

Comparative of acid drainage process types between two streams of the Cobica river in the environment of the Iberian Pyrite Belt (Huelva, Spain) and impact on the Andévalo Dam.

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ABSTRACT

The present work describes the process of acid water discharge into the Andévalo Dam (Iberian Pyrite Belt, Huelva-Spain) starting from the interpretation of rainfall data and chemical analyses regarding pH, conductivity, metal and sulphate content in water, from a time series corresponding to the sampling of two confluent channels that discharge water into the referred dam. Statistical data treatment allows us to conclude the existence of acid mine drainage processes in the Chorrito Stream, which are translated into very low pH values and high sulphate and metal concentrations in the water coming from Herrerías Mine. On the other hand, the Higuereeta Stream shows, for the same parameters, much lower values that can be interpreted as the channel response to acid rock drainage processes in its drainage basin induced by the rocky outcrops of the Iberian Pyrite Belt.

INTRODUCTION

General Setting

The recently created Andévalo Dam is located at the junction of the Malagón and Cobica rivers, both tributaries to the Chanza River in the SW of Spain, very close to the border with Portugal (Figure 1). It presents a storage capacity of 630 million cubic metres, which can be extended up to 1025 million cubic metres (López and Sanz, 2001).

The reservoir is fed from the Malagón River as its main watercourse, with a catchment area of 405 sq. km, receiving the Cobica River as its tributary before the dam (Figure 1). This river also receives discharges from two streams, Chorrito and Higuereeta, where samples were taken for the present work. The channel regime in the environment is directly associated to precipitation given by the impermeable nature of the outcropping rocks in the basin. This fact gives the channel its practically torrential characteristics with large floods in winter and almost null flow in low water periods (Grande et al., 2003a).

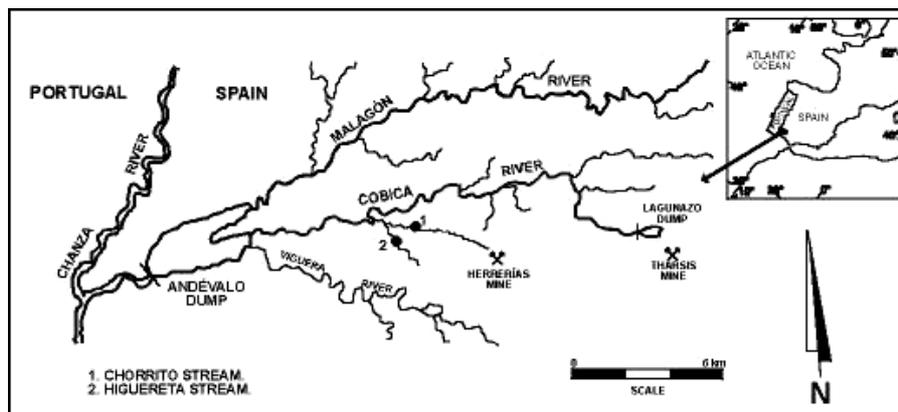


Figure 1: Location map

A determining factor of the subsequent use of the dam is the chemical makeup of the Cobica River water. It is a typically mining channel that receives discharges from two abandoned mine operations, Herrerías Mine and Tharsis Mine (Figure 1). A.M.D. and A.R.D. processes undergone by the drainage network in the regional environment have been widely described for the Tinto and Odiel rivers by different authors (Borrego, 1992;

Borrego et al., 2002; Braungardt et al., 1998, Davis et al., 2000; Elbaz-Poulichet et al., 1999-2001; Leblanc et al., 2000; Sáinz, 1999; Sáinz et al., 2002-2003a-2003b; Grande et al., 2000-2003b-2003c).

Geologically, the described sector is located in the Iberian Pyrite Belt, in the Spanish South-West, with numerous huge and over-huge paleozoic massive sulphide deposits, the biggest in the world according to Sáez et al. (1999). The massive sulphide bodies contain pyrite to which sphalerite, galena and chalcopyrite and other minor stages are associated (Sáez et al., 1999). These deposits have been exploited for more than 2000 years. As a result, many large abandoned mine operations, as well as several million tones of old slag dumps of different composition (Pinedo, 1963), have remained from this activity.

