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Time Evolution of an AMD-Affected River Chemical Makeup

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Abstract Acid mine drainage is the main problem encountered by sulphide mining operations, not only because of its ecological aspects, but also because, once it appears, it is very difficult to remediate both technologically and economically. This paper characterises the response of an acid mine drainage-affected channel in the Iberian Pyrite Belt (Southwest of the Iberian Peninsula, Huelva, Spain) to the stimulus of rainfall in its drainage basin by studying the cause–effect relationships between sulphate, iron, copper, zinc, manganese, arsenic and cadmium concentrations in water samples taken at three points and rainfall in the zone.

Keywords Acid mine drainage · Sulphate · Heavy metals · Rainfall

1 Introduction

Traces of an intense old mining activity, associated with the Iberian Pyrite Belt, can be found in the Southwest of the province of Huelva (Spain). The main geological characteristic of this area is the existence of large and extra-large Palaeozoic massive sulphide deposits (Sáez et al. 1999). These sulphides are essentially made up of pyrite associated with sphalerite, galena, chalcopyrite and many smaller phases. These

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deposits have been mined for some 2,000 years. As a result, traces of this activity still remain at present, with large abandoned mining works and several million tons of old slag (Pinedo 1963) in vast areas occupied by mine dumps of various compositions. Only the area of the Riotinto Mines has an extension of over 2,000 ha (Sáinz et al. 2004).

These mining works are a very important polluting source. Acid rock drainage (ARD) and acid mine drainage (AMD) originate when a sulphurous mineral comes in contact with oxygen and atmospheric humidity. As a result, a complex mechanism begins on the mineral ore surface, starting with sulphide oxidation, releasing heavy metals (Fe, Cu, Zn…), and producing sulphates and hydrogenions, the latter giving the water an extremely acid pH ($\text{pH} < 3$). Along with this oxidation, a series of secondary reactions are generated, which affect the minerals that make up the rock (Förstner and Wittmann 1983). Finally, contaminant particles are obtained, which adhere to the mineral ore surface and are later dissolved by rain water and swept out to river channels. Although the kinetics of this reaction is very slow, it can be accelerated in the presence of ferric ion (Dogan 1999) and catalyzing bacteria (Nicholson 1994).

Although ARD is a natural process, it can be distinguished from AMD as an anthropogenic process, since it is accelerated by mineral massive extraction, its accumulation and the increase of the reaction surface, as grain size decreases, for mining purposes (EMCBC 1996).

AMD is the main problem mining operations have to cope with, not only because of its ecological effects, but also because, once it appears, it is virtually impossible to remediate, since its treatment with today technology costs millions of dollars and its effects can last for many centuries (EMCBC 1996).

The most serious ecological aspects of this kind of contamination are the lack of biodegradability of heavy metals, their bioaccumulation and transfer through the trophic chain, and their toxicity, both of metals that are essential for human beings and of those that are not, as they go far beyond tolerability limits (Sáinz et al. 2002).

The Cobica River (Fig. 1) springs from the Lagunazo reservoir waters, in the municipal district of Tharsis (Huelva, Spain, SW Iberian Peninsula). It flows along the wastes of abandoned mine operations in the area and, as a result, is affected by AMD processes. Downstream, it flows through Puebla de Guzmán municipal district, where it still keeps its mining nature and meets the Chorrito Stream. This stream springs from the ponds at Herrerías Mine, an old mining site in Puebla de Guzmán, and is also affected by contamination of various mine wastes scattered along its basin. The importance of these two channels is that their waters flow into the recently built Andévalo Dam, which will supply water for irrigation and human consumption to the whole area. When entering the dam, the Cobica river water mixes with uncontaminated water, producing a sharp increase in pH. As a result, heavy metals precipitate and remain dormant in the bottom sediments, at the expense of possible environmental changes that can cause their re-dissolution and introduction into the trophic chain. Hence the vital importance of monitoring the global behaviour of these heavy metals, starting from the study of their concentration evolution as a result of one of the external agents that can affect them, i.e. rainfall.

The main contribution to this dam is made by the Malagón River, of high hydrological relevance, with a basin of 405 km^2. The hydrological conditions of the area, mainly made up of impermeable materials, cause that practically all the rainfall received by these basins flows as runoffs into these channels and, therefore, into the dam. This results in hydric regimes with torrential characteristics, with large floods in winter and almost empty channels in summer (Grande et al. 2003c).

2 Objectives and Methods

The main aim of this paper is to characterise the response of an AMD-affected channel to the stimulus caused by rainfall in its drainage basin by establishing cause–effect relationships between rainfall values and variations in Fe, Cu, Zn, Mn, As, Cd and sulphate concentrations at two points of the Cobica River and at one point of its mining tributary, the Chorrito (Fig. 1).

