Study of the transit and attenuation of pollutants in a water reservoir receiving acid mine drainage in the Iberian Pyrite Belt (SW Spain)
M. Santisteban, J. A. Grande, M. L. de la Torre, T. Valente, E. Perez-Ostalé and M. Garcia-Pérez

ABSTRACT

The Sancho Dam was built in 1962 and is fed by the Meca River, which receives water from subsidiary tributaries affected by acid mine drainage (AMD), mostly generated by the abandoned Tharsis mining complex. This study focuses on the hydrochemical relations observed between the water at the entrance of the reservoir and a point located further away, specifically at the dam. The main aim is to analyze the water parameters in both monitored points, in order to evaluate possible attenuation processes and to propose a spatial evolution model of the pollutants’ load by using cross-correlation functions. Concentrations of metals and sulfates put in evidence their contamination by acid mine drainage, with greater pollution load at the entrance of the reservoir than in the dam, due to the reduction of the same in the course between the two points. This attenuation results from the precipitation of iron oxyhydroxysulfates produced by the increase in the pH as well as by dilution and sorption phenomena. The cross-correlation functions show the close relationship between the two sampling points with a transit time of contaminants less than 1 week ($t = 0$) for most cases, due to the small distance between the two points (about 300 meters).

Key words | AMD, cross-correlation, Iberian Pyrite Belt, metals, sulfates, water dam

INTRODUCTION

The sulfides have high potential to react with oxygen and water, and weathering involves a series of geochemical and microbiological reactions that result in acid drainage and extremely high concentrations of sulfate, metals (e.g., iron, copper, lead, zinc) and metalloids (arsenic, antimony) (Lowson 1982, Parker & Robertson 1999; Younger et al. 2002). The heavy metal contamination has three major issues (Sáinz et al. 2002): they are not biodegradable, they suffer bioaccumulation and biomagnification and they are toxic and degrade the ecosystems.

The environmental literature usually distinguishes between two different processes of water pollution caused by sulfide oxidation: the first, named ARD (acid rock drainage), is a geochemical natural process of temporal patterns, common in geology; the second, called AMD (acid mine drainage), is produced when massive amounts of effluents are generated by the mining activity (Sainz et al. 2002).

AMD generation can persist hundreds of years after the mines have closed, affecting the water resources and causing deleterious effects on aquatic life (Demchack et al. 2004 in Casiot et al. 1999).

The Iberian Pyrite Belt (IPB) is located in the west of the Iberian Peninsula (Figure 1), forming a metallogenic province of 230 km long and 30 km wide. It contains numerous giants and supergiants massive sulfide deposits of Paleozoic age, the largest in the world according Sáez et al. (1999). These authors estimated reserves of above 1,500 Mt, in eight supergiant deposits (>100 Mt) and an undetermined number of smaller deposits, commonly associated with a mineralization of stockwork type and
footwall alteration haloes. Pyrite, with greater or lesser proportion of copper, is the major mineral with an average content of 46–49% sulfur, 40–45% iron, 0.6–1% Cu, 0.5–1, 5% Pb, 1–3% zinc, 0.1–0.6% of arsenic and other metals (Ortiz 2003). Associated with pyrite there are other mineral phases, such as sphalerite, galena, chalcopyrite and many other minor ones (Sáez et al. (1993)).

The intense mining activity in this metallogenic region has left a legacy of 87 abandoned mines (Pérez-Ostale 2014), with wells, tunnels and other mining structures. These many kilometers of tunnels and 200 million m³ of wastes are scattered throughout hundreds of tailings and mining dams, being sources of contamination of water and sediments of the river basins and coastal zone of influence (Sáinz et al. 2004).

The Spanish Society of Dams and Reservoirs (SEPREM), officially recognizes the existence of 30 AMD sites, which arrives at the reservoirs with low pH and high metal and sulfate dams and reservoirs in the IPB, of public and private ownership, and used for agricultural, industrial or urban supply. Many of these reservoirs are located in channels affected by loads. On arrival at the reservoirs, the waters of these channels undergo a strong increase in pH which causes precipitation in the reservoir of most of the metal load transported by the mining channel accumulating in its bed (Santisteban et al. 2013). These processes have been described by Cerón et al. (2013a, b), Grande et al. (2013) and Santisteban et al. (2013, 2014).

