Hydrochemical changes in a reservoir that receives water contaminated by acid mine drainage

M. L. de la Torre, J. A. Grande, T. Valente, M. Santisteban and J. C. Cerón

ABSTRACT

The aim was to characterize hydrochemical changes that take place in the Sancho reservoir, which receives waters contaminated by acid mine drainage (AMD) from the Meca River (Iberian Pyrite Belt, SW Spain). The sampling procedure comprised bimonthly campaigns carried out between October 2011 and May 2012, in the entrance of the reservoir and in the input river waters. In addition to *in situ* parameters, heavy metals and sulphate were analysed in the laboratory by photometry and atomic absorption spectrometry, respectively. The database was submitted to statistic treatment through the STATGRAPHICS Centurion XVI.I software. The results show a clear relationship between the sampling site in the entrance of the reservoir and in the watercourse, with an almost instantaneous cross-correlation. At the beginning of the sampling period a small rise in pH at both sites was detected, coinciding with a reduction in the concentration of heavy metals. This attenuation results from the dilution process caused by rain as well as the sorption by iron oxyhydroxysulphates that precipitate as a consequence of the above-mentioned rise in pH. The time changes that were detected in this system are due to the influence of input waters from the waste dumps of the Tharsis mines.

Key words | AMD, Iberian Pyrite Belt, pollution attenuation, reservoir

M. L. de la Torre (corresponding author)
J. A. Grande
T. Valente
M. Santisteban
J. C. Cerón
Centro de Investigación para la Ingeniería en Minería Sostenible,
Escuela Técnica Superior de Ingeniería,
Universidad de Huelva, Ctra,
Palos de la Frontera, s/n 21819,
Palos de la Frontera, Huelva,
Spain
E-mail: *mltorre@uhu.es*

T. Valente
Centro de Investigação Geológica,
Ordenamento e Valorização de Recursos,
Departamento de Ciências da Terra,
Universidade do Minho,
Campus de Gualtar,
4710-057 Braga,
Portugal

INTRODUCTION

The oxidation of sulphide minerals (e.g., pyrite) to produce acid mine drainage (AMD) has been widely studied (Grande *et al.* 2010a; Gray & Vis 2013; Valente *et al.* 2013). AMD with high levels of sulphate and heavy metals at low pH (Mylona *et al.* 2000) decreases the biodiversity of water-ecosystems (Tordoff *et al.* 2000; Sydnor & Redente 2002), contaminates the soil and plants, and endangers human health (Zhao *et al.* 2012).

The composition of AMD from mining areas is collectively controlled by means of local hydrology, geology and geochemistry. All over the world, AMD is discharged from millions of abandoned mine drainage tunnels and tailings piles (Cheng *et al.* 2009).

The Iberian Pyrite Belt (IPB), corresponding to an area of approximately 230 km long and 30 km wide, is located in SW Europe. It stretches from Seville in southern Spain to the western coast of Portugal, crossing the province of Huelva. This province is known for its metallogenic importance, as it contains numerous giant and supergiant massive sulphide ore deposits (Sáez *et al.* 1999). Therefore, the IPB has long been one of the world's most important mining regions, exploited since ancient times. The first mining works date back to the Copper Age (Nocete & Linares 1999), a period which is characterized by the production of copper obtained from carbonates (azurite and malachite), oxides (cuprite and tenorite) and even sulphides (calcosite and covelite) (Sáez *et al.* 2003; Nocete *et al.* 2005). As a result of this long intensive activity, the region has numerous abandoned and active mining works that are considered to be an important source of acid, sulphates and heavy metals (Azcue 1994).

