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TECHNICAL COMMUNICATION

Characterisation of AMD Pollution in the Reservoirs of the Iberian Pyrite Belt

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Abstract A number of water-supply dams have been built in the semi-arid Iberian Pyrite Belt (SW Spain) in a fluvial network affected by acid mine drainage (AMD). There are almost a hundred mines, most of which are closed, which emit low pH leachates with high metal and sulphate loads to reservoirs intended for urban supply. The Iberian Pyrite Belt contains 23 of these reservoirs spread along the Tinto and Odiel river basins, which are the main water courses affected by AMD, and the Chanza and the Guadiamar river basins, which are affected to a lesser extent. We characterised the degree of pollution in the various reservoirs that receive AMD-affected waters; this will eventually allow the development of a risk map of the overall extent of the problem in reservoirs in the Iberian Pyrite Belt.

Keywords AMD · Reservoir · Iberian Pyrite Belt · Risk map

Introduction

Southwestern Europe has a semi-arid climate. This, together with the scarcity of exploitable aquifers, has led the agencies responsible for managing water resources to build dams for the storage and subsequent distribution of surface waters to answer the needs of the urban, agricultural, and industrial users. In the Iberian Pyrite Belt study area, these dams (Fig. 1) are located in a river network affected by acid mine drainage (AMD) associated with the intensive mining of metal sulphides. The exploited bodies of massive sulphides contain pyrite, with which sphalerite, galena, chalcopyrite, and many minor phases are associated (Saez et al. 1999). These deposits have been exploited for over 2,000 years with numerous extensive mine workings left, along with several million tons of slag of varying composition from the distant past (Pinedo 1963). There are almost a hundred mines in the Iberian Pyrite Belt, some of them known on a worldwide scale, such as Rio Tinto, Tharsis, and Aznalcóllar Sotiel. Most of these mines closed before environmental guidelines regulated the activity, and therefore have no preventive or corrective measures to protect the water medium. This is why, now that mining has stopped, that these former mines continue to emit acidic leachates.

The result is a fluvial network that is intensely affected by AMD (Aroba et al. 2007; Borrego 1992; Borrego et al. 2002, 2012; Braungardt et al. 1998; Carro et al. 2011; Davis et al. 2000; de la Torre et al. 2009, 2010, 2011; Elbaz-Poulichet et al. 1999, 2000, 2001; Grande 2011; Grande et al. 2000, 2003a, b, 2005a, b, 2010a, b, c, d, e, 2011a, b; Jiménez et al. 2009; Leblanc et al. 2000; Sáinz et al. 2002, 2003a, b, 2004, 2005; Sánchez-España et al. 2005, 2006a, b, 2007). AMD contributions to reservoirs intended for urban supply leads to waters with low pH and a high metal and sulphate load reaching these reservoirs. This is what happens in the River Cobica, which collects water from Herrerías Mine and the Tharsis mines in the Iberian Pyrite Belt (Grande et al. 2005a, b; Jiménez et al. 2009). Table 1 shows typical values for pH, sulphate, and

