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Acid mine drainage in semi-arid regions: the extent of the problem in the waters of reservoirs in the Iberian Pyrite Belt (SW Spain)

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

ABSTRACT

There are many reservoirs in the Iberian Pyrite Belt (IPB), SW Spain, which receive contributions from watercourses affected by acid mine drainage processes, characterised by low pH values and high concentrations of heavy metals and sulphates. When they reach the reservoirs, the waters increase its pH, which will cause most of the metal load carried by the mining channel to precipitate into the reservoir itself and accumulate on its floor. The silting of reservoirs is an environmental problem which can affect the loss of storage capacity, their general functioning and aquatic ecosystems. A study of these is vital to allow both preventative and corrective measures to be established. Climatic conditions are the most significant external controlling factors in terms of the degree and type of mining pollution. The study area presents characteristics typical of the semi-arid Mediterranean climate, with annual precipitation of around 630 mm/year; moderate temperatures with average annual values of 17.1°C and a temperature range of 50°C. The aim of this study is to carry out a physical–chemical characterization of the waters where they enter the reservoirs located in the IPB over the course of a hydrological year and to establish possible interdependencies between the various parameters.

Key words | acid mine drainage, Iberian Pyrite Belt, metals, mine, mining pollution, reservoirs

INTRODUCTION

At present, the silting of reservoirs is an environmental problem of the highest order, which goes beyond the loss of storage capacity and can affect their general functioning as aquatic ecosystems.

The silting of reservoirs gives rise to a series of well-known effects, from a loss of water storage capacity to a change in the longitudinal slope of the channel, the formation of wetlands, a limitation in recreational use or a tendency towards the eutrophication of their waters. However, the silting of a reservoir also leads to a clear loss of efficiency in the reservoir itself with the corresponding cost that affects both the profitability of the initial investment in the actual hydrological engineering, and the operating accounts (Palau 2002).

Spread throughout the Iberian Pyrite Belt (IPB) are numerous reservoirs intended for industrial, agricultural or recreational use. Many of these reservoirs are located in watercourses affected by acid mine drainage (AMD) processes, which means that the water that reaches the dams is low in pH and has a high metal and sulphate load. When the mine-water contributions arrive at the reservoir, there is a sharp increase in the pH of the acid waters upon encountering the huge volume of the receiving basin. This increase in pH is translated into a violent reduction in the dissolving capacity of the mixing waters, which causes most of the metal load carried by the mining watercourse to precipitate into the reservoir itself. In any case, the metal precipitate accumulates in the form of sediment on the floor of the dam, always remaining subject to variations in the pH of the medium and redox potential, which can lead
to silting of the sedimentary medium (Grande et al. 2005a).

The newly formed metal sulphides that accumulate in the sediment and the particulate matter containing sulphates transported by mining effluent are a potential environmental risk because they can oxidise rapidly and release metals, producing a greater increase in the acidity of the medium. Variations in pH and oxygen are the greatest factors that affect the mobility of trace metals (Wen & Allen 1999). Oxidation of the sediment on the floor can occur during periods of rotation (periods of oxygenation) and is also due to remobilisation and transport during high rainfall events and strong water currents.

The impact of the climate on the polluting process of AMD as it affects pyritic materials exposed on the surface is more than well known. Climatic conditions, and especially precipitation, are the most significant external controlling factors in terms of the degree and type of mining pollution in any area.

The study area presents characteristics typical of the semi-arid Mediterranean climate, with annual precipitation of around 650 mm/year; moderate temperatures with average annual values of 17.1 °C and a temperature range of roughly 50 °C. The precipitation occurs principally in the autumn and winter months, producing situations of drought in summer and part of the spring.

In semi-arid climates, the construction of dams is one of the most common alternatives to cover the water needs of the population and industry. The vulnerability of these surface waters to pollution is much greater than that of underground waters (Grande et al. 2010a).