Both AMD and acid rock drainage processes affecting the regional drainage network have been broadly described by several authors, such as Amils *et al.* (2011) who have studied the Tinto River for its extreme characteristics,

apparently quite similar to Mars, regarding sulphate and iron oxide deposits. Fernández-Remolar *et al.* (2005) have also analysed the implications of the sedimentary mineralogy and geobiology of the Tinto River, leading to a subsequent interpretation about the Mars rocks. Another research line was pursued by Braungardt *et al.* (2003), who focused their attention on the geochemistry of the Tinto and Odiel river estuaries. Similarly, Carro *et al.* (2011) studied both estuaries (from the Tinto and Odiel rivers) to determine the existence of three geochemical zones, while Elbaz-Poulichet *et al.* (2001) conducted research about metal biogeochemistry in the Tinto and Odiel rivers. These two rivers have also been studied by Sáinz *et al.* (2005), who have applied a system analysis to model the

contamination by AMD. As far as pit lakes are concerned, the work conducted by Santofimia & López-Pamo (2013) is also worth mentioning, by focusing on the role of surface water and mine groundwater in the chemical stratification of an acidic pit lake. From a broader perspective, Sánchez-España *et al.* (2005) reported on the physical properties and water chemistry of 64 AMD discharges from 25 different mines in the IPB.

In semiarid climates, reservoir construction is one of the most common alternatives to cover the water needs of both population and industry alike. The vulnerability of these water surfaces to contamination is much greater than in underground waters (Grande *et al.* 2010a, b). The Sancho reservoir was built in 1962 and is nourished by the waters
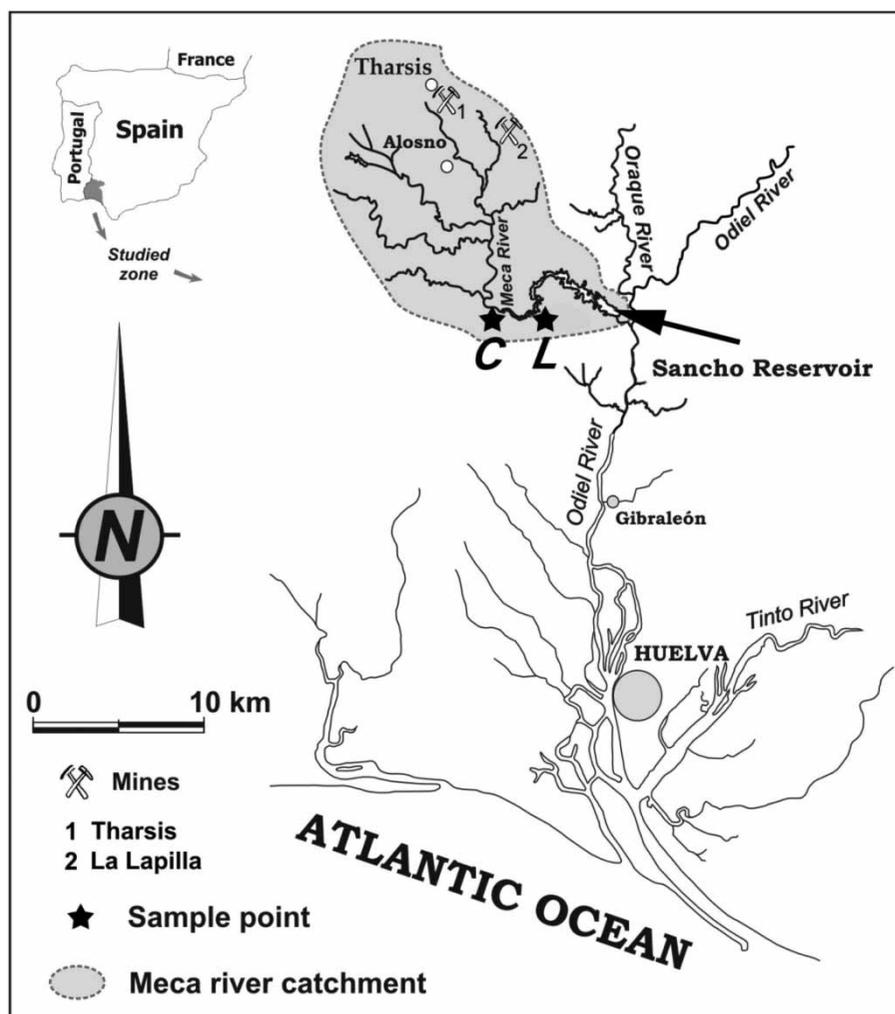

Figure 1 | Location map in which are situated the Sancho reservoir and water sampling points.

of the Meca River (Figure 1). The reservoir has a maximum storage capacity of $58 \, Hm^3$ and the impounded water covers an area of 427 ha. The watershed area totals $314 \, km^2$. The crest length is 224 m and it is located 56 m above sea level.