Potentially Pollutant Mining Activities:

Mining liquid pollution arriving to the Cobica watercourse is produced by mine underground water, waste dump leachate and general washout of all pyrite waste dispersed through the numerous mining operations. Liquid contamination in these settings can become solid contamination by means of several sorption, precipitation and co-precipitation mechanisms (Kwong and Lawrence, 1998); however, together with these indirect mechanisms, it should be reminded that certain mining activities can cause contamination with solid particles (Johansen and Asmund, 1999).

A.M.D. and A.R.D. Processes

Two liquid contamination processes caused by sulphide oxidation can be distinguished in this environment: a geochemical natural process called ARD (Acid Rock Drainage), by means of which surface rock outcrops of sulphide masses undergo meteorization and oxidize spontaneously; and another one, anthropogenic, called AMD (Acid Mine Drainage), that is the result of the appearance of effluents produced by mining operations (Sáinz et al., 2002).

A.M.D. processes are one of the most hazardous types of water pollution due to their nature, extent and difficult solution (Azcue, 1999), as well as to their remediation economic costs (Commonwealth of Pennsylvania, 1994). Rivers affected by this type of contamination are characterised by their acidity, as well as by the high sulphate and heavy metal content in their waters, and by the metallic content of their sediments (Lew and Sheppard, 2001).

OBJETIVES AND METHOD

This work intends to characterize A.M.D. (Acid Mine Drainage) and A.R.D (Acid Rock Drainage) geochemical processes in two confluent streams, Chorrito, whose drainage basin undergo AMD processes, and Higuera, enduring ARD phenomena, both discharging into a public-supply reservoir.

Sampling and analytical methodology

The sampling campaign was carried out daily from December 2000 to March 2001 during the rainy period, when water runs along both streams, and was finished when watercourses stopped running in the studied sector. Water samples were taken at two points, one in the Chorrito Stream, and the other in the Higuera Stream, these points being near the junction of both streams (figure 1).

Analytical procedures

Metal concentrations in sample waters were determined by Atomic absorption spectrometry using flame FAAS (Fe, Cu, Mn and Zn). The accuracy of the analytical procedures for total metal determinations was checked with CRM 609 (Trace elements in groundwater) from BCR. Replicate analysis was done if this CRM showed good accuracy, with all results comparable with certified values.

Sulfates were determined by Ion Chromatography with Chemical Suppression of Eluant Conductivity (Standard Methods, 4110). The accuracy of the analytical procedures for anion sulfate determinations were checked with CRM 408 (Major compounds in simulated Rainwater) and CRM 609 (Trace elements in groundwater) from BCR. Replicate analysis was done if this CRM showed good accuracy, with all results comparable with certified values. Total dissolved and total suspended solids were determined by gravimetric method.

Statistical Methods

After studying the statistical summary of variables and the correlation matrix, the posing of the initial hypothesis was approached using graphic treatment of time series for its subsequent statistical contrast with autocorrelation and cross-correlation functions by means of the statistical package Statgraphics Plus for Windows 5.1.

RESULTS

Statistical Summary

	Rainfall (mm)	pH	COND (mS/cm)	LEVEL (cm)	SO ₄ (mg l ⁻¹)	Fe (mg l ⁻¹)	Mn (mg l ⁻¹)
MEAN	3.176	7.168	0.288	11.069	42.994	0.286	0.037
VARIANCE	47.709	0.473	0.0027	21.471	78.114	0.249	0.015
MINIMUM	0.0	5.68	0.135	7.5	19.07	0.0	0.0
MAXIMUM	35.0	7.93	0.351	30.0	60.3	2.817	0.602
RANGE	35.0	2.25	0.216	22.5	41.23	2.817	0.602

Table 1: Statistical summary for Higuera Stream

	Rainfall (mm)	pH	COND (mS/cm)	LEVEL (cm)	SO ₄ (mg l ⁻¹)	Fe (mg l ⁻¹)	Mn (mg l ⁻¹)
MEAN	3.176	2.953	3.271	32.965	1583.14	219.095	13.60
VARIANCE	47.706	0.393	1.073	81.850	349121.0	7514.36	20.46
MINIMUM	0.0	2.29	0.856	26.0	337.5	39.5	4.49
MAXIMUM	35.0	4.46	5.89	70.0	3453.0	396.3	23.0
RANGE	35.0	2.17	5.034	44.0	3115.5	356.8	18.51

Table 2: Statistical Summary for Chorrito Stream

The statistical summary of variables (tables 1 and 2) allows the observation of the following phenomena: mean pH value in the Higuiereta stream is 7.16, reaching a minimum of 5.68 and a maximum of 7.93, whereas in the Chorrito stream the mean value is 2.95, with minimum and maximum values of 2.29 and 4.46, respectively. pH variance in both streams is similar, with a slightly higher value in the Higuiereta.