The scientific literature is replete with numerous studies aimed at quantifying the environmental effects of AMD in water, from the point of view of the processes that take place in the affected waters (Grande 2011; Grande et al. 2000, 2005a, b, 2005a, b, 2010a, b, c, d, e, 2011; Younger 2001; Sáinz et al. 2003; Sarmiento 2007; Cánovas et al. 2008; de la Torre et al. 2009; Hubbard et al. 2009; Jiménez et al. 2009; Egal et al. 2010; Loredo et al. 2010; Ochieng et al. 2010; Romero et al. 2011); the sediments (Borrego et al. 2002; López-González et al. 2006; Vicente-Martorell et al. 2008; Ruiz et al. 2009; Couceiro & Schettini 2010) or the biota (Valente & Leal Gomes 2007; Casiot et al. 2009; Gray & Delaney 2010; Gunn et al. 2010; Haf et al. 2010; Hao et al. 2010; Amaral-Zettler et al. 2011).

**GEOGRAPHICAL AND GEOLOGICAL LOCATION**

The study area that the present work focuses on is located in the IPB, in the southwest of the Iberian Peninsula, containing a total of 23 reservoirs spread mainly along the basins of the rivers Tinto and Odiel (Figure 1), which are the main watercourses affected by AMD, and the river basins of the Chanza and the Guadiamar, which are affected to a lesser extent.

The Odiel, which belongs to the Andalusian Atlantic Basin, rises in Marimateos at an altitude of 660 m in the Arcena mountains and covers more than 140 km before losing its fluvial nature in Gibraleón, where it has its confluence with the River Tinto in what is known as the ‘Marismas del Odiel’, an estuary complex of salt marshes with great ecological value declared a Biosphere Reserve by UNESCO. The River Tinto belongs to the Guadiana basin, rises in the Padre Caro mountains, in the district of Nerva, and covers almost 100 km to its mouth. Both rivers have a natural torrent and are located in a climate zone with extremely irregular rainfall (Sáinz et al. 2003). Their waters descend towards the zone of tidal influence with an average pH of less than 2.5 and an enormous dissolved metal load. In a single day the River Odiel carries more heavy metals into the Atlantic shelf than the total released by the Aznalcollar disaster (Sáinz et al. 2003).

The rivers Tinto and Odiel have been widely studied by a number of authors: Borrego et al. (2002); Braungardt et al. 1998, 2003; Davis et al. 2007; Elbaz-Poulichet et al. (1999, 2000, 2001); Grande 2011; Grande et al. 2000, 2005a, b, 2005a, b, 2010a, b, c, d, e, 2011; Leblanc et al. (2000); Sáinz (1999); Sáinz et al. (2000a, b, c, 2002, 2003, 2004, 2005); de la Torre et al. (2009); Jiménez et al. (2009).

The IPB is a geological formation that is 230 km long and on average 50 km wide, and constitutes one of the largest deposits of sulphides in the world (Leistel et al. 1998) with approximately 1,700 MT of reserves. These massive bodies of sulphides contain pyrite, with which sphalerite, galena and chalcopyrite and many minor phases are associated (Sáez et al. 1999). These deposits have been exploited
for more than 2000 years, with numerous extensive mining workings remaining as evidence of this activity, as well as several million tonnes of ancient slag of various composition (Pinedo Vara 1965). The waters which emerge from inside the mines through the tunnels, leachate from slag heaps, mountains of ash, pools, cementation channels and calcination areas, run-off from washing pyrite residue, low-grade sulphur ore, slag and pyrite ash spread by the mines, all produce liquid pollution, which, once it has reached the closest watercourses, enters the main course of the rivers Tinto and Odiel by means of a network of tributaries and sub-tributaries (Sáinz et al. 2005c).

**OBJECTIVES**

The concentration of metals and sulphates in a mining river close to the productive source is 10 times greater than the concentrations measured in the same river near its mouth, above the limit of tidal influence (Grande et al. 2005b). This fact suggests that there are precipitation processes along the watercourse and when it reaches the reservoir, which change the hydrochemical conditions.

Depositing of the materials carried by the water currents occurs in the reservoirs. In this case, both the bed load and the load in suspension are deposited, but the dissolved load (including the microcolloidal fraction) could even be carried outside the reservoir by the water it releases. The presence of
significant quantities of organic matter in this sediment is due to the depletion of oxygen and the reduction of sulphates by sulphate-reducing bacteria (Heijs & Van Gemerden 2000). The sulphide produced by the reduction of sulphates can react chemically with the metals to form insoluble sulphides, such as FeS, FeS₂, ZnS, etc. (Rickard & Morse 2005). The newly formed metal sulphides accumulate in the sediment, forming a potential risk from an environmental point of view, because they can oxidise and release metals, producing a greater increase in the acidity of the medium.

