots. *N* represents the number of data; the length of the box represents the interquartile range, which contains 50% of the values, and the heavy horizontal line inside the box indicates the median. The "whiskers" are lines that extend from the box to the highest and lowest values excluding outliers (○) and extremes (*). Outliers are defined as cases in which the values are between 1.5 and 3 times larger than the length of the box from its upper or lower border; those greater than 3 times are extremes.

This figure also displays the seasonal evolution of the mean monthly river flow over the time period, which, due to its high variability, has been plotted on a logarithmic scale. River flow distribution is strongly linked to rainfall, with increasing values in autumn, maximum in December and January and diminishing values after this and until August when it is common to experience zero flow (represented on the logarithmic scale as a flow rate of 0.001 $m^3 s^{-1}$). During April, in response to the spring rains, the downward trend is broken and a slight increase is produced (Fig. 2).

The pH values (Fig. 2) remain constant around 3 for most of the year, except during the winter months (especially January and February) when it is slightly higher but always with the 75th percentile below 4. On occasions, extreme values above 6 can be reached. These constant values are due to the buffer effect of the precipitation of iron oxyhydroxides.

The sulphate content decreases in the winter months, reaching minimum values in January and February, coinciding with the highest pH values (Fig. 2). Throughout the spring and summer, the sulphate concentration increases, reaching maximum values in September and October (Fig. 2). The electrical conductivity, calcium, magnesium and the rest of the major ions are not represented in the figure as they exhibit a similar pattern.

Cd, Mn and Zn (the last represented in Fig. 2) also display a similar pattern to the sulphates, with maximum values during autumn and the first winter months, minimum in January and an increase during spring and summer. Cu exhibits a similar behaviour, with lowest values in January and February and greatest values in the autumn, although the evolution is not as clear as the previously described metals.

In the case of Pb, there exist few data in the winter months due to it being frequently below the detection

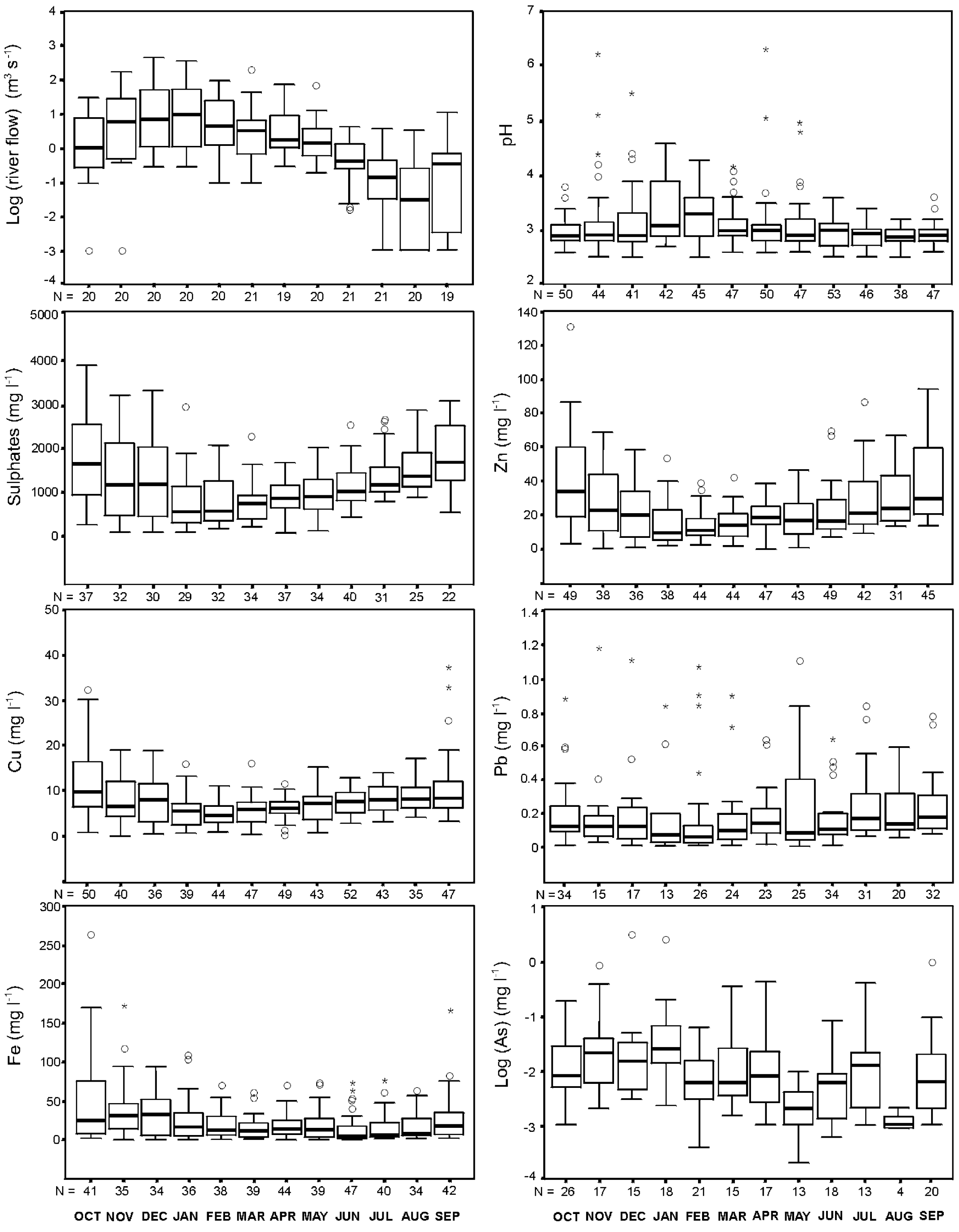

Fig. 2. Box-and-whisker plots of the monthly evolution of some of the variables typical of mining pollution. See text for discussion.