Mean conductivity in the Higuiereta is 0.28 (mS/cm) and 3.27 (mS/cm) in the Chorrito. The variance for the latter is approximately 400 times higher than that of the Higuiereta.

Regarding mean sulphate content, the Higuiereta stream shows a value near 43 mg l⁻¹ whereas in the Chorrito the mean value is 1583 mg l⁻¹, with a variance 5 times higher than that of the Higuiereta.

Mean dissolved iron content in the Higuiereta stream is low, around 0.3 mg l⁻¹, as opposed to what happens in the Chorrito stream, where mean content reaches 219.1 mg l⁻¹, some 800 times higher. Variance for this variable in the acidic environment is 25 times higher.

Manganese mean values in the Higuiereta is 0.04 mg l⁻¹, reaching 13.6 mg l⁻¹ in the Chorrito. Variance in this case is also higher in the acidic stream, some 600 times.

Correlation Matrix

Table 3 shows the correlation coefficients for each pair of variables. Outstanding is the fact that in both streams precipitation presents a high correlation, positive with water level and negative with conductivity, the latter being superior in the Higuiereta than in the Chorrito.

	Precip.	pH HIG	COND HIG	HEIG. HIG	SO ₄ HIG	Fe HIG	Mn HIG	pH CHA	COND CHA	HEIG. CHA	SO ₄ CHA	Fe CHA	Mn CHA
Precip.	1												
pH HIG	-0.3295	1											
COND HIG	-0.6783	0.5435	1										
HEIG. HIG	0.7818	-0.3505	0.8736	1									
SO ₄ HIG	-0.4433	0.5533	0.7197	-0.6293	1								
Fe HIG	0.3194	-0.3892	0.5861	0.5755	-0.4404	1							
Mn HIG	-0.0033	0.1537	0.0711	-0.0644	0.2341	0.2114	1						
pH CHA	0.2963	-0.8753	-0.5397	0.4391	-0.4824	0.3070	-0.1310	1					
COND CHA	-0.3411	-0.2516	0.5000	-0.6653	0.2302	-0.3837	0.0606	0.0365	1				
HEIG. CHA	0.6532	-0.6096	-0.8548	0.8588	-0.6961	0.7140	-0.1101	0.5865	-0.3910	1			
SO ₄ CHA	-0.2335	-0.1314	0.4708	-0.5541	0.2749	-0.4098	0.0132	0.0111	0.7058	-0.4318	1		
Fe CHA	-0.3760	0.2390	0.3919	0.0298	0.1839	-0.3390	-0.0869	-0.3798	0.4420	-0.3604	0.2523	1	
Mn CHA	-0.3919	0.4404	0.8134	-0.6780	0.6133	-0.4366	0.1125	-0.4373	0.4514	-0.6572	0.4098	0.1574	1

Table 3: Correlation Matrix

Conductivity shows a high and negative correlation with water level in the Higuiereta and moderate in the Chorrito, where it is high and positive with sulphates in both watercourses. In the Chorrito stream a positive though moderate correlation of this variable with metals (Fe and Mn) can be observed.

Regarding pH, a different behaviour can be stated in both watercourses, since this variable positively correlates with conductivity in the Higuiereta stream, but not in the Chorrito. In Higuiereta, pH positively correlates with sulphates, but this is not the case for the Chorrito. Correlation between pH and level in the Higuiereta stream is moderate and negative, whereas it is positive in the Chorrito.