The present study aims to carry out a physical–chemical characterisation of the waters where they enter the reservoirs in the IPB affected by AMD over the course of the hydrological year 2011–2012 and to establish possible relations.

**MATERIALS AND METHODS**

The sampling phase was carried out on a 2-weekly basis in the period between October 2011 and May 2012 during the period of rainfall which causes the water to flow in the watercourses, with the sampling finishing once the channels in the sector being studied have stopped running. During this period we simultaneously proceeded with analysis of the samples in the laboratory, using a variety of analytical techniques.

Once the study area had been delimited and the water relations were understood, both in terms of natural watercourses and contributions from mining leachates, the next step was to determine the points at which the water samples would be taken. A sampling point was chosen where the waters enter the reservoirs affected by AMD, and which is covered by the waters during the measuring period, close to the maximum capacity limit of the dams. The reservoirs to be sampled are gathered together in Table 1 and Figure 1.

During the sampling campaign, determination of pH, electrical conductivity (EC) and total dissolved solids (TDS) was carried out in situ using a Crison MM40 portable multimeter.

Following the measurements in the field, two water samples were taken in sterilised polyethylene containers at each point, one to determine the sulphates and another 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 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. The water distiller used was the Optic Ivymen System AC-L4.

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

The equipment used to carry out the metals analysis was a Perkin-Elmer AAnalyst 800 atomic absorption spectrophotometer equipped with a graphite furnace and an air/acetylene-flame atomiser. 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.

The data from the analytics, as well as the parameters measured in the field, were submitted to graphical/statistical treatment in order to apply cluster analysis, which allows approximation dendrograms to be obtained using the STATGRAPHICS Centurion XVI.I software package.

**RESULTS**

**Physical–chemical characterisation**

Based on measurement of the physical–chemical parameters and analyses of metals and sulphates carried out in the laboratory, a huge volume of data was obtained, with the average values gathered together in Tables 2 and 3.

It can be observed that the pH ranges from 2.18, being the minimum value recorded, to values close to neutral, with 6.66 being the maximum value. The average pH values measured at the various sampling points were as follows:
The maximum TDS and electrical conductivity values recorded were 3,120.78 μS/cm and 5,849.31 mg/L, respectively, both measured in the Marismillas reservoir. The minimum values for these parameters could be measured in the La Joya reservoir, with a value of 141.74 μS/cm for electrical conductivity and 90.69 mg/L for TDS.

The average concentrations of electrical conductivity measured in the various reservoirs were in the following order: Aguas Ácidas > Marismillas > Gossan > Cueva de la Mora > Andévalo-Cobica > Sancho > Andévalo-Chorrito > Herrerías > Grande > Lagunazo > Chanza > Agrio > Del Pino > Corumbel > Campanario > Dique II > Puerto León > Silillos I > Garnacha > Dique I > Silillos II > La Joya.

The highest average concentration recorded for TDS was in the Marismillas reservoir, followed by the Aguas Ácidas reservoir > Gossan > Cueva de la Mora > Olivargas > Andévalo-Cobica > Sancho > Andévalo-Chorrito > Herrerías > Grande > Lagunazo > Chanza > Agrio > Del Pino > Corumbel > Campanario > Dique II > Puerto León > Silillos I > Garnacha > Dique I > Silillos II > La Joya.

As regards the sulphates analysed, the maximum concentration obtained was 3,086.35 mg/L in the Aguas Ácidas reservoir, while the minimum concentration was