limit (0.001 mg l^{-1} for most of the samples). The seasonal pattern is unclear, with many outliers and extremes. However, it can be suggested that the lowest contents are recorded in winter.

Iron displays a different distribution where during the autumn and first winter months, maximum values are reached and, in contrast to the other metals, during summer, minimum concentrations are experienced.

Due to its great variability (Table 1), arsenic concentration is represented on a logarithmic scale and displays a distribution similar to Fe, with maxima in winter and minima in summer. Few As data are available for the summer period as concentrations are commonly below detection limit (0.001 mg l^{-1} for most of the samples).

3.3. Relationships between the contaminant elements

With the aim of analysing the relationship between variables typical of mining related contamination, a correlation matrix was prepared and, given that the majority of variables do not show a normal distribution, the Spearman correlation coefficient was used (Davis, 1986). In Table 2, the correlations obtained to a significance level of 0.01 ($p < 0.01$) are displayed.

Evident in the data is the existence of a tightly related group of variables: electrical conductivity and sulphate, Mn, Zn and Cd concentrations (correlation coefficient above 0.87). Sulphate concentration fundamentally controls the electrical conductivity of the water, given that the rest of the ions exhibit much lower concentrations (Table 1) and thus the very high observed correlation between these two variables. The association of Mn, Zn and Cd with sulphate and electrical conductivity is produced by their similar distribution throughout the year (Fig. 2). This group also displays significant, but lower, correlations with Cu, and even lower with Fe and Pb (Table 2). All of these variables display a negative correlation with pH (Fig. 3).

River flow exhibits a positive relationship with pH and a negative correlation with the rest of the variables, although the correlation is notably lower with respect to Fe and Pb. The negative correlations are caused by the diluting effect produced during large storms, although in times of heavy rain, there is an increase in the amount of contaminant mining waste load (Sáinz et al., 2002). During the mixing of large volumes of noncontaminated runoff water, the pH increases and the sulphate and metal content decrease (except As), and as a result, the electrical conductivity decreases. When the river flow decreases during the spring and summer, the concentrations of contaminants begin to recover, reaching maxima in the summer due to sulphide-oxidising bacterial activity increasing with the temperature; and simultaneously, a concentrating effect of the dissolved pollutants occurs in the water due to water evaporation.

The correlation between flow and the other variables is best defined when using data from only one hydrological year instead of the entire series. Fig. 4 shows the relationship between flow and electrical conductivity in years 1996/97 and 2000/01. In 1996/97, which has the greatest number of measurements, the correlation is worse although all of the points that diverge from the general trend correspond to the

Table 2
Matrix of Spearman correlation coefficients of the variables associated with mining pollution (only shown values with $P < 0.01$)

	Flow	pH	EC	SO_4^{2-}	As	Cd	Cu	Fe	Mn	Pb	Zn
Flow	1.00										
pH	0.42	1.00									
EC	– 0.61	– 0.78	1.00								
SO_4^{2-}	– 0.60	– 0.76	0.95	1.00							
As					1.00						
Cd	– 0.52	– 0.76	0.87	0.89		1.00					
Cu	– 0.46	– 0.72	0.81	0.85		0.91	1.00				
Fe	– 0.22	– 0.72	0.68	0.65	0.38	0.70	0.73	1.00			
Mn	– 0.61	– 0.71	0.93	0.95		0.93	0.85	0.63	1.00		
Pb	– 0.23	– 0.70	0.62	0.57	0.34	0.66	0.53	0.54	0.55	1.00	
Zn	– 0.52	– 0.79	0.92	0.92		0.93	0.89	0.78	0.94	0.69	1.00

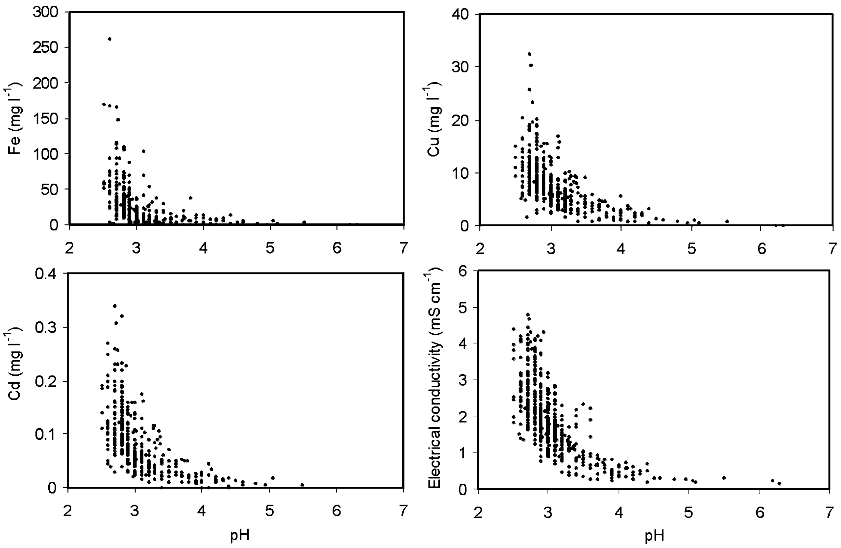

Fig. 3. Relationship of pH versus Fe, Cu and Cd concentrations and electrical conductivity.

