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Negative pH values in an open-air radical environment affected by acid mine drainage. Characterization and proposal of a hydrogeochemical model

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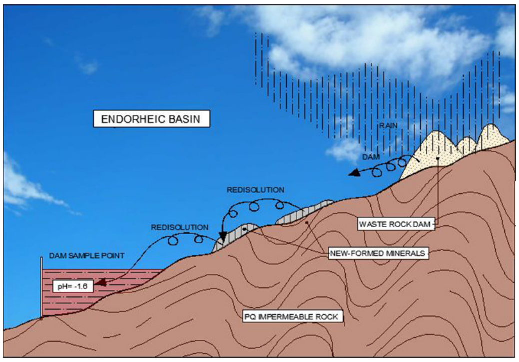
HIGHLIGHTS

- Negative pH values analysed in an open air environment
- Extreme pollution by acid mine drainage in the Iberian Pyrite Belt
- High toxicity assessed by the presence of diatoms species
- Radical pollution values in an endorheic basin

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents the finding of a singular environment polluted by acid mine drainage in the Iberian Pyrite Belt. This situation is regulated by particular conditions, thus the analysed values can be considered as extreme, not only because of the high concentrations of toxic elements, but also due to the extreme low pH, reaching an average negative pH of −1.56, never found before in open-air environments contaminated by acid mine drainage. Concentrations up to 59 g/L of Fe, 2.4 g/L of Al, 740 mg/L of As, 4.3 mg/L of Co, 5.3 mg/L of Ge, 4.8 mg/L of Sb, inter alia, can be found dissolved in these polluted waters. The main aims of the present work are the physicochemical characterization and the toxicity assessment of these radical polluted waters. In addition, a hydrogeochemical model of the system will be proposed, which justifies the extreme pH value and the extraordinarily high concentrations of toxic elements, even for acid mine drainage polluted environments. Extreme acidity and metal and sulphate concentrations in the Radical Environment are due to several processes of different nature, mainly driven by the geochemistry of the minerals presents in the endorheic character of the basin. The extremely acidic nature of these waters control the Fe species present in them, being $FeHSO_4^+$

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the mainly Fe specie representing 94% of total. High toxicity of these waters has been detected due to the absence of any diatoms species.

1. Introduction

Acid Mine Drainage (AMD) is one of the most serious problems of fluvial pollution worldwide, a global problem affecting the five continents without a generic solution to be applicable to the different scenarios. Although precise scale quantification of this pollution is difficult, Johnson and Hallberg (2005) estimated that, in 1989, approximately 19,300 km of rivers and 72,000 ha of lakes and reservoirs throughout the world were severely affected by mining effluents.

The acid water load from sulphide minerals mining operations, and occasionally from coal, to the river networks is the main factor responsible for the modification of the physical-chemical characteristics of the waters, increasing the acidity of them as well as heavy metals and sulphates contents coming from the oxidation of sulphides, reaching extreme values (USEPA, 1994).

One of the main implications of pollution through the oxidation of sulphides is the low pH of the affected waters. Table 1 lists some of the environment contaminated by heavy metals where the lowest pH values found in the scientific literature have been measured. The lowest described values (pH 0.9) belong to the Iberian Pyrite Belt (IPB, SW of Europe, Fig. 1), or are related to volcanic environments (Russo et al., 2008). Note that the negative pH values measured by Nordstrom et al. (2000) belong to the dripping of melanterite stalactites and other sulphates found inside an underground mine. From our knowledge, lower pH values have not yet been found in open-air environments.

This paper presents the finding of a singular environment, regulated by particular conditions, thus the analysed values can be considered as extreme, not only because of the high concentrations of toxic elements, but also due to the extreme low pH, reaching a negative pH value never found before, in contaminated environments by AMD.

On the other hand, in rivers highly contaminated by AMD, the use of conventional environmental quality biomarkers is not possible due to the absence of macroinvertebrates. So, AMD polluted rivers have a huge gap in terms of water toxicity assessment, making impossible the estimation of the environmental recovery. Some toxicity studies have been performed in polluted streams of IPB (Sarmiento et al., 2011) and tested using bivalves as a biomonitor tool for metal contamination (Sarmiento et al., 2016; Bonnail et al., 2016). However, these studies had only been possible through laboratory tests.

In recent times, studies in metal/acid-polluted streams have addressed the diatoms as important bioindicators in the water quality assessment (Luis et al., 2009, 2011), due to their short generation time, ubiquity and easiness of collection. Diatoms respond to these toxic effects not only at the community level through shifts in dominant taxa (Hirst et al., 2004), but also through changes in diversity (Luis et al., 2009, 2016), normally decreasing in contaminated sites, thus less diatom species in affected sites.

The main aims of the present work are the physicochemical characterization and the toxicity assessment of these AMD polluted waters which present the most extreme and radical pH value found in an open air mine environment. In addition, a hydrogeochemical model of the system will be proposed, which justifies the extreme pH value and the extraordinarily high concentrations of toxic elements, even for AMD polluted environments.

2. Site description

To diagnose the processes that regulate this unusual situation, a description the different AMD-scenarios that the Iberian Pyrite Belt presents is necessary. These scenarios could be classified as regional background area (Tinto and Odiel Basins, Fig. 1) and local background area (Cobica Basin, Fig. 1).

2.1. Regional background area: Tinto and Odiel Basins

Throughout the Regional Background Affected by AMD, >4000 ha. of land are occupied by tailings from 88 old sulphide mines (Grande, 2016). The intensive mining activity carried out over the course of >4500 years in the IBP (Fig. 1) has caused an almost countless number of mines to appear, scattered throughout the area. The environmental regulations were previously absent and less restrictive. This issue led to extraordinary levels of pollution throughout the affected drainage networks (Grande et al., 2014). Iberian Pyrite Belt has a special relevance by the magnitude and extension of the AMD problem, being the Tinto and Odiel rivers the best known cases, which are widely described in the scientific literature by a large number of authors (De la Torre et al., 2009; Davis Jr et al., 2000; Elbaz-Poulichet et al., 1999, 2000, 2001; Gonzalez et al., 2012; Grande et al., 2005; Jiménez et al., 2009; Leblanc et al., 2000; Sainz et al., 2005; Sánchez-España et al., 2005; Sarmiento et al., 2009a, 2009b; Grande et al., 2005, 2014, 2017; Jiménez et al., 2009; Nieto et al., 2007; inter alia).