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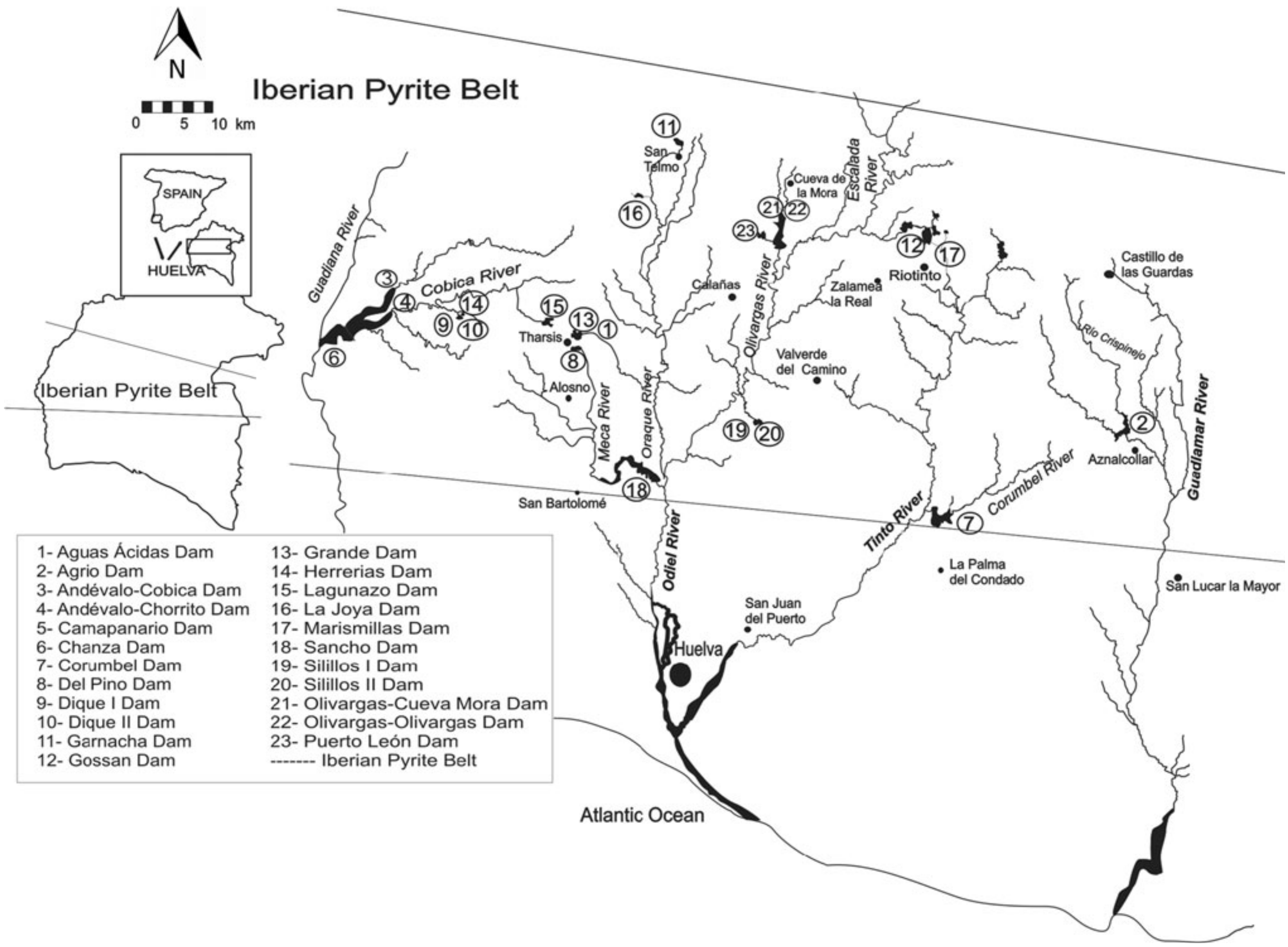


Fig. 1 Location map of the sampled reservoirs

Table 1 Statistical summary of the Cobica River (Grande et al. 2010a)

	Average	Variance	Minimum	Maximum
pH	2.80	0.20	2.10	6.40
EC (µS/cm)	2,200	3.100	300.0	10,300
SO_4 (mg/L)	1,215.6	3.1000	94.000	13,680
Fe (mg/L)	96.50	6,802	0.400	709.8
Cu (mg/L)	5.600	63.900	0.200	54.000
Zn (mg/L)	8.90	222	0.20	120
Mn (mg/L)	15.50	871	0.200	210.00
As (mg/L)	0.11	104,197	0.00	3.36
Cd (mg/L)	0.033	3,581	0.000	0.360

metals in the Cobica watercourses, which carry their waters to the Andévalo Dam (Grande et al. 2010e).

When the mine water reaches the reservoir and encounters the huge volume of the receiving basin, there is a sharp increase in pH. This translates into a dramatic reduction in the carrying capacity of the mixing waters, which causes most of the metal load carried by the mining watercourse to precipitate in the reservoir and to accumulate in the sediment on the floor of the dam, subject to variations in the pH of the medium (Grande et al. 2010e). Contaminants such as arsenic deserve particular attention; it enters the fluvial network as trivalent As at a pH close to 3, and once dissolved, oxidises to pentavalent As. Then, it remains in solution, since precipitation only occurs at a pH close to 12.

The study area, which is located in the Iberian Pyrite Belt in the southwestern Iberian Peninsula, contains a total of 23 reservoirs spread along the Tinto and Odiel river basins (Fig. 1), which are the main water courses affected by AMD, and the Chanza and the Guadiamar river basins, which are affected to a lesser extent.

Directive 75/440/EEC defines the standards that continental surface waters in all member countries of the European Union must meet if they are intended for use in the production of drinking water, restricting the use of the aforementioned waters on the basis of their composition. However, this regulation allows lower-quality water to be used in exceptional circumstances, if suitable treatment, including blending, is used to improve the water quality. Therefore, this paper aims to characterise the degree of pollution in the various Iberian Pyrite Belt reservoirs that receive AMD-affected waters by modifying the methodology proposed by Grande (2011). This will eventually allow a risk map of the overall extent of the problem to be developed.