2.1 Sampling and Treatment

Sampling was conducted for 236 correlative days, within the same hydrological year, from October 3, 2003 to May 25, 2004. It was performed at three different points forming a ‘Y’ system from two contributions: Cobica River before meeting the Chorrito (this point is called ‘Puente’), Chorrito Stream, and Cobica River after meeting the Chorrito (Fig. 1). At the moment of the sampling, pH and conductivity were measured in situ, taking two water samples from each point using sterile polypropylene 100 ml bottles. One of the collected samples was acidified with a dissolution of low nitric acid concentration to avoid metal precipitation. The other one was left unmodified for sulphate analysis. After collection, all samples were kept in a portable fridge at 4°C and immediately taken to the laboratory.

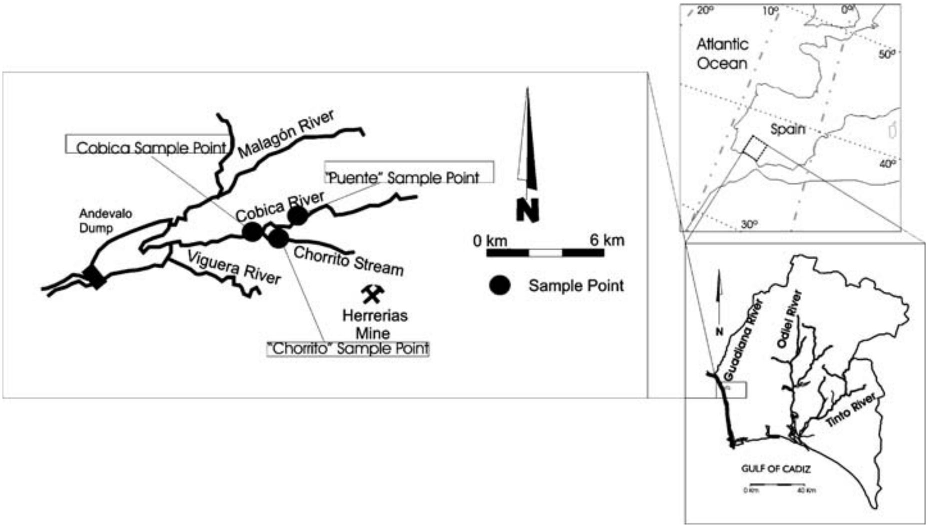

Fig. 1 Location map

The rainfall data from the station that is nearest to the studied area, “Tharsis Mines”, were obtained from the local meteorological service.

2.2 Reagents and Apparatus

To determine pH and conductivity in situ, a Crison pHmeter, model 507, and a Crison conductimeter, model 524, were used.

Measurement of sulphates dissolved in water was performed with a Machery–Nagel photometer, model PF-11.

For the analysis of heavy metals (Fe, Cu, Mn and Zn), a Varian SpectrAA 50B atomic spectrometry equipment was used. The technique used was atomic absorption with air-acetylene flame, using Varian hollow cathode lamps as the source of energy. As and Cd determination was made using a Jobin Yvon Ultima2 equipment.

The preliminary treatment of the sample consisted of a filtering using 0.45 micra cellulose nitrate filters (Sartorious 11406-47-ACN). All reagents used were of analytical grade or higher, from Merck or Panreac. Certified patterns were used for A.A. Panreac. All the analyses were performed with distilled water (Milli-Q quality).

2.3 Analytical Procedure

Fe, Cu, Mn and Zn concentration in the water was analysed by means of atomic absorption spectrophotometry with (air-acetylene) flame, whereas arsenic and cadmium were determined by atomic emission spectroscopy, using inductively coupled Ar plasma.

Sulphate concentration was determined using the chloride precipitation reaction method, which forms a precipitate that can be measured by turbidity at 405 nm wavelength.

2.4 Statistical Methods

After studying the statistical summary of variables and the correlation matrix, posing of the initial hypothesis was approached using graphic treatment of time series by means of the statistical package Statgraphics Plus for Windows 5.1.

Correlation matrix: Each box shows Pearson’s ‘R’ correlation coefficient, which ranges between 1 and -1 for each pair of variables.

Time series analysis: It studies the evolution throughout time of a given magnitude. In this case, the parameters considered are rainfall and variations induced by it in the water chemical composition to determine possible relationships between both of them (Bisquerra 1989).

3 Results

With the data resulting from the analyses described above and the rainfall data coming from the meteorological station nearest to the sampling points, a statistical analysis of the time series was performed in order to characterise the target channels and find the response of the sampled water chemical conditions to rainfall.