month of October. In the graphs representing annual evolution (Fig. 2), the sulphate (and therefore electrical conductivity), Zn, Mn, Cu and Fe concentrations show maxima during September and October as a result of the first rains of the hydrological year. The runoff waters produce a washing effect and redissolution of the weathering products of pyrite, which have accumulated during the summer months, becoming themselves contaminated with these products. In this way, intermediate flow rates show the maximum values for electrical conductivity, sulphate, Zn, Mn, Cd, Cu and Fe. If the data corresponding to the month of October are removed, a good linear correlation between river flow (on a logarithmic scale) and electrical conductivity is observed (Fig. 4a). If not especially intense rainfalls are recorded in autumn, the aforementioned increase in the contaminant contents can be observed in winter (Fig. 4b).

3.4. Behaviour of contaminant elements

3.4.1. Sulphates, manganese, zinc and cadmium

Sulphates, manganese, zinc and cadmium possess strong correlations, given their common origin and their similar behaviour in acidic waters. Sulphate is a very mobile anion and the precipitation of gypsum and other sulphate salts can only occur when high concentrations are reached.

Mn does not form part of the massive sulphide ores. However, Fe/Mn mineralizations commonly occur close to the massive sulphide, forming chert caps. There are almost 100 previously worked Mn deposits within the IPB (Sáez et al., 1999). The acidic waters, on contact with these deposits, rapidly dissolve large quantities of Mn. In oxidising acidic conditions, manganese is present in the +2 oxidation state, behaving in a similar way to Zn and Cd. These metals are strongly sorbed in neutral or alkaline pH conditions, although in acidic conditions are desorbed and are stable in solution, thus the strong correlation with the sulphates.

The concentration of these elements in the water is conditioned by seasonal river flow variation. During the summer, an intense weathering of the sulphides occurs due to the rise in temperature and increased evaporation leads to soluble iron hydroxysulphates precipitation in the mine dumps, tailings dams and on the margins of the acid rivers. The most abundant minerals precipitated are copiapite $[Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 20H_2O]$, coquimbite $[Fe_2(SO4)_3 2H_2O]$, melanterite ($FeSO_4 7H_2O$) and rozenite ($FeSO_4 4H_2O$), all containing large amounts of Cu, Zn, Cd and Pb amongst others (Buckby et al., 2003). These minerals are highly soluble salts dissolving rapidly with the arrival of the first autumn rains. The lowest concentrations of these elements, due to dilution effects,

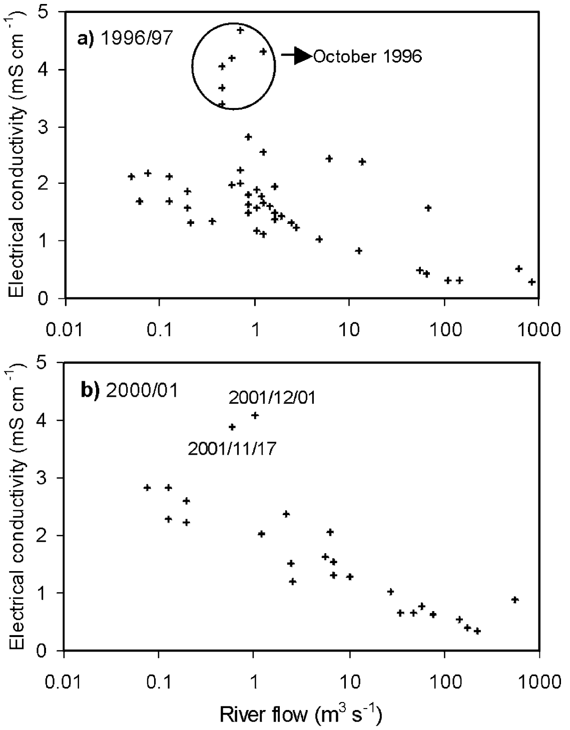

Fig. 4. Relationship of river flow rate versus electrical conductivity during (a) 1996/97 and (b) 2000/01.

occur during the period when river flows are at their highest.

Nevertheless, some differences exist between the behaviour of Mn on one side and Cd and Zn on the other. In Fig. 5, it is possible to see how, during summer, the Cd values increase less than Mn. The Zn/Mn and Zn/SO_4^{2-} relationships present the same annual distribution patterns. This behaviour could be due to a certain coprecipitation or sorption of Cd and Zn on iron oxyhydroxides and hydrosulphates which is commented on later.