Among the water dams constructed in the IPB for public supply there is the Sancho reservoir, which is the object of study in the present work. The Sancho Dam was built in 1962 and is fed by the Meca River which receives water from subsidiary tributaries affected by AMD, mostly generated by the abandoned Tharsis mining complex. The stored water is used for industrial purposes, supplying a pulp mill located 15 km downstream, in San Juan del Puerto (SW-Spain). The Tharsis mining complex is responsible for the maximum levels of contamination by AMD recorded in the Odiel basin (Sarmiento et al. 2009).

This study focuses on the hydrochemical relations observed between the water at entrance of the reservoir and
a point located further away, specifically at the dam. The main goal is to analyze the water parameters at both monitored points, in order to evaluate possible attenuation processes and to propose a spatial evolution model of the pollutants’ load.

MATERIALS AND METHODS

Sampling methodology

A weekly sampling campaign was carried out during the hydrological year 2012–2013, yielding a total of 32 days of sampling. The water samples were collected at a point where the river waters enter in the reservoir and at the dam.

During the sampling campaign, determination of pH, electrical conductivity and total dissolved solids was carried out in situ using a Crison MM40 portable multimeter. Following the measurements in the field, two water samples were taken and stored in sterilized polyethylene containers at each point: one to determine the sulfates and the other to determine the heavy metals. Nitric acid was added to obtain a pH < 2 in order to prevent the precipitation of the metals during transportation to the laboratory, which was carried out in 100 mL 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). Once filtered, the water samples were stored in hermetically sealed polyethylene containers in a refrigerator at a temperature of between 1 and 4°C.

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.

A Macherey-Nagel PF-11 photometer was used to determine the sulfate concentration.

The equipment used to carry out the metals and arsenic analyses was a Perkin-Elmer AAnalyst 800 atomic absorption spectrophotometer equipped with a graphite furnace and an air/acetylene-flame atomizer. The samples were introduced using the Perkin-Elmer AS800 Autosampler. Perkin-Elmer Lumina™ hollow cathode lamps (HDL and LDL) were used as sources of radiation.

Statistical methods

The data from the analytics, as well as the parameters measured in the field, were submitted to graphical/statistical treatment in order to apply cross-correlation, using the STATGRAPHICS Centurion XVI.I software package.

The cross-correlation function estimates the correlation that exists between a time series at a ‘t’ time and a second series at a ‘t + k’ instant as the function of delay or differential time ‘k’. It is particularly useful if two series are related with each other and, if they are, to determine whether one leads to the other.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Count</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Coefficient of variation</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (mg/L) - Tail</td>
<td>32</td>
<td>3.69</td>
<td>2.74</td>
<td>0.74</td>
<td>0.43</td>
<td>11.88</td>
<td>11.45</td>
</tr>
<tr>
<td>Cu (mg/L) - Tail</td>
<td>32</td>
<td>1.98</td>
<td>1.00</td>
<td>0.74</td>
<td>0.02</td>
<td>10.04</td>
<td>10.02</td>
</tr>
<tr>
<td>Pb (mg/L) - Tail</td>
<td>32</td>
<td>0.16</td>
<td>0.11</td>
<td>0.76</td>
<td>0.01</td>
<td>0.42</td>
<td>0.41</td>
</tr>
<tr>
<td>Cd (mg/L) - Tail</td>
<td>32</td>
<td>0.36</td>
<td>0.35</td>
<td>0.66</td>
<td>0.14</td>
<td>0.89</td>
<td>0.80</td>
</tr>
<tr>
<td>Zn (mg/L) - Tail</td>
<td>32</td>
<td>0.36</td>
<td>0.35</td>
<td>0.66</td>
<td>0.14</td>
<td>0.89</td>
<td>0.80</td>
</tr>
<tr>
<td>Ni (mg/L) - Tail</td>
<td>32</td>
<td>0.11</td>
<td>0.07</td>
<td>0.63</td>
<td>0.01</td>
<td>0.32</td>
<td>0.31</td>
</tr>
<tr>
<td>Mg (mg/L) - Tail</td>
<td>32</td>
<td>57.46</td>
<td>28.65</td>
<td>0.50</td>
<td>10.10</td>
<td>105.00</td>
<td>94.90</td>
</tr>
<tr>
<td>Ca (mg/L) - Tail</td>
<td>32</td>
<td>27.34</td>
<td>15.05</td>
<td>0.55</td>
<td>7.44</td>
<td>61.77</td>
<td>54.33</td>
</tr>
<tr>
<td>Al (mg/L) - Tail</td>
<td>32</td>
<td>0.54</td>
<td>0.20</td>
<td>0.36</td>
<td>0.09</td>
<td>0.89</td>
<td>0.80</td>
</tr>
<tr>
<td>As (mg/L) - Tail</td>
<td>32</td>
<td>0.02</td>
<td>0.10</td>
<td>4.91</td>
<td>0.00</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>Sb (mg/L) - Tail</td>
<td>32</td>
<td>0.01</td>
<td>0.03</td>
<td>2.16</td>
<td>0.00</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$ (mg/L) - Tail</td>
<td>32</td>
<td>278.50</td>
<td>153.45</td>
<td>0.55</td>
<td>95.00</td>
<td>764.00</td>
<td>671.00</td>
</tr>
</tbody>
</table>
RESULTS