Table 1 Statistical summary of the parameters analysed in the samples from Puente

	Number of data samples	Average	Variance	Minimum	Maximum
pH	236	2.8	0.32	1.6	5.4
Cond (mS/cm)	236	1.61	0.33	0.2	2.7
SO_4 (mg/l)	236	662.5	128,725	42	1,290
Fe (mg/l)	236	83.7	8,299	0.9	518
Cu (mg/l)	236	2.14	1.65	0	4.7
Zn (mg/l)	236	3.4	6.6	0.1	21
Mn (mg/l)	236	2	1.6	0.1	6
As (mg/l)	236	155.7	31,821.6	0	767.5
Cd (mg/l)	236	13.8	62.7	0	29.8

3.1 Statistical Summary

The statistical summary of the analysed parameters was obtained in order to determine a preliminary characterization of each of the channels. From the results shown in Tables 1, 2, and 3, the following is deduced:

- pH mean value at all sampling points is extremely acid in all cases: 2.8 at ‘Puente’, 2.5 at Chorrito, and 2.8 at Cobica. It can be observed that extreme values for acidity reach 1.0 at Chorrito, followed by Puente (1.6) and Cobica (2.1).
- Conductivity has a mean value of 1.61 mS/cm at Puente, 2.54 at Chorrito, and 2.19 mS/cm at Cobica. It must be remarked that the maximum value reached for this parameter at Puente only amounts to 2.77 mS/cm. However, in the other two channels, Chorrito and Cobica, this value reaches a maximum around 10 mS/cm.
- As regards sulphates, there are considerable differences in the three channels. Whereas mean value for sulphate content remains at 662.5 mg/l at Puente, this mean value reaches 2,051.68 mg/l at Chorrito (three times higher than that at Puente) and 1,215.57 mg/l at Cobica (almost double as that at Puente). The maximum values reached at the beginning of the sampling campaign at Chorrito (14,800 mg/l) and Cobica (13,680 mg/l) must be emphasized. Besides, variance of sulphate values at Puente is of 128,725, while that at Chorrito reaches 4.3×10^6 and that at Cobica, $3.1\ 10^6$.
- Fe has a mean value of 83.7 mg/l at Puente, 131.2 mg/l at Chorrito and 96.5 mg/l at Cobica. The highest variance is reached at Chorrito (18,342), more than double the ones reached at Puente (8,299) and Cobica (6,802).

Table 2 Statistical summary of the parameters analysed in the samples from Chorrito

	Number of data samples	Average	Variance	Minimum	Maximum
pH	236	2.5	0.1	1.04	4.06
Cond (mS/cm)	236	2.5	3.3	0.1	10.9
SO_4 (mg/l)	236	2,051.7	4.3×10^6	176	14,800
Fe (mg/l)	236	131,2	18,342.8	4	1,170
Cu (mg/l)	236	9.7	58.7	0.47	51
Zn (mg/l)	236	11	152.3	0.21	90
Mn (mg/l)	236	20.2	431.3	1.1	160
As (mg/l)	236	409.5	422,867	0	4,419.1
Cd (mg/l)	236	49	2,984.3	0	328.6

Table 3 Statistical summary of the parameters analysed in the samples from Cobica

	Number of data samples	Average	Variance	Minimum	Maximum
pH	236	2.8	0.2	2.1	6.4
Cond (mS/cm)	236	2.2	3.1	0.3	10.3
SO_4 (mg/l)	236	1,215.6	3.1	94	13,680
Fe (mg/l)	236	96.5	6,802.4	0.4	709.8
Cu (mg/l)	236	5.6	63.9	0.2	54
Zn (mg/l)	236	8.9	221.5	0.2	120
Mn (mg/l)	236	15.5	871.2	0.2	210
As (mg/l)	236	110.7	104,197	0	3,360.6
Cd (mg/l)	236	33.3	3,580.6	0	367.9