Time Evolution Charts:

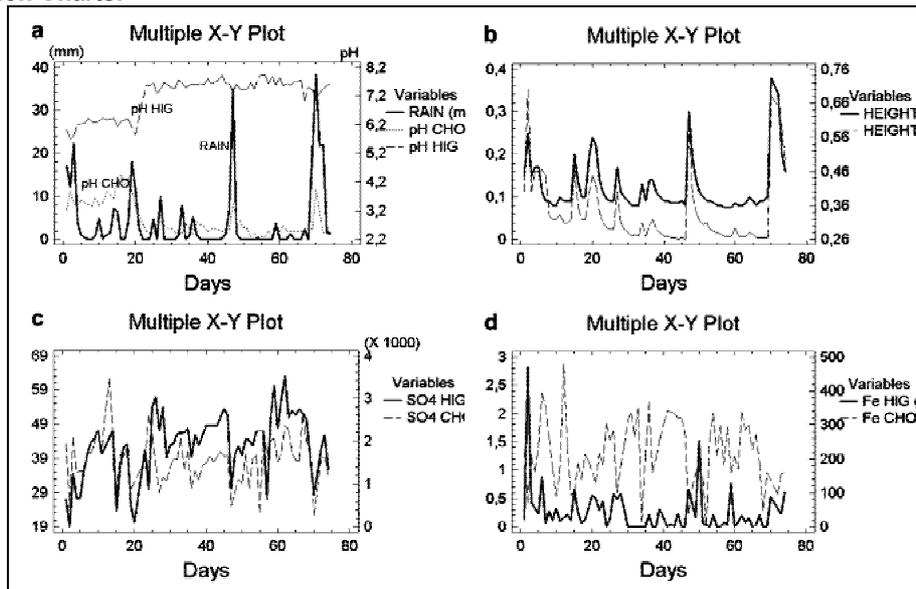


Figure 2: Time evolution Chart

The time evolution chart for precipitation (Figure 2a) shows the existence of rainfall events with maximums on days 2, 19, 47 and 70. pH evolution is different in the acidic basin and in the clean one. In the former, starting from values close to pH 3.5 it remains around these values with small oscillations until day 19, when it undergoes a remarkable decrease to values near pH 2, remaining there until the end of the sampling period, with the exception of two instant rises to pH 3.5 on days 47 and 70. In the meantime, the Higereta stream has a different evolution: starting from values around pH 6, it remains practically constant until day 20, when it undergoes an increase that sets it around pH 7 until the end of the series, with the exception of two concrete decreases on days 47 and 68.

Water level (Figure 2b) measured in both watercourses as flow function shows very similar behaviours in both charts, with great level increases on days 47 and 70. At the same time, the Chorrito stream presents a great flood on the second sampling day, not so sharp in the Higereta. The last flood on day 70 shows how both channels grow rapidly but, whereas the Higereta recovers the original flow almost vertically, the Chorrito offers a more time-softened recovery curve.

Time evolution of sulphate content (Figure 2c) is also similar in both basins, logically affected by higher concentration values in the Chorrito. Iron content (Figure 2d) evolves differently according to the channel, with much higher variations in the Chorrito, resulting in a much more irregular line, whereas in the Higereta the variations are much more discrete and maximums and minimums do not match those of the other stream. For both parameters, it can be observed that increases of pH correspond to concentration decreases in both streams. This fact is more stressed in the Chorrito.

Autocorrelation Function:

