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Hydrochemical characterization and evaluation of the impact of AMD processes on river basin areas in the Iberian Pyrite Belt

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Abstract

The hydrographic network in the Iberian Pyrite Belt (IPB) (south-west Europe) is intensively affected by acid mine drainage (AMD) processes. This represents a unique worldwide scenario of extractive mining activity for more than 4,000 years. In order to be able to achieve possible restorations, it is necessary to reduce the scale of possible actions for future environmental improvements, at the river basin level. Therefore, the delineation of watersheds and subwatersheds in the IPB has been carried out, as well as the definition of the degree of impact by AMD processes in these basins in the dry season and in the rainy season. The results show that all basins are affected by AMD processes during the entire hydrological year, with pH values between 2 and 3, for most cases, and high concentrations of sulfates, metals and arsenic.

Keywords: Affected areas; AMD; Iberian Pyrite Belt; Metals; Waste rock dumps

Introduction

The hydrographic network in south-west Europe is intensively affected by acid mine drainage (AMD) processes, due to 88 sulfide mining exploitations located in the Iberian Pyrite Belt (IPB) (Pérez-Ostale *et al.*, 2013). This represents a unique worldwide scenario of extractive mining activity for more than 4,000 years.

The IPB is the biggest metallogenic region in the world, 230 km long and 60 km wide, which extends from the province of Seville (south-west Spain) as far as Portugal. It contains reserves in the order of 900 million tonnes of sulfides, and constitutes one of the most important metallogenic regions in the world. Its mines have been exploited since the second millennium BC by Tartessians, Phoenicians, Romans and Arabs. In more recent times (19th century until nowadays), mainly Spanish, Portuguese and English companies have followed one another in the mining of copper, silver, iron and gold (Sainz *et al.*, 2003). Over a period of more than 30 centuries, the mineral extracted is estimated at 30

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million tonnes (Pinedo, 1963). Between the second half of the 19th century and the first half of the 20th that quantity of mineral extracted was multiplied by 10 (Sainz *et al.*, 2003).

As a result of this activity in the past and due to the lack of preventive or corrective measures, there is a large contaminant load into the rivers of the basin areas, affecting the water quality of this region.

There are many abandoned mines without restoration in this area, which emit acid leachates loaded with metals and sulfates, which may constrain the use of the water in the affected watercourses. At the same time, European Regulations mandate the preservation of water resources and the restoration of the affected areas. This is the case with the Alcolea dam on the Odiel River, currently under construction.

Nowadays, mining activity in the IPB has been reactivated due to the copper demand for electrification of emerging countries. There are in operation a total of two mines, and at least another 20 will reopen in the near future.

The AMD impact in this area has been extensively described in the scientific literature over the last two decades (Grande, 2011; Grande *et al.*, 2000a, 2000b, 2005a, 2011a, 2011b; Leblanc *et al.*, 2000; Elbaz-Poulichet *et al.*, 2001; Borrego *et al.*, 2002; Younger *et al.*, 2002; Braungardt *et al.*, 2003; Sainz *et al.*, 2003, 2005; López-González *et al.*, 2006; Valente & Leal Gomes, 2007; Cánovas *et al.*, 2008; Vicente-Martorell *et al.*, 2008; Campaner Luiz-Silva, 2009; Casiot *et al.*, 2009; de la Torre *et al.*, 2009, 2013; Ruiz *et al.*, 2009; Couceiro & Schettini, 2010; Egal *et al.*, 2010; Gray & Delaney, 2010; Gunn *et al.*, 2010; Hafs *et al.*, 2010; Hao *et al.*, 2010; Loredo *et al.*, 2010; Ochieng *et al.*, 2010; Amaral-Zettler *et al.*, 2011; Romero *et al.*, 2011; Cerón, 2013a, 2013b; Santisteban *et al.*, 2013).

The Spanish sector of the IPB is delimited by two major river courses: the Guadiana River on the west side, and the Guadalquivir River on the east side. In the present work four main river basins have been considered, corresponding to the Chanza, Odiel, Tinto, and Guadiamar Rivers. Table 1 shows the main characteristics of the river networks in the study.