Compared with other cases in the world, the Sancho reservoir is an extreme case of AMD pollution (Galvan *et al.* 2009) due to the input waters from the Meca River (Figure 1), which actually receives contaminated waters from different subsidiary tributaries affected by AMD, mostly from the abandoned Tharsis mine (SW Spain). Here, waste dumps occupy an area of more than 300 ha. In addition, there are two big open pits and a large number of mining facilities, thus contributing towards the particularly degraded scenario resulting from industrial activity, ultimately responsible for AMD generation. Reservoir water is used for industrial purposes to supply the pulp mill located 15 km downstream, namely in San Juan del Puerto (SW Spain) (Grande *et al.* 2012).

Several authors have described the processes which affect the Sancho water reservoir: Sarmiento *et al.* (2009) describe natural attenuation processes, while Torres *et al.* (2010) make a proposal for the reservoir's geochemistry control process.

The aim of this study is to model the hydrochemical changes that take place in a reservoir (Sancho reservoir), at the confluence of a river contaminated by AMD, as well as the possible attenuation of the corresponding polluting load. The study is based on the comparison of the water properties analysed in two sites: namely, in the entrance of the reservoir and upstream in the Meca River, which contributes to AMD influence.

The importance of this study is due to the fact that it may serve as a methodological basis for the possible definition of processes to be adopted in similar cases on a worldwide scale (for example, Dillon reservoir, Colorado, USA or Spring Creek reservoir, Iron Mountain, California, USA). Similarly, at a local scale, it may also be applied to the forthcoming construction of the La Alcolea and La Coronada reservoirs, located in the Odiel River (the IPB, SW Spain), to be used for irrigation purposes.

MATERIALS AND METHODS

Between October and May, a bimonthly sampling was carried out during the hydrological year 2011–2012. The water samples were collected at a specific point on the River Meca, the watercourse responsible for the contamination of the Sancho reservoir by AMD, and at another point already located in the reservoir (namely, in the so-called confluence zone), thus accounting for a total of 17 days of sampling collection. At each of these points, pH, conductivity and total dissolved solids (TDS) were measured *in situ* using a Crison MM40 portable multimeter. Two water samples were also taken at each point in sterilized polyethylene containers, one to determine the sulphates and the other to determine the heavy metals. Nitric acid was then added to obtain a pH <2 in order to prevent the precipitation of metals during transportation to the laboratory. Transportation was carried out in 100 and 200 mL PVC containers, respectively, in a portable refrigerator at a temperature of 4 °C.

In the laboratory, the water samples were vacuum-filtered using 0.45 micron cellulose nitrate filters (Sartorius 11406-47-ACN) with a glass Büchner flask connected to a vacuum pump in order to accelerate the flow. Once filtered, the water samples were then stored in hermetically sealed polyethylene containers in a refrigerator at a temperature between 1 and 4 °C, and later on, they were analysed for sulphates, Fe, Cu, Zn, Mn, Cd, Ni, Co, As, Sb, Pb and Al. All the reagents used were analytical grade or of *Suprapur* quality (Merck, Darmstadt, Germany). The standard solutions were Merck AA Certificate. Milli-Q water was used in all the experiments. The Optic Ivymen System AC-L4 was used as the water distiller.

The measurement of sulphates was carried out by photometry using a MACHERY-NAGEL PF-11 photometer. The heavy metals analysis was conducted through a Perkin Elmer AAnalyst 800 Atomic Spectrometer. These elements were analysed by atomic absorption air-acetylene flame using hollow-cathode lamps as a source of energy. Cadmium analysis was performed by electrothermal atomic absorption spectrometry, using the AAnalyst 800 graphite furnace, equipped with a Zeeman background

corrector and an EDL (electron discharge lamp). Arsenic was determined using Perkin Elmer Fias 100 flow injection equipment.