2.2. Local background area: Cobica River basin

The Cobica River basin (Fig. 1) collects AMD-polluted waters coming from Lagunazo Mine and Herrerias Mine (Grande et al., 2005) after flowing along the wastes of abandoned mine operations. The importance of these processes is that their leachates, carried by the Cobica

Table 1
Extreme hydrochemical parameters measured at other mines worldwide. Concentration in mg/L, Eh in mV.

	pH	Eh	SO_4	Fe	Al	Cu	Zn	Mn	As	Cd	Pb	
Iron Mountain, USA	−2.5		760,000	124,000		4760	2600		340	211	12	Nordstrom et al. (2000)
Rocky Mountains, USA	2.35		2720			98.6	228					Verplanck et al. (2009)
Carnoules mine, France	2.2	130	7590	2650			63.6		324		1.3	Leblanc et al. (1996)
Licor de Cu, Huelva, Spain	0.9		78,000	34,500	1600	500	500	57	41	0.3		Unpublished data
Peña del Hierro mine, Spain	1.5	575	114,322	20,829	2885	22	16	54	13	2.9	2.7	Sarmiento et al. (2009b)
Río Agrio, Argentina	1.8/2.2			191/2650	79–921		0.3–7.7	8.6–79.8	0.3–4.8			Russo et al. (2008)
Caviahue Lake, Argentina	2.7			23.4	20.2		0.03	0.99	0.01			Russo et al. (2008)
Woods Weir, Canada	2.57		4784		72.83	1.09	22.2	8.28		0.1	0.1	Moncur et al. (2006)
Acid Pond, Canada	2.33		7150	3700	252	15.8	50.5	22.3		0.6	1	Moncur et al. (2006)
Boomerang Lake, Canada	2.8		680		6	0.75	38					Kalin et al. (2006)
São Domingo mine, Portugal	2.6	481		4210	1480	100	2,448,000		6.2		30	Abreu et al. (2008)
Lower Lusitania, Germany	2.5		425	38.3								Hünken and Mutz (2007)

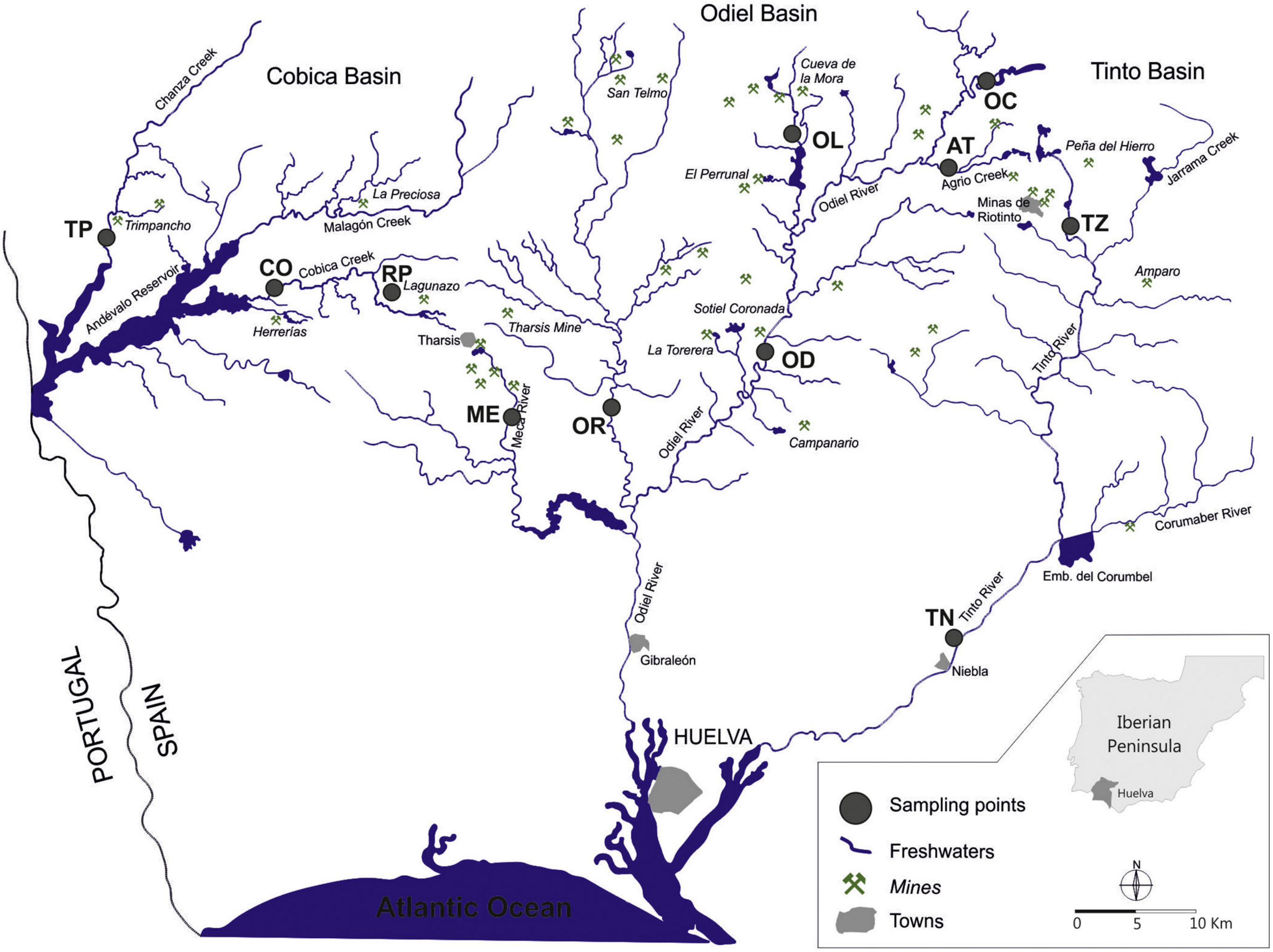

Fig. 1. River networks location map indicating sampling points.

River, flow into the Andevalo Dam which will supply the water for irrigation and human consumption to an area of 20,000 km^2. The main contribution to this dam is made by the Malagon River, of high hydrological relevance, with a watershed of 405 km^2 and to which the Cobica River is a tributary (Fig. 1). The waters presenting a radical pH value and extreme concentrations of toxic elements, and subject of this study, belong to this basin. This Radical Point collects acid lixiviates from Lagunazo Mine.

Rainfall data recorded at the station nearest to the study area (Tharsis mine) were obtained from the local Meteorological Service. Annual rainfall was 613 mm for the hydrological year 2016/2017, 75% of which occurred between November and March.

The Radical Point studied is part of an endorheic basin defined by the natural topographic limits in the highest areas. The lower zone of the basin is affected by the presence of an anthropic closure for the storage of acid water. This polluted water was destined to the irrigation of open-air "teleras", and the later current of the acid water through channel systems, some of them still present in the working area. In fact, the existence of remnants of "teleras" and channel systems indicates that the mine could be at least 130 years old (previous to 1888). In addition to the "teleras" waste, in the radical watershed, considerable surface area occupied by other mining waste with very high contaminating capacity can be found. It is due to its low granulometry and high weathering degree (Younger, 2007). These are more recent accumulations (1982–1998) from the pyrites roasting at the Chemical Complex of Huelva that were returned to the mining areas after the entry into force of the Spanish environmental regulations in 1982.