3.4.2. Copper

Copper concentration undergoes a lower increase in summer than the sulphates, Mn, Zn, and Cd (Fig. 2). This is confirmed if we represent, for example, the annual evolution of the Cu/Mn relationship (Fig. 6), in which a clear seasonality can be observed, with maxima in winter and minima in summer. Hence, with respect to the aforementioned elements, copper concentration decreases during the summer and increases during winter. Thus, Cu displays slightly weaker correlations with sulphates, Mn, Zn and Cd (values between 0.85 and 0.91) than those that exist within this group itself (between 0.89 and 0.95).

As is the case of the variations of Zn and Cd in relation to Mn and sulphates, this behaviour appears to be related to the coprecipitation of Cu together with iron oxyhydroxides and hydroxysulphates. During the precipitation of these compounds, the sorption or coprecipitation of Cu would occur in greater proportions than Cd, Mn and Zn. For the same reason, sulphates and Mn would become enriched in the water with respect to Cd and Zn.

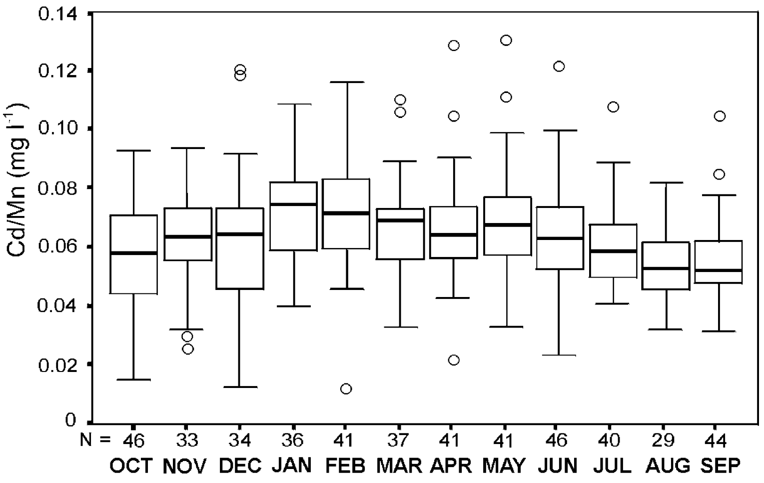

Fig. 5. Box-and-whisker plot of the monthly evolution of the Cd/Mn ratio.

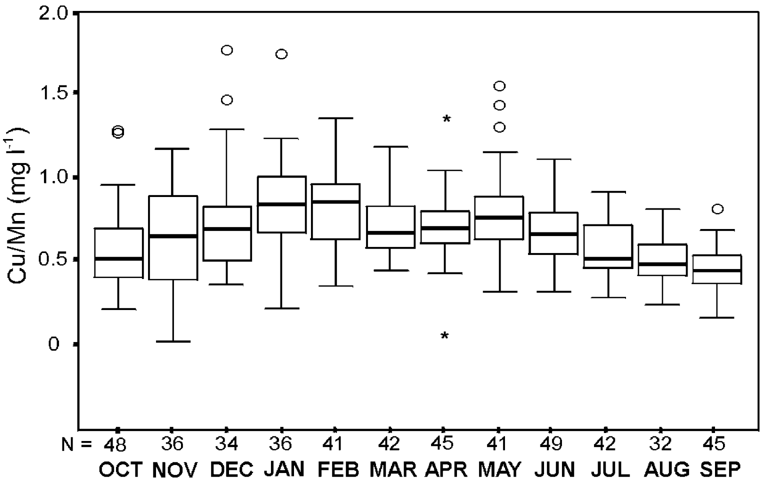

Fig. 6. Box-and-whisker plot of the monthly evolution of the Cu/Mn ratio.

These results are in agreement with those of Alpers et al. (1994a) and Gray (1998), such that in acid mine drainage, Zn becomes enriched relative to Cu during the summer; this being attributed to the formation of secondary sulphate minerals such as melanterite ($FeSO_47H_2O$) which would preferentially incorporate Cu before Zn. In the Rio Tinto basin, Buckby et al. (2003) found that the most abundant hydroxysulphates that precipitate during summer (copiapite, coquimbite, melanterite and rozenite) contain higher proportions of Cu than Zn. Also in agreement with our work are the findings in the study of the sediments of the Odiel River by Galán et al. (2003) who describe that proportionally higher Cu concentrations, relative to Mn, Zn and Cd, are found associated with the reducible fraction.