Data from the analytics, as well as the parameters measured in the field, were then entered into a matrix and subject to graphical and statistical treatment using the STATGRAPHICS Centurion XVI.I software package. The following statistical procedures were also performed. (1) Time series analysis to study the evolution throughout a given time interval. In this case, the parameters to be considered were precipitation and variations induced by it in the water chemical composition in order to determine possible relationships between both of them. (2) Cross-correlation gives relevant information about the relationship between two variables as a function of a time-lag applied to one variable.

RESULTS

Statistical summary

Table 1 shows the average values for the parameters analysed at the sites, both in the watercourse and in the

Table 1 | Average values for the parameters analysed at the watercourse site and the reservoir site and percentage comparison

Parameter	River Meca	Reservoir	% Comparison
pH	2.53	3.3	23.4
EC (μS cm^{-1})	1,051.59	892.70	15.11
TDS (mg L^{-1})	667.35	563.58	15.55
Fe (mg L^{-1})	20.34	4.95	75.66
Cu (mg L^{-1})	9.20	2.32	74.78
Zn (mg L^{-1})	4.09	3.88	5.13
Mn (mg L^{-1})	6.71	3.94	41.28
Cd (mg L^{-1})	0.80	0.12	85.00
Ni (mg L^{-1})	0.22	0.12	45.45
Co (mg L^{-1})	0.55	0.38	30.90
As (mg L^{-1})	0.13	0.03	76.92
Sb (mg L^{-1})	0.007	0.006	14.28
Pb (mg L^{-1})	0.36	0.33	8.33
Al (mg L^{-1})	0.49	0.44	10.20
SO$_4^{2-}$ (mg L^{-1})	781.92	323.88	58.58

reservoir. One can observe that the average pH value in the watercourse (2.53) is lower than that at the reservoir site (3.3). All the other parameters have reached average values which are higher in the watercourse – in particular, electrical conductivity (EC) ranges from about 1,052 (μS cm^{-1}) to around 893 (μS cm^{-1}); furthermore, Fe has an average concentration of 20.34 (mg L^{-1}) in the watercourse, throughout the sampling campaign, falling to 4.95 (mg L^{-1}) in the reservoir, that is, the average Fe concentration drops by 76% from the sampling site in the watercourse thus contributing to AMD influence to the sampling site in the Sancho reservoir. Cu goes from 9.20 (mg L^{-1}) in the watercourse, to 2.32 (mg L^{-1}) in the reservoir, falling by nearly 75%. Cd falls by 85% from 0.80 (mg L^{-1}) to 0.12 (mg L^{-1}) from the watercourse to the Sancho reservoir. The element As has an average concentration of 0.13 (mg L^{-1}) and 0.03 (mg L^{-1}) both in the watercourse and the reservoir, falling by 77%. This decrease in concentration was also observed in the other analysed parameters, although in a less profound manner.

Cross-correlation function

In order to establish the possible correlations between these parameters – not at a single site, but between both sampling sites – a cross-correlation analysis was conducted between pairs of variables from both sites, as can be observed in Figure 2. At the same time, cross-correlation is aimed at determining how the changes in concentrations which take place in the watercourse actually affect the reservoir, as well as the possible delay in such correlation. Each unit was fixed at 15 days since the sampling process occurred with a 15-day interval, as described in the Materials and methods section.