### Table 1 | General data of the sampled dams

<table>
<thead>
<tr>
<th>Points</th>
<th>Dams</th>
<th>Coordinates UTM</th>
<th>Uses</th>
<th>Volume (hm³)</th>
<th>Surface (ha)</th>
<th>River location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Andévalo-Cobica</td>
<td>650,803 4,167,417</td>
<td>–</td>
<td>634</td>
<td>3,630</td>
<td>Cobica</td>
</tr>
<tr>
<td>2</td>
<td>Andévalo-Chorrito</td>
<td>649,240 4,165,762</td>
<td>–</td>
<td>634</td>
<td>3,630</td>
<td>Chorrito</td>
</tr>
<tr>
<td>3</td>
<td>Agrio</td>
<td>738,737 4,161,112</td>
<td>Supply, industrial</td>
<td>20.37</td>
<td>192.2</td>
<td>Agrio</td>
</tr>
<tr>
<td>4</td>
<td>A. ácidas</td>
<td>666,964 4,163,520</td>
<td>–</td>
<td>–</td>
<td>1.16</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>Chanza</td>
<td>637,578 4,173,754</td>
<td>Supply, fishing, irrigation</td>
<td>341</td>
<td>2,239</td>
<td>Chanza</td>
</tr>
<tr>
<td>6</td>
<td>Campanario</td>
<td>691,692 4,155,967</td>
<td>Recreation</td>
<td>–</td>
<td>4 ha</td>
<td>Aguas Agrias</td>
</tr>
<tr>
<td>7</td>
<td>Corumbel</td>
<td>717,217 4,147,612</td>
<td>Supply, irrigation</td>
<td>19</td>
<td>396</td>
<td>Corumbel</td>
</tr>
<tr>
<td>8</td>
<td>Del Pino</td>
<td>666,784 4,162,493</td>
<td>–</td>
<td>–</td>
<td>1.9</td>
<td>Rivera de la Angustinos</td>
</tr>
<tr>
<td>9</td>
<td>Dique I</td>
<td>651,528 4,165,736</td>
<td>–</td>
<td>–</td>
<td>7.7</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>Dique II</td>
<td>651,387 4,165,068</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>Herrerías</td>
<td>651,471 4,165,235</td>
<td>–</td>
<td>–</td>
<td>5</td>
<td>Chorrito</td>
</tr>
<tr>
<td>12</td>
<td>Garnacha</td>
<td>678,806 4,186,885</td>
<td>Supply, industrial</td>
<td>6.5</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>Gossan</td>
<td>712,690 4,179,052</td>
<td>Mining, industrial</td>
<td>2,200</td>
<td>125</td>
<td>–</td>
</tr>
<tr>
<td>14</td>
<td>Grande</td>
<td>666,764 4,163,634</td>
<td>–</td>
<td>–</td>
<td>24.28</td>
<td>Aguas Agrias</td>
</tr>
<tr>
<td>15</td>
<td>Lagunazo</td>
<td>662,731 4,165,639</td>
<td>Industrial, fishing</td>
<td>3</td>
<td>18</td>
<td>Cobica</td>
</tr>
<tr>
<td>16</td>
<td>La Joya</td>
<td>673,647 4,180,222</td>
<td>Industrial</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>17</td>
<td>Marismillas</td>
<td>715,238 4,175,219</td>
<td>Industrial</td>
<td>–</td>
<td>18</td>
<td>Tinto</td>
</tr>
<tr>
<td>18</td>
<td>Silillos I</td>
<td>700,515 4,162,637</td>
<td>Supply, fishing, recreation</td>
<td>1.05</td>
<td>28</td>
<td>Buitrón</td>
</tr>
<tr>
<td>19</td>
<td>Silillos II</td>
<td>701,078 4,161,423</td>
<td>Supply</td>
<td>–</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>20</td>
<td>Sancho</td>
<td>670,111 4,147,929</td>
<td>Supply, industrial</td>
<td>58</td>
<td>427</td>
<td>Meca</td>
</tr>
<tr>
<td>21</td>
<td>Olivargas</td>
<td>692,476 4,182,511</td>
<td>–</td>
<td>29</td>
<td>240</td>
<td>Olivargas</td>
</tr>
<tr>
<td>22</td>
<td>Cueva de la Mora</td>
<td>693,586 4,180,337</td>
<td>–</td>
<td>29</td>
<td>240</td>
<td>Barranco de la Malena</td>
</tr>
<tr>
<td>23</td>
<td>Puerto León</td>
<td>689,958 4,176,833</td>
<td>Fishing, supply, industrial</td>
<td>11</td>
<td>19</td>
<td>Naranjo</td>
</tr>
</tbody>
</table>
2.18 mg/L in the Corumbel reservoir. The order of abundance in the other reservoirs was: Aguas Ácidas > Marismillas > Gossan > Cueva de la Mora > Olivargas > Andévalo-Cobica > Andévalo-Chorrito > Sancho > Grande > Agrio > Lagunazo > Del Pino > Garnacha > Herrerías > Camapanario > Puerto León > Chanza > Silillos II > Dique II > Silillos I > Dique I > La Joya > Corumbel.