Tables 1 and 2 show the results of the statistical summary corresponding to the chemical parameters analyzed weekly in both points: at the entrance of the reservoir (point that was named ‘tail’) and at the dam of Sancho reservoir (point called ‘dam’).

The results show that most parameters have a higher average concentration at the tail point of the reservoir than that of the dam (Figure 2). The highest values of sulfates are present at the tail with an average concentration of 278.50 mg/L, decreasing at the dam until it reaches a concentration of 225.50 mg/L. The remaining parameters have much lower concentration obeying the following order: Mg > Ca > Zn > Fe > Cu > Al > Pb > Ni > Cd > As > Sb. Mg has a still high concentrations, which decreases from 57.46 mg/L at the tail to 44.08 mg/L at the dam, as well as Ca, decreasing from 27.34 mg/L to 24.78 mg/L. With considerably lower concentration is Zn, with a presence of 3.14 mg/L at the tail to 2.90 mg/L at dam; Fe decreases from 3.69 mg/L to 1.18 mg/L; Cu has concentrations of 1.98 mg/L at the tail and 1.05 mg/L at dam; Al decreases its concentration from 0.54 mg/L at the tail to 0.52 mg/L at dam; Pb keeps its concentration of 0.16 mg/L at both points; Ni decreases from 0.11 mg/L to 0.08 mg/L; Cd and Sb maintained their values of 0.6 mg/L and 0.1 mg/L, respectively at both points; and As descends from 0.2 mg/L to 0.1 mg/L from one point to another.

Regarding the maximum and minimum values obtained at each point, these depend on the monitored parameter. Independent of being the maximum, the standard deviation, and the coefficient of variation, they are always higher at the tail than at the dam.

To determine what is the relationship between the concentrations of the parameters at the dam and the modifications of concentrations at the tail, as well as the possible delay (set each unit 1 week), cross-correlation function between pairs of variables of both sampling points have been carried out (Figure 3).

This figure indicates that most parameters are closely related at both points, reaching correlation coefficients of 1, for some cases, such as Pb and As. For Cd the correlation is of 0.9 between the two points, while Mg and Zn reaches a

Table 2  | Statistical summary of the parameters analyzed in the dam of Sancho reservoir

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Count</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Coefficient of variation</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (mg/L)</td>
<td>32</td>
<td>1.18</td>
<td>0.56</td>
<td>0.47</td>
<td>0.17</td>
<td>2.34</td>
<td>2.17</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>32</td>
<td>1.05</td>
<td>0.38</td>
<td>0.36</td>
<td>0.15</td>
<td>1.81</td>
<td>1.66</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>32</td>
<td>0.16</td>
<td>0.09</td>
<td>0.57</td>
<td>0.02</td>
<td>0.37</td>
<td>0.35</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>32</td>
<td>0.06</td>
<td>0.05</td>
<td>0.78</td>
<td>0.00</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>32</td>
<td>2.90</td>
<td>0.85</td>
<td>0.29</td>
<td>1.68</td>
<td>5.67</td>
<td>3.99</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>32</td>
<td>0.08</td>
<td>0.05</td>
<td>0.61</td>
<td>0.01</td>
<td>0.17</td>
<td>016</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>32</td>
<td>44.08</td>
<td>21.22</td>
<td>0.48</td>
<td>9.19</td>
<td>89.00</td>
<td>79.81</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>32</td>
<td>24.78</td>
<td>8.70</td>
<td>0.35</td>
<td>12.75</td>
<td>61.96</td>
<td>51.21</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>32</td>
<td>0.52</td>
<td>0.15</td>
<td>0.29</td>
<td>0.24</td>
<td>0.78</td>
<td>0.55</td>
</tr>
<tr>
<td>As (mg/L)</td>
<td>32</td>
<td>0.01</td>
<td>0.02</td>
<td>3.37</td>
<td>0.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Sb (mg/L)</td>
<td>32</td>
<td>0.01</td>
<td>0.01</td>
<td>1.11</td>
<td>0.00</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>SO4(^{2-}) (mg/L)</td>
<td>32</td>
<td>225.50</td>
<td>46.86</td>
<td>0.21</td>
<td>138.00</td>
<td>284.00</td>
<td>146.00</td>
</tr>
</tbody>
</table>

Figure 2 | Representation of the average values of the parameters analyzed at the tail and at the dam of the Sancho reservoir.
Figure 3 | Cross-correlation function between pairs of variables at the tail and at the dam of the Sancho reservoir.
maximum of 0.7. For the remaining parameters a correlation of about 0.6 is observed, being Fe the elements that correlates worst, with a value of 0.2.