Time-evolution graphs

In order to provide a thorough in-depth hydrochemical comparison of both sites, Figure 3 shows the time-evolution graphs, with rain to the left of the y-axis in each graph, together with a parameter for the watercourse and reservoir sites, both to the right of the y-axis. In all cases it can be observed that the line that represents
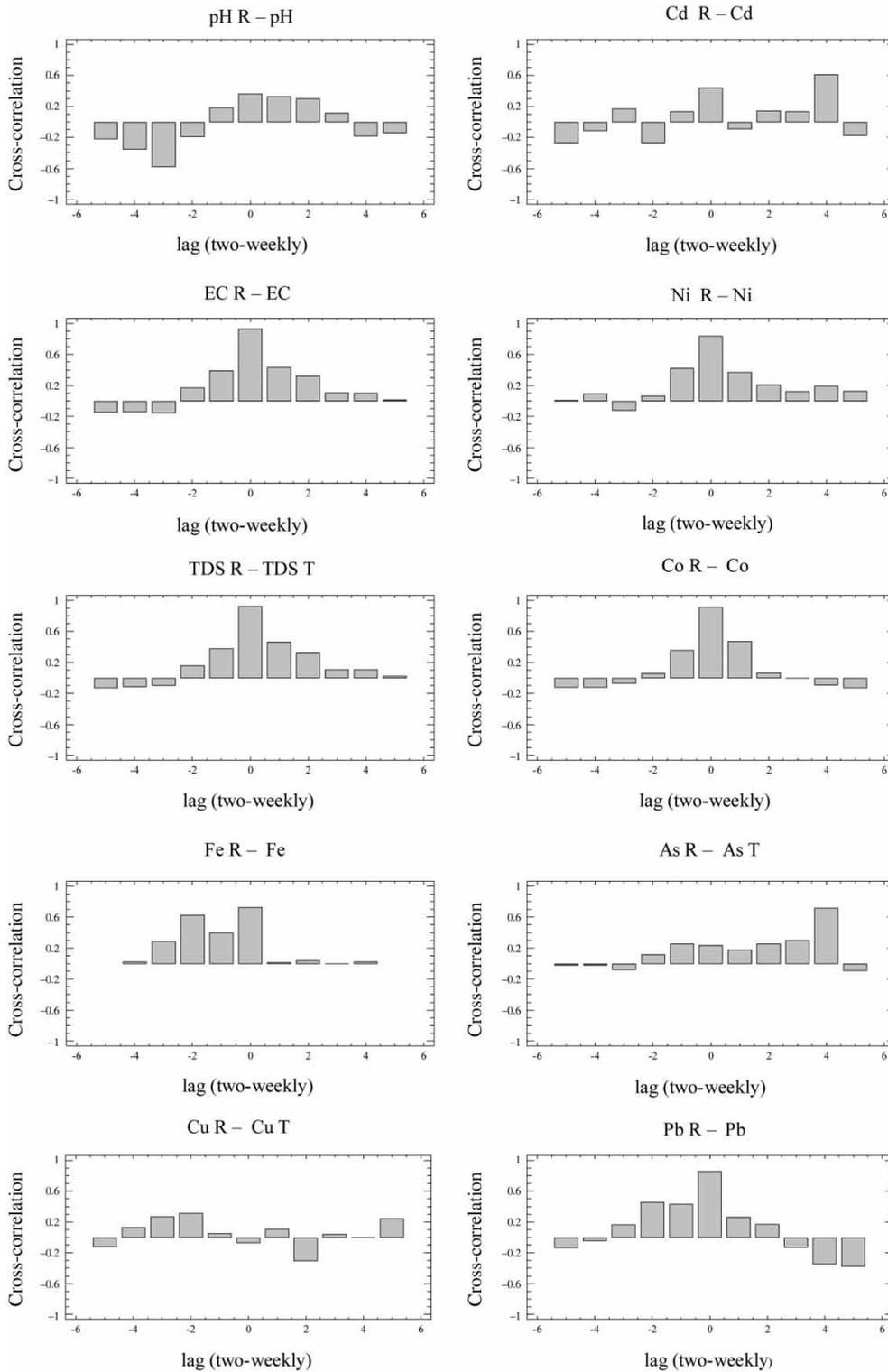
Figure 2 │ Cross-correlation functions between parameters to determine how the changes in concentrations that take place at the site in the watercourse affect the site in the tailwater, as well as the possible delay.
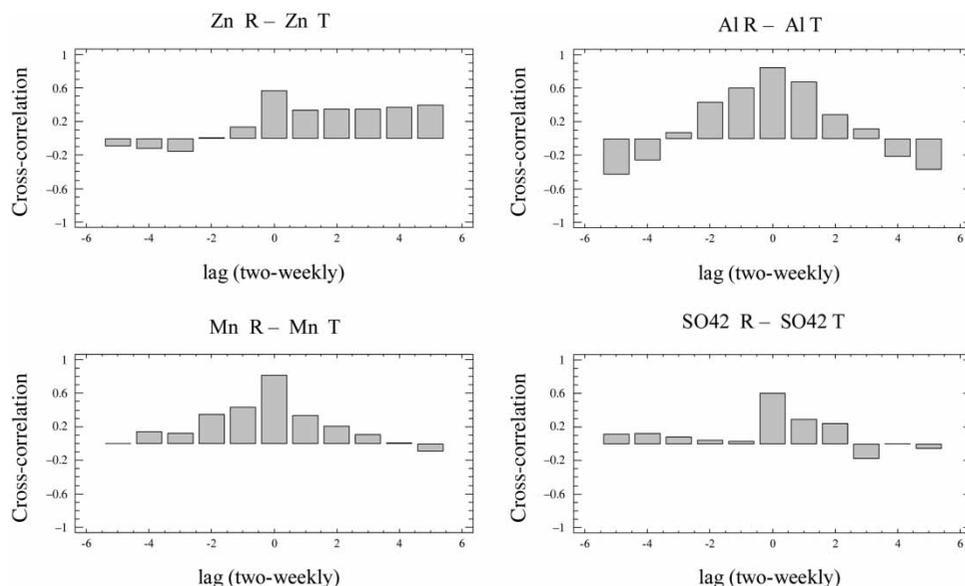
Figure 2 │ Continued.