- Cu reaches a mean value of 2.14 mg/l at Puente, 9.78 at Chorrito and 5.6 mg/l at Cobica. Variance is not very high in any case; however, it reaches a value of 63.9 at Cobica, 58.7 at Chorrito, and 1.65 at Puente (of the order of 30 times lower than in the other cases).
- Zn shows a mean value of 3.4 mg/l at Puente, 10.99 mg/l at Chorrito and 8.89 mg/l at Cobica. The maximum value reached by Zn at Cobica is of 120 mg/l, 90 mg/l at Chorrito, and only 21 mg/l at Puente.
- Mn presents a mean value of 2 mg/l at Puente, 20.2 mg/l at Chorrito and 15.49 mg/l at Cobica. The maximum value reached by this parameter at Puente was only of 6 mg/l, whereas it was of 160 mg/l at Chorrito, and of 210 mg/l at Cobica.
- Mean concentration of As at Puente was of 155.7 mg/l, of 409.49 mg/l at Chorrito and 110.7 mg/l at Cobica. Concentration maximum value for As reached at Chorrito was of 4,419.1 mg/l, and of 3,360.6 mg/l at Cobica, whereas at Puente it was of 767. 58 mg/l.
- As for Cd, mean concentration value at Puente was of 13.8 mg/l, 48.9 mg/l at Chorrito, and 33.26 mg/l at Cobica. If we observe the eventual maximum value reached by Cd concentration in the water sampled at Puente, it can be seen that its value is of 29.8 mg/l, whereas at Chorrito it reaches 328.6 mg/l (11 times higher), and 367.9 mg/l at Cobica (12 times higher than at Puente).

3.2 Correlation Matrix

Also, the correlation matrix was obtained (Tables 4, 5, and 6). Taking into account only those correlations with a Pearson's R higher than 0.6 or lower than −0.6 and with a significance level of 100% (P value = 0), the following relationships stand out:

- Sulphates at Cobica (Table 6) correlate positively with Cu (0.86), Zn (0.87), Mn (0.86), and Cd (0.91), but they do not with Fe (0.38) and As (0.35). (A similar case to that between conductivity and metals at this same sampling point). At Chorrito (Table 5) we observe correlations higher than 0.6 in all cases (0.6 Cu; 0.71 Zn; 0.71 Mn; 0.68 As and 0.95 Cd), except for Fe (0.53). In the case of Puente (Table 4) the behaviour is similar to that of Chorrito (0.46 Fe; 0.69 Cu; 0.64 Zn; 0.62 Mn; 0.66 As; 0.83 Cd).
- As regards correlation values between metals, it can be emphasized that Fe does not correlate with any metal at Puente (Table 4), it only correlates with As at

Table 4 Correlation matrix for Puente

		SO_4	Fe	Cu	Zn	Mn	As	Cd	Rainfall
SO_4	Pearson Correlation	1							
	Sig.								
Fe	Pearson Correlation	0.464	1						
	Sig.	0.000							
Cu	Pearson Correlation	0.690	0.421	1					
	Sig.	0.000	0.000						
Zn	Pearson Correlation	0.648	0.405	0.794	1				
	Sig.	0.000	0.000	0.000					
Mn	Pearson Correlation	0.624	0.246	0.607	0.687	1			
	Sig.	0.000	0.000	0.000	0.000				
As	Pearson Correlation	0.661	0.431	0.632	0.460	0.285	1		
	Sig.	0.000	0.000	0.000	0.000	0.000			
Cd	Pearson Correlation	0.832	0.388	0.860	0.733	0.643	0.724	1	
	Sig.	0.000	0.000	0.000	0.000	0.000	0.000		
Rainfall	Pearson Correlation	−0.219	−0.137	−0.202	−0.168	−0.162	−0.173	−0.230	1
	Sig.	0.000	0.018	0.001	0.005	0.006	0.004	0.000	

Table 5 Correlation matrix for Chorrito

		SO_4	Fe	Cu	Zn	Mn	As	Cd	Rainfall
SO_4	Pearson Correlation	1							
	Sig.								
Fe	Pearson Correlation	0.530	1						
	Sig.	0.000							
Cu	Pearson Correlation	0.607	0.635	1					
	Sig.	0.000	0.000						
Zn	Pearson Correlation	0.713	0.686	0.790	1				
	Sig.	0.000	0.000	0.000					
Mn	Pearson Correlation	0.718	0.564	0.795	0.928	1			
	Sig.	0.000	0.000	0.000	0.000				
As	Pearson Correlation	0.689	0.609	0.330	0.351	0.326	1		
	Sig.	0.000	0.000	0.000	0.000	0.000			
Cd	Pearson Correlation	0.952	0.494	0.625	0.717	0.744	0.692	1	
	Sig.	0.000	0.000	0.000	0.000	0.000	0.000		
Rainfall	Pearson Correlation	−0.037	−0.097	−0.092	−0.115	−0.113	−0.015	−0.059	1
	Sig.	0.573	0.140	0.159	0.080	0.084	0.822	0.365	