This study considers AMD pollution parameters at a river basin level, considering that at present it is impossible to remediate this problem on the receiving environment. This is due to several factors: (i) the high dispersion of the polluting sources along the IPB, (ii) the torrential rainfall, and (iii) the high water flow of the rivers during the winter season. To accomplish possible restoration, a more precise knowledge of water flows at a smaller scale is needed.

Any restoration project must fulfill three requirements: it must be technically viable, economically profitable, and environmentally sustainable. Under this premise, most of the techniques employed, both passive and active treatments, in other mining regions are not suitable in this study area. Therefore,

Table 1. Characteristics of the fluvial network of the study area.

Basin	Source	River mouth	River length (km)	Basin surface (km^2)	Sub-basins
Chanza	Cortegana (Huelva)	Guadiana River	117	985	Trimpancho Malagón Cobica
Odiel	Sierra de Aracena (Huelva)	Ria de Huelva	140	2,333	Meca Oraque Olivargas Odiel
Tinto	Nerva (Huelva)	Ria de Huelva	100	1,039	
Guadiamar	Castillo de las Guardas (Sevilla)	Guadalquivir River	1,300	137	

it is necessary to reduce the scale of the potential actions for future environmental improvements, considering minor fluxes of water flows near the generating sources with high levels of pollution loads.

Firstly, a diagnosis of the impact of AMD processes on the river basins is needed in order to study appropriate remediation alternatives for each of them. Therefore, the objectives considered in the present study are: (i) delimitation of the river basins in the IPB; and (ii) definition of the degree of impact on the basins and sub-basins by AMD processes in the IPB in the rainy season and in the dry season. The study during the dry season and its comparison with the rainy season, taking into account precipitation, allows us to model the process during the entire hydrological year.

Materials and methods

Initially the definition of the acidic contributions to the sub-basins was carried out, and subsequent sampling and analytical determinations were carried out.

The existing mining and cartographic data were revised using Map Source Software and aerial photos (Grande *et al*., 2013a, 2013b; Pérez-Ostale *et al*., 2013). With this information, nine mining basins and sub-basins have been defined, according to the presence of mining exploitations in the river basins (Figure 1).