the time evolution of the corresponding parameter at the watercourse is above that of the reservoir site for the greater part of the year. The pH is an exception, thus revealing an opposite behaviour. Throughout the campaign conducted in the watercourse, the values are always more acid than in the reservoir. One can also observe that in most of the graphs (EC, TDS, Fe, Zn, Mn, Ni, Co, Sb and sulphates) there is a similar increase in the concentration of the parameters from week 11 onwards, with a sharp increase in such concentration taking place in week 16 in both sites. This increase coincides with a spike in rainfall.

DISCUSSION

Statistical summary

Table 1 shows that the Meca River, with low pH values and high heavy metals concentrations, is contaminated by AMD. This pollution ends up affecting the Sancho reservoir, where it persists. However, some attenuation is also observed in this contamination, namely when the waters from the river and reservoir mix. In particular, an increase can be detected in the average pH, together with a large fall of around 75% in the average concentrations of Fe, Cu, Cd and As, as well

as somewhat lower drops in Mn, Ni and sulphates. Smaller reductions of less than 30% were observed for Zn, Co, Sb, Pb and Al. This attenuation can be explained by the dilution process and the iron oxyhydroxysulphates precipitation resulting from a rise in pH, as well as the subsequent metals sorption phenomena. Sanchez-España *et al.* (2006) stated that up to 70% of the Fe and nearly 95% of the As initially dissolved in the AMD emissions can actually be removed from the solution, at some mine sites in the IPB, at a distance of 1 km or less from the discharge points. On the other hand, the most soluble cations (Cu^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}) actually remain essentially as dissolved solutes until the pH is near-neutral.