Table 6 Correlation matrix for Cobica

		SO_4	Fe	Cu	Zn	Mn	As	Cd	Rainfall
SO_4	Pearson Correlation	1							
	Sig.								
Fe	Pearson Correlation	0.380	1						
	Sig.	0.000							
Cu	Pearson Correlation	0.865	0.434	1					
	Sig.	0.000	0.000						
Zn	Pearson Correlation	0.873	0.333	0.945	1				
	Sig.	0.000	0.000	0.000					
Mn	Pearson Correlation	0.867	0.349	0.928	0.974	1			
	Sig.	0.000	0.000	0.000	0.000				
As	Pearson Correlation	0.354	0.631	0.283	0.212	0.225	1		
	Sig.	0.000	0.000	0.000	0.001	0.001			
Cd	Pearson Correlation	0.919	0.362	0.909	0.940	0.920	0.372	1	
	Sig.	0.000	0.000	0.000	0.000	0.000	0.000		
Rainfall	Pearson Correlation	−0.018	−0.064	−0.072	−0.072	−0.068	−0.008	−0.032	1
	Sig.	0.782	0.335	0.274	0.272	0.300	0.900	0.631	

Cobica (Table 6), and it correlates with all metals but Cd at Chorrito (Table 5). Regarding As, it can be observed that it correlates with Cd at Chorrito and Puente, but not at Cobica.
- Precipitation does not have correlations higher than 0.6 or lower than −0.6 with any other of the parameters studied.

3.3 Time Evolution Charts

The graphic treatment of time evolution for the parameters analysed at each of the sampling points, along with the rainfall values provided by the nearest meteorological station (Tharsis) shows the following (Figs. 2, 3, and 4):

- Rainfall eventual maximum values are observed on days 25 October 2003; 21 November 2003; 20 February 04 and 23 February 04.
- The charts representing time evolution for sulphates, copper, zinc, manganese and cadmium, in the case of Puente (Fig. 2), have a very similar evolution. On the day after heavy rainfall, a decrease in the value of these parameters is observed, although the general evolution is an increase throughout the campaign. The case of Fe is different: the charts are sharper and no immediate response to rainfall is observed.
- At Chorrito (Fig. 3), in the case of sulphates, copper, zinc, manganese, cadmium and also arsenic, decreases in these parameters concentration on the day after heavy rainfall occurs can be observed. However, the general evolution is a decrease throughout the campaign. On the contrary, iron has a much sharper evolution that does not seem to be related with rainfall.
- The behaviour observed in the case of Cobica (Fig. 4) is a general soft increase in the concentration of sulphates, copper, zinc, manganese, cadmium and arsenic with an eventual sharp decrease a day after a heavy rainfall episode. Also in this case, iron does not seem to be related with rainfall and shows a sharper evolution.
- A very high concentration can be observed at all sampling points at the beginning of the sampling campaign, except for iron, arsenic and zinc at Puente (Fig. 2).

4 Discussion

Previous studies by different authors (Borrego 1992; Borrego et al. 2002; Braungardt et al. 1998; Davis et al. 2000; Elbaz-Poulichet et al. 1999, 2000, 2001; Leblanc et al. 2000; Sáinz 1999; Sáinz et al. 2002, 2003a, b; Grande et al. 2000, 2003a, b, 2005a) and, more specifically, that by Grande et al. (2005b) (where the authors characterise AMD and ARD processes in the same area of study, taking samples from the Chorrito Stream and from another stream called Higuereta, which flows into the Cobica and has no acid contributions), are useful as a reference for the discussion and for obtaining the conclusions of our study.

It is evident that there are different responses at each sampling point, although all of them are framed within the general characteristics of AMD processes. In fact, in all cases, pH mean values are acid ones, around 2.7, and consequently, high metal dissolution can be observed. Within this context, it can be seen how in all cases the