Most of these materials have experimented calcination in "teleras" until 1888, giving a product known locally as "morrongo". These appears in the form of heterometric fragments of a size not exceeding 3 cm, being able to find abundant particles within the slime - clay granulometric fraction. In some areas scattered Roman or posterior lupias from metallurgy are found which were surely transported for building of roads and railways. In the area there are also pyrite ashes from the Chemical Complex of Huelva. The environmental regulations from that time required the return of ashes from pyrite roasting of the chemical industries to the areas where the exploitation was granted.

3. Methodology

3.1. Radical Point setting

The sampling point where the extreme pH values were found (Radical Point) is located in a small mining leachates dam belonging to the Cobica River watershed. This dam was built to collect the infiltrations of two other larger dams located upstream within the same basin, which were built at the end of the 19th century to retain acid mine waters that were used in "canaleos" (local name for leaching copper production) for the copper recovery from "teleras" (local name for open air calcination of copper) (Grande et al., 2010a, 2010b).

Related to the types of waste present in the watershed, there are two conditioning factors to be described in the sampling area: hydrodynamic characteristics and mining-geochemical characteristics. Regarding the hydrodynamic factors, the studied dam has a medium-small size for scenarios of sulphide mining (80 m^2). The water level in the dam remains practically constant throughout the hydrological year, regardless of the season. There are no mapped aquifers or fractures causing upwelling of groundwater in the area that feed the dam, receiving only rainwater from the small watershed and sponge water from slag heaps located in it. Slag heaps of different lithologies (pyrite ash and mineral in stock) and different grain sizes (especially fine to very fine size) are found in the watershed (Fig. 2). These residues occupy a surface $>$39 ha. (Fig. 2) originating a system generating acidic waters that discharge into the studied dam (Grande, 2016). This basin drains as an endorheic basin due to not receiving external contributions of groundwater or surface from outside (Jimenez, 2009). In addition, the water balance of the dam is clearly negative for this environment, being of 650 L/m^2 of mean annual precipitation and an annual potential evapotranspiration of 912 L/m^2 (Jiménez et al., 2009). Regarding the mining-geochemical factors, pyritic materials that have undergone mineralogical and metallurgical processes can be observed in the receiving basin (Fig. 2). Also can be detected stockpiles of crushed ore that were stored temporarily in the 1980s because they were low-grade copper ores and were mixed with richer ones until they reached the optimum copper percentage for commercialization. The closure of the mining operations has left these highly polluting mineral accumulations exposed to rain as the stocks are not waterproofed.

3.2. Collected samples

From October 2003 to January 2007, five surface water samples were collected at the Radical Point (RP in Fig. 1) (October 2003, February and August 2004, September 2005 and January 2007).

In addition, a total of 13 measurements of pH were performed monthly throughout the hydrological year 2016–2017 in the Radical Point site. Beside, in the dry season (October 2017), surface water samples were taken at 11 different points along the whole Iberian Pyritic Belt: 8 points belonging to the Regional Background Affected (Fig. 1); one point of the regional background not affected (OC in Fig. 1) taken at the headwaters of the Odiel river, upstream of the mining influence; one point belonging to the local bottom (CO in Fig. 1); a corresponding point with the Radical Point (RP in Fig. 1).

Water samples were filtered immediately in the field through 0.22 μm Millipore filters fitted on Sartorius polycarbonate filter holders. Samples for cations and metal analysis were acidified in the field to pH < 2 with suprapur HNO$_3$ (2%) to avoid precipitation and then stored in the dark at 4 °C in polyethylene bottles for less than two weeks until analysis. Samples collected for sulphate determination were filtered but not acidified.

3.3. Analytical methods

Several physicochemical parameters were measured in the field. Temperature, pH, specific conductance, redox potential and total dissolved solids were measured using a multiparametric portable device (CrisonMM40) with a measuring scale of up to −2 pH units. The measured negative pH values were tested with other portable instruments. The pH meter was calibrated using WTW standard solutions (pH 2.00, 4.01 and pH 7.00) and redox potential was checked using Hanna standard solutions (240 mV and 470 mV).

Concentration of trace metal analysis for the samples were performed with an Agilent Technologies 7700 Series inductively coupled plasma mass spectrometer (ICP-MS) and an Iris Intrepid Model atomic emission spectrometer (ICP-AES). Detection limits were calculated using average and standard deviations from ten blanks and were <0.5 mg/L for Zn, Fe, Al, Ca, Cu, K, Na and Mn; <1 μg/L for As, Cd, Cr, Ge, Li, Ni, Pb, Rb, Ba, Co, Ga, Se and Sr; and <0.5 μg/L for the rest of the