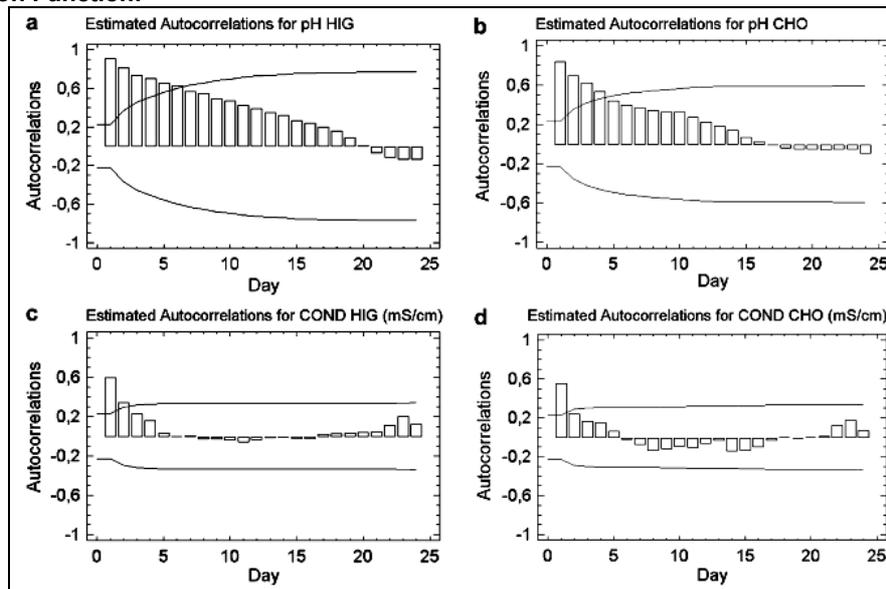


Figure 3: Autocorrelation function

The autocorrelation function applied to the studied series shows the value for correlations between each variable on one day, and the same variable on the previous days. The plot (Figure 3) contains vertical bars that represent the coefficient for each day and a pair of dotted lines at a distance from the baseline that are a multiple of the standard error at each day. For pH we can see how in the Chorrito (Figure 3b) there are four values above the point line, which means they are significantly different from zero, implying the existence of a 4-day memory for the system. That is, pH correlates positively with values of up to 4 previous days, and from that moment on the system does not remember. In the case of the Higereta (Figure 3a) this value is 6. For conductivity autocorrelation functions, the Higereta (Figure 3c) presents a two-day memory, whereas the Chorrito (Figure 3d) remembers one day.

Cross-correlation Function:

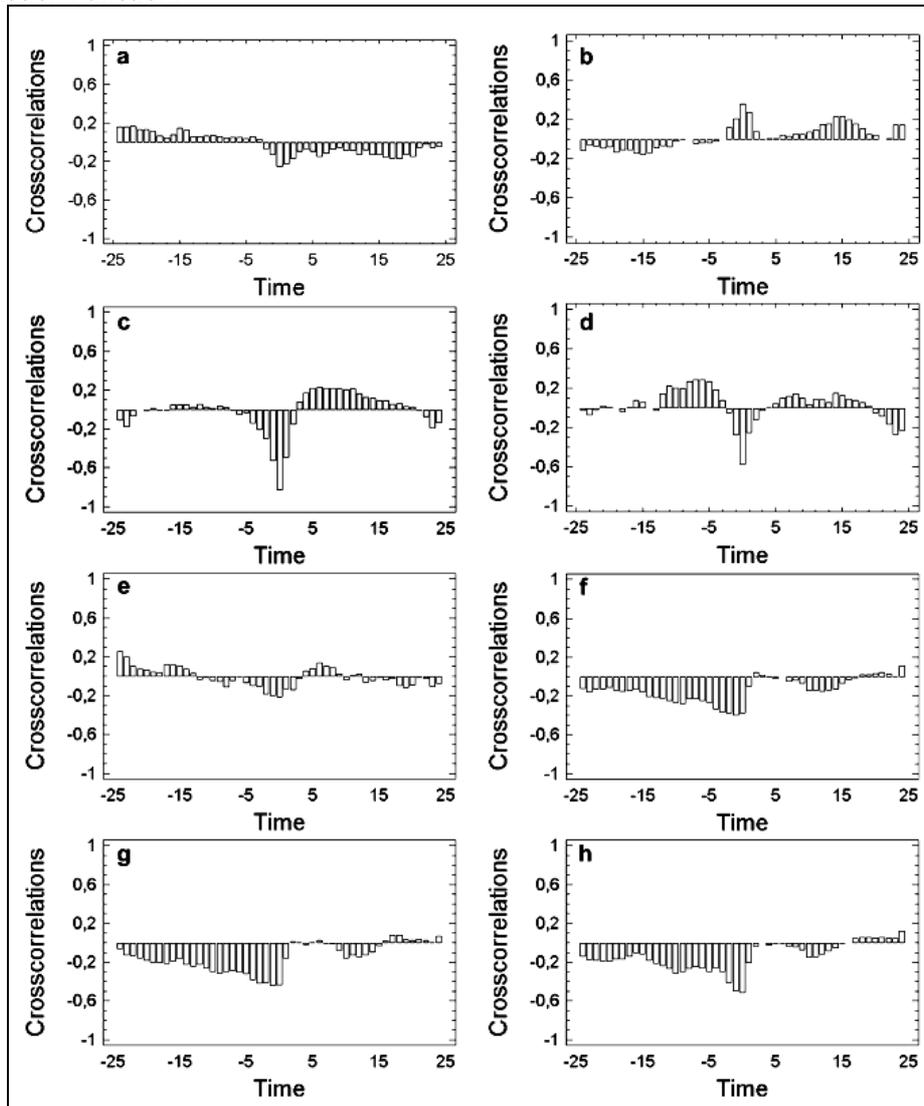


Figure 4: CrossCorrelation Function

The Crosscorrelation Function analysis displays a plot (Figure 4) of the estimated correlations between a time-series variable at time t and a second time-series variable at time $t + k$ as a function of the time differential k . The cross-correlation chart between Higereta pH and precipitation (Figure 4a) shows how correlation coefficients take positive and discrete values from $t = -25$ to $t = -3$, and from that moment they decrease rapidly reaching the minimum at $t=0$. They remain with negative values until the end. The same chart applied to the Chorrito (Figure 4b) shows a very different pattern. Coefficients take discrete and negative values up to $t = -3$. At this point, a rapid growth with a maximum at $t=0$ starts, with a new decrease to a new minimum at $t=3$. Later on a new slightly softer maximum appears at $t=15$.

Water level as opposed to conductivity reaches a maximum coefficient close to 0.8 and negative at $t=0$ in the Higereta (Figure 4c), showing a similar pattern with a lower correlation (0.6) in the Chorrito (Figure 4d).

Fe as opposed to pH no such apparent correlation can be seen in the Chorrito (Figure 4e), but a relative negative maximum appears again at $t=0$. The rest of metals in the Chorrito correlate with mean and negative coefficients and absolute maximum at $t=0$; from that moment on the coefficient is near zero (Figures 4f, 4g, 4h).

DISCUSSION

The values observable in the statistical summary of variables (Table 1 and table 2) show the existence of different responses in one and another channel, which can be associated at first to different phenomena. In this sense, in the Chorrito stream mean pH values and variance, conductivity and sulphate and metal content show a phenomenon of extraordinarily high water channel acidification and metal dissolution, which are not compatible with ARD processes and, as a result, can be associated to AMD processes in the environment. On the other hand, these values in the Higuiereta can be associated to the action of ARD processes in the studied geological context.

The correlation matrix between variables (Table 3) allows us to establish hypotheses about the existence of cause-effect relationships in the river system. Precipitation gives negative Pearson's coefficients with conductivity in both channels, but much higher in absolute values in the Higuiereta. In both cases it is evident that precipitation causes a decrease of ion concentration by dissolution in water, which is more remarkable in the Higuiereta due to the absence of great sulphide masses to be leached in this drainage basin. The same phenomenon can be observed when conductivity correlates with water level.

In the Higuiereta stream, pH has a mean and positive coefficient in relation to conductivity, which informs of the moderate impact of the metal load on water conductivity, having into account that the lower the pH, the greater dissolution capability and, as a result, the more metals available. Consequently, if they are related to conductivity, as occurs in estuarine environments, they should yield negative coefficients (Borrego et al., 2002; Grande et al., 2000-2003b; Sáinz et al., 2002-2003). In the studied case, sulphate load is more directly implied in the environment acidification process. In this same channel pH values correlate negatively with water level. This value indicates that the increasing flow causes a pH decrease, that is, rainfall causes the waters acidification process almost simultaneously to the level increase in this stream, since there are no waste dumps or mining workings that may delay the arrival of the water to the channel.

The absence of correlation between pH and conductivity in the Chorrito is difficult to interpret, even attending to Lyew and Sheppard's work (2001), who suggest that conductivity changes do not always match pH changes in waters under AMD processes. In our case, conductivity appears closely linked to sulphate content and, to a lesser extent, to metal load. In this context we understand that high correlation between pH and conductivity should be expected if we admit that the process of sulphide oxidation generates, on the one hand, sulphates (that increase with conductivity), and on the other, hydrogenions (that acidify the water). This can be explained considering that at the pH values registered (2.29-4.46), all the considered metals remain in solution, as their precipitation as hydroxides and oxides occurs at higher pH (Fe^{3+} 3.5 – 4.5, Cu^{2+} 6.5 – 7.5, Zn^{2+} 8.0 – 9.5, Mn 8.5 – 9.5) (Singh and Rawat, 1985).

In many fluvial environments iron oxy-hydroxides have a great influence on the behaviour and distribution of heavy metals, because due to their large surface area they are very efficient metal ion scavengers, and therefore they exert strong control over the concentration and migration of these elements in natural waters. However, in the samples of El Chorrito a low correlation level between Fe and Mn. This may be due to the fact that Fe oxides start precipitating with pH values ranging from 3 to 4.5, while the rest of metals remain in the dissolved phases. Because in this environment pH holds at very low values, only Fe oxides, and not the rest of metals, are incorporated to the particulated phases. Many of these Fe oxides form ferruginous crusts and accumulations of yellowish Fe-oxide rich loams such as hematites, which are usually found on fluvial channel banks.