Materials and Methods

Once the study area was established and the water relationships were understood, in terms of natural watercourses and contributions of mining leachates, the next step was to determine where water samples would be taken. Sampling points were chosen where the waters enter the reservoirs affected by AMD. During the sampling campaign, pH, electrical conductivity (EC), and total dissolved solids (TDS) were determined in situ using a Crison MM40 portable multimeter. Samples were collected every 2 weeks between October 2011 and May 2012, when the dry season arrived and water largely ceases to flow in the watercourses. The reservoirs sampled are displayed in Table 2 and Fig. 1.

Following the field measurements, two water samples were collected in sterilised polyethylene containers at each point, one to determine sulphate concentrations and the other for metal analysis. Nitric acid was added to obtain a pH <2 to prevent precipitation of the metals during transportation to the laboratory. The samples were kept 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 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. Metals were analysed using a Perkin-Elmer AAnalyst 800 atomic absorption

Table 2 General data of the sampled reservoirs

Points	Dams	Cordinates UTM		Uses	Volume (hm^3)	Surface (ha)	River location
		X	Y				
1	Andévalo-Cobica	650803	4167417	–	634	3,630	Cobica
2	Andévalo-Chorrito	649240	4165762	–	634	3,630	Chorrito
3	Agrio	738737	4161112	Supply, industry	20.37	192.2	Agrio
4	A.ácidas	666964	4163520	–	–	1.16	–
5	Chanza	637578	4173754	Supply, fishing, irrigation	341	2,239	Chanza
6	Campanario	691692	4155967	Recreation	–	4 ha	Aguas Agrias
7	Corumbel	717217	4147612	Supply, irrigation	19	396	Corumbel
8	Del Pino	666784	4162493	–	–	1.9	Rivera de los Angustinos
9	Dique I	651528	4164736	–	–	7.7	–
10	Dique II	651387	4165068	–	–	3	–
11	Herrerias	651471	4165235	–	–	5	Chorrito
12	Garnacha	678806	4186885	Supply, industry	6.5	3	–
13	Gossan	712690	4179052	Mining, industry	2,200	125	–
14	Grande	666764	4163634	–	–	24.28	Aguas Agrias
15	Lagunazo	662731	4165639	Industry, fishing	3	18	Cobica
16	La Joya	673647	4180222	Industry	–	–	–
17	Marismillas	715238	4175219	Industry	–	18	Tinto
18	Silillos I	700515	4162637	Supply, fishing, recreation	1.05	28	Buitrón
19	Silillos II	701078	4161423	Supply	–	8	–
20	Sancho	670111	4147929	Supply, industry	58	427	Meca
21	Olivargas	692476	4182511	–	29	240	Olivargas
22	Cueva de la Mora	693586	4180337	–	29	240	Barranco de la Malena
23	Puerto León	689958	4176833	Fishing, supply, industry	11	19	Naranjo

Table 3 Parametric and weighted values for pollution (Grande 2011)

Pollution	Parametric value	Weighted value
None	Not detected	0
Slight	Below legal limit	1
Moderate	Between 1 and 2 times the limit	2
Average	Between 2 and 10 times the limit	3
High	Between 10 and 50 times the limit	4
Extremely high	Over 50 times the limit	5

Table 4 Highest parametric values admissible by Directive 75/440/EEC concerning the quality of drinking water

Parameter	Values
Antimony (Sb)	0.005 mg/L
Arsenic (As)	0.010 mg/L
Aluminum (Al)	0.200 mg/L
Cadmium (Cd)	0.005 mg/L
Copper (Cu)	2.000 mg/L
Iron (Fe)	0.200 mg/L
Manganese (Mn)	0.050 mg/L
Nickel (Ni)	0.02 mg/L
Lead (Pb)	0.010 mg/L
Conductivity (EC)	2,500 µs/cm at 20 °C
Sulphates	250.00 mg/L

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^{TM} 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 using the STATGRAPHICS Centurion XVI.I software package; CorelDRAW software was used to graphically present the results.

To characterise the degree of pollution in the various reservoirs that receive AMD-affected waters, we took as a reference the classification model proposed by Grande (2011), which had been used to assess an AMD-affected watercourse in the Iberian Pyrite Belt. By applying a simple weighting formula, this classification model (Table 3) allows the level of the problem a watercourse suffers from to be diagnosed for each pollutant by measuring the pH in situ. Based on the average values of each contaminant for the specific pH in the table produced by Gray (1996), a weighted value is defined for each concentration. This corresponds to the number of times this parameter exceeds the limit established by Directive 75/440/EEC for the public supply of drinking water (Table 4).