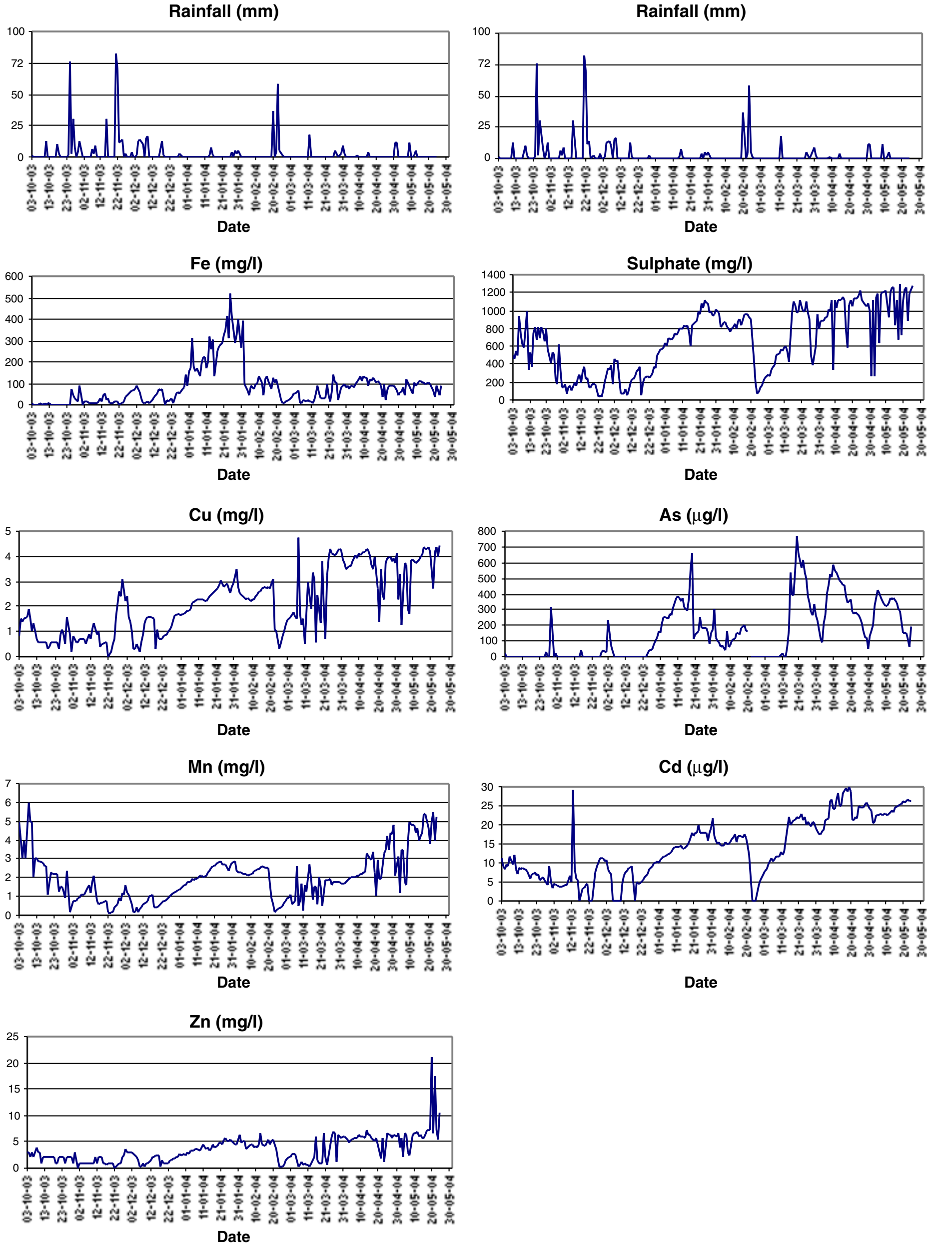

Fig. 2 Temporal series analysis for Puente

highest mean concentration of dissolved metals is found at the sampling point of the Chorrito Stream, followed by the Cobica and, finally, by the Puente, these mean values being a half or a third of the value for the other points. In this way we can observe how the dissolved metal contribution into the Chorrito Stream decreases as