It must be taken into account that in fluvial systems that are not affected by AMD, the most frequent Fe compounds are poorly ordered amorphous ferric gels, with a strong capacity to collect free metal ions, i.e., those associated to the dissolved phases. Fe-precipitates in acid mine drainage are mainly Fe (III)-oxyhydroxysulphides (oxyhydroxysulphates) and oxy-hydroxides, and they seem to be structurally different from amorphous ferric gels. In fact, the sediments and suspended particulated matter (SPM) object of study in the Tinto River are dominated by Fe oxy-hydroxides. However, adsorption studies always relate metals to ferric gels. The adsorption margin for Cd, Cu and Zn in freshwater appears at pH 4, under which capture does not occur, always referred to ferric gels. If Fe compounds involved in adsorption processes are oxyhydroxysulphides (oxyhydroxysulphates) and oxy-hydroxides, the pH that allows the beginning of the transfer of metals from dissolved to particulated phases is probably over 4.

Time evolution charts (Figure 2) warn of the existence of cause-effect relationships between precipitation and the channels pH variations, and at the same time, between these and the waters chemical makeup.

The appearance of a temporary connection between the rainfall occurred in the drainage basin around sampling day 19 and pH variations (Figure 2a) induced in both streams seems evident. So, whereas in the Higuiereta these rains would have caused a pH increase from values close to pH 6 to values slightly above pH 7, in the Chorrito they would have generated a decrease from values close to pH 3.6 down to pH 2.5. The justification of this phenomenon is the following: in the Higuiereta we start from slightly acid values that would be the consequence of the slight acidification imposed by ARD processes, since there are no mining operations in the drainage basin. The rains on day 19 cause an immediate decrease of almost one pH unit on day 20 as a result of soils washout and outcrops in the drainage basin. From that moment on, the increase of available inflow causes the dilution of the stream water and therefore the increase of pH, which becomes stable at around 7. In the Chorrito, a channel under the influence of mining activity, the rains would have caused an initial dilution that is shown by a slight pH increase. From that moment on, waste dumps and mining operations would have started discharging water in its drainage basin, releasing water affected by AMD processes with pH of around 2.5. Rainy events on days 47 and 70 would have caused the immediate dissolution of the acidic channel water for one or two days, and these

instant increases of the inflow would have caused pH peaks that appear on these dates. These pH peaks coincide, considering the torrential nature of these channels, with water level increases corresponding to floods induced by precipitation and with decreases of iron and sulphate concentrations. As a result of the drainage process in waste dumps and mining workings, these peaks also appear temporarily more softened in the Chorrito. Kim and Chon (2001) justify a similar behaviour of mine water in Youngdong (South Korea) as the consequence of dissolution processes of salts formed on the surface during pore water evaporation.

The autocorrelation function applied to pH values shows a higher 'inertia' for the Higuiereta time series (Figure 3a). This phenomenon can be interpreted as a consequence of the greater stabilisation of this parameter around pH 7 and of the lower relative abundance of external stimuli that might modify this value. Conversely, in the Chorrito (Figure 3b) we find that pH only correlates with those values from the 4 previous days, as opposed to the 6 days in the Higuiereta. This lower inertia can be justified as a consequence of the great amount of external agents (waste dumps, mining workings, channelling, etc.) potentially implied in leaching processes, final responsible for pH variations. The same can be said about conductivity series (figures 3c and 3d).

The cross-correlation function for pH as opposed to precipitation shows different behaviours in each stream. In the Higuiereta (Figure 4a) we find a maximum at $t=0$ but of negative sign, which informs us of the almost immediate acidification process (less than one day, the sampling interval) in this channel waters. As a result, precipitation would be leaching surface sulphate outcrops in the drainage basin, which considering the scarce infiltration and the absence of waste dumps and mining workings in the basin would be rapidly transported by surface runoff to the Higuiereta channel. The correlogram shows how coefficients take negative values and are temporarily softened around time zero in a three-day interval. This allows us to propose a 'surficial' washout time of three days, after which outcrops become clean until a new meteorization process takes place, causing surficial alteration and leaving a new load available to rainfall. This will be reflected on the water pH in the following rainy event.