Results

Table 5 summarises the average values of the parameters analysed for all of the reservoirs. The average pH was 4.70, with the minimum being 2.18 and the maximum 6.66, corresponding to the Marismillas and Herrerías reservoirs, respectively. EC averaged 945.2 µS/cm, with a maximum of 6,074 µS/cm measured in the Aguas Ácidas Reservoir and a minimum of 141.7 µS/cm for the La Joya Reservoir. The highest measured concentration for the TDS was 5,849 mg/L in the Marismillas Reservoir, while the lowest was 90.69 mg/L in the La Joya Reservoir. The average TDS concentration was 772.8 mg/L. The average sulphate concentration was 454.98 mg/L, with a maximum of 3,086.4 mg/L in the Aguas Ácidas Reservoir and a minimum of 2.1760 mg/L in the Corumbel Reservoir. The average concentrations for the metals analysed followed the order: Fe > Zn > Cu > Mn > AL > Pb > Cd > As > Sb. The maximum and minimum values were respectively: Fe (2,266 and 0.127 mg/L); Cu (207.0 and 0.037 mg/L); Mn (35.22 and 0.174 mg/L); Cd (1.495 and 0.068 mg/L); As (1.853 and 0.001 mg/L); Sb (0.110 and 0.001 mg/L); Pb (0.590 and 0.245 mg/L) and Al (0.699 and 0.058 mg/L).

In general, a high level of variance was observed, both in the measured physical–chemical parameters and the metals and sulphate concentrations. Variance was highest for EC, followed by TDS > sulphate > Fe > Cu > Zn > Mn. The other parameters had much lower variance values. Tables 6 and 7 show the average values for all of the reservoirs in the study.

The lowest pH values were recorded in the following reservoirs: Marismillas < Gossan < Aguas Ácidas < Gossan < Cueva de la Mora < Andévalo-Cobica < Sancho, with all of them presenting values below 4. The Marismillas Reservoir had the most acidic pH, with an

Table 5 Statistical summary of the average values for the parameters obtained at the different sampled reservoirs

	Average	Variance	Minimum	Maximum
pH	4.70	2.04	2.18	6.66
EC (µS/cm)	945.2	1,900,000	141.7	6,074
SO_4 (mg/L)	454.98	620,265	2.1760	3,086.4
TDS (mg/L)	772.8	1,900,000	90.69	5,849
Fe (mg/L)	117.1	223,704	0.130	2,266
Cu (mg/L)	10.25	1,845	0.040	207.05
Mn (mg/L)	5.442	101.5	0.170	35.22
As (mg/L)	0.125	0.152	0.001	1.850
Cd (mg/L)	0.220	0.097	0.070	1.490
Sb (mg/L)	0.015	0.001	0.001	0.109
Pb (mg/L)	0.344	0.01	0.245	0.590
Al (mg/L)	0.370	0.03	0.058	0.699

Table 6 Average values for the measured physical–chemical parameters

Points	Dams	pH	T (°C)	EC (μS/cm)	TDS (mg/L)	SO_4^{2-} (mg/L)
1	Aguas Ácidas	2.47	14.17	6,074	3,890	3,086.4
2	Agrio	5.52	16.20	322.0	205.8	137.24
3	Andévalo-Cobica	3.07	17.48	956.9	612.4	426.35
4	Andévalo-Chorrito	3.65	17.34	652.2	417.1	412.00
5	Camapanario	5.66	13.08	265.8	171.5	53.647
6	Chanza	5.89	17.59	346.3	221.6	30.059
7	Corumbel	5.84	16.72	266.6	170.4	2.1765
8	Del Pino	3.64	15.81	300.6	189.4	126.88
9	Dique I	5.97	18.19	183.6	116.9	9.5882
10	Dique II	6.23	19.07	245.7	159.0	25.529
11	Garnacha	5.84	16.83	197.2	126.5	72.294
12	Gossan	2.64	16.65	2,633	1,658	1,415.7
13	Grande	4.04	15.02	483.6	309.0	209.82
14	Herrerias	6.66	19.57	559.5	362.3	71.118
15	Lagunazo	5.64	17.61	406.7	260.1	127.41
16	La Joya	5.93	19.12	141.7	90.69	6.1765
17	Marismillas	2.18	17.51	3,121	5,849	2,168.0
18	Sancho	3.34	17.65	793.3	505.4	323.88
19	Sililos I	5.85	14.02	206.9	155.7	23.176
20	Sililos II	5.02	15.37	168.4	123.5	29.000
21	Olivargas	4.74	16.14	1,100	704.2	494.65
22	Cueva de la Mora	2.72	15.49	2,088	1,309	1,167.2
23	Puerto León	5.74	17.22	227.7	167.9	46.294

average value of 2.18, while values close to neutral (6.66) could be observed in the Herrerías Reservoir. The extent of the problem in each of the reservoirs that have an average pH below 7 is summarised in Fig. 2.