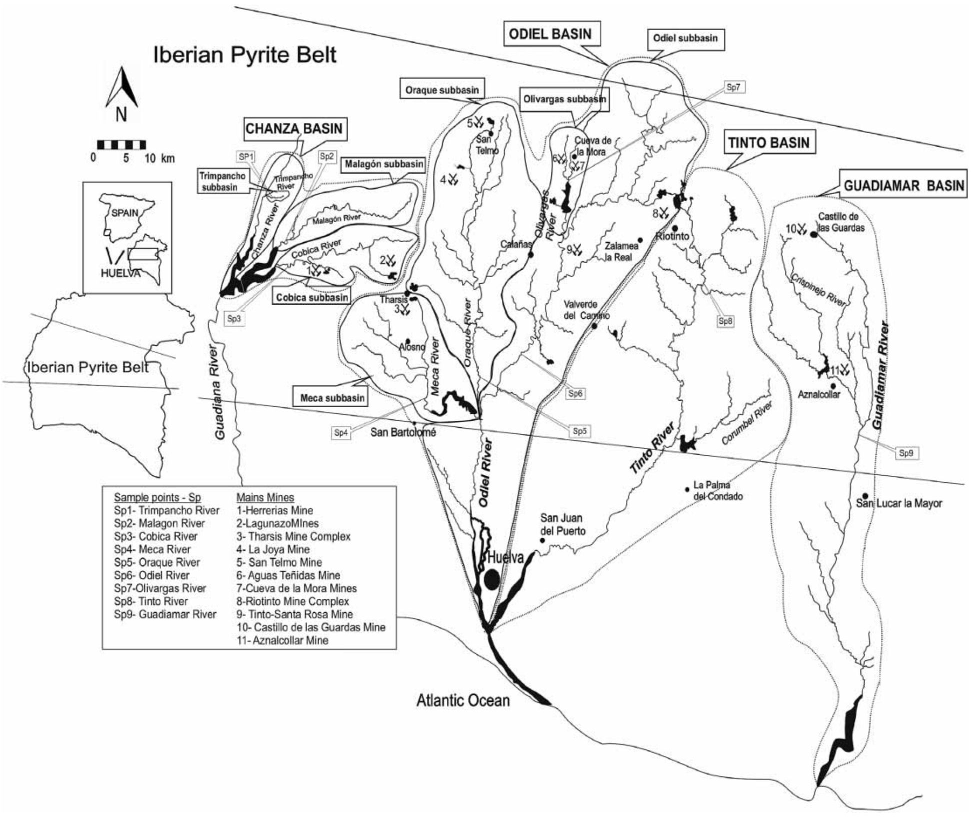

Fig. 1. Location map.

The climate of the studied area is Mediterranean, with hot summers and mild winters, when most of the rain falls. In the period between the years 1980 and 2010, November and December were the wettest months with average rainfall around 124 mm/month, and July and August were the driest months with average rainfall close to 8 mm/month. In the same period the average rainfall ranges from 468 mm in the south to 1,134 mm in the north. The distribution of rainfall, the high average annual temperature (15.9–17.9°C), and the high potential evapotranspiration values (around 915–1,323 mm/year) produce a strong seasonal effect (Galván, 2011).

Basic assumptions are considered to achieve the defined objectives. First of all, the main pollution sources are the waste rock dumps (WRDs). Secondly, the annual precipitation is clearly lower than the evapotranspiration, so open pits act as endorheic systems with a negative balance, and therefore without contribution to the river networks (Pérez-Ostale, 2014). Water upwelling through wells and galleries is negligible for this type of mining, due to the impermeable character of the hydrogeological scenario. Therefore, WRDs with no restoration are the main cause of pollution of the water network of the IPB (Sainz *et al*., 2002). WRDs leach only during rainfall and for some days afterwards, depending on the size of the WRD and the water that they accumulate. It can be assumed that the rain that falls on WRDs will deteriorate the watercourses of the river basins. Hence, WRDs behave as a 'polluted and polluting aquifer' of anthropogenic origin. This study does not take into account the WRDs belonging to the mines currently in operation, Aguas Teñidas and Cobre las Cruces, which do not produce acid leachates and comply with environmental legislation.

One sampling point was chosen for each sub-basin, considering that the following requirements had to be fulfilled:

1. Sampling was performed at the beginning of the dry season (June 2013), when the rivers transport water that is stable from a chemical and hydrological point of view, without sudden changes due to recent rainfall that may redissolve existing precipitates along the river bed. Also, another sampling was carried out in the rainy season (March 2013), coinciding with the period in which all the WRDs, including those of a small area, emit leachate.
2. Each sampling point has to be representative of all the water inputs in the sub-basin. Therefore, each sampling point has to consider the leachates of the mining exploitations within each sub-basin, including the AMD generated by the sulfide oxidation corresponding to different mineral paragenesis.
3. The sampling point is indicative of the chemical characteristics of the emitting sources within the sub-basin. Hence, the sampling point was chosen downstream close to the acid water input of the last emitting source. We consider that the present approach focused at a sub-basin level is representative and useful for characterization of the water quality, considering its eventual usage.
4. Possible sampling points with indicators of anomalous organic matter content (presence of algae) were also discarded, as this may alter the analytical results.

At each sampling point (Figure 1), samples were taken every 15 days in duplicate for the coordinator of the results in the laboratory, following established procedures for water affected by AMD processes. The results obtained were processed with other data already obtained in previous campaigns. For the study and comparison of the obtained results, the average values for each sampling point for the entire campaign were taken into account.

The 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 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). Merck AA Certificate solutions were used in all experiments as standard solutions. Milli-Q water (Millipore, Bedford, MA, USA) was used in all the experiments.