3.4.3. Iron

Fe displays a lower negative correlation coefficient with river flow than the elements mentioned above. Fe also has weaker correlation with electrical conductivity, sulphates, Zn, Cd, Mn, etc., indicating a different

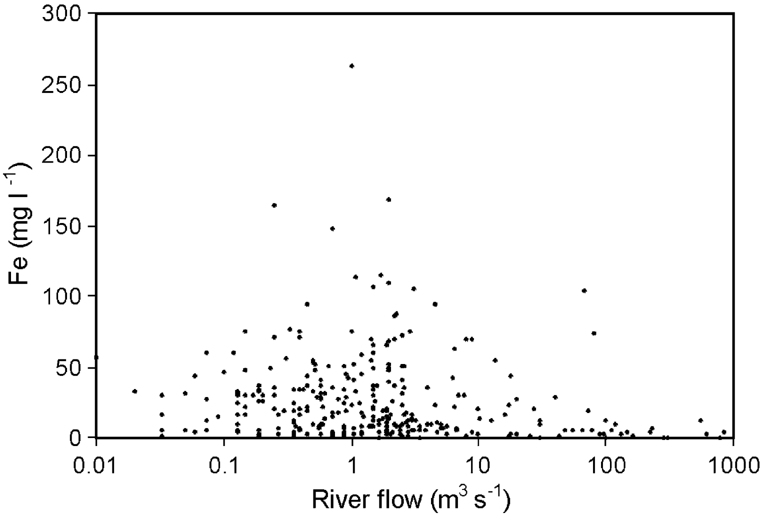

Fig. 7. Relationship of river flow rate versus Fe content.

hydrochemical behaviour. In the seasonal variation of Fe concentrations (Fig. 2), it can be seen how this element, opposite to the others, has lowest concentrations during summer.

The correlation between Fe and river flow is weaker owing to the fact that in summer, (with low flow rates) the Fe content is lower (Fig. 7) contrary to the case of others variables (Figs. 2 and 4). The most plausible explication for this is the great precipitation of iron oxyhydroxides during summer.

During the pyrite oxidation process, two moles of sulphate are produced for every mole of Fe; this relationship equates in mg l^{-1} terms of Fe/SO_4^{2-} to 0.29. This relationship is similar to that found by Sáinz et al. (2003) for mining wastes in the Odiel basin, which contained average pH values between 2.2 and 2.6. On mixing these leach products with more alkaline waters, or due to the hydrolysis of silicate minerals that may come in to contact, the acidity reduces and the precipitation of iron oxyhydroxides occurs, buffering the pH of the water to around 3. As this process occurs, the concentration of Fe in the water reduces although the pH remains constant.

A relationship of Fe/SO_4^{2-} closer to 0.29 indicates a composition closer to the leach products derived from the weathering of pyrite. As the relationship is lower, this indicates a "more evolved" water, where through mixing or mineral hydrolysis processes, it loses Fe whilst the sulphate remains in solution (or become weakly diminished due to the precipitation of sulphated salts). Although sulphates do not have exactly a conservative behavior, sulphate concentrations are sufficiently high compared to Fe that they can be considered as conservative (Berger et al., 2000). Fig. 8 represents the variation of the Fe/SO_4^{2-} relationship over the year where the highest values are observed in winter and the lowest in summer. In winter, the circulation of water is rapid within the basin, such that the water flowing in the Odiel River has a higher Fe/SO_4^{2-} relationship caused by a lower ferric oxyhydroxide precipitation. For this reason, the Fe content does not show such a strongly defined decrease in winter when compared to sulphate, Mn, Zn, and Cd. In summer, the water drained by the Odiel River has a slower circulation through the basin and is in contact with minerals in the soil and subsoil for a longer period, producing more efficient hydrolysis of silicate minerals, and therefore, a greater precipitation of Fe and a lower Fe/SO_4^{2-} relationship. In addition, the precipitation of ferric oxyhydroxide in summer is favoured by increased rate of bacterial oxidation of Fe^{2+} to Fe^{3+} due to higher temperatures (Jaynes et al., 1984).

In Fig. 9, it can be seen how the waters with higher Fe content have a stronger Fe/SO_4^{2-} relationship where a decreasing Fe content due to the precipitation of oxyhydroxides causes the relationship to decrease. In the same way, increased Fe oxyhydroxide precipitation during summer increases the amount of Mn, Zn, Cd, Cu and Pb, compared to Fe and, in contrast, in

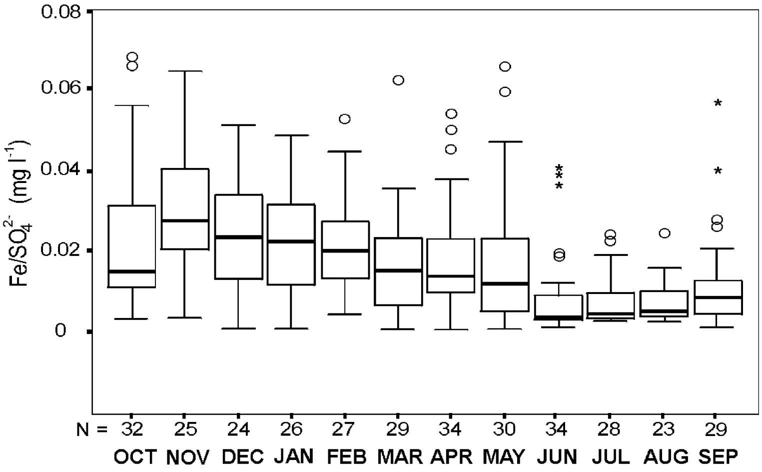

Fig. 8. Box-and-whisker plot of the monthly evolution of the Fe/SO_4^{2-} ratio.