The average values for EC, TDS, and sulphate have also been presented as a bar chart (Fig. 3), which show noticeably high levels of EC, TDS, and sulphate in the Aguas Ácidas, Marismillas, Gossan, Cueva de la Mora, Olivargas, Andévalo-Cobica, Sancho, and Andévalo-Chorrito reservoirs.

Figure 4 shows the percentage of reservoirs that exceed limits established by Directive 75/440/EEC (Table 4). All of the reservoirs studied exceeded the regulations for Mn, Cd, and Pb; 96 % of the reservoirs were above the limit laid down for Fe; 48 % of the reservoirs exceeded the Sb limit; 35 % exceeded the sulphate limits; 30 % did so for As, while only 26 % and 13 %, respectively, were above the maximum permitted limit for Cu and EC.

Figure 5 is based on the Grande model (Grande 2011) (Table 2), and shows the number of reservoirs defined for each element within each degree of pollution. For Fe, only one reservoir did not exceed the limits set by the regulations and was therefore within the weighted value of 0, in which contamination is considered to be nil. Within this same range, we find 17 reservoirs that show no signs of being affected in terms of Cu pollution. These are 16 reservoirs for As, 12 reservoirs that do not exceed the permitted limits for Sb, and 3 reservoirs for Al. In terms of EC, 20 reservoirs are seen to be below the permitted maximum, and 15 reservoirs do not exceed the regulations for sulphate. All the reservoirs exceed the regulations for Mn, Cd, and Pb.

Only 2 reservoirs are seen to show slight pollution (a weighted value of 1) for Fe, and only 1 reservoir for Al. No reservoirs are observed with this level of pollution for the rest of the parameters.

Two reservoirs had a moderate degree of pollution (a weighted value of 2), in terms of Fe, three for Cu, eight for Al and four for sulphate. Only 2 reservoirs present levels of EC that indicate moderate pollution.

A weighted value of 3 indicates a medium level of contamination. Eight reservoirs had this level of pollution for Fe, two for Cu, nine for Mn, four for As, 10 for Sb, 11 for Al, and only one reservoir for EC and sulphate.

Cd and Mn stand out in the high pollution range, with 20 reservoirs presenting a weighted value of 4. We find two reservoirs with this degree of contamination for Fe, six for Mn, two for As, and only one reservoir for Sb and sulphate. No reservoirs were observed with this level of pollution for the other parameters.

Table 7 Average values (in mg/L) for the analysed metals and sulphates

Points	Dams	Fe	Cu	Mn	Cd	As	Sb	Pb	Al	∑ metals
1	Aguas Ácidas	315.8	9.054	34.03	0.110	0.344	0.006	0.590	0.145	385.0
2	Agrio	0.456	0.180	1.342	0.074	0.003	0.001	0.245	0.480	3.021
3	Andévalo-Cobica	34.83	1.388	3.102	0.162	0.047	0.002	0.300	0.525	42.84
4	Andévalo-Chorrito	11.59	2.191	6.411	0.256	0.003	0.014	0.299	0.554	24.34
5	Camapanario	0.457	0.092	2.356	0.133	0.004	0.021	0.274	0.342	3.872
6	Chanza	0.236	0.113	0.194	0.084	0.001	0.001	0.307	0.172	1.369
7	Corumbel	0.246	0.074	0.391	0.083	0.003	0.002	0.279	0.257	1.644
8	Del Pino	0.397	0.182	0.653	0.128	0.001	0.001	0.339	0.515	3.075
9	Dique I	0.127	0.051	0.174	0.068	0.003	0.002	0.281	0.310	1.267
10	Dique II	0.182	0.058	0.494	0.092	0.004	0.083	0.258	0.235	1.645
11	Garnacha	0.204	0.037	0.263	0.102	0.001	0.019	0.398	0.268	1.570
12	Gossan	34.25	6.314	10.71	0.130	0.015	0.004	0.387	0.451	63.49
13	Grande	0.441	0.120	2.706	0.109	0.003	0.001	0.338	0.430	4.736
14	Herrerias	0.358	0.083	0.514	0.092	0.088	0.005	0.256	0.188	1.739
15	Lagunazo	0.943	0.068	0.469	0.131	0.002	0.007	0.323	0.375	2.665
16	La Joya	0.358	0.535	0.390	0.151	0.001	0.003	0.349	0.220	2.431
17	Marismillas	2,266	207.0	35.22	0.769	1.853	0.110	0.561	0.058	2,601
18	Sancho	4.957	2.322	3.948	1.495	0.370	0.006	0.331	0.444	18.27
19	Sililos I	1.444	0.740	0.364	0.161	0.045	0.002	0.301	0.560	3.896
20	Sililos II	0.506	0.557	0.176	0.179	0.005	0.001	0.301	0.408	2.341
21	Olivargas	2.552	1.328	2.303	0.176	0.091	0.037	0.364	0.699	9.198
22	Cueva de la Mora	15.80	2.311	17.66	0.230	0.015	0.002	0.544	0.468	149.64
23	Puerto León	0.542	0.940	1.324	0.161	0.012	0.033	0.298	0.394	4.043