The determination of sulfate was carried out using a photometer manufactured by Macherey-Nagel's (Photometer FP-11).

The concentration of metals in the water (Fe, Cu, Cd, Mn, Co, Ni and As) was analyzed in the laboratory by means of an Aanalyst 800 atomic absorption spectrometer (Perkin-Elmer, Norwalk, USA). Analysis was performed in duplicate to guarantee the accuracy of the measurements.

The analytical data were entered into a data matrix, from which a cluster analysis was performed (STATGRAPHICS Centurion XV software). The aim is to look for associations that indicate affinities in behavior between variables strictly from a hydro-geochemical perspective (Davis, 1986).

Results and discussion

Cartography of the basins and sub-basins of the Spanish IPB affected by AMD has been defined and shown in Figure 1, which shows the river network within the study area. Four main basins have been defined, corresponding to the Chanza, Odiel, Tinto, and Guadiamar rivers. The Chanza basin, located on the western side of the IPB, has been divided into three smaller sub-basins, corresponding to its main tributary rivers, Trimpancho, Malagón, and Cobica Rivers. The Odiel basin has been divided into four sub-basins: the sub-basin on the Odiel River itself, and those of its three main tributaries: Meca, Oraque, and Olivargas Rivers. Finally, the Tinto and Guadiamar River basins, on the east of the IPB, configure the rest of the water network.

In previous works, the Olivargas basin has not been considered as a sub-basin on the Odiel River (Sarmiento, 2007; Grande *et al*., 2013b). In the present work, however, we have considered that an independent sub-basin should be considered, as particular and distinctive hydrodynamic and hydrochemical parameters can be related to the AMD inputs coming from important mining exploitations, such as Cueva de la Mora, Aguas Teñidas and La Zarza-Perrunal.

Table 2 shows the WRDs' surface areas for each basin and sub-basin of the study area and the mean values of physicochemical parameters obtained at each sampling point for the entire campaign.

The results in Table 2 show that the majority of pH values ranged from 2.33 in the Meca River, up to 3.12 for the Odiel River, except in the Malagón River that shows a pH of 8.05. The Tinto River presents the maximum values of EC (9,920 μS/cm), TSD (5,900 mg/L) and Fe (102.40 mg/L). The Meca River shows the maximum values of Cu (15.01 mg/L), Mn (22.92 mg/L), Co (0.24 mg/L), Ni (28.24 mg/L)

Table 2. WRDs' surface areas and physicochemical parameters of the river basins in the dry season.

Parameter	Trimpancho	Malagón	Cobica	Meca	Oraque	Olivargas	Odiel	Tinto	Guadiamar
WRDs (ha)	7.9	5.2	81.4	383.6	132.3	136.5	636.7	824.2	355.8
pH	2.53	8.05	2.52	2.33	2.84	2.83	3.12	2.52	2.60
EC (μS/cm)	8,420	363	5,140	2,910	2,680	4,700	2,810	9,220	4,440
TDS (mg/L)	5,430	233	3,290	1,863	1,728	3,010	1,799	5,900	2,840
Fe (mg/L)	74.54	2.58	70.27	43.18	26.28	91.97	11.03	102.40	61.98
Cu (mg/L)	7.76	4.87	5.27	15.01	4.91	10.27	6.74	13.52	6.36
Cd (mg/L)	0.62	0.61	0.62	0.73	0.64	1.09	0.68	0.86	0.62
Mn (mg/L)	20.86	1.17	10.00	22.92	1.71	16.77	15.25	22.04	10.62
Co (mg/L)	0.04	0.03	0.07	0.24	0.13	0.21	0.04	0.10	0.03
Ni (mg/L)	1.88	0.39	0.84	28.24	0.91	2.38	1.10	0.31	0.76
As (mg/L)	0.20	0.01	0.04	8.39	0.29	2.09	0.18	2.93	0.09
SO_4^{2-} (mg/L)	2,832	51	1,656	1,656	1,920	2,000	1,596	2,112	1,524

and As (8.39 mg/L). In the Trimpancho River the maximum concentration of sulfates was detected (2,832 mg/L). The minimum levels are associated generally with the Malagón River.