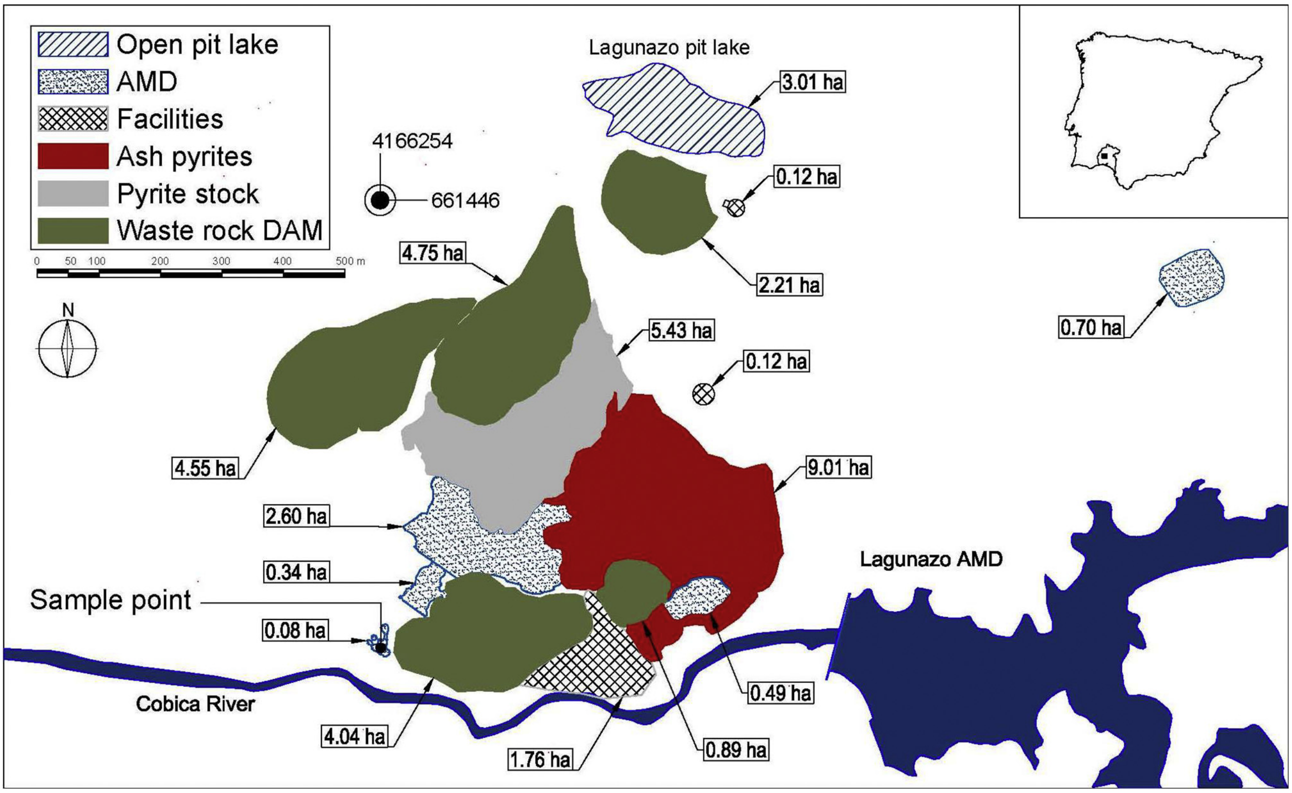

Fig. 2. Leachate collection basin location.
Modified from Grande (2015).

elements. The relative standard of deviations (RSDs) were <10% for all the analysed elements, indicating good repeatability of the procedures.

Specific conductivity and pH were measured in the first five sampling at point RP (Fig. 1) (October 2003 to January 2007). Concentrations of Fe, Cu, Zn and As were measured with a Perkin-Elmer Atomic Absorption Spectrophotometry (AAnalyst 800) with air acetylene flame using hollow cathode lamps as the source of energy. Detection limits were <0.5 mg/L for all elements.

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 sulphate was carried out using a photometer manufactured by Macherey-Nagel's (Photometer FP-11). Detection limits was 10 mg/L.

3.4. Diatoms samples

Epipsammic diatom samples were collected by removing the top layer of the sediment surface with a syringe, following the sampling of protocol (Prygiel and Coste, 2000). Alive samples were immediately taken to the laboratory to exclude the possibility of the presence of dead diatoms in order to avoid abundance errors. Then, an aliquot was treated with HNO_3 (65%) and potassium dichromate ($K_2Cr_2O_7$) at room temperature for 24 h, followed by three centrifugations (1500 r/min) to wash off the excess of acid. Then, permanent slides were prepared using Naphrax®. Diatoms were identified and semi-quantified under a light microscope (Leitz Biomed 20 EB) using a 100× objective (N.A. 1.32). Taxonomy was based on Krammer and Lange-Bertalot (1986, 1988).

3.5. Geochemical modelling

Water chemistry was interpreted with the assistance of the equilibrium chemical-speciation/mass-transfer model PHREEQC (Parkhurst and Appelo, 1999) using the thermodynamic database WATEQ4F (Ball and Nordstrom, 1991). The degree of saturation is expressed as the saturation index (SI), where SI is equal to the difference of logarithms of ion activity product and solubility constant (SI = logIAP − logKsp). WATEQ4F was used to calculate the saturation indexes for discrete minerals that may be controlling the concentrations of dissolved species in the waters. Published solubility constants were used for other minerals, such as schwertmannite.

Table 2
Physicochemical parameters in studies samples.

	pH	EC (mS/cm)	TDS (g/L)	T (°C)	Eh (mV)
Regional Background Unaffected					
OC	8.69	0.33	na	28.5	376
Regional Background Affected					
AT	2.33	14.6	9.34	32.7	777
TZ	1.77	16.2	10.5	24.9	535
ME	2.71	4.44	2.84	35.4	712
OR	2.52	2.66	1.7	28.4	677
TP	1.78	31.8	20.4	27.2	795
TN	2.53	9.09	5.82	29	639
OL	2.55	4.35	2.78	31	787
OD	3.38	1.87	1.19	31.3	612
Mean	2.45	10.6	6.82	30	692
Range	1.77–3.38	1.9–31.8	1.19–20.4	24.9–35.4	535–795
Local Background					
CO	2.8	5.08	3.25	34.5	767
Radical Point					
RP	−1.56[a]	118	75.9	36.8	635

EC: specific conductance; TDS: total dissolved solids; na: not analysed.

[a] Average value (standard deviation of 0.3, n = 13).

4. Results and discussion

4.1. Hydrochemical characteristic of samples points

Table 2 shows the physicochemical parameters measured "in situ" for the samples measured and collected in the Radical Point (RP), Local Background point (CO) and in several AMD-affected streams, which could be the hydrochemical characteristics indication of the Regional Background Affected (RBA) by AMD in the Iberian pyrite belt. This table also shows data taken in the Odiel River sampled before the influence of sulphide mines (OC). Therefore, this point could represent the Regional Background Unaffected of the zone, showing pH values of 8.7 and bicarbonates concentration up to 190 mg/L. Parameters measured in Local Background point show values around 2.8 of pH and 31.8 mS/cm and 3.25 g/L of specific conductance and total dissolved solids, respectively. Alike, Regional Background Affected present values range between 1.8 and 3.4 of pH, 2–32 mS/cm of specific conductance and between 3 and 1700 g/L of total dissolved solids.

Radical Point presents a specific conductance around 120 mS/cm and total dissolved solids of 75.9 g/L. Also presents average pH values of −1.56 (standard deviation of 0.3, n = 13), the lowest found in open-air environments contaminated by AMD. It is important to consider the extreme pH values found by Nordstrom et al. (2000), in the Richmond Mine at Iron Mountain (USA), as low as −3.6 of pH, however, these values were taken in waters coming from the drippings of a cluster of melanterite stalactites and others sulphate minerals efflorescences in an underground mine (Nordstrom et al., 2000). As stated above, other negative pH values have also been measured in some leachates of unstable salt precipitates in the zone. These precipitates had been observed on the bed surface of pyritic sludge and after periods of heavy rainfall. The crystallization of these salts is mainly due to the diffusion and capillary action of the strongly ionic water flooding the pyrite sludge pores to the surface. This pH negative lixiviates flow down to the lower zone of the basin and but they are occasional.