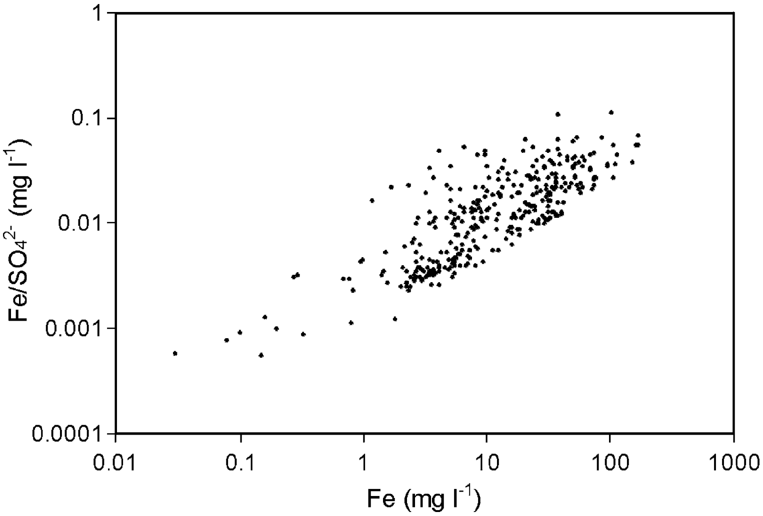

Fig. 9. Relationship of the Fe content versus the Fe/SO_4^{2-} ratio.

winter, the proportion of Fe relative to the other metals increases.

3.4.4. Arsenic

Arsenic is an element with a pattern clearly different from the other variables, showing a much higher variation coefficient than the rest and only significant correlations with Fe and Pb (Table 2). Fig. 2 shows how the arsenic content undergoes an increase during the winter months, with minima during the summer.

In oxidising acidic conditions, as experienced in the Odiel River, arsenic is present in a 5+ oxidation state and is mostly found as arsenate anions. The arsenates form strong complexes with the surface of the ferric oxyhydroxides, as they are strongly adsorbed by them (Williams, 2001; Casiot et al., 2003). This process is pH dependent, where, in more

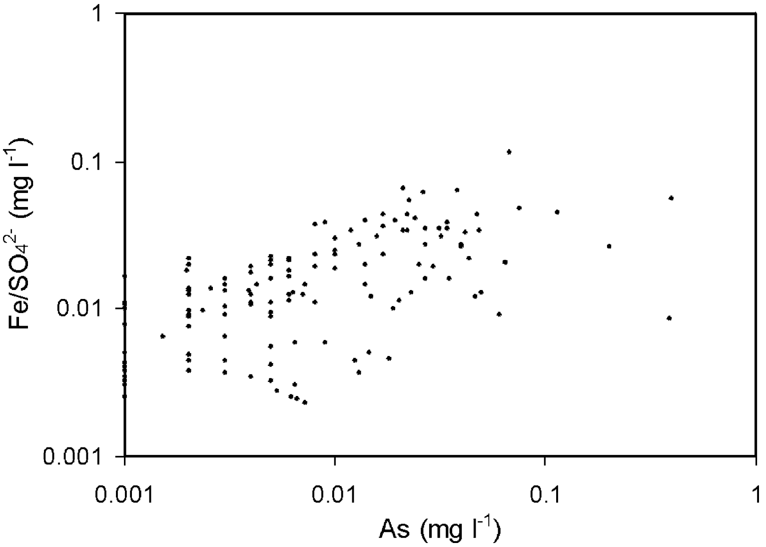

Fig. 10. Relationship of As content versus the Fe/SO_4^{2-} ratio.

alkaline conditions, the degree to which the arsenates are adsorbed decreases (Smedley and Kinniburgh, 2002). This is to say that the arsenic liberated during the oxidation of arsenical pyrite will be adsorbed on commencement of ferric oxyhydroxide precipitation, thus lowering the As concentration in the water. In Fig. 10, it can be seen that the As content decrease in parallel with the decrease of the Fe/SO_4^{2-} relationship, that is, during increased precipitation of Fe oxyhydroxides.

During periods of high river flows, when the waters circulating through the Odiel River exhibit a high Fe/SO_4^{2-} relationship, or in other words have undergone little ferric oxyhydroxide precipitation, As concentrations will be at their highest. The results for sediments reported by Galán et al. (2003) support this hypothesis: the authors' finding that As in sediments of the Odiel and Tinto Rivers is almost exclusively contained within the reducible fraction, which represents the ferric oxyhydroxides.

The slightly higher pH values during winter (Fig. 2) can also influence the increase of arsenic in this period, favouring the desorption of arsenate ions from the surface of the ferric oxyhydroxides (Williams, 2001). Fig. 11 shows how, by increasing the pH, the As concentration relative to Fe also increases, which may be due to this desorption process caused by the raising of the pH.

3.4.5. Lead

The mobility of Pb in acid mine waters is low due to the low solubility of anglesite ($PbSO_4$), causing concentrations of Pb in such waters not to be very high (Alpers et al., 1994b). Other minerals that can retain Pb in considerable amounts, and whose existence is known in the Tinto River basin, are beudantite [$PbFe^{+3}(AsO_4)(SO_4)(OH)_6$; Nieto et al., 2003] and beaverite [$Pb(Fe,Cu)_3(SO4)_2(OH)^6$; Hudson-Edwards et al., 1999]. Buckby et al. (2003) also report that Pb can be found in high quantities in gypsum in the Tinto basin.