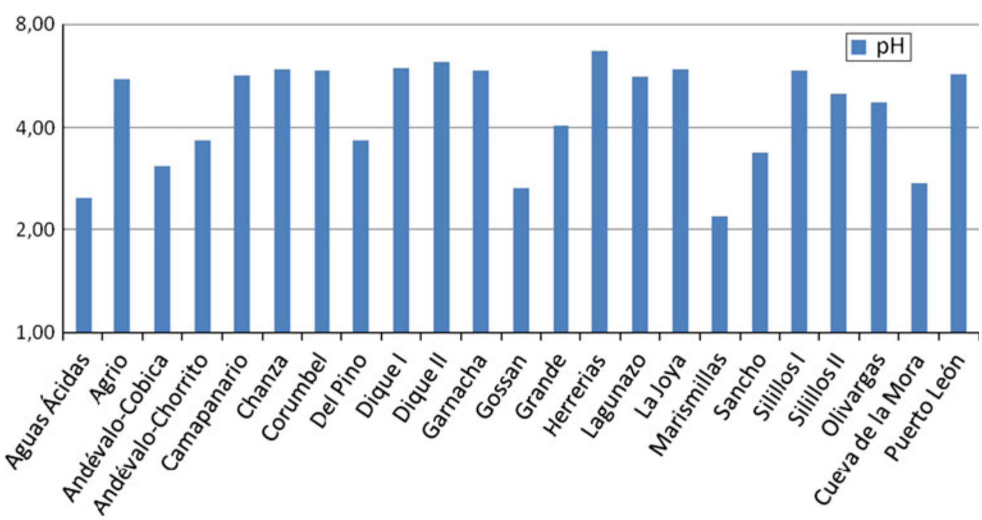


Fig. 2 Average values for pH measured at the different sampled reservoirs

A weighted value of 5 indicates extremely high pollution, with six reservoirs noted with this degree of pollution for Fe. Only one reservoir exceeded 50 times the regulations for Cu, whereas there were eight reservoirs with an extremely high value for Mn, three for Cd, one for As, and three reservoirs in this range for Pb. Sb, EC, and sulphate did not reach this range of extremely high pollution.

Figure 6 shows all of the radial diagrams, which represent the number of times that each element exceeded the permitted limits for each reservoir, helping us to visualize the results. Bearing in mind that it was necessary to reduce the scale in many of them due to the large difference between the concentrations of some of the parameters analysed, we can observe similar behaviours in those reservoirs with the highest concentrations of metals and