Figs. 3 and 4 shows the concentrations of the dissolved parameters measured in the samples from Regional Background Affected and Radical Point (Fig. 3) and those belonging to the Regional Background Unaffected and Local Background (Fig. 4). Fig. 3 also shows the maximum value found in the samples included in the RBA. It can be observed that the concentrations at the Radical Point are unusually high compared to the values found in the literature worldwide (Table 1). Concentrations of up to 187 g/L of sulphates, 60 g/L of Fe, 742 mg/L of As, 5 mg/L of Sb, 4.5 mg/L of Pb, 2 g/L of Mn, and elevated concentration of other elements considered as ultratrace elements in these contaminated environments, such as Tl (2.3 mg/L), Li (7 mg/L), V (3 mg/L), Bi (0.3 mg/L), inter alia (Table 3).

Dissolved elements such as, sulphates, Fe, As, Sb, Pb, Zn, Cu, etc., come from the oxidation of sulphur minerals, and they are in high concentration compared to the maximum found in samples from RBA (Fig. 3). The chemical data of the studied sampling point (Radical Point), suppose the finding of a singular space with values extraordinarily high of pollution by AMD. It is true not only for a neighboring scenario also polluted such as Cobica Stream (Fig. 4), but also for the regional hydrological environment affected by the mining activity in the area (Fig. 3).

On the other hand, a large number of other elements, coming from the acid solution of the surrounding rock, are observed (2.4 g/L of Al, 485 mg/L of Mg, 394 mg/L of Ca, etc., Fig. 3), but not in such a high concentration compared to those found in the Regional Background Affected (maximum up to 3.1 g/L of Al, 4.2 g/L of Mg, 479 mg/L of Ca, etc. Fig. 3, Table 3). All of them show values within the range obtained for the RBA, although much higher than the local background. Except for K, which has a fairly high and unusual value (146 mg/L of K, maximum Regional Background Affected found of 3.7 mg/L). This high values of K concentration could be due to a redissolution of minerals type

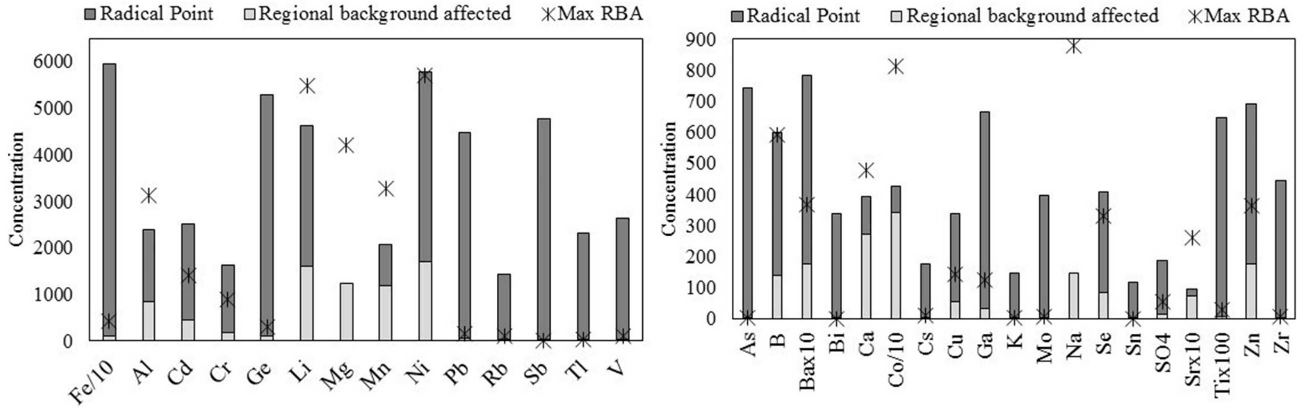

Fig. 3. Dissolved concentrations of several elements analysed in the Radical Point and comparison with Regional Background Affected. Asterisk symbol shows the maximum value found in Regional Background Affected (elements in μg/L, except Fe, Al As, Ca, Cu, K, Mg, Mn, Na, Sr, Ti and Zn in mg/L, and sulphates in g/L).

potassium jarosite, which were precipitated in the past when the raft did not have this ultra-acid character.

Composition of the AMD waters is strongly linked to the interaction between geochemical and hydrogeological processes. The relative content to iron and sulphate has been evaluated and compared to the theoretical composition of pyrite (Table 3). The most outstanding characteristic of the Radical Point is the existence of higher Fe/SO$_4$ molar ratios (0.55) than the theoretical one for pyrite (0.50), indicating an enrichment of Fe over sulphate. The AMD polluted waters often have Fe/SO$_4$ ratios lower than the theoretical one for pyrite, as it is the case of the other studied samples (Table 3). It is attributed to ferrous iron oxidation and the subsequent Fe(III) minerals precipitation or the occurrence of evaporitic Fe sulphates (Sarmiento et al., 2009a).

The roasting of pyrite forms a series of Fe secondary minerals such as hematite, magnetite and iron sulphates, while most sulphur is released as gaseous sulphur dioxide. As it has been said before, ashes from pyrite roasting from the chemical industries were return to the mining area, explaining the enrichment of Fe over sulphate in the studied sample. In addition, pyrite roasting has been carried out in "teleras" for a long time in the Iberian Pyrite Belt. Inefficient combustion of pyrite can form porous pyrrhotite (Fe$_{(1-x)}$S, $x = 0$–0.17), whose Fe/SO$_4$ molar ratio is close to 1 (Hu et al., 2006). So, the oxidation of the pyrrhotite could also explain the increase of the Fe/SO$_4$ ratios in the Radical Point.

Fig. 5 draws the studied samples in a Ficklin diagram, which classifies waters based on their pH and the sum of base metals Zn, Cu, Pb, Cd, Co and Ni. Samples belong to the Regional Background Affected can be considerate as high-acid and high or extreme metal, included the Local Background sample. However, the Radical Point sample is considerate as Ultra-acid and extreme-metal water.

4.2. Speciation and saturation indices

A speciation analyses has been carried out using the PHREEQC code (Parkhurst and Appelo, 1999). Usually, ion pair between metal and sulphate (Me-SO$_4$) are the dominant species in these environments affected by AMD, where the sulphate concentration is elevated. The most important metal species in the pH range 2 to 3.5 are FeSO$_4^+$, followed by Fe^{3+}, Fe^{2+} and FeSO$_4$ (Langmuir, 1997). In the studied Radical Point, Fe speciation shows interesting differences with respect to similar studies in rivers from the Iberian Pyrite Belt and the other studied samples (Table 4). In the Tinto River, FeSO$_4^+$ is by far the predominant species, representing 70% of the total Fe (Fig. 6, Cánovas et al., 2007). Similar results can be found in other studies of the IPB (Durães et al. 2017). In the Radical Point, the predominant Fe species is FeHSO$_4^+$, representing 94% of total, followed by FeSO$_4^0$ (6%) (Fig. 6). In any case, species of Fe(II) represent 100% of the whole, while the main species in the Tinto River are Fe(III) species. This result would also be in accordance with the Fe/SO$_4$ molar ratio very close to the theoretical for pyrite, as seen above. The MeSO$_4^0$ followed by Me^{2+} are the dominant species in the studied sample for Cd, Cu, Mg, Mn, Ni, Pb and Zn.