Table 3 shows the physicochemical parameters of the sampling campaign in the rainy season for each basin and sub-basin of the study area. The Tinto River presents the highest concentration of Cu (12.70 mg/L), Co (0.279 mg/L) and As (0.012 m/L). The pH reached a minimum value of 2.13 for Tinto River and a value close to neutrality in the Malagón River (above 8). The highest values of TDS (1,123 mg/L) and EC (1,521 μS) were obtained in the Olivargas basin.

Figure 2 compares the values of each parameter in the dry season and rainy season. Overall, lower pH values have been observed in the dry period than during the rainy season for the different rivers. The contribution of clean rainwater to channels produces dilution of the river, which translates into a rise of pH. The dynamic behavior of the channel responds to the sum of external stimuli caused by rains. The seasonal memory depends on the time of the hydrologic year and, finally, the hydrochemical inertia of the basin. For the same reason, the concentrations of metals, arsenic, sulfates, and the EC and TDS values are higher in the summer.

Table 3. Physicochemical parameters of the river basins in the rainy season.

Parameter	Trimpancho	Malagón	Cobica	Meca	Oraque	Olivargas	Odiel	Tinto	Guadiamar
pH	2.45	8.32	2.57	2.57	2.93	3.25	3.41	2.13	6.49
EC (μS/cm)	781	204	498	746	302	1,521	382	771	187
TDS (mg/L)	500	145	310	475	193	1,123	244	493	120
Fe (mg/L)	30.26	0.304	32.18	34.13	4.905	22.1	1.46	62.24	0.303
Cu (mg/L)	6.59	0.011	4.85	7.14	1.41	2.98	3.614	12.7	0.001
Cd (mg/L)	0.078	0.248	0.05	0.038	0.006	0.011	0.025	0.047	0.278
Mn (mg/L)	9.54	0.029	1.506	6.549	0.08	3.92	4.752	4.644	0.067
Co (mg/L)	0.161	0.043	0.023	0.531	0.052	0.089	0.101	0.279	0.042
Ni (mg/L)	0.133	0.008	0.007	0.193	0.006	0.2	0.022	0.068	0.008
As (mg/L)	N.D.	N.D.	0.001	0.007	0.001	0.001	0.005	0.012	0.003
SO_4^{2-} (mg/L)	1,060	31	510	720	188	430	384	690	130