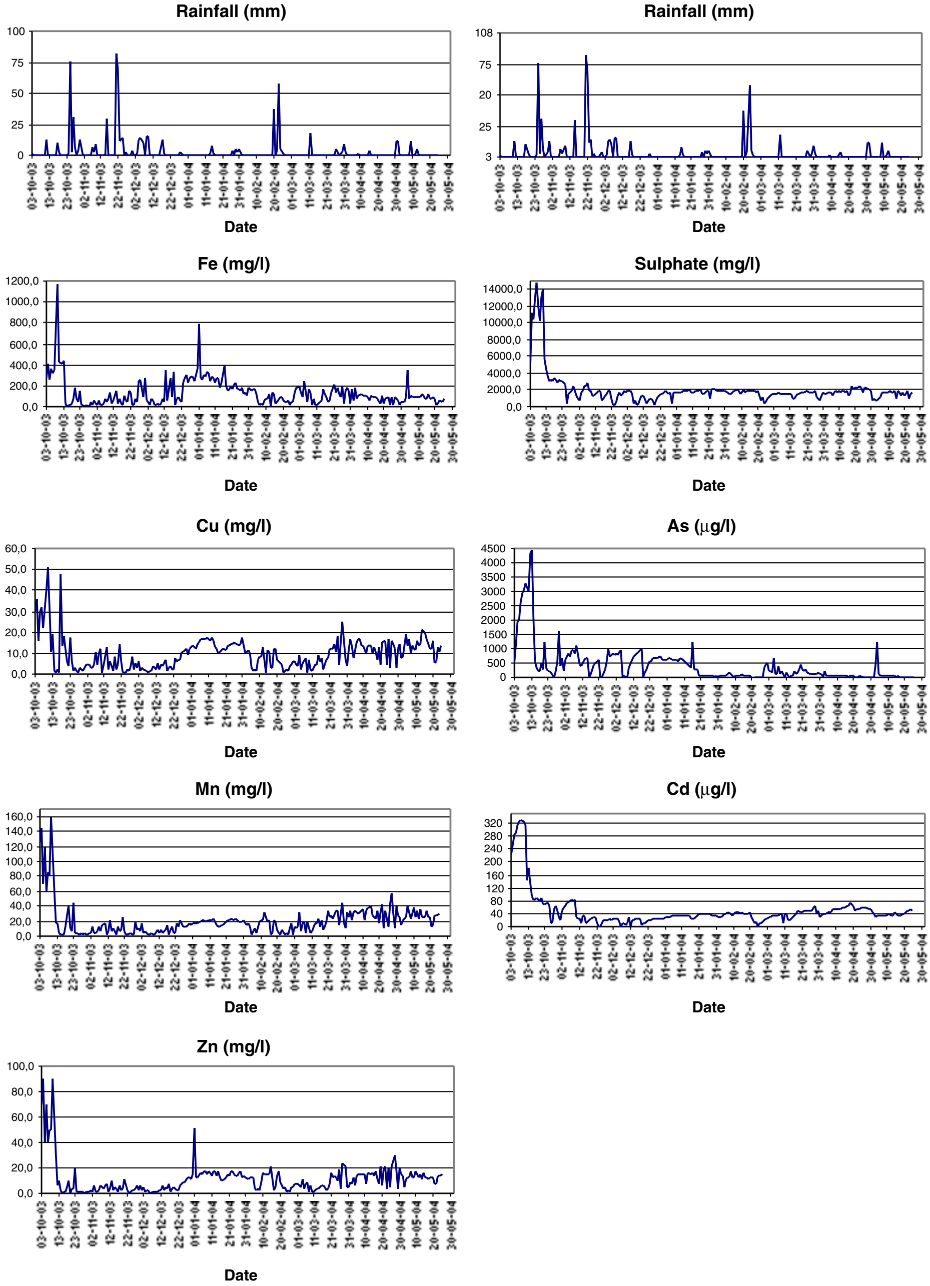

Fig. 3 Temporal series analysis for Chorrito

its water meets the Cobica, this concentration becoming smaller downstream of the junction. More specifically, the high mean values for sulphates (2,051.70 mg/l) and arsenic (409.49 mg/l) at the Chorrito must be emphasized.