If we look at the summation of the average concentrations of metals analysed we see that the Marismillas reservoir presents the highest value with 2,601.24 mg/L of total average metals. The Aguas Ácidas and Cueva de la Mora reservoirs also present very high values, 384.95 and 149.64 mg/L, respectively. The lowest recorded value was 1.27 mg/L for the Dique I reservoir. The order of abundance for the rest of the reservoirs was: Gossan > Andévalo-Cobica > Andévalo-Chorrito > Sancho > Olivargas > Grande > Puerto León > Silillos I > Camapanario > Del Pino > Agrio > Lagunazo > La Joya > Silillos II > Herrerías > Dique II > Corumbel > Garnacha > Chanza.

Figures 2(a) and b presented below show the distribution of the values for the physical–chemical parameters and the sulphates measured in each reservoir. Three groups clearly stand out: those reservoirs which present high pH values and low values for the other parameters (TDS, EC, sulphates and $\sum$ metals), intermediate values for pH and the other values, and low pH values and high values for the other parameters.

### Cluster analysis

With the aim of establishing possible relationships between the variables for a single reservoir, the mass of
data was submitted to statistical treatment using cluster analysis.

In this case, and after comparing various vicinity measures and different agglomeration methods, the ‘Euclidean distance’ was chosen as vicinity measure, and the ‘Ward method’ as agglomerative method. The Ward method or ‘second-order central method’ is a hierarchical method whose procedure is to calculate the average of all the variables for each cluster. Next, it calculates the Euclidean distance between each factor and the mean of its group. Then, it adds the distance for each case. At each stage, the clusters formed are those which produce the smallest increase in the total sum of the distances within the cluster (Bisquerra 1989). In this way, using this technique, the variables studied may be classified into different ‘categories’. The vicinity measure used is the Euclidean distance, which is the square root of the sum of the differences between the variables squared. The reason for choosing the stated method and the vicinity measure is that they produce the clearest and most easily interpreted dendrograms.

Some of the most representative clusters obtained are presented below in the groups defined previously (Figures 3–5).

The relationship between electrical conductivity and TDS stands out in the clusters of variables for all the reservoirs.

<table>
<thead>
<tr>
<th>Points</th>
<th>Dams</th>
<th>Fe (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Zn (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Cd (mg/L)</th>
<th>Ni (mg/L)</th>
<th>Co (mg/L)</th>
<th>As (mg/L)</th>
<th>Sb (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Al (mg/L)</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aguas Ácidas</td>
<td>315.82</td>
<td>9.05</td>
<td>20.10</td>
<td>34.03</td>
<td>0.11</td>
<td>1.22</td>
<td>3.54</td>
<td>0.34</td>
<td>0.01</td>
<td>0.59</td>
<td>0.15</td>
<td>384.95</td>
</tr>
<tr>
<td>2</td>
<td>Agrio</td>
<td>0.46</td>
<td>0.18</td>
<td>0.16</td>
<td>1.34</td>
<td>0.07</td>
<td>0.03</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.25</td>
<td>0.48</td>
<td>3.02</td>
</tr>
<tr>
<td>3</td>
<td>Andévalo-Cobica</td>
<td>34.83</td>
<td>1.39</td>
<td>2.31</td>
<td>3.10</td>
<td>0.16</td>
<td>0.08</td>
<td>0.09</td>
<td>0.05</td>
<td>0.00</td>
<td>0.30</td>
<td>0.53</td>
<td>42.84</td>
</tr>
<tr>
<td>4</td>
<td>Andévalo-Chorrillo</td>
<td>11.59</td>
<td>2.19</td>
<td>2.63</td>
<td>6.41</td>
<td>0.26</td>
<td>0.17</td>
<td>0.22</td>
<td>0.00</td>
<td>0.01</td>
<td>0.30</td>
<td>0.55</td>
<td>24.34</td>
</tr>
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<td>Camapanario</td>
<td>0.46</td>
<td>0.09</td>
<td>0.10</td>
<td>2.36</td>
<td>0.13</td>
<td>0.04</td>
<td>0.05</td>
<td>0.00</td>
<td>0.02</td>
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<td>3.87</td>
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<td>0.19</td>
<td>0.08</td>
<td>0.02</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.31</td>
<td>0.17</td>
<td>1.37</td>
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<td>7</td>
<td>Corumbel</td>
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<td>0.07</td>
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<td>0.39</td>
<td>0.08</td>
<td>0.03</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.28</td>
<td>0.26</td>
<td>1.64</td>
</tr>
<tr>
<td>8</td>
<td>Del Pino</td>
<td>0.40</td>
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<td>0.64</td>
<td>0.65</td>
<td>0.13</td>
<td>0.14</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.34</td>
<td>0.52</td>
<td>3.08</td>
</tr>
<tr>
<td>9</td>
<td>Dique I</td>
<td>0.13</td>
<td>0.05</td>
<td>0.14</td>
<td>0.17</td>
<td>0.07</td>
<td>0.08</td>
<td>0.03</td>
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studied, with both linked to sulphates on occasions. The only reservoir where this relationship is not observed is in the Marismillas reservoir, where the variable pairs electrical conductivity-Pb and pH-TDS can be observed.