Due to the relatively lower solubility of these minerals, Pb generated by galena oxidation is relatively immobile and has low concentrations (Table 1). Thus, Pb displays a low correlation with the other elements; maximum correlation coefficients are with Zn (0.69) and Cd (0.66). The seasonal distribution of Pb does not show a clear evolution throughout the year.

4. Conclusions

As a consequence of the intensive mining of the massive sulphide deposits that has occurred historically in the Odiel River basin, its waters have pH values below 3 and have elevated metal and sulphate

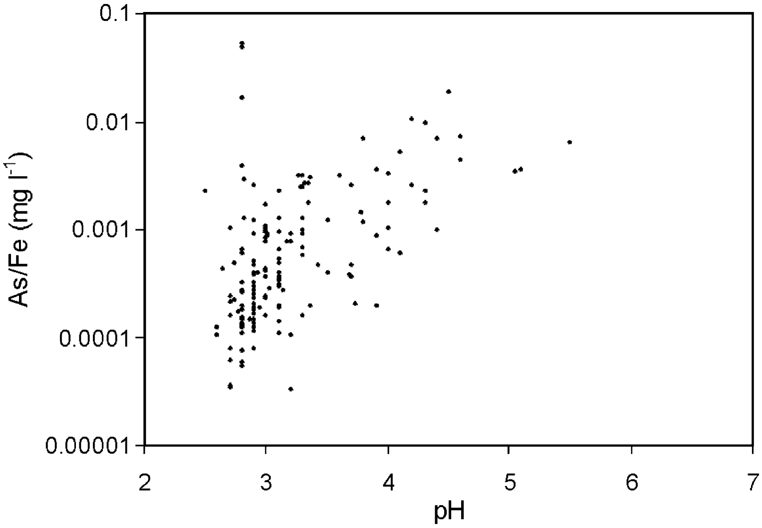

Fig. 11. Relationship of pH versus the As/Fe ratio.

contents most of the year round. The average concentrations of dissolved pollutants prior to entry in to the estuary between 1980/81 and 2001/02 were 1204 mg l^{-1} of sulphates, 24.2 mg l^{-1} Zn, 23.5 mg l^{-1} Fe, 13.7 mg l^{-1} Mn and 7.6 mg l^{-1} Cu. Pb, Cd and As are found in much lower concentration, with means below 0.3 mg l^{-1}.

During September and October, the highest electrical conductivity readings and Cd, Cu, Fe, Mn and Zn concentrations are recorded, coincident by the first rainfalls, which provoke redissolution of sulphate salts that have precipitated during summer due to the intense weathering of pyrite. During the winter, dilution by superficial runoff water causes a slight increase in pH, and at the same time, the concentrations of sulphates and previously mentioned metals contained in the waters decrease. In spring and summer, pH again decreases and sulphate, Cd, Mn and Zn concentrations increase because of increased pyrite oxidation rate and water evaporation.

Although sulphates, Mn, Zn, Cd and Cu display similar evolution trends during the year, some important behavioural differences do exist. Cu is absorbed or coprecipitated preferentially in the Fe oxyhydroxides and hydrosulphates such that, its concentration diminishes in summer with respect to the other variables. Cd and Zn also appear to be affected by this process, although to a lesser degree than Cu, displaying lower concentrations in summer when compared to sulphates and Mn. Compared to the other elements, Pb shows a more erratic behaviour.

Fe has a distinctive behaviour pattern compared to the other metals. During summer, the concentrations are very low due to the intense precipitation of ferric oxyhydroxides such that, during this period, the Fe/SO_4^{2-} relationship reaches minimum values, and reaches maxima in the winter. For the same reason, the Fe concentration decreases with respect to the other heavy metals during summer and increases during autumn and winter.

The concentration of As in the waters maintains low levels during summer due to the strong surface adsorption on the ferric oxyhydroxides. In contrast to the other metals, the highest concentrations of As occur in winter when there is a low precipitation of ferric oxyhydroxides (higher Fe/SO_4^{2-} relationship). The slight pH increase produced in winter can also contribute to an increase in the concentration of As.

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References

Achterberg EP, Herzl VMC, Braungardt CB, Millward GE. Metal behaviour in an estuary polluted by acid mine drainage: the role of particulate matter. Environ Pollut 2003;121:283–92.

Alpers CN, Nordstrom DK, Thompson JM. Seasonal variations of Zn/Cu ratios in acid mine water from Iron Mountain, California. In: Alpers CN, Blowes DW, editors. Environmental geochemistry of sulfide oxidation. New York: American Chemical Society; 1994a. p. 323–44.

Alpers CN, Blowes DW, Nordstrom DK, Jambor JL. Secondary minerals and acid mine-water chemistry. In: Jambor JL, Blowes DW, editors. Short course on environmental geochemistry of sulfide mine-wastes. Ontario: Mineralogical Association of Canada; 1994b. p. 247–70.

Amaral Zettler LA, Gómez F, Zettler E, Keenan BG, Amils R, Sogin ML. Eukaryotic diversity in Spain’s river of fire. Nature 2002;417:137.