Arsenic is probably one of the most toxic and dangerous elements associated with AMD Usually, arsenic is present as several distinct chemical forms that have different mobility and toxicity. As(III) and As(V) are the primary species found in AMD, As(III)

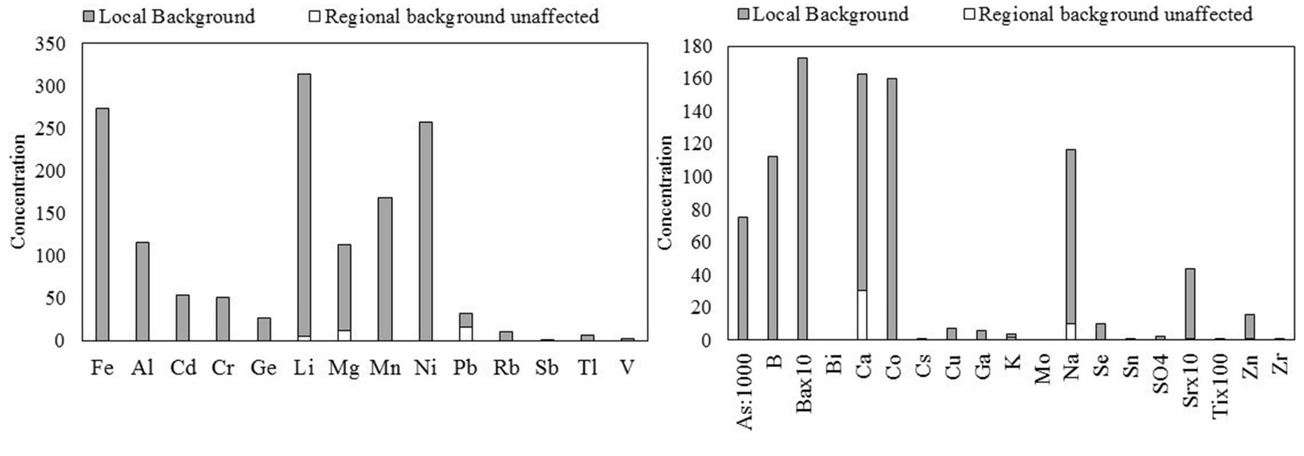

Fig. 4. Dissolved concentrations of several elements analysed in Local Background and Regional Background Unaffected samples (elements in μg/L, except Fe, Al As, Ca, Cu, K, Mg, Mn, Na, Sr, Ti and Zn in mg/L, and sulphates in g/L).

Table 3
Several element concentrations in the studied samples.

	AT	TZ	ME	OR	TP	TN	OL	OD	CO	RP
mg/L										
Al	1974	393	297	70.7	3122	703	89.2	82.5	115	2400
Ca	412	410	155	100	479	176	345	104	163	394
Cu	108	7.70	25.2	6.80	135	143	2.25	7.08	7.24	339
Fe	790	4183	90.4	13.8	1615	1752	152	0.54	274	59,513
K	bdl	bdl	3.73	2.64	bdl	bdl	2.06	2.28	3.49	146
Mg	2553	1383	345	159	4207	803	292	142	113	485
Mn	3268	1043	492	141	3197	766	386	161	168	2073
Na	24.0	29.8	100	46.2	878	46.8	27.1	30.2	117	84.1
SO_4	24,901	19,180	2384	1816	56,520	9821	5117	1226	2556	186,707
Zn	364	111	78.4	31.1	308	219	276	19.6	15.4	690
Molar ratio										
Fe/SO_4^{2-}	0.05	0.38	0.07	0.01	0.05	0.31	0.05	–	0.18	0.55
μg/L										
As	35.7	143	13.1	3.69	857	2074	14.6	1.76	75.3	741,916
B	109	64.3	104	58.3	594	111	28.9	36.1	112	601
Ba	9.22	3.66	23.4	36.6	17.9	10.7	15.3	24.2	17.3	78.3
Bi	bdl	bdl	bdl	bdl	1.48	bdl	bdl	bdl	bdl	340
Cd	1412	74.4	166	73.5	613	925	308	76.9	53.0	2524
Co	8132	4451	2476	624	5001	5280	934	436	160	4262
Cr	186	51.2	92.7	10.5	897	123	5.99	2.74	51.0	1639
Cs	6.33	6.92	bdl	bdl	11.4	6.87	1.09	bdl	0.59	176
Ga	42.1	16.1	7.35	2.43	127	39	24.4	2.58	5.83	666
Ge	103	298	12.9	3.52	197	180	31.9	2.73	27.0	5300
Li	4323	671	592	177	5492	1014	442	203	314	4620
Mo	6.14	0.71	bdl	bdl	bdl	bdl	bdl	bdl	bdl	398
Ni	5701	571	1077	324	3990	1061	718	238	257	5787
Pb	6.39	8.12	101	52.1	43.0	97.9	151	35.8	31.4	4484
Rb	9.72	45.3	6.12	3.27	110	20.4	8.86	2.82	11.0	1442
Sb	bdl	bdl	bdl	bdl	4.96	0.84	bdl	bdl	bdl	4783
Se	146	17.7	24.0	11.2	304	53.1	59.5	9.60	9.83	405
Sn	0.15	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	118
Ti	81.5	79.7	8.49	8.34	306	91.2	8.73	8.30	9.37	6473
Tl	3.20	2.79	bdl	0.81	9.05	24.7	4.46	0.63	6.10	2318
V	16.5	44.8	2.64	1.02	101	87.4	2.17	0.82	2.20	2638
Zr	2.27	0.62	bdl	bdl	7.00	4.58	0.53	bdl	bdl	447

being more toxic than As(V). Concentration of total arsenic in samples belonging to Regional Background Affected range between 1.8 and 2074 μg/L, being the mainly specie As^{3+} due to the oxidized specie is strongly adsorbed on the Fe oxihydroxisulphates (Sarmiento et al., 2009b). In the Radical Point the arsenic species found are mostly the reduced one (98% As^{3+} and 2% As^{5+}), mainly as H_3AsO_3 and $H_4AsO_3^+$ (47% and 52%, respectively). Concentration of As is up to 742 mg/L, which can give an idea of how dangerous these waters can be in terms of toxicity. Also taking into account that a rupture of this dam could originate an important load of contamination to the reservoir that provide drinking water to the city of Huelva.