Cross-correlation

As far as cross-correlation functions (Figure 2) are concerned, it is clear that there is a close relationship between most of the parameters in the watercourse and in the reservoir. Such a correlation occurs with $t = 0$, as a consequence of the short distance between both points (roughly 300 metres). This suggests that rises or falls in a specific parameter in the watercourse will have an almost immediate consequence at the sampling site in the reservoir. Data show that pH, EC and TDS, Fe, Zn, Mn, Ni, Co, As, Sb, Pb, Al and sulphates are very closely related at both sites,
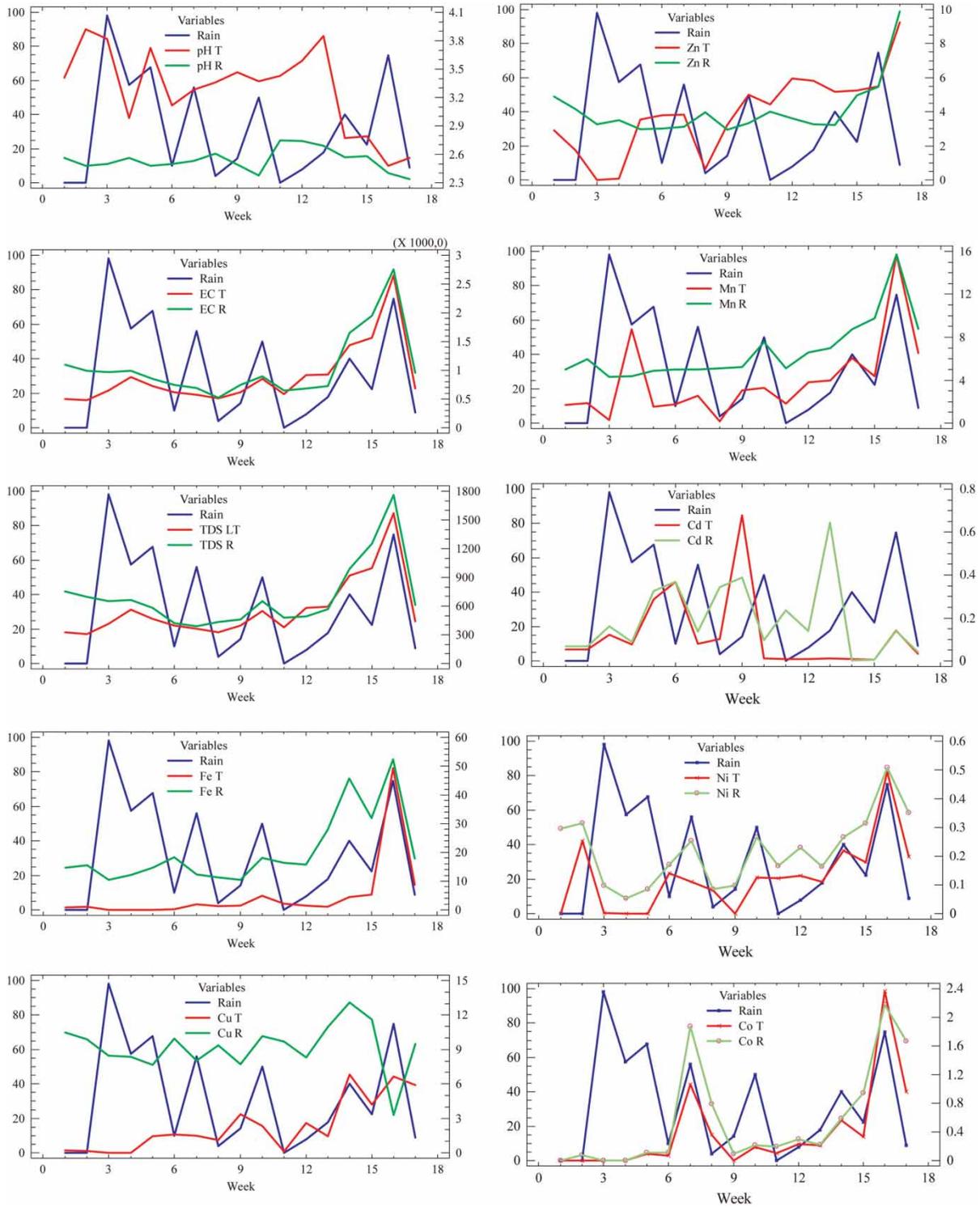
Figure 3 | Time-series graphs for each parameter in the watercourse and the tailwater with rain in order to provide a hydrochemical comparison of both sites in greater depth. The units in which the parameters are expressed are: rain in mm, EC in μS cm^{-1}, TDS in mg L^{-1}, SO$_4^{2-}$ in mg L^{-1} and all the metals in mg L^{-1}.

with the maximum correlations set above 0.6. This maximum correlation appears in a time frame less than 15 days, which is less than the sampling period in all cases, with the exception of the As, which has a 60-day delay. The result associated with As indicates that a rise or fall in its watercourse concentration actually leads to increases or decreases in the reservoir 60 days later. Additionally, the oxidation of Fe(II) to Fe(III) is completed in all the mine waters after a time span of between 1 and 2 weeks (Sanchez-España *et al.* 2006), thus coinciding with the time elapsed between samplings. With reference to cross-correlation functions, one also observes that As has a delay of 60 days between the reservoir and the watercourse, possibly as a consequence of the rapid scavenging of As near its source by sorption on hydrous iron oxides. The As(V) uptake by schwertmannite can take place by either coprecipitation (displacing structural SO_4^{2-} in the schwertmannite stoichiometry) or post-precipitation sorption (via ligand exchange with SO_4^{2-}). Regenspurg & Peiffer (2005) have reported large-scale substitutions of sulphate by arsenate in schwertmannite. Therefore, As could have been either coprecipitated and/or sorbed by schwertmannite during oxidation. Moreover, at low pH, acidic solutions are commonly saturated with respect to a number of iron minerals like jarosite, schwertmannite and goethite, although schwertmannite is usually the mineral favoured to precipitate at pH less than 3.5 as well as in high redox conditions (Eh >700 mV) (Sanchez-España *et al.* 2006; Valente *et al.* 2012).