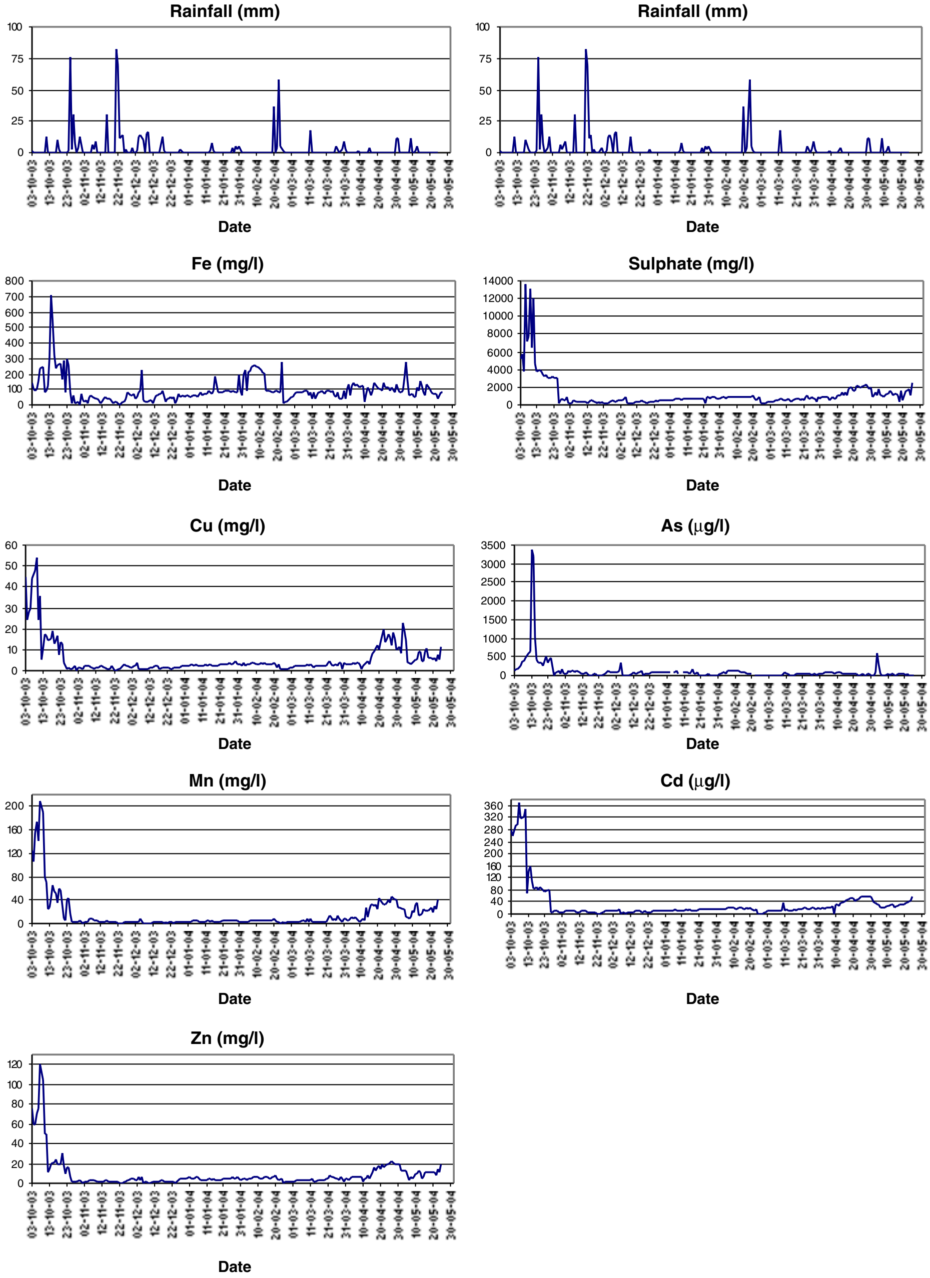

Fig. 4 Temporal series analysis for Cobica

In the Pearson matrix, the absence of correlation with rainfall and the different behaviours of Fe at the three sampling points are remarkable. The same, but with a different pattern, happens with As concentrations.

In the time analysis, the relationship between rainfall on days 25 October 2003; 21 November 03; 20 February 2004 and 23 February 2004, and sulphate, zinc, manganese and cadmium values is evident. This implies an immediate decrease in these parameters after a heavy rainfall episode because heavy rain causes immediate dilution, which implies a decrease in concentration of these parameters. This phenomenon shows that no dissolution of sulphate salts takes place and that the dilution effect prevails. In other AMD-affected river systems (Tinto and Odiel rivers) precipitation of sulphate salts occurs during periods of scarce rainfall, serving as acidity and metals depot. Later, subsequent rainfalls give rise to the re-dissolution of these salts and cause an evident increase in sulphate and metal concentration, and a decrease in pH. This phenomenon is much more frequent during the first autumn rains, after the dry summers that are typical in these latitudes. The reason why this system is different is maybe that channels are much smaller and the amounts of precipitated salts are very small, and their re-dissolution does not alter the water chemical makeup significantly.

5 Conclusions

The high concentration levels at all sampling points at the beginning of the campaign can be explained by the first rainfall after a dry period, producing increase in sulphate and metals due to the re-dissolution of salts precipitated on the river margins. These salts have a very important role in the chemical variation of the water, and are a temporal reserve of acidity, sulphates and metals.

Subsequent rainfall causes a decrease in sulphate and metal concentration due to the dilution caused by clean runoff water.

Among all metals, it is iron which is less affected by the coming of rainfall, due to the hydrolysis and precipitation processes of oxyhydroxides or oxihydroxisulphates which take place with pH higher than 3. Here, a tamponed reaction of pH occurs, as H^+ ions are released during these processes.

Increase in Cu, Zn and Cd as rainfall begins is due to their higher content in the re-dissolved soluble salts with respect to their concentration in the water. The higher or lower capability of metals to be adsorbed or to coprecipitate on Fe oxydydroxides or oxyhydroxisulphates which precipitate after floods is the factor controlling their concentration in water.

From the analysis of the variations in the concentration of dissolved metals after rainfall we obtain the order of affinity to precipitate on these phases. From higher to lower affinity grade, this order would be:

$$\mathrm{Cu} > \mathrm{Cd} > \mathrm{Zn} > \mathrm{As} > \mathrm{Mn}$$

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