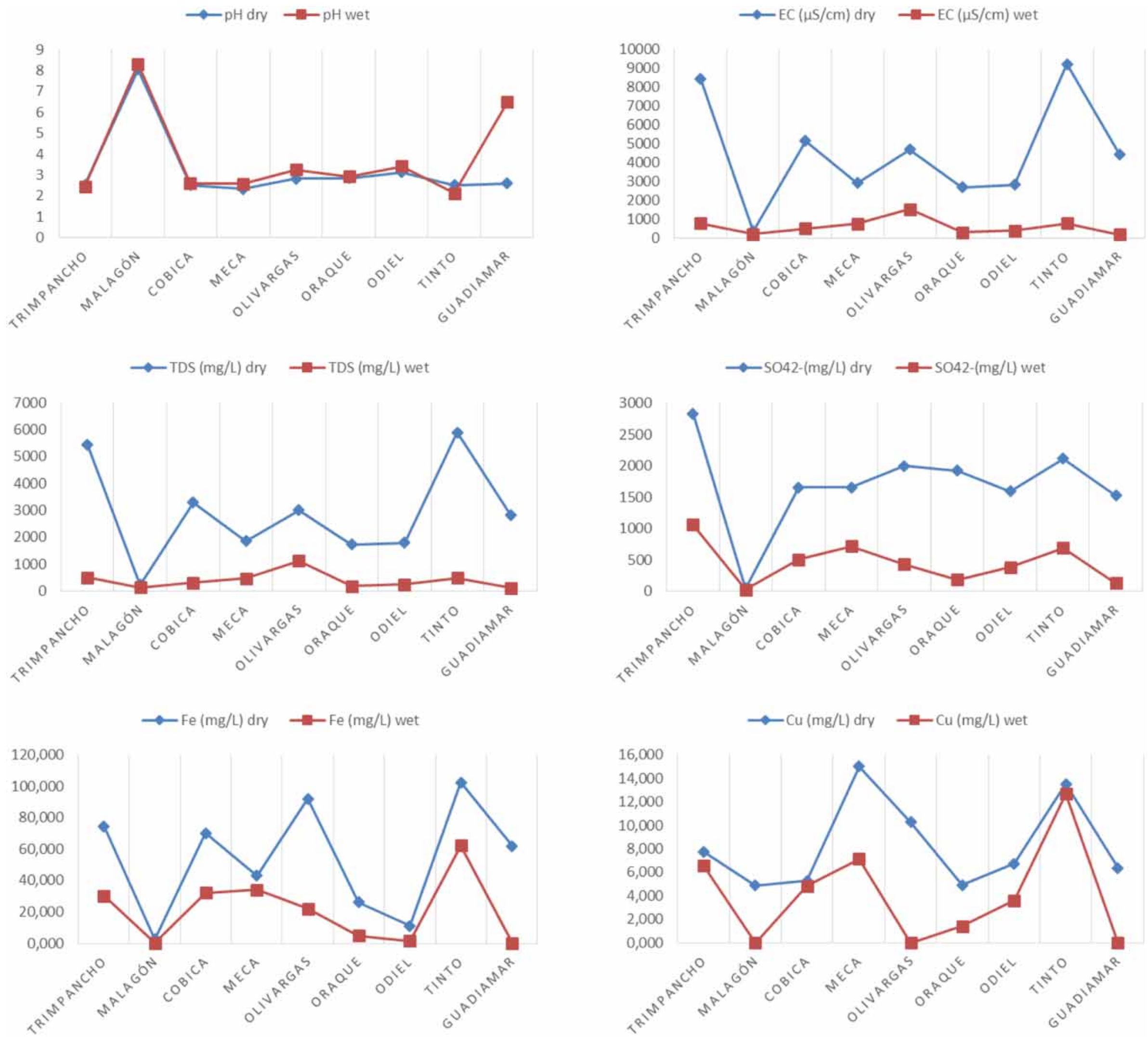

Fig. 2. Comparison of physicochemical parameters, heavy metals and As in dry and rainy seasons. (*Continued*.)

To analyze the relationships between the various parameters, dendrograms were obtained (Figures 3 and 4), in the dry and rainy season, respectively.

The dendrogram in Figure 3 shows two families. The first one brings the pH and the elements Cd, Ni, Co and As, with the pair Cu–Mn, and in turn, with Fe. The second group is formed by the triplet EC, TDS and sulfates.

The dendrogram in Figure 4 also shows two large groups. In the first, the pH–Fe pair associated with another sub-cluster containing Cd, Co, Ni and As, Mn and Cu grouped appears. The second major group related to TDS and sulfates with EC.

The grouping of parameters EC, TDS and sulfates in both dendrograms reflects the suitability of the process. This behavior is consistent with that contained in the scientific literature (Lyew & Seppard,