All the clusters present two large differentiated groups, with a limited relationship between them for the different sampling points. That is to say, if we take the Agrio reservoir as an example, two main families are observed: that formed by the pair Fe-Pb together with Zn, As and Sb, and another family in which the vicinity relation between electrical conductivity and TDS together with sulphates, and the associations between the remainder of the variables stand out.

**DISCUSSION**

By examining the average pH values measured, a classification of the sampling points was produced, creating a
distinction between those reservoirs which present pH values <3, pH values between 3 and 5 and pH values >5.

The most acid reservoirs, with a pH <3, are: Marismillas (pH: 2.18) < Aguas Ácidas (pH: 2.47) < Gossan (pH: 2.64) < Cueva de la Mora (pH: 2.72).

These reservoirs in turn present the highest average values analysed for electrical conductivity and TDS, as well as metals and sulphates.

A relationship is observed between the variables electrical conductivity and TDS in the clusters of variables obtained for the entry points of these reservoirs, with the Marismillas reservoir the only one where this grouping was not detected. The variable pairs electrical conductivity-Pb and pH-TDS are observed in this reservoir, together with sulphates.

The reservoirs where average pH values between 3 and 5 could be measured were: Andévalo Cobica (pH: 3.07) < Sancho (pH: 3.34) < Del Pino (pH: 3.64) < Andévalo Chorrito (pH: 3.65) < Grande (pH: 4.04) < Olivargas (pH: 4.74).

These reservoirs present average values for electrical conductivity, TDS, metals and sulphates.

There is also a direct relationship observed between electrical conductivity and TDS in all the reservoirs, except in the Marismillas reservoir. This fact may be due to the discharge of residual urban waters from the town of Nerva directly into the waters of the reservoir, which may mask the results obtained.

There are no common groupings observed for the rest of the parameters at the different sampling points, which is interpreted as a consequence of the great heterogeneity and geographical dispersion of the reservoirs studied, with each of them belonging to different river basins, each of which has its own particular characteristics. They are therefore also subject to the arrival of contributions contaminated by a variety of mineral parageneses and with very different levels of pollution controlled essentially by the clean contributions that cause dilution.

It can be concluded that all the reservoirs present acid pH values with high concentrations of metals and sulphates, characteristic of processes of AMD. The reservoirs which present the most acid pH values are Marismillas, Aguas Ácidas, Gossan and Cueva de la Mora, presenting in turn the highest average values for electrical conductivity, TDS, sulphates and metals. There are also reservoirs whose waters possess values of pH >5, close to neutral, with the lowest values recorded for electrical conductivity, TDS, metals and sulphates. The rest of the reservoirs have intermediate values, always with an inverse proportionality between pH and the rest of the parameters.

The clusters of variables for the entry points of these reservoirs the relationship electrical conductivity-TDS stands out, linked on some occasions to sulphates, pH, Cu, Ni or As.

CONCLUSION

Low values for electrical conductivity, TDS, metals and sulphates are observed in these reservoirs.

In the clusters of variables for the entry points of these reservoirs the relationship electrical conductivity-TDS stands out, linked on some occasions to sulphates, pH, Cu, Ni or As.
in contrast to the homogeneous lithology of the adjoining rock in the reference domain. These huge paragenetic and therefore mineralogical differences, together with the diversity in size and ecological nature of the river basins and watersheds in the study, might produce the lack of geographical homogeneity of the redox potential, which would lead to the development of reactions that would give rise to the presence of the various elements in solution analysed.

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REFERENCES


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