Time-evolution graphs

According to Sánchez-España *et al.* (2006), the metal–sulphate ionic complexes are the dominant dissolved forms under which Fe(III) and Al(III) are present in the solutions at low pH, with the hydroxyl-containing ionic complexes having very minor or even negligible presence. As the pH increases, the sulphated ions become less abundant and are progressively replaced by the hydroxide forms (e.g., $Fe(OH)_2^+$, $Fe_3(OH)_4^{5+}$), which become dominant under neutral conditions. The divalent metal cations (Mn^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}) can be present either as free aqueous ions or as sulphate species. This process can explain the rise in concentrations of some parameters from week 11 onwards

(Figure 3), which coincides with a fall in pH. This change in trend detected in week 11, as a result of the fall in pH from this date onward, takes place due to the swelling factor in the waste dumps. The rainfall which occurred at the beginning of the campaign loads the waste dumps. According to Sáinz *et al.* (2002), and considering the climate context of the IPB, the rainfall at the beginning of the hydrologic year promotes accumulation of water in the waste dumps. After saturation, they start to discharge contaminated water. Therefore, from week 11 onwards the rainfall led to an increase in flow from the waste dumps, and, consequently in the metals concentration observed both in the watercourse and in the reservoir.

These results highlight the influence of waste dumps, as the major source of AMD in the region (Sainz *et al.* 2003), in the Sancho reservoir. Such a significant impact is due to the high surface occupied by waste dumps without restoration in the catchment of the Meca River (more than 300 ha; Valente *et al.* 2013). The magnitude of the impact of the AMD from the Meca River becomes evident by the high level of contamination in the Sancho reservoir. The pH values below 4, together with the high metals concentration, restrain the use of water, thus preventing its use for domestic and agricultural uses (Grande *et al.* 2010b; Cerón *et al.* 2013).

Furthermore, one should bear in mind that the River Meca is not a generating medium; the waters are evolving. The values ascribed for the metal load in a generating medium are 100 times greater (Grande *et al.* 2010b).

CONCLUSIONS

Being used for industrial purposes, the Sancho reservoir is contaminated by AMD from the contributions of the River Meca, a typical mining watercourse which carries the contamination from the Tharsis mines. However, some attenuation is detected in this contamination when the waters in the watercourse mix with those in the reservoir. There is a rise in pH and significant falls in the average concentrations of most of the heavy metals analysed. This attenuation is a consequence of the precipitation of the iron oxyhydroxysulphates produced by the rise in pH, as well as the subsequent phenomena of sorption and dilution.

According to the majority of the parameters, a clear relationship is seen between the reservoir and the water-course, with an almost instantaneous cross-correlation.

The cross-correlation function turns out to be an effective tool for establishing relationships of cause-and-effect temporality between hydrochemical parameters before and after they merge with the reservoir. In addition, it allows for determining the corresponding response times to the stimulus produced by the precipitation, something which seems to be useful beyond a sole regional level, especially when applied to other reservoirs with similar problems.

At the beginning of the campaign, there was a small rise in pH at both sites, which was later reversed starting from week 11, together with a sharper fall in week 16. However, this initial increase coincided with a reduction in the concentration of heavy metals, which started to rise from week 11 onwards and with a sharp rise in week 16. This time behaviour is due to the discharge from waste dumps of the Tharsis mines, which discharged the maximum volume of water at the beginning of the campaign. Such a discharge was a consequence of the first rains, and as the campaign went on, the flow gradually decreased, despite an increase in the concentration of heavy metals and acidity.

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