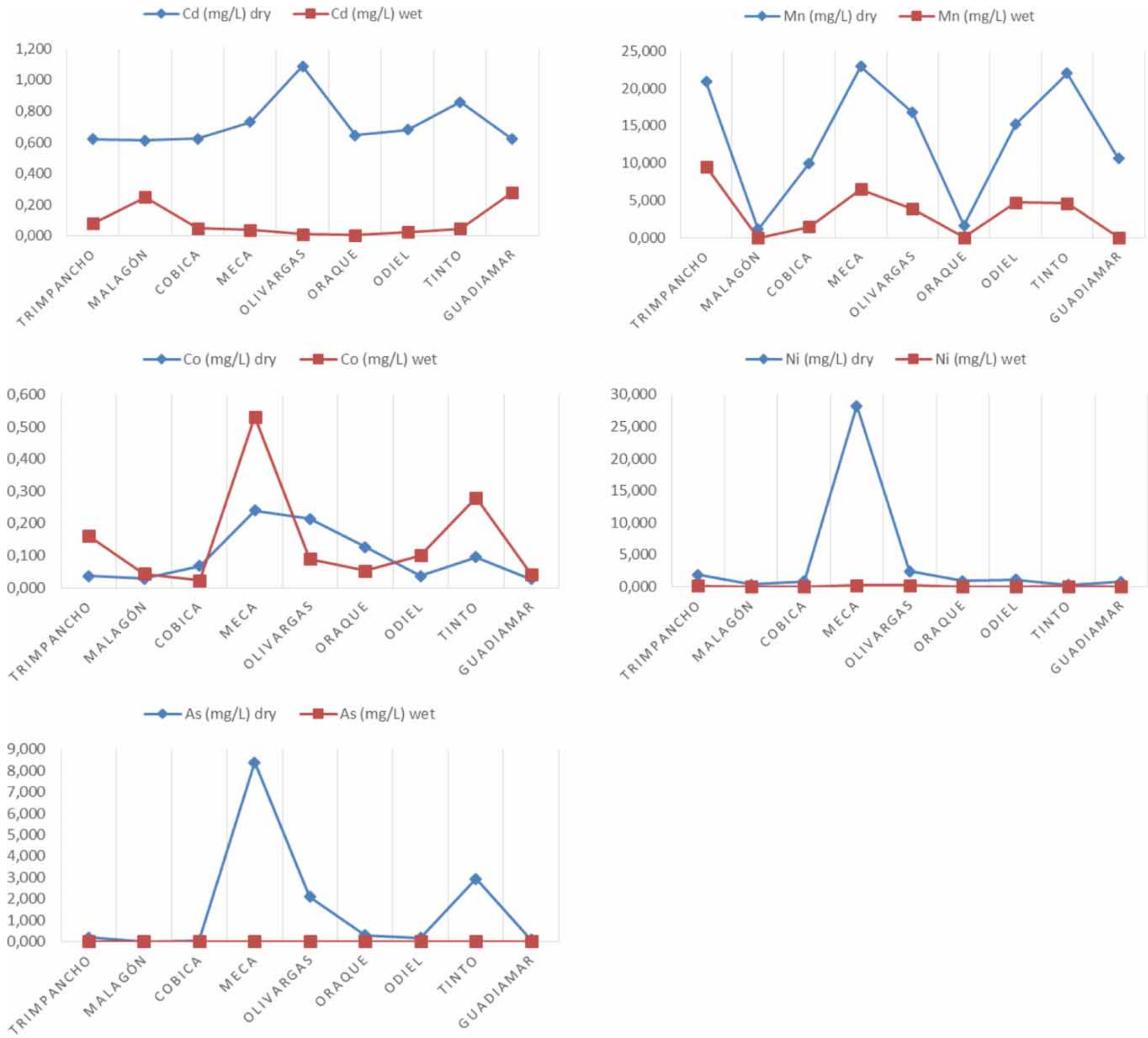

Fig. 2. Continued.

2001; de la Torre *et al.*, 2011; Grande *et al.*, 2005b). Sulfates and TDS are responsible for variations in conductivity. This happens in the absence of chlorides, which are potentially responsible for significant increases in conductivity that could mask the dependency relationships between this and sulfates, as usually happens in an estuarine environment within the zone of tidal influence in coexistence with AMD fluvial processes (Grande *et al.*, 2003a, 2003b).