Berger AC, Bethke CM, Krumhansl JL. A process model of natural attenuation in drainage from a historic mining district. Appl Geochem 2000;15:655–66.

Braungardt CB, Achterberg EP, Elbaz-Poulichet F, Morley NH. Metal geochemistry in a mine-polluted estuarine system in Spain. Appl Geochem 2003;18:1757–71.

Buckby T, Black S, Coleman ML, Hodson ME. Fe-sulphate-rich evaporative mineral precipitates from the Río Tinto, southwest Spain. Mineral Mag 2003;67:263–78.

Casiot C, Morin G, Juillot F, Bruneel O, Personné JC, Leblanc M, et al. Bacterial immobilization and oxidation of arsenic in acid mine drainage (Carnoulès creek France). Water Res 2003;37: 2929–36.

Davis JC. Statistics and data analysis in geology. Singapore: John Wiley & Sons; 1986. 646 p.

Elbaz-Poulichet F, Dupuy C. Behaviour of rare earth elements at the freshwater–seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia Spain). Appl Geochem 1999;14: 1063–72.

Elbaz-Poulichet F, Braungardt C, Achterberg E, Morley N, Cossa D, Beckers JM, et al. Metal biogeochemistry in the Tinto–Odiel rivers (Southern Spain) and in the Gulf of Cadiz: a synthesis of the results of TOROS project. Cont Shelf Res 2001;21:1961–73.

Fernández-Remolar D, Gómez-Elvira J, Gómez F, Sebastián E, Martín J, Manfredi JA, et al. The Tinto River, an extreme acidic environment under control of iron, as an analog of the Terra Meridiani hematite site of Mars. Planet Space Sci 2004;52:239–48.

Galán E, Gómez-Ariza JL, González I, Fernández-Caliani JC, Morales E, Giráldez I. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. Appl Geochem 2003;18:409–21.

Gray NF. Acid mine drainage composition and the implications for its impact on lotic systems. Water Res 1998;32:2122–34.

Hudson-Edwards KA, Schell C, Macklin MG. Mineralogy and geochemistry of alluvium contaminates by metal mining in the Rio Tinto area, southwest Spain. Appl Geochem 1999;14:1015–30.

Jaynes DB, Rogowski AS, Pionke HB. Acid mine drainage from reclaimed coal strip mines: 1. Model description. Water Resour Res 1984;20:233–42.

Johnson CA. The regulation of trace element concentrations in river and estuarine water contaminated with acid mine drainage: the adsorption of Cu and Zn on amorphous Fe oxyhydroxides. Geochim Cosmochim Acta 1986;50:2433–8.

Leblanc M, Morales JA, Borrego J, Elbaz-Poulichet F. 4.500 year old mining pollution in Southwestern Spain: long-term implications for modern mining pollution. Econ Geol 2000;95:655–62.

Morillo J, Usero J, Gracia I. Partitioning of metals in sediments from the Odiel River (Spain). Environ Int 2002;28:263–71.

Nelson CH, Lamothe PJ. Heavy metal anomalies in the Tinto and Odiel Rivers and Estuary System, Spain. Estuaries 1993;16:495–511.

Nieto JM, Capitán MA, Sáez R, Almodóvar GR. Beudantite: a natural sink for As and Pb in sulphide oxidation processes. Trans.-Inst Min Metall., B, Appl Earth Sci 2003;112:293–6.

Nieto JM, Nocete F, Sáez R. Environmental impact of copper mining and smelting activities in southwest Spain during the third millennium B.C. Environ Pollut. [in press].

Ruiz MJ, Carrasco R, Pérez R, Sarmiento AM, Nieto JM. Optimización del análisis de elementos mayores y traza mediante UN-ICP-OES en muestras de drenaje ácido de mina. Proceedings IV Iberian Geochemical Meeting, 14-18 July. Coimbra, Portugal: University of Coimbra; 2003a. p. 402–4.

Ruiz MJ, Carrasco R, Pérez R, Sarmiento AM, Nieto J. 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, 14–18 July. Coimbra, Portugal: University of Coimbra; 2003b. p. 414–6.

Sáez R, Pascual E, Toscano M, Almodóvar GR. The Iberian type of volcano-sedimentary massive sulphide deposits. Miner Depos 1999;34:549–70.

Sáinz A, Grande JA, de la Torre ML. Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers. Environ Manage 2002;64:345–53.

Sáinz A, Grande JA, de la Torre ML. Odiel River, acid mine drainage and current characterisation by means of univariate analysis. Environ Int 2003;29:51–9.

Sáinz A, Grande JA, de la Torre ML. Characterisation of heavy metal discharge into the Ria of Huelva. Environ Int 2004;30:557–66.

Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. Appl Geochem 2002;17:517–68.

van Geen A, Adkins JF, Boyle EA, Nelson CH, Palanques A. A 120 yr record of widespread contamination from mining of the Iberian Pyrite Belt. Geology 1997;25:291–4.

Williams M. Arsenic in mine waters: an international study. Environ Geol 2001;40:267–78.

Younger PL. The longevity of minewater pollution: a basis for decision-making. Sci Total Environ 1997;194/195:457–66.