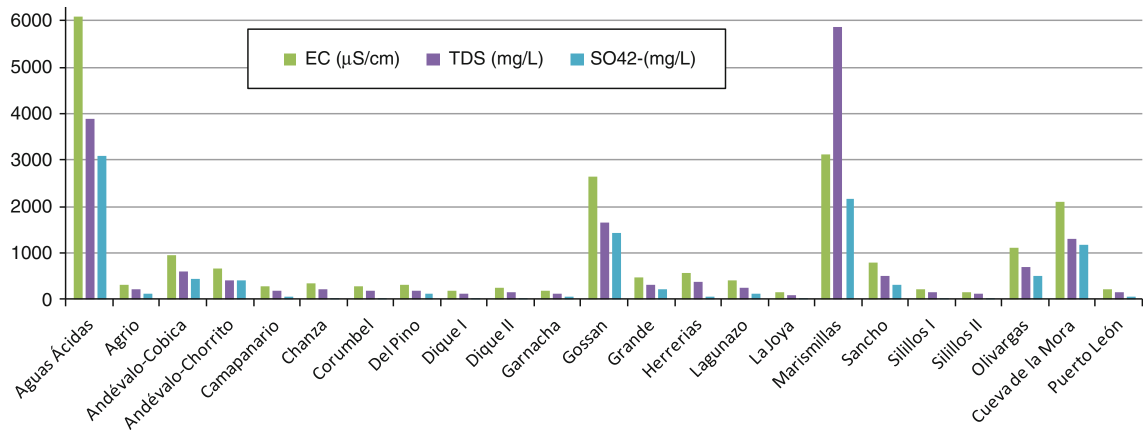


Fig. 3 Average values for EC, TSD and sulphates measured at the different sampled reservoirs

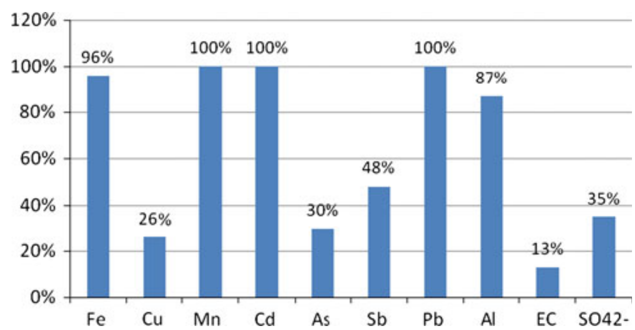


Fig. 4 Rate of reservoirs exceeding Directive 75/440/EEC for the different studied contaminants

sulphate. The Marismillas, Aguas Ácidas, Gossan, Andévalo-Cobica, Cueva de la Mora, Andévalo-Chorrito, Sancho, and Olivargas reservoirs stand out as having high average concentrations of Fe, Zn, Cu, and Mn, as well as sulphate.

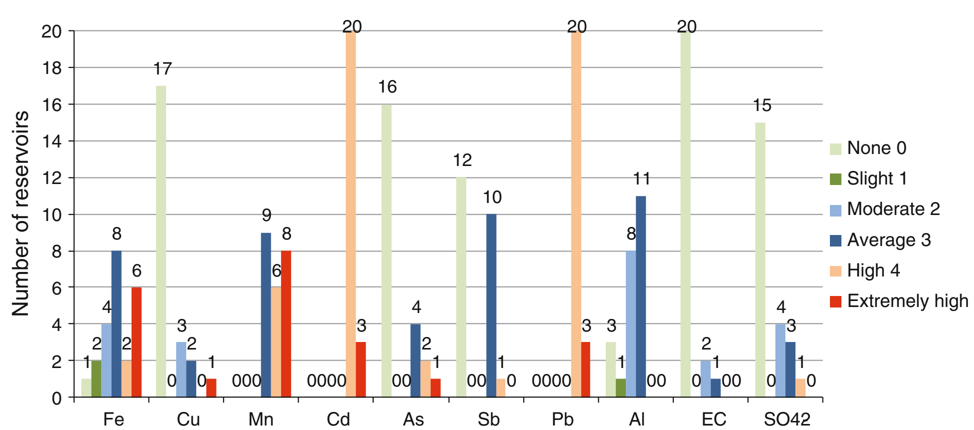
The Dique 1, Dique II, Herrerías, and Chanza reservoirs, which are all located in the upper part of the Guadiana river basin (Fig. 6), are heavily affected by Pb and Cd. The Andévalo-Chorrito and Andévalo-Cobica reservoirs have elevated levels of Fe and Mn. In the other reservoirs, the diagrams present a similar pattern of Mn, Cd, Pb, and Al concentrations.

Discussion and Conclusions

In general, we can say that all the reservoirs studied in the Iberian Pyrite Belt exceeded the maximum concentrations established by Directive 75/440/EEC for most of the parameters determined. Mn, Cd, Pb, Fe, and Al stand out because they present values that exceed the limits by the highest percentages, though the rest of the parameters were also found to exceed the established maximum levels.

On an individual level, according to the comparison established using the model proposed by Grande (2011), each reservoir presents a different range of pollution, due to the great heterogeneity and geographic dispersion of the reservoirs studied. Each reservoir belongs to a different hydrographic basin, has individual characteristics, and receives contaminant contributions by different mineral paragenesis at very different levels of pollution and dilution.