The second sub-cluster shows a different behavior in the rainy season. The behavior of the tailings determines the chemical characteristics of the channel in direct relation to the cleaner contributions. When high rainfall occurs, contributions are plentiful and modify the values of pH, dissolved oxygen or redox potential. Conversely, when it does not rain, there is no input of clean water and salt precipitation occurs at the expense of solutes present in water. Part of the pollutant load is removed from the

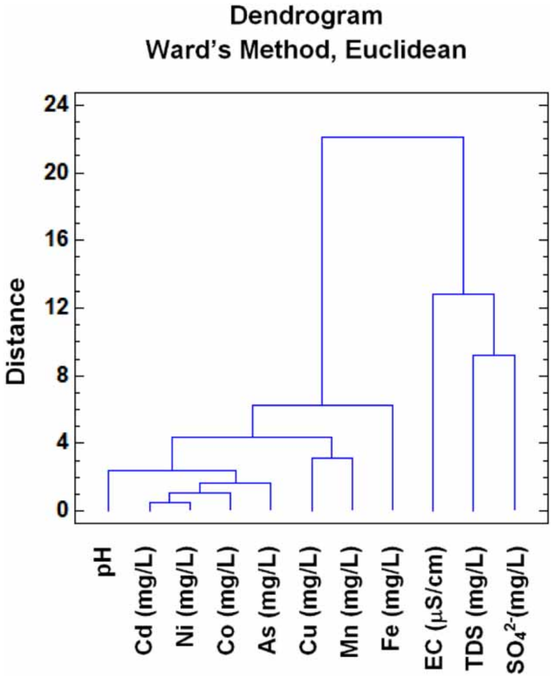

Fig. 3. Cluster analysis for all parameters in the dry season.

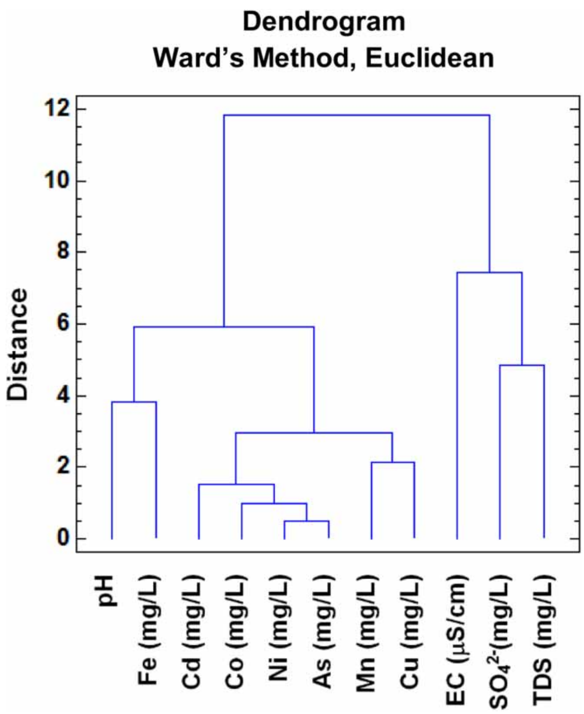

Fig. 4. Cluster analysis for all parameters in the rainy season.

water environment going to form the solid phase, and all of it is subject to formation of new mineral species regulated by pH, dissolved oxygen or redox potential.

Conclusions

The definition of the nine basins and sub-basins considered in this study, located in the Spanish IPB, allows the observation that all are affected by AMD.

In times of drought, the AMD impact in the water of other basins is similar, with pH values found between 2 and 3, except in the Malagón River. In the rainy season, lower concentrations of metals, arsenic and sulfates, due to the processes of dilution by rainwater contributions, are obtained. The pH is higher, with values between 2 and 3, except in the Guadiamar River and Malagón River.

Cluster analysis is an effective tool for modeling process pollution by AMD, providing observations of the association of TDS, EC and sulfates, both in the rainy and the dry season. However, the grouping of pH, metals and As shows a different behavior during the rainy season from the dry season, because of the relationship between the chemical characteristics of the channel, contributions and emissions from dumps.

This work, besides contributing to the literature and allowing a more accurate planning of measures aimed at rehabilitation, will serve as a methodological basis for implementation in other sectors affected by similar problems.

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