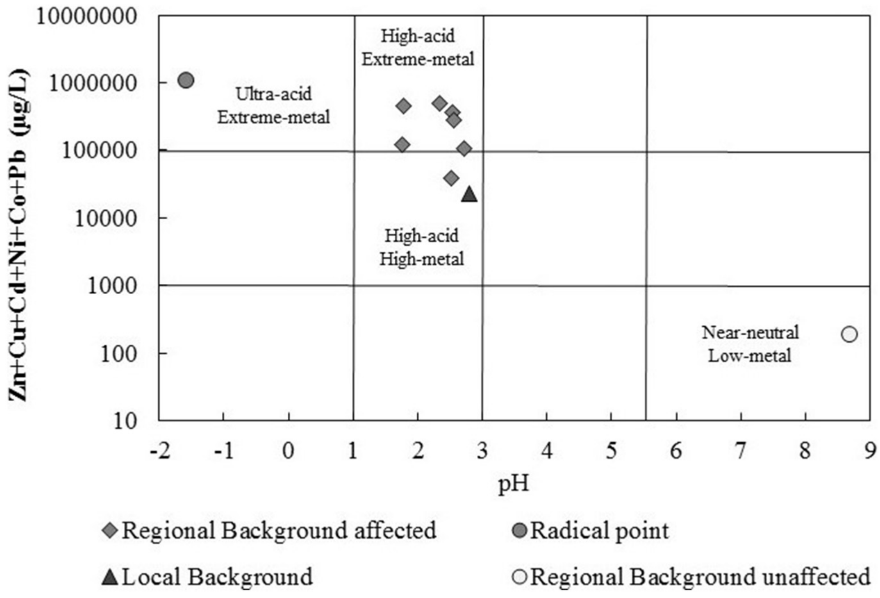

Fig. 5. Flicklin diagram projection of the studied samples (Plumlee et al., 1992).

Table 4
Percentage of main iron species in studied samples (<2% no data).

	AT	TZ	ME	OR	TP	TN	OL	OD	CO	RP
Fe^{+3}	4.8	–	8.4	2.9	–	–	4.2	–	4.8	–
$FeOH^{+2}$	2.1	–	15	3.0	–	–	4.0	4.3	12	–
$Fe(OH)_2^+$	–	–	–	–	–	–	–	2.6	–	–
$Fe(SO_4)_2^-$	21	–	3.7	4.0	37	3.6	16	–	8.6	–
$FeSO_4^+$	68	–	52	37	55	17	73	4.8	69	–
$FeHSO_4^{+2}$	2.2	–	–	–	5.8	–	–	–	–	–
Fe^{+2}	–	53	14	36	–	49	–	66	–	–
$FeSO_4$	–	40	3.5	16	–	26	–	21	–	6.0
$FeHSO_4^+$	–	6.6	–	–	–	–	–	–	–	94

The sulphate species formed in the Radical Point could provide information concerning the precipitation of sulphate minerals. However, the Fe^{3+}-SO_4^+ species only represent 0.2% of total Fe species, being the Fe^{2+}-HSO_4^- the main species.

A value not too high of redox potential (635 mV, Table 2) and the extreme acidity of this water, produces that all the Fe species are in the reduced and dissolved form (Langmuir, 1997). This could explain the nonexistence of sulphate minerals (efflorescences) in the seasonal variation limit of water table in the Radical Point. In fact, the calculations of the saturation indexes show sub-saturation in all the studied minerals, except for those insoluble even at low pH, such as anglesite (saturation index value of 3.4) and barite (saturation index value of 3.9).

4.3. Seasonal variations of the Radical Point

From October 2003 to 2007, a seasonal variation study of several parameters was performed at the Radical Point (Fig. 7). It can be observed the pH evolves from around 1.5 units to negative values. In the same way, the concentrations of the elements analysed increase during the studied period, with ranges of 31–197 g/L of sulphates, 9–60 g/L of Fe, 140–460 mg/L of Cu, 190–690 mg/L of Zn and 119–740 mg/L of As.

The results indicate that the waters of the studied Radical Point evolve towards more extreme values, increasing the concentration of dissolved elements and decreasing the pH to negative values. This variation is due to the accumulation of salts in the receiving basin, for years. The point of study has received contributions of highly contaminated waters due to several processes of different nature: the geochemistry of the minerals presents in the endorheic basin. Pyrite and arsenopyrite of nearby local paragenesis and responsible of the release of acidity, loading of metal and sulphates through oxidation mechanisms of sulphides. The particle size of the materials is small. The surface area exposed to weathering is an important factor in the development of the sulphide oxidation process. The studied scenario is an acidity generator system, especially influenced by the endorheic character of the basin. Cyclic processes of precipitation/dissolution in a closed system originate a different response in the flow. This response does not fit into a general model of operation of mining waste rock dumps as described by Sainz et al. (2002). The climatology of the area is an important factor to consider. The average annual rainfall in the area is 650 L/m^2 (Jiménez et al., 2009), often subjected to torrential rain periods, which means that there are runoff moments with a high capacity for mechanical transport of particulate matter to the studied dam. The particulate matter can be both, the primary type minerals above described, and the particles of the secondary minerals newly formed by the processes of evaporation in the basin. In addition, mine tailings operate as free aquifers of anthropogenic origin (Sainz et al., 2002).

4.4. Toxicity assessment by diatoms presence

Samples from Cobica (a receiver channel of Lagunazo-Radical Point) has 3 species already found in similar environments from Lousal and Aljustrel mining areas, located in the Portuguese part of the Iberian Pyritic Belt (IPB). The 3 dominant species were, in descendent order of dominance: 61% *Brachysira vitrea*, 22% *Eunotia exigua* and 7% *Pinnularia* c.f. *acidophila*.

1) *Brachysira vitrea* (Grunow) Ross in Hartley, which is a pH tolerant species and was the most abundant diatom species in Cobica sites. *B. vitrea* is known as metal tolerant (Dixit et al., 1991; Luis et al., 2011), which justifies its dominance in Cobica sites affected by acid mine drainage, with important metal contamination. In the bibliography, the data related with this species optimum pH are contradictory. Hofmann (1994) considered it as indifferent. On the other hand, Monteith and Evans (2005) found it dominating in acidic sites, which is in agreement with the present study and with other from Lousal mining area in Portugal (Luis et al., 2011).
2) *Eunotia exigua* (Brebisson ex Kützing) is considered as acidobiont: optimal occurrence in pH < 5.5 (Patrick, 1977; Van Dam et al., 1994) and is one of the common species in rivers and lakes influenced by AMD, in pH < 5 (Kwandrans, 1993) in North America and Europe. Lessmann et al. (2000) found this taxon in lignite-influenced lakes with pH of 2 and 3 in Germany. *E. exigua* is known to show high tolerance to contamination and to large spectra of chemical pollutants (Guasch et al., 1998). In the present study, samples with low pH (2–6) and high metal concentration had high

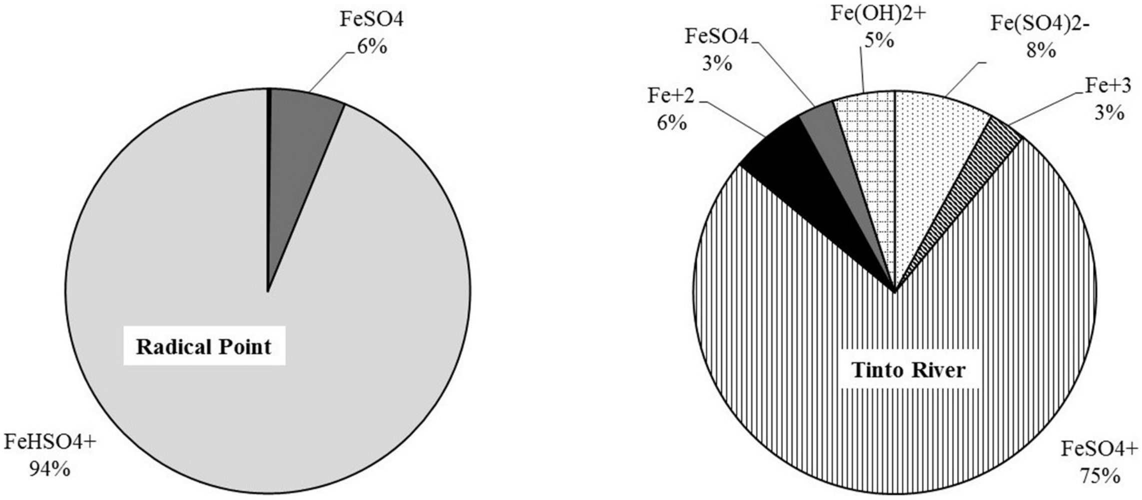

Fig. 6. Main iron species in the Radical Point and the Tinto River.
Modified from Cánovas et al. (2007).

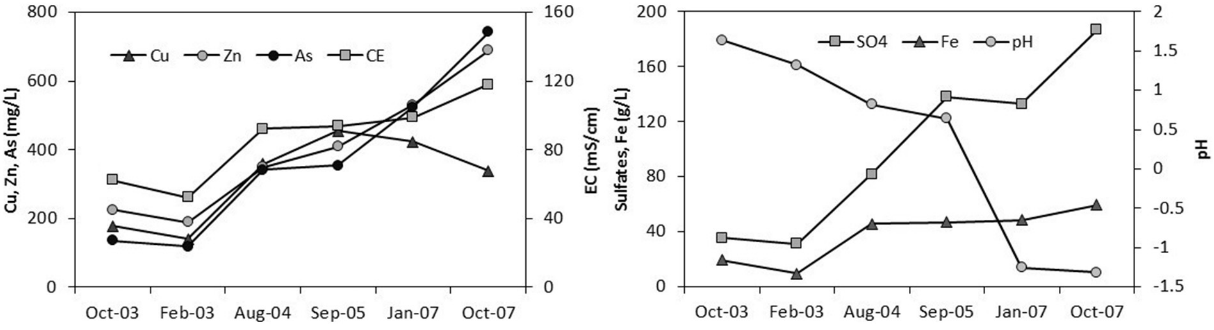

Fig. 7. Seasonal variation of some parameters in the Radical Point.

relative abundances in *E. exigua*, as found in other studies (De Nicola, 2000; Passy, 2006; Luis et al., 2009, 2011, 2016).

3) *Pinnularia* c.f. *acidophila* Hofmann et Krammer is acidophilic: occurrence in pH < 7 and in this study co-dominating the diatom communities of Cobica. It was discovered in an opencast mining lake (Krammer, 2000) of low pH. *Pinnularia aljustrelica* Luís, Almeida et Ector (first discovered in Luis et al., 2012) and *Pinnularia acoricola* Hustedt are close species to *P. acidophila* and sometimes confused in the bibliography. All showing an ecological preference of pH 2 to 3 (Luis et al., 2009, 2011, 2016).

However Lagunazo-Radical Point didn't have diatoms due to its low pH: the lowest found until now in AMD contaminated systems. Contrary to Cobica, were some extreme diatoms were found.

In recent reviews of eukaryotic diversity in extreme environments (Aguilera, 2013; Amaral-Zettler, 2013), the lowest pH, where eukaryotics were found, was 2. Thus our study contributes to the affirmation: no eukaryotic microorganisms, including diatoms, were found in such extreme pH of Lagunazo-Radical Point.

5. Conclusions

This paper presents the finding of a singular environment, regulated by particular conditions, and polluted by acid mine drainage in the Iberian Pyrite Belt. This radical environment has been compared with others polluted scenarios in the same area. The obtained results can be considered as extreme values, due to the low pH, reaching an average negative pH of −1.56, never found before in open-air environments contaminated by acid mine drainage. Dissolved concentrations up to 59 g/L of Fe, 2.4 g/L of Al, 187 g/L of SO_4^{2-}, 740 mg/L of As, 4.3 mg/L of Co, 5.3 mg/L of Ge, 4.8 mg/L of Sb, inter alia, can be found in these polluted waters, considered as Ultra-acid and extreme-metal water. Extreme acidity and metal and sulphate concentrations in the Radical Environment is due to several processes of different nature, mainly driven by the geochemistry of the material wastes presents in the endorheic character of the basin: pyrites roasting wastes, "morrongos" from pyrite calcination in situ, accumulation of evaporitic sulphate salts in the receiving basin, inter alia. These processes occur continuously over the years, causing water to evolve towards extreme pH and very high concentrations of dissolved elements. Values of Fe/SO_4 molar ratios higher than 0.50 indicate an enrichment of Fe over sulphate possibly due to the presence of pyrrhotite in the mine tailing wastes. Hydrochemical modelling shows $FeHSO_4^+$ as the main Fe specie in this waters, representing 94% of total Fe species. The use of diatoms as bioindicators of water toxicity assessment shows three dominant species in the studied points. They are, in descendent order of dominance: *Brachysira vitrea*, *Eunotia exigua* and *Pinnularia* c.f. *acidophila*. However, no species of diatoms have been found in the Radical environment, indicating a high toxicity of these waters.

The present study could open up an important line of research in extreme environments, hitherto unknown in the open air. The absence of typical diatoms in environments contaminated by acid mine draining does not eliminate the possibility of finding new organisms not described until now, as well as hydrogeochemical processes that may expand new knowledge in this subject.

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