Fig. 5 Affection rate of the reservoirs based on the model proposed by Grande (2011)



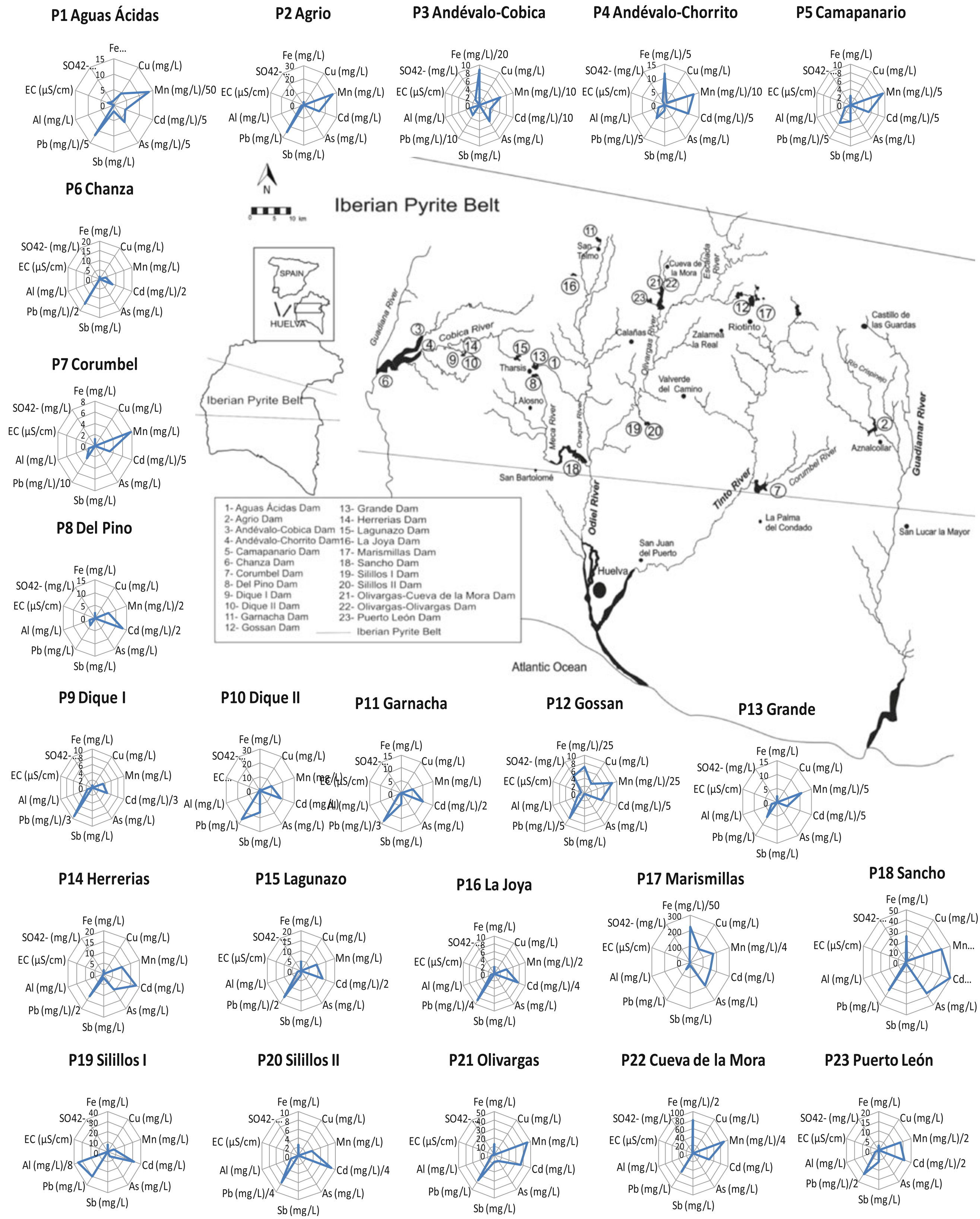


Fig. 6 Affection map based on Directive 75/440/EEC for the different sampled reservoirs

The lowest average pH values, the highest measured average values for the physical–chemical parameters, and the highest metals and sulphate concentrations were recorded in the Marismillas, Aguas Ácidas, Gossan, Andévalo-Cobica, Cueva de la Mora, Andévalo-Chorrito, Sancho, and Olivargas reservoirs, which are the reservoirs most affected by AMD. These reservoirs exceed the maximum concentrations laid down by Directive 75/440/EEC by the greatest margin (Grande 2011). The methodology used allows the degree of pollution in the waters stored in reservoirs to be precisely defined and a regional risk map to be formulated. The AMD that flows into these reservoirs translates to pollution indices that vastly exceed EEC regulations.

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