The results also show that maximum correlation occurs at a time \( t = 0 \) (less than 1 week) in most cases (Pb, As, Sb, Cd, Mg, Al), that is, higher or lower concentrations of these elements in a point over the other, reflect an increase or decrease in less than a week time. There are cases such as Cu or Ni, which reach this maximum correlation a week later; Fe and Ca in \( t = 2 \), and sulfates that reach the maximum at \( t = 3 \).

**DISCUSSION**

The statistical summary shows that Sancho reservoir is affected by AMD processes due to the high metal load and sulfates. Nevertheless, there is an attenuation of contamination between the tail point and the dam of the reservoir. In fact, it can be seen as all parameters have a higher concentration at the tail of the reservoir than at the dam, in the following order of abundance: sulfates > Mg > Ca > Zn > Fe > Cu > Al > Pb > Ni > Cd > As > Sb.

The parameters presenting the highest percentage of reduction between the two sampling points are the Fe (70%), As (50%) and Cu (47%). The other parameters change their concentration to a lesser extent, presenting the following percentages of reduction: 27% for Ni; 24% for Mg; sulfates decreased 20%; Ca 10%; Zn varies by 7% and Al by 4%. It can be seen that Cd, Sb and Pb maintain their concentrations relatively constant between the two points (Figure 4).

These variations are very similar to those presented by de la Torre et al. (2014b), in which the authors evaluated the attenuation capacity of the metal load in this reservoir, between the channel that brings water to the reservoir (Meca River), and the entry of the reservoir, coinciding this latter point with the sampling point, called tail in the present work.

The acid solutions are saturated in iron minerals such as jarosite, goethite and schwertmannite, with precipitation of these mineral phases being controlled by pH and redox conditions. For instance, schwertmannite precipitates preferably at pH 3.5 at high redox potential (\( \text{Eh} > 700 \text{ mV} \)) (Sánchez-España et al. 2006; Valente et al. 2012). In such conditions, removal of metals and As (V) may occur due to the co-precipitation and sorption processes on schwertmannite, as well as possible subsequent precipitation (through a via exchange with \( \text{SO}_4^{2-} \)) (Sánchez-España et al. 2006).

The cross-correlation function shows the close relationship between the two sampling points, with a transit time of contaminants less than 1 week (\( t = 0 \)), for most cases, due to the small distance between both points (about 300 meters). This means that an increase or decrease at the tail has a consequence on a period of less than a week at the dam point, although there are parameters in which this time is some what higher. This will depend on the effect of dilution on element. The order in which the parameters decrease in concentration is not related to the order that makes the percentage of reduction or the transit time because these two latter depend on the processes of precipitation, sorption and dilution that suffer each of them.

**CONCLUSIONS**

Concentrations of metals and sulfates determined in the Sancho reservoir are evidence of its contamination by acid mine drainage, observing a higher abundance of the pollution load at the tail of the reservoir than that of the dam, due to the attenuation during the course between the two points. This attenuation results from the precipitation of iron oxyhydroxy sulfates produced by raising the pH, and the subsequent dilution and sorption phenomena.

The standard deviation, the range of oscillation and the variation coefficient at the tail are greater than that at the dam. This may be explained by the concept of ‘chemical inertia’ (Grande et al. 2010; Santisteban et al. 2014), which is higher at the dam due to the large volume of water.
Therefore, at this point the hydrochemistry will be less sensitive to variations due to external stimuli.

The cross-correlation function allowed quantifying the process of advance of pollution load from the entrance to the dam. Thus, a transit time of less than 1 week is proposed for most of the contaminants.

The cross-correlation function revealed as an effective tool for establishing temporal cause–effect relationships between hydrochemical parameters before and after its incorporation into a reservoir, as well as for the determination of response times to stimuli-induced precipitation. This can be of regional interest for application to other reservoirs in similar conditions.

REFERENCES


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