The Chorrito (Figure 4b) undergoes a different process. The absolute maximum at $t=0$ now takes a positive value, which implies that precipitation causes an initial dilution of the channel waters without substantial ionic discharge, and therefore an increase of pH, since there are no surficial outcrops to be exploited in the drainage basin. From the third day after the start of rainfall the coefficient turns negative, that is, the channel would be receiving acidic inputs with a maximum on day 15. It is remarkable how the function takes negative values for the whole interval after rainfall starts. This can be explained because of the discharge time of waste dumps and mining workings in the zone into the drainage basin. The maximum absolute value found at $t=+15$ instant shows a greater correlation between precipitations occurred at an instant and the pH value 15 days after, or more exactly, in a four-day interval around day 15. It is a relative increase that in absolute terms does not reach extreme values. However, we understand that its significance is remarkable given that it is an environment under multiple variations that result into this evident coupling behind the time in 15 days. This result can be suggested as mean time of waste dumps discharge. pH values around day 15 show the previous progressive increase in absolute values as water coming from waste dumps arrives to the channel and its subsequent decrease as the system becomes homogeneous by dilution in clean waters.

Cross-correlation function correlograms of level/conductivity show a close dependency between these variables in both channels (Figures 4c and 4d), much more evident in the Higuiereta. The chart illustrates that conductivity highest values match the moments of minimum flow. This is a consequence of the fact that, in the absence of AMD phenomena, the more abundant the flow, the greater dilution, and therefore conductivity.

Finally, correlograms of metals (Figures 4f, 4g, 4h) with respect to pH in the Chorrito suggest that as pH decreases, metal concentration in water increases, except for Fe (Figure 4e). All this happens starting from a certain pH value that is different according to each metal solubility, and with $t=0$ as the instant when pH reaches the necessary value for dissolution to occur. In this sense, Chen and Lin (2001) suggest that the metal solubilization in the bioleaching process is highly dependent on the pH and its relationship with pH is non-linear. Similarly, Yukselen and Alpaslan (2001), test in a lab experiment and state that according to the results of column leaching tests, it was found that, the degree of heavy metal leaching is highly dependent of pH.

CONCLUSIONS

In short, for this sector the river network presents two types of channels with different behaviours:

Higuiereta stream. Channel undergoing ARD processes

Mean pH values range from 5.6 to 7.9. Conductivity has mean values around 0.3 mS/cm. Fe has a value of 0.3 mg l⁻¹, Mn of 0.1 mg l⁻¹, and sulphates of 43 mg l⁻¹.

A high correlation between pH and conductivity can be observed in this channel as a consequence of the moderate impact of metal load on conductivity.

Rainfall causes an almost immediate acidification process due to the washout of surficial sulphide outcrops, estimated to last for three days, and to the absence of waste dumps and mining workings that may delay the arrival of water to the channel.

Chorrito stream. Channel undergoing AMD processes

Mean pH values do not reach 3 with minimums close to 2. Conductivity is close to 3.3 mS/cm, and variance is 400 times higher than in ARD. Mean content in Fe is close to 220 mg l⁻¹ (800 times higher), in Mn is over 13.5 mg l⁻¹, whereas in sulphates it is close to 1600 mg l⁻¹ (37 times higher than in ARD).

In contrast to the observed behaviour in ARD environment and to what would be expected, there is no correlation between pH and conductivity, probably because in the pH interval where this water is set, practically all metals are in dissolution.

Rainfall initially causes an increase of pH due to the initial dilution of the channel waters without a substantial ionic input. From the third day on a decrease of pH occurs, which corresponds with the waste dumps and mining workings water discharge, estimated to last 15 days.

It may be expected that with the arrival of mine water discharges into the reservoir an abrupt rise of pH will occur in the acidic waters given the great volume of the catchment area. This pH increase will translate into a significant reduction of the dissolution capacity in the mixing waters that will cause the metal load carried by the mining channel to precipitate into the reservoir itself. A similar way to what happened in the Tinto and Odiel rivers estuarine zone when acid waters undergo the action of tidal clash (Grande et al., 2000). In any case, the metal and sulphate load will be accumulated in the reservoir, that will always be subject to pH variations of the environment, thus conditioning the chemical makeup of